1. Introduction
Lab-scale chalcopyrite thin film solar cells have had a slow but steady climb in power conversion efficiency in the last decade, marked by the National Renewable Energy Laboratory (NREL) reaching the 20% milestone with a co-evaporated Cu(In,Ga)Se$_2$ (CIGS) solar cell in 2007 [1]. At the time, it was presented that the record cell had measured efficiency of 19.9%, but later on it was corrected to 20.0% due to a new standard solar spectral irradiance reference. In 2013, ZSW presented several co-evaporated CIGS solar cells above 20% [2] and later a new record cell of 20.8% [3]. In early 2014, Solar Frontier announced a new record at 20.9% for a 0.5 cm$^{-2}$ CIGS solar cell [4], and in June 2014 Solibro presented a CIGS solar cell with 21.0% efficiency [5]; both cells were verified by the Fraunhofer Institute. Swiss Federal Laboratories for Materials Science and Technology (EMPA) holds the current record for CIGS thin film solar cells on...
flexible substrates, with 20.4% efficiency [6]. As the efficiency increases towards the ideal Shockley-Queisser limit, it is becoming more difficult to improve it. Much effort has been put into investigation of the absorber layer and its interfaces where the material parameters are critical to the device performance. One of these parameters is the compositional ratio of Ga to In, which is known to influence the conduction band edge energy level [7]. We define this compositional parameter as GGI ≡ Ga/(Ga + In), where we use atomic ratios of respective elements, and the variation of GGI through the depth of the absorber is defined as the Ga-profile. With the ability to control the bandgap throughout the absorber layer, it is possible to introduce quasi-electrical fields, change conduction band alignment, change the absorption regions and suppress recombination pathways.

To study the influence of a GGI-graded absorber one can use modeling, and there are several studies on this topic [8–15]. The conclusions of these studies are diverse, however, where some argue that CIGS absorbers have a double-graded Ga-profile with the highest efficiency of notch yield [8–10, 15]. The primary argument for a notch-type Ga-profile is because of high current density due to absorption in the low bandgap region (notch), while also maintaining high voltage though a larger bandgap in the space charge region (SCR). Other studies are more critical of notch-type GGI-grading, arguing that front grading is detrimental to cell efficiency [11], or that front grading could be detrimental in certain conditions, and that the benefits of any GGI-grading are smaller than commonly believed and dominated by positive effects of the added Ga in itself [12]. Decock et al conclude that alternative back grading (flat step in GGI towards the back contact) is redundant for thick absorber layers and that front grading (mainly in the valence band) might be beneficial if it is engineered in such a way that it moves generation to a region with a lower probability of recombination [13]. In general, the consensus is that notch-type GGI-grading is or could be beneficial rather than detrimental, but it is hard to decouple the benefits from grading and the benefits from deposition processes. One example is the three-stage-process, known for yielding high quality CIGS films, where the notch-type Ga-profile is formed as a consequence. Also, one should take care to have a solid framework when comparing different profiles, as pointed out in previous studies [12, 13], and be aware that a varying GGI will also introduce changes in other parameters, e.g. the recombination rate [16]. Moreover, when doing simulations, one needs to be aware that the net effects of GGI-grading are dependent on defect levels and their distributions [13, 15, 17]. Thus, it becomes important to build models on the basis of experimental data in order to be able to predict the effects of changing the Ga-profile. Moreover, the use of data from high quality solar cells is important in order to correctly predict possible enhancements for high efficiency devices.

In this work, we simulated the role of the Ga-profile in the SCAPS software [18] on the basis of experimental data from a reference solar cell. This device is a representative state-of-the-art in-house CIGS solar cell with efficiency η ≈ 19%. This reference device was created in a similar fashion to our baseline process [19], with a Mo back contact on top of a soda lime glass, a CIGS absorber layer, a CdS buffer layer, a non-doped ZnO layer (i-ZnO) as well as an Al-doped ZnO layer (ZnO:Al) in connection to the grid fingers. Some small modifications of the baseline process were done to the back and front contacts. The back contact was created by sputtering a thicker Mo layer, with a 15 nm thick evaporated layer of NaF on top, to ensure that enough Na was available during the growth of the CIGS layer. We also used a thinner ZnO and the addition of MgF2 on top to minimize reflection and parasitic absorption, respectively. The absorber layer deposition for the reference device was done in a batch evaporation tool at 540 °C with a simulated in-line process, see figure 1. This deposition process is similar to our in-line evaporation baseline process [19], but with a small modification towards the end where a front grading is formed. The metal deposition rates shown are the values measured with a quadruple mass spectrometer and corrected with the known composition from x-ray fluorescence (XRF) analysis. In our deposition process, with no temperature gradients during deposition or sharp steps in metal evaporation rates, the Ga-profile is thought to be more decoupled from the absorber film quality as compared to the classical three-stage-process. According to the evaporation data, seen in figure 1, where the integrated CGI ≡ Cu/(Ga+In) and GGI are shown on the right-hand y-axis, the CIGS was in slightly Cu-rich state in the first half of the deposition window: CGI peaks at 1.15. The notch is formed 12 min into the deposition process.

The simulations were done in four different models: two simple defect models with a constant or Ga-dependent absorber defect concentration placed in the middle of the bandgap, and variations of these models with a donor/double acceptor amphoteric defect complex with constant distribution in the CIGS layer. Within these models, single-graded (SG) and double-graded (DG) Ga-profiles were optimized and compared with each other.
value 107 to 10 6 cm s−1 based on a more recent study in the
several spots of the images.

Different layer thicknesses were estimated and averaged from
microscopy images of the full stack of the reference device. The
$S_b$ was decreased from the previous baseline
were set, where $S_b$ contacts fixed surface, recombination velocities,
in order to minimize the metal-semiconductor barrier. At the
of states and the doping concentration, but no other defects,
i.e. the electron affinity, the band edge energies, the density
work function is dependent on the contacting semiconductor,
in SCAPS was used at both contacts, meaning that the metal
measurements of the same device.

Each model consists of a four-layer structure, representing the
CIGS, CdS, i-ZnO and ZnO:Al of the reference device. The thickness of each layer is an average of the thicknesses
measured with cross-section transmission electron microscopy
(TEM), see figure 2.

There are three interfaces considered in the models: the
front contact, the interface between the CIGS and CdS
layers, and the back contact. The option to have flat bands in
SCAPS was used at both contacts, meaning that the metal
work function is dependent on the contacting semiconductor,
i.e. the electron affinity, the band edge energies, the density
of states and the doping concentration, but no other defects,
in order to minimize the metal-semiconductor barrier. At the
contacts fixed surface, recombination velocities, $S_b$ and $S_f$,
were set, where $S_b$ was decreased from the previous baseline
value $10^7$ to $10^6$cm s$^{-1}$ based on a more recent study in the
group [21]. In addition, there is an optical filter at the front
contact, whereas no reflection is assumed at the back contact.
The optical filter corresponds to the reflectance measured with
a spectrophotometer with an integrating sphere. This measure-
ment was done on the complete reference solar cell stack.
Carrier generation, in each layer, is calculated with wave-
length-dependent absorption coefficients [22] and an AM1.5
spectrum. The composition of the CIGS layer was measured with
energy dispersive x-ray spectroscopy (EDS) for three
individual CIGS grains from our reference device. On each
grain we performed and averaged 10 parallel measurements,
with a step width of 25 nm. The EDS data were calibrated
using the average composition XRF analysis. For this study,
the XRF calibration was refined by comparing the absorption
edge from EQE of flat Ga-profile CIGS devices with varying
Ga content. We used the following empirical expression in the
models and for extracting the bandgap from EQE: $E_g = 1.01 +
0.626x - 0.167(x - x^2)$, where $x = \text{GGI}$ [23]. In the models an
average Ga-profile was used, created from the EDS data of the
three individual grains. The shallow acceptor concentration
of the CIGS layer was estimated from temperature-dependent
capacitance (CV-T) measurements. The reference device was
either in a relaxed state, treated at 330 K in darkness for one
hour, or in a light-soaked state where it was light-biased with
white LED light for one hour at room temperature (RT), and
then cooled with constant light bias. A JV-measurement was
performed under a halogen lamp with a cold mirror (ELH)
and the light intensity was calibrated with the $J_{sc}$ from an EQE
measurement [24]. From a dark JV-measurement, the series
resistance and the shunt conductance, used as one-diode
model parameters in SCAPS, were extracted according to the
method presented by Hegedus and Sharfarman [25]. In all
models, the recombination centers were placed in the middle
of the bandgap in order to act as efficiently as possible; we are
not attempting to model the exact and complicated nature of
the defect-rich and highly self-compensated CIGS material.
Instead, we model an equivalent recombination behaviour to
replicate the behaviour of the reference device. The concen-
tration of the recombination centers in the CIGS bulk and the
interface trap density at the absorber/buffer interface in each
model were set by comparing the simulated four figures of
merit, $V_{oc}$, $J_{sc}$, FF and $\eta$, with their measured counterpart, as
well as by comparing the overall shape of the JV-curves. The
amphoteric defect concentration was set using CV-T data.

The four different models in this work are described in
detail below:

(a) Model A is our simple defect model with bulk and
interface mid-gap donor defects, uniformly distributed
through the depth of the CIGS layer.

(b) In model B, the bulk defects are set similarly to model
A, but with a Ga-dependent concentration in line with
previous findings [16]: it is empirically known that for
the CIGS, $V_{oc}$ deficit increases with increasing GGI,
and classically the best devices have been made with
GGI ≤ 0.3 [26]. Two criteria when setting the defect
distribution were to set its concentration one order of
magnitude higher at GGI = 1 compared to GGI = 0, and
the minimum defect concentration at GGI = 0.3.

(c) In model C, the simple defect model is assumed with
an additional metastable amphoteric defect complex,
treated in previous modeling [18] and set to behave as
the Cu and Se di-vacancy ($V_{Cu-}V_{Se}$) complex [27], with
electron/hole capture and emission energies from an
experimental investigation [28]. Naturally, with this
and $E_f$ respectively, and $E_i$ is the intrinsic energy in the middle of the bandgap. In the amphoteric defect model, the position of the Fermi level, $E_F$, in relation to the amphoteric transition energy, $E_{TR}$, determines the configuration of the defect complex. In the case shown here, the band bending thus enhances the p-doping of the front region of the CIGS layer, while the back region is compensated.

all individual defects in these models are set with a uniform energy distribution, i.e. single energy level, in the bandgap. The distribution as discussed in this work refers to the depth of the CIGS layer.

2.2. Simulations

Three main sets of simulations were performed in this study: (1) to finalize model A, B, C and D in order to fit them with the reference device data by setting the magnitude of the defect concentrations, (2–3) to see how the efficiency could be improved by changing the CIGS composition and optimizing the Ga-profiles in each model. In detail:

1. The bulk defect concentration, distinguished by the model, was varied together with the interface trap density in order to fit the measurement of the reference device.

2. The optimum SG Ga-profile was found by varying the value of GGI at the CIGS/CdS interface and at the back interface of the CIGS layer.

3. The optimum DG Ga-profile was found with the same steps mentioned in part (2), and by additionally varying GGI at the notch in between the two interfaces, as well as the position of the notch in the CIGS layer.

Figure 3. The band diagram of a CIGS device in equilibrium, including (from left to right), ZnO:Al, i-ZnO, CdS and CIGS. The conduction and valence band edge energies are represented as $E_C$ and $E_V$ respectively, and $E_i$ is the intrinsic energy in the middle of the bandgap. In the amphoteric defect model, the position of the Fermi level, $E_F$, in relation to the amphoteric transition energy, $E_{TR}$, determines the configuration of the defect complex. In the case shown here, the band bending thus enhances the p-doping of the front region of the CIGS layer, while the back region is compensated.

Radiative recombination is taken into account in each model; it was not present in the previous baseline model due to a dominating Shockley–Read–Hall (SRH) recombination. However, it was observed that radiative recombination had an impact for highly efficient CIGS with low bulk defect concentration, especially in the case of notch-type Ga-profiles allowing accumulation of minority carriers at a notch [29].

All individual defects in these models are set with a uniform energy distribution, i.e. single energy level, in the bandgap. The distribution as discussed in this work refers to the depth of the CIGS layer.

3. Results and discussion

3.1. Material characterization

In this section, the results from the material characterization are presented, and a list of model parameters, based on the material characterization, fitting of JV-data and previous studies, can be found in table 1. A TEM image of the reference device from which the layer thicknesses were estimated, can be seen in figure 2. Marked is the average measured CIGS absorber thickness. The window layers are both thinner (310 nm) in our reference device than in the baseline (440 nm), and the Mo back contact is 550 nm in our device instead of 350 nm which is the baseline. The CIGS and CdS thicknesses are similar to those normally used in the group. The EDS data of Ga-profiles for three different grains can be seen in figure 4. The difference in composition at the notch is 5% GGI between grain 1 and grain 3, which corresponds to a bandgap variation of about 25 meV. The thickness of the absorber varies 225 nm between grain 2 and grain 3. Note that the position of the notch from the CIGS/CdS interface is similar for all three grains even if the total thickness varies. The average profile (line in figure 4) was used in order to fit the models with the reference data, but the thickness of this profile was chosen according to the average CIGS thickness from the measurement seen in figure 2, and correlates with the thickness of grain 1. The composition of the reference sample is CGI = 0.87, an average measured with XRF, and GGI = 0.24, calculated for the average EDS profile using the refined XRF data.

The doping concentration of the CIGS layer was estimated from the derivative of the Mott-Schottky plot of the CV-T measurements seen in figure 5. According to Cwil et al, the doping concentration is given by the minimum of the net doping concentration curve [29]. In models A and B, this apparent concentration of Ga-profiles for three different grains can be seen in figure 4. The optimum DG Ga-profile was found with the same steps mentioned in part (2), and by additionally varying GGI at the notch in between the two interfaces, as well as the position of the notch in the CIGS layer.

SCAPS allows the user to create layers with a spatial resolution of 1 nm or manipulate a certain layer with even higher resolution. For simplification in the process of optimizing the Ga-profiles, a spatial resolution in the order of 10 nm was used, and the optimized Ga-profiles were restricted to linear gradients in between points of interest.
Table 1. The model parameters used for simulations in the SCAPS software. CB DOS and VB DOS stand for conduction band and valence band effective density of states, respectively.

| Layer parameter | Symbol (unit) | ZnO:Al | i-ZnO | CdS | CdS/CIGS | CIGS |
|-----------------|---------------|--------|-------|-----|----------|------|
| **General**     |               |        |       |     |          |      |
| Thickness       | \(d\) (nm)    | 230    | 80    | 50  | —        | 1950 |
| Bandgap         | \(E_g\) (eV)  | 3.3    | 3.3   | 2.4 | —        | 1.0–1.6 (Ga-dep.) |
| Electron affinity | \(\chi\) (eV) | 4.4    | 4.4   | 4.2 | —        | 4.5–3.9 (Ga-dep.) |
| Rel. permittivity | \(\varepsilon_r\) | 9      | 9     | 5.4 | —        | 13.6 |
| CB DOS          | \(N_C\) (cm\(^3\)) | \(3 \times 10^{18}\) | \(3 \times 10^{18}\) | \(1.3 \times 10^{18}\) | — | \(6.8 \times 10^{17}\) |
| VB DOS          | \(N_V\) (cm\(^3\)) | \(1.7 \times 10^{19}\) | \(1.7 \times 10^{19}\) | \(9.1 \times 10^{19}\) | — | \(1.5 \times 10^{19}\) |
| Effective mass  | \(m_e^*, m_h^*\) | \(0.78, 0.24\) | \(0.78, 0.24\) | \(0.51, 0.14\) | 0.72, 0.09 | 0.72, 0.09 |
| Mobility        | \(\mu_h, \mu_e\) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) | 31, 100 | 31, 100 | 20, 72 | — | 13, 100 |
| Doping:         |               |        |       |     |          |      |
| Type            | —             | Donor  | Donor | Donor| —        | Acceptor |
| Conc.           |               | \(N_{A}, N_{D}\) (cm\(^{-3}\)) | \(10^{20}\) | \(10^{17}\) | \(5 \times 10^{17}\) | — |
| Radiative rec.  | \(R_B\) (cm\(^3\) s\(^{-1}\)) | \(10^{-10}\) | \(10^{-10}\) | \(10^{-10}\) | \(10^{-10}\) | — |
| S. rec. velocity | \(S_f, S_b\) (cm s\(^{-1}\)) | \(10^7\) (front) | — | — | — | \(10^9\) (back) |
| Defects I       |               |        |       |     |          |      |
| Type            | —             | Acceptor | Acceptor | Acceptor | Donor | Donor |
| Distribution    | —             | Constant | Constant | Constant | — | Constant (A, C), Ga-dep. (B, D) |
| Conc., density  | \(N_{T}, N_{IF}\) (cm\(^{-3}\), cm\(^{-2}\)) | \(10^{16}\) | \(10^{16}\) | \(2 \times 10^{17}\) | \(10^{12}\) | Model dep., see figure 7 |
| Energy level    | \(E_T\)       | \(E_i\) | \(E_i\) | \(E_i\) | \(E_i\) | \(E_i\) |
| Cap. cross-sec. | \(\sigma_p, \sigma_n\) (cm\(^2\)) | \(5 \times 10^{-13}, 10^{-15}\) | \(5 \times 10^{-13}, 10^{-15}\) | \(5 \times 10^{-13}, 10^{-15}\) | \(10^{-15}, 5 \times 10^{-13}\) | \(10^{-15}, 5 \times 10^{-13}\) |
| Defects II      |               |        |       |     |          |      |
| Type            | —             | —      | —     | —   | —        | Amphoterically (C, D) |
| Distribution    | —             | —      | —     | —   | —        | Constant |
| Conc.           | \(N_T\) (m\(^{-3}\)) | — | — | — | — | \(9 \times 10^{15}\) |
| Energy level    | \(E_T\) (eV); above \(E_V\) | — | — | — | — | 1.00 (+0) / 0.06, 0.85 (0/-, -/2-) |
| Cap. cross-sec. | \(\sigma_p, \sigma_n\) (cm\(^2\)) | — | — | — | — | \(10^{-17}, 10^{-17}\) |

Figure 4. GGI as a function of the depth of the CIGS layer, i.e. the Ga-profiles, for three individual grains of the reference device, measured with energy dispersive x-ray spectroscopy. Each individual Ga-profile is an average from 10 separate line scans performed on each grain, with a step width of 25 nm. In the simulations, we use a calculated average of the three individual Ga-profiles (line).

Figure 5. The net acceptor concentration derived from the CV-measurements of the reference device. The relaxed (Rel., black curves) device was kept in darkness at 330 K for one hour and then cooled. The light-soaking (L-S, red curves) was achieved with about 0.1 W cm\(^{-2}\) white LED light for one hour at 330 K, and then cooled with constant light bias before the measurement.
CV-measurement for the relaxed reference device is included in figure 5.

In models C and D, when introducing the $V_{Se} - V_{Cu}$ amphoteric defect complex, we also introduce the availability of more shallow acceptors or compensational shallow donors depending on the configuration of the defect complex. In theory [27], the $V_{Se} - V_{Cu}$ complex in a relaxed solar cell will appear in the acceptor configuration close to the CIGS/CdS interface, where the band bending causes the Fermi level to rise above the amphoteric transition energy ($E_{TR} = 0.23$ eV in our models), and it will appear in a donor configuration some distance from the CIGS/CdS interface, where the Fermi level is below $E_{TR}$ for a device in equilibrium. The assumption is made that for a low temperature CV-measurement of the relaxed reference device, the minimum of the net acceptor concentration corresponds to maximum compensation, i.e. the $V_{Se} - V_{Cu}$ complex in 100% donor configuration. In contrast, the peak net acceptor concentration, measured from the light-soaked CIGS reference device at low temperature, was assumed to correspond to the $V_{Se} - V_{Cu}$ complex in 100% acceptor configuration. From these assumptions, the doping and amphoteric metastable defect concentrations were derived. The value of the amphoteric defect concentration at $N_T = 9 \times 10^{15}$ cm$^{-3}$ in this work corresponds well with the values presented in previous studies [18, 29].

The optical reflectance data from the reference device is seen in figure 6, and the minimum around 770 nm corresponds to negligible reflection. This agrees very well with the chosen MgF$_2$ thickness at around 140 nm, optimized to fit the peak photon flux of the AM1.5 spectra. The plot shows the reflectance of active area and was used as an optical filter for EQE simulations. For JV-simulations the reflectance was uniformly shifted up 2.5% absolute corresponding to the shadowing area of the front contact grid fingers.

3.2. Models

The fit between simulations and JV-measurement data from the reference device was made by adjusting the defect concentrations in each model, as seen in figure 7 and table 1. The plots of corresponding JV-simulations and JV-parameters can be seen in figure 8 and table 2, respectively. Noticeable is the low bulk defect concentration that has been used in all models, in the order of $10^{12}$ cm$^{-3}$. In reality, CIGS is defect-rich, and this low number represents an effective concentration of recombination centers in the absorber layer that makes the best fit in our models. The recombination rate is exponentially decaying with the increasing difference of the defect energy level in respect to the intrinsic level. In other words, with fixed
Table 2. The simulated JV-parameters for the four models and the measured JV-parameters from the reference device from which many of the input parameters have been taken. Assuming a one-diode model behavior, $J_0$ and $A$ were extracted by fitting the one-diode model equation to the corresponding JV-data.

| Model | $V_{oc}$ (mV) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | $\eta$ (%) | $J_0$ (A cm$^{-2}$) | $A$ |
|-------|---------------|-------------------------|--------|-------------|---------------------|-------|
| A     | 680           | 38.1                    | 75.7   | 19.6        | $4.5 \times 10^{-10}$ | 1.45  |
| B     | 681           | 38.0                    | 75.4   | 19.5        | $6.1 \times 10^{-10}$ | 1.47  |
| C     | 687           | 37.8                    | 75.6   | 19.6        | $3.7 \times 10^{-10}$ | 1.45  |
| D     | 685           | 37.6                    | 75.8   | 19.5        | $4.5 \times 10^{-10}$ | 1.46  |
| Reference | 685         | 36.8                    | 75.9   | 19.1        | $1.38 \times 10^{-9}$ | 1.56  |

capture cross-sections, the defect concentration set here is the minimum defect concentration for this recombination rate for a single level defect of this type with uniform distribution through the depth of the absorber. In these models, back contact surface recombination has an impact equivalent to, or higher than, the recombination in the bulk absorber. The cause of this effect is that the low defect concentrations make the electron diffusion length longer, so the influence of the back contact extends further into the CIGS absorber.

The CIGS/buffer layer interface trap density is much debated and in this work was set to a nominal value $[20]$, 10$^{12}$ cm$^{-2}$. In one simulation study, Song et al mention only a 'high recombination interface layer' $[9]$, while others do not include any interface traps due to their negligible influence for positive conduction band offset (CBO) $[12]$ (true for CBO between around 0 and +0.2 eV), or simply do not mention it at all. A sensitivity analysis shows that in our four SCAPS models, with the reference Ga-profile, the JV-parameters do not change substantially for an interface trap density variation spanning from 10$^{11}$ to 10$^{13}$ cm$^{-2}$. Recently, NREL presented a study based on time-resolved photoluminescence concluding that SRH and surface recombination are insignificant for high-efficiency CIGS solar cells $[31]$: this is in accordance with the low bulk defect concentrations and insensitivity to CIGS/buffer layer interface trap densities modeled in this work.

Regardless of the low bulk defect concentrations set in our models, $V_{oc}$ in models A and B was in both cases slightly lower than the experimental value of the reference device. The difference of 4 mV is not considered substantial, but it is interesting to note that, even without recombination in the bulk of the CIGS layer and at the CIGS/CdS interface, the $V_{oc}$ does not increase more than an additional 6 mV, indicating that it is limited by the bulk shallow acceptor concentration, i.e. the doping concentration. In models C and D, with higher shallow acceptor concentration assumed, the measured $V_{oc}$ is no longer on the limit set by the doping.

$J_{sc}$ is higher in all models compared to the reference device, and as seen in figure 9 the simulations overestimate the current generated for all wavelengths, except for long wavelengths at the absorption edge. The general difference in EQE is assumed to originate from the dead cell area. Since the reflection was measured on the full stack, however, and the model is restricted to absorption as the only other optical input parameter, some of the difference in EQE at shorter wavelengths could be caused by interference at the buffer/window layer interface. Also, the difference could partly originate from low absorption coefficients for the CdS and the ZnO in the models. Contribution to the photocurrent in terms of the hole injection from the CdS is small in the models, and is not the cause of the overestimated current in EQE. A quantitative analysis shows that for wavelengths between 300 and 514 nm the overestimated current is 0.84 mA cm$^{-2}$, about half of the total difference in $J_{sc}$. A more complex simulation tool with the optical constants of each layer would be required to further analyse this difference. For the reverse relationship at wavelengths longer than about 1100 nm, this could be attributed to reflection at the back contact which is absent in the models. As an effect of $J_{sc}$ being overestimated in the simulations, the efficiency is slightly overestimated as well.

The overall shape of the JV-curve in the forward bias regime $V > V_{mp}$ fits considerably better for models C and D which include amphoteric defects, and where the doping concentration was set higher, as compared to models A and B. In this regime, the diode diffusion current becomes large enough to impact the solar cell performance. The simpler models A and B with lower mid-gap defect concentrations fit better for $V < V_{mp}$, where it is clear that the current collection loss is smaller than for models C and D. Shunt conductance and series resistance were set to equal values in all four models.

3.3. Optimization of single-graded Ga-profiles

The optimum SG Ga-profiles were found by simulating different values for GGI at the back contact and at the CIGS/CdS interface, and the results can be seen in figure 10. The optimized SG Ga-profiles are similar to each other, and compared to the EDS-measured Ga-profile the efficiency is increased by 0.9–1.3%. The JV-parameters are found in table 3, where...
the highest efficiency for an optimized SG Ga-profile was achieved in model B, at 20.8%. The overall Ga concentration is higher for these profiles compared to the measured Ga-profile in the reference device, indicating that the efficiency could be improved by increasing GGI in the CIGS layer according to these results, provided that the absorber film quality is unaffected by the compositional variation.

By comparing the Ga-dependent/constant defect concentration models, models B/A, and D/C, it is observed that the models with a Ga-dependent defect distribution have, in general, a lower optimum bandgap value than their counterparts. This difference can be explained by the increase in defect concentration for higher GGI and by the fact that the lowest defect concentration at GGI = 0.3 is lower than the compared constant defect concentration in models A and B. The latter fact means that the total defect concentration of a profile in models B and D is allowed to be smaller than in models A and C, leading to an increase of efficiency for model B compared to A, and model D compared to C. No quantification of the profile differences has been done due to the nature of the selection of the Ga-dependent defect distribution. Experimental verification would be required for cells made with our process, and while the Ga-profile trend is clear, especially for the A/B comparison, the differences are not substantial.

By comparing the models with/amphoteric defects, models C/A and D/B respectively, we see that optimum GGI towards the back contact is lower for the models with amphoteric defects compared to their counterparts, while optimum GGI at the CIGS/CdS interface is slightly higher. This difference is an effect predominantly caused by the increased doping in the models with amphoteric defects; a tradeoff between $J_{SC}$ and $V_{OC}$, with a small net efficiency gain, makes it more beneficial with a lower GGI towards the back contact for models C and D as compared to models A and B, where optimum GGI is higher towards the back contact. The increase towards the CIGS/CdS interface is partly a net benefit of efficiency due to the tradeoff between $V_{OC}$ and $J_{SC}$, and partly due to the mitigation of recombination in the SCR via the deep acceptor state of the amphoteric defect complex. The increase in FF originates from the reduced SCR, lowering the recombination that otherwise causes the FF to drop.

In a comparison between respective optimized Ga-profiles, the efficiency is still lower in models C/D, mainly due to a lower $V_{OC}$ caused by higher recombination in the bulk due to a higher mid-gap defect concentration, compared to models A/B. Moreover, there is additional recombination in models C/D via the deep acceptors at 0.85 eV above the valence band, which is especially effective in the SCR close to the interface.

### 3.4. Optimization of double-graded Ga-profiles

For optimization of the DG Ga-profiles, it is observed that the position of the notch can play a crucial role depending on the other parameters in the model, e.g. the value of GGI towards the CIGS/CdS interface. In the case of steep front grading, a notch situated in the SCR can suppress detrimental effects, also noted by Gloeckler and Sites [12]. However, in cases of lower front Ga-grading, it is not detrimental to cell performance to have the notch further away from the CIGS/CdS interface. These situations are illustrated in figure 11.

![Figure 10](image1.png)

**Figure 10.** The optimum single-graded Ga-profile, where the distance starts at the front interface. When compared between the models, the results are similar to each other, and the narrow spread at the front interface corresponds to 4% GGI (comparing models B and C). At the back contact the difference is about 10% GGI (between models A and C).

| Model | $V_{OC}$ (mV) | $J_{SC}$ (mA cm$^{-2}$) | FF (%) | $\eta$ (%) | $J_0$ (A cm$^{-2}$) | $A$ |
|-------|--------------|-------------------|-------|-----------|-----------------|-----|
| A-SG  | 757          | 34.5              | 78.9  | 20.6      | $7.9 \times 10^{-11}$ | 1.48 |
| B-SG  | 746          | 35.1              | 79.4  | 20.8      | $2.8 \times 10^{-11}$ | 1.39 |
| C-SG  | 747          | 34.6              | 79.3  | 20.5      | $2.6 \times 10^{-11}$ | 1.38 |
| D-SG  | 739          | 35.0              | 79.7  | 20.6      | $0.7 \times 10^{-11}$ | 1.29 |
| Reference | 685          | 36.8              | 75.9  | 19.1      | $1.38 \times 10^{-9}$ | 1.56 |

### Table 3. The JV-parameters of the optimized single-graded Ga-profiles.

![Figure 11](image2.png)

**Figure 11.** The efficiency as a function of the position of the notch from the CIGS/buffer layer interface. In the unrestricted case, the maximum efficiency was achieved by having the notch 30 nm from the front interface with a very high front grading; however, when placing the notch at 200 nm from the front interface and optimizing the Ga-profile at this point, the efficiency is not lowered more than 0.1%. Moreover, the lower Ga-grading in such a profile lessens the detrimental effects of having the notch further into the bulk.
A maximum efficiency is observed for a notch situated around 80 nm from the CIGS/CdS interface in models A and B, while for models C and D the maximum was observed for a notch situated 30–40 nm into the CIGS layer. In addition, the optimum GGI towards the CIGS/CdS interface, in the cases of models C and D, are 0.8 and 0.7 respectively. These changes of GGI over such short distances are problematic in terms of stability of the CIGS film, and in practice are impossible to realize. Limited control of the CIGS deposition processes, in part due to thermal diffusion, and inter-diffusion that might take place on a larger time scale are the main factors. Therefore, the constraint not to have the notch closer than 200 nm from the CIGS/CdS interface was introduced for the DG Ga-profile optimization process. Figure 11 shows two cases of the extent of the efficiency variation, compared to an optimized point (highlighted), as a function of the notch position in the absorber. The two illustrated cases consider the constrained case where the Ga-profile is optimized for a notch 200 nm from the CIGS/CdS interface, and the unconstrained case where the position of the notch is 30 nm from the CIGS/CdS interface. The two examples mentioned here come from simulations performed in model D, but the constraint on the optimized DG Ga-profile is applied to all four models, see figure 12. Noteworthy is the insensitivity to the notch position observed for the constrained case as seen in figure 11, and more importantly that it exhibits high efficiencies over a wide range of notch positions. In the unconstrained case, the efficiency drops rapidly when the notch is moved further than 100 nm from the CIGS/CdS interface, and this drop is attributed to a rapid drop of FF.

The JV-parameters for the optimized DG Ga-profiles in the four models can be found in table 4 where the parentheses mark the values from the unconstrained process. The highest efficiency of 21.4% is achieved in model B, and 21.2% is achieved in model A. These are the models without amphoteric defects, and the difference is a tradeoff between $V_{oc}$ and $J_{sc}$, where the simulation in model B has a higher FF due to the lower front grading. When comparing these simulations with the optimum DG Ga-profiles of models C and D, in the former models we see a higher back grading, lower GGI at the notch and therefore a steeper front grading. The difference in back grading is attributed to the difference in doping between the models, similar to the case of optimized SG profiles. The lower and more pronounced notch of models A and B can be attributed to the more extended SCR of these models, due to the lower doping concentration. The simulations show that models C and D, contrary to models A and B, suffer higher SRH recombination via the deep acceptors in the SCR at forward bias due to an increase of minority carriers injected from the buffer layer. Models C and D are in general dominated by SRH recombination throughout the absorber layer. On the other hand, models A and B suffer a dominating radiative recombination current at the notch, which constitutes the critical recombination path due to a high concentration of minority carriers accumulated at the notch. The higher bandgap gradient towards the back contact provides a higher quasi-electrical field, increasing the effective electron diffusion length towards the notch.

3.5. General discussion

The optimized Ga-profiles and the corresponding JV-parameters vary between each model. This shows that there is a dependence on defect-related properties, such as recombination rates and doping concentrations, when optimizing the Ga-profile. Furthermore, it means that a more rigorous electrical analysis is required to have a better understanding and correctly predict the optimum Ga-grading that results in the highest efficiencies for real CIGS thin film solar cells.

Overall, there is a higher efficiency increase in models A and B, when comparing the optimized DG profiles with optimized SG profiles, as compared to models C and D. It increases as much as 0.6% in models A and B, but only 0.1–0.2% in models C and D. Nonetheless, the trend is clear: the optimum DG Ga-profiles perform better in simulations than SG profiles within these models, even if the benefit of the DG Ga-profile is marginal. It turns out that interface traps as set in these models play an important role for simulations with SG Ga-profiles. The interface trap density in the four models play an important role for simulations with SG Ga-profiles. The interface trap density in the four models was set when simulating the measured Ga-profile; however, the power conversion efficiency only changed $+0.1\%$ between the case of nominal ($10^{12}$ cm$^{-2}$) and negligible ($<10^{11}$ cm$^{-2}$) interface trap densities. In the case of optimized Ga-profiles, the same variation—from the nominal value to negligible amounts of interface trap densities—caused the efficiency of the optimized DG Ga-profiles to have a maximum change of $+0.2\%$, while the optimized SG Ga-profiles had an efficiency change of up to $+1.0\%$. Table 5 summarizes these simulations, and in figure 13 there is a comparison of how the efficiency in model A, with the measured Ga-profile (figure 13(a)) and the optimized SG Ga-profile (figure 13(b)), varies with bulk...
defect concentration and interface trap densities. Due to the nature of these simulations, with the Ga-profile being optimized in only one case (figure 13(b)), although not for every point), one cannot compare the absolute values of efficiencies between the two plots. Even so, the trend tells us that if the interface traps can be minimized, the DG Ga-profiles might be redundant. Similar findings were found by Hirai et al [15].

There are several indications that a more advanced simulation tool would be required in order to achieve a better understanding of the complex behaviour exhibited by our device, such as lateral bandgap fluctuations, electromagnetic interference, interfacial parameter-dependence on the underlying bulk material, metastable transitions, and so on. All of these would be of importance to better understand CIGS. The results from the simulations in all the models point towards the same thing: if the quality of our CIGS can be maintained, compared to the measured Ga-profile of the reference device, we would benefit from increasing the overall GGI in the Ga-profile.

### 4. Conclusion

In this work, four SCAPS models were studied and compared with experimental data. The models were different in defect concentration and doping values of the CIGS layer: (A) a simple defect model with a constant concentration of mid-gap recombination centers, (B) a model with a Ga-dependent defect concentration, (C) a model with high doping due to...
the addition of amphoteric defects, and (D) a combination of models B and C. These models were set to fit a high efficiency reference device with a power conversion efficiency of 19.1%. The device was made with a single stage co-evaporation process and characterized with electrical and optical methods, providing input data for the models. Models A and B exhibited better fit with the reference device measurement for JV-simulation at $V < V_{MP}$, while models C and D exhibited better fit for $V > V_{MP}$. Good fits were achieved with all four models by setting a mid-gap defect concentration in the order of $10^{12}$ cm$^{-3}$ in the CIGS layer. Simulations with this low defect concentration indicate that bulk SRH recombination is not the dominant limiting factor for our high efficiency CIGS reference device, and one should also consider that, for long minority carrier diffusion lengths, the back contact surface recombination plays a larger part than for more defective CIGS devices.

In each model, single- and DG Ga-profiles were optimized and compared by using JV-simulations. The optimum DG Ga-profiles yielded 0.2–0.6% higher power conversion efficiencies than the SG counterpart in each model. While the original models were insensitive to the interface trap density between the CIGS absorber layer and the CdS buffer layer, it was clear that for the optimized SG Ga-profile the interface trap density plays a role. Back contact surface recombination impacts the choice of optimum Ga-profile as well, and if the back contact could be passivated, the back grading would be less important. Moreover, if the CIGS/buffer layer interface could be passivated, the front grading would become useless, meaning that a SG Ga-profile might be as effective as a DG Ga-profile.

With the effects of different doping concentrations between the complex and simple defect models in mind, the results are consistent. It is obvious that there is potential to change the Ga-profile in the CIGS layer, and thereby enhance the efficiency of solar cells with a simulated in-line deposition process. If the quality of the CIGS absorber layer can be maintained for this deposition process, power conversion efficiency of 21% or above can be achieved by increasing the GGI and deposit Ga-profiles as proposed in this work.

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