Potential-induced optimization of ultra-thin rear surface passivated CIGS solar cells

Bart Vermang1, 2, Fredrik Rostvall1, Viktor Fjällström1, and Marika Edoff1

1 Ångström Solar Center, University of Uppsala, Uppsala 75121, Sweden
2 ESAT-KU Leuven, University of Leuven, Leuven 3001, Belgium

Received 14 August 2014, revised 9 September 2014, accepted 9 September 2014
Published online 15 September 2014

Keywords solar cells, thin films, CuInGaSe2, surface passivation, sodium

Ultra-thin Cu(In,Ga)Se2 (CIGS) solar cells with an Al2O3 rear surface passivation layer between the rear contact and absorber layer frequently show a “roll-over” effect in the J–V curve, lowering the open circuit voltage (VOC), short circuit current (JSC) and fill factor (FF), similar to what is observed for Na-deficient devices. Since Al2O3 is a well-known barrier for Na, this behavior can indeed be interpreted as due to lack of Na in the CIGS absorber layer.

In this work, applying an electric field between the backside of the soda lime glass (SLG) substrate and the SLG/rear-contact interface is investigated as potential treatment for such Na-deficient rear surface passivated CIGS solar cells. First, an electrical field of +50 V is applied at 85 °C, which increases the Na concentration in the CIGS absorber layer and the CdS buffer layer as measured by glow discharge optical emission spectroscopy (GDOES). Subsequently, the field polarity is reversed and part of the previously added Na is removed. This way, the J–V curve roll-over related to Na deficiency disappears and the VOC (+25 mV), JSC (+2.3 mA/cm²) and FF (+13.5% absolute) of the rear surface passivated CIGS solar cells are optimized.

1 Introduction The two latest hot topics in CIGS (Cu(In,Ga)Se2) solar cell research are potassium fluoride (KF) “front surface passivation” and aluminium oxide (Al2O3) “rear surface passivation”. The KF front surface passivation achieved its name as it essentially embodies passivation improvements located at the front part of CIGS solar cells (absorber-layer/buffer-layer). It consists of a post-deposition potassium treatment of the CIGS absorber layer, which mainly results in enhanced passivation (grain boundaries and donor-like defects) and increased junction depth, but also in thinning of the CdS buffer layer and an increased band-gap (larger Ga content) [1–3]. On the other hand, the Al2O3 rear surface passivation leads to a reduction in interface recombination at the rear of CIGS solar cells (rear-contact/absorber-layer). It consists of an Al2O3 film with nano-sized point openings between the rear contact and the CIGS absorber layer, which results in a reduction of interface recombination by chemical (a reduction in interface trap density) and field-effect passivation (a reduction in surface minority charge carrier concentration), while the point openings allow for contacting [4–6].

Unfortunately, this Al2O3 rear surface passivation layer also acts as a barrier for Na diffusion during CIGS growth, occasionally resulting in underperforming rear passivated CIGS solar cells. Although the actual influence of Na is still debated in the CIGS solar cell research community, it is generally accepted that provision of Na (from the soda lime glass (SLG) substrate and/or a NaF precursor layer) during CIGS growth has a positive effect on device performance. The commonly recognized explanation for this effect is an increase in free carrier density of the CIGS layer by at least one order of magnitude, which can be associated with a lower number of compensating donors [7]. A more detailed description of the influence of Na during CIGS growth can be found in [8]. Unfortunately, the Al2O3 films used as CIGS rear surface passivation layer are also
known to be excellent diffusion barriers [9, 10], and typically only 2% to 5% of their total area is opened [5]. Hence, the Al$_2$O$_3$ passivation layer is a physical barrier for Na and consequently limits Na diffusion from the SLG to the CIGS absorber layer. Therefore, additional Na provided by a NaF precursor layer is required for the rear passivated solar cells [4, 5]. However, it occasionally happens that the NaF layer is too thin resulting in underperforming rear passivated cells, due to a lack of Na as apparent by $J–V$ curves with characteristic “roll-over” effects [4, 5].

In this work it is investigated if the low-performing rear surface passivated CIGS solar cells can be cured (improved) by applying electrical fields in the finished solar cells. It is known that a typical way to migrate Na in CIGS solar cells is to use an electric field between the backside of the SLG and the SLG/rear-contact interface [11–13]. Therefore, the impact of such electrical fields on the cell performance of Al$_2$O$_3$ rear surface passivated CIGS solar cells is investigated and correlated to elemental Na depth profiles in the absorber layer.

### 2 Experimental

The Al$_2$O$_3$ rear surface passivated CIGS solar cell fabrication process is summarized in Table 1. After a glass cleaning step, a Mo layer is deposited as the rear cell contact in an inline sputtering system. It has a sheet resistance of 0.6 $\Omega/\Omega$ and a typical thickness of 350 nm. On top of this rear contact, a CdS layer rich of nano-sphere shaped precipitates is deposited by chemical bath deposition (CBD), and then coated by the Al$_2$O$_3$ rear surface passivation layer. Next, removing the CdS nano-particles successfully generates the nano-sized point openings in the passivation layer. After the formation of this rear passivation structure, first a 15 nm NaF layer is evaporated, followed by co-evaporation of an ungraded CIGS absorber layer of about 400 nm thickness ($[\text{Ga}] / ([\text{Ga}] + [\text{In}]) = 0.3$). As shown in [4–6], these ultrathin ungraded CIGS absorber layers with uniform low Ga concentration are exemplary characterization devices to assess rear surface passivation and rear internal reflection. Next, the buffer layer is deposited using a standard CBD CdS process. Then the shunt-reducing intrinsic ZnO layer (i-ZnO), and subsequently the Al-doped ZnO (ZnO:Al) front contact are sputtered. As front contact grid, a Ni/Al/Ni stack is deposited by evaporation through a shadow mask. This ZnO and Ni/Al/Ni stack have a total thickness around 400 nm and 3000 nm, respectively. Finally, 0.5 cm$^2$ solar cells are defined by mechanical scribing. A more detailed description of the applied cell processing steps can be found in [4–6]. Note that the unpassivated reference cells have the same processing sequence, but without the formation of the advanced rear passivation structure (steps 3–5 in Table 1).

An electrical field strength of +50 or -50 $V_{SC}/mm$ glass thickness is applied between the backside of the SLG and the SLG/Mo interface, two approaches previously called “potential induced degradation” (PID) or “accelerated recovery”, respectively [11–13]. To be able to induce such electrical fields to those cells, first a few extra steps are needed: (i) the sample backside and edges are etched with dilute HCl to remove any conductive paths between the contacts for the external voltage created by the deposition of CdS and/or ZnO:Al; (ii) an electrical contact is applied to the backside of the substrate by means of aluminium tape; and (iii) an electrical contact is soldered to the Mo back contact of the solar cell stack, see [13] for a picture and sketch. This way, an electrical field can be applied between the backside of the SLG and the SLG/Mo interface. The samples are exposed to a temperature of 85 °C in air atmosphere with an applied bias of ±50 V between the glass substrate and the Mo (ground). In case of +50 V, this approach is called PID, as designated and explained in [11–13]. In case of -50 V, the approach is called accelerated recovery, as designated and explained in [13].

Current–voltage ($J–V$) and glow discharge optical emission spectroscopy (GDOES) measurements are performed as described in more detail elsewhere [12, 13]. The $J–V$ measurements are done under illumination from a tungsten halogen lamp, calibrated to match the total photon flux of the AM1.5 G spectrum using a Si-calibration photodiode. The elemental depth profiles are recorded with GDOES in a Spectrums GDA750 (Spectrums Analytik GmbH, Germany).

### 3 Results

Average cell characterization results and representative $J–V$ curves of unpassivated reference CIGS solar cells before and after PID, and after additional accelerated recovery can be found in Table 2 and Fig. 1(a), respectively. Table 2 gives the average cell characteristics of six reference cells (i) as-finished (= before PID), (ii) after 50 h of PID (= after PID), and (iii) 186 h of accelerated recovery later (= after recovery); and also a representative $J–V$ curve is shown for each status in Fig. 1(a).

Average cell characterization results, and representative $J–V$ curves and Na depth profiles in the CIGS absorber layer of Al$_2$O$_3$ rear surface passivated CIGS solar cells before and after PID, and after accelerated recovery can be found in Table 2, and Fig. 1(b) and Fig. 2, respectively.

### Table 1

<table>
<thead>
<tr>
<th>step</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>glass cleaning</td>
</tr>
<tr>
<td>2</td>
<td>Mo rear contact sputtering</td>
</tr>
<tr>
<td>3</td>
<td>CdS particle-rich CdS deposition</td>
</tr>
<tr>
<td>4</td>
<td>Al$_2$O$_3$ passivation layer deposition</td>
</tr>
<tr>
<td>5</td>
<td>CdS particle removal</td>
</tr>
<tr>
<td>6</td>
<td>NaF evaporation</td>
</tr>
<tr>
<td>7</td>
<td>CIGS co-evaporation</td>
</tr>
<tr>
<td>8</td>
<td>CBD CdS buffer deposition</td>
</tr>
<tr>
<td>9</td>
<td>(i-ZnO;Al) window sputtering</td>
</tr>
<tr>
<td>10</td>
<td>0.5 cm$^2$ solar cell scribing</td>
</tr>
</tbody>
</table>
Table 2 Average cell characterization results (AM1.5G) and standard deviation for 0.5 cm² unpassivated reference CIGS solar cells and Al₂O₃ rear surface passivated cells, before and after potential-induced degradation, and after accelerated recovery.

<table>
<thead>
<tr>
<th>status</th>
<th>cell type</th>
<th>( V_{OC} ) (mV)</th>
<th>( J_{SC} ) (mA/cm²)</th>
<th>FF</th>
<th>eff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>before PID</td>
<td>unpass. ref.</td>
<td>574 ± 06</td>
<td>20.8 ± 0.5</td>
<td>70.6 ± 2.1</td>
<td>8.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>rear pass.</td>
<td>618 ± 13</td>
<td>26.1 ± 0.3</td>
<td>54.4 ± 1.6</td>
<td>8.8 ± 0.4</td>
</tr>
<tr>
<td>after PID</td>
<td>unpass. ref.</td>
<td>3 ± 03</td>
<td>5.2 ± 4.5</td>
<td>4.1 ± 10.1</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>rear pass.</td>
<td>234 ± 19</td>
<td>21.8 ± 1.6</td>
<td>22.1 ± 2.3</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>after recovery</td>
<td>unpass. ref.</td>
<td>602 ± 02</td>
<td>21.0 ± 0.3</td>
<td>68.4 ± 0.8</td>
<td>8.7 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>rear pass.</td>
<td>644 ± 06</td>
<td>28.4 ± 0.2</td>
<td>67.8 ± 1.7</td>
<td>12.4 ± 0.3</td>
</tr>
</tbody>
</table>

In the same experiment as the reference cells, also rear passivated cells have been made. Likewise, the average cell characteristics and a representative \( J-V \) curve are given in Table 2 and Fig. 1(b). Additionally, elemental depth profiles have been defined on neighbouring rear passivated cells and the Na profiles are shown for each status in Fig. 2.

4 Discussion Before PID, the rear passivated CIGS solar cells have a higher average \( V_{OC} \) (+44 mV) and \( J_{SC} \) (+5.3 mA/cm²) compared with corresponding unpassivated reference cells, but lose FF (–16.2%) due to Na deficiency in the absorber layer. As-finished, higher \( V_{OC} \) and \( J_{SC} \) can be seen in Table 2 for the Al₂O₃ rear passivated cells. This can be explained by an increase in rear surface passivation and rear internal reflectance thanks to the passivation layer, as already discussed in [6]. However, the FF of these passivated cells is lower than is the case for the reference cells. This is most probably due to a lack of Na in the CIGS absorber layer, as can be seen from the “roll-over” effect shown in the \( J-V \) curve; see Fig. 1(b) and [4, 5]. It is indeed known that this Al₂O₃ passivation layer is an effective barrier layer for Na diffusion [10]. Hence, Na deficiency will occur if the contacting area is too small. As the formation of openings in the passivation layer by removal of nanoparticles is a statistical process step, it can indeed result in too small (this work) or sufficient (as reported in [6]) contacting area.

After 50 h of PID, both cell types have degraded, but the rear passivated cells still show diode behaviour while the reference cells show resistive behaviour. After degradation, the average efficiency of the passivated and unpassivated cells is reduced to respectively 1.1% and 0.0%, due to losses in \( V_{OC} \), \( J_{SC} \) and FF. However, Fig. 1 clearly indicates that the passivated cell still is a diode after degradation, which is not the case for the reference cell. In [12], the degradation of unpassivated reference cells after PID has been correlated to Na migrating into the CIGS absorber and CdS buffer layer. It is the same degradation mechanism – but slower – that applies to the rear passivated cells. Indeed, also in the rear passivated cells, a noticeable increase in Na concentration in the CIGS absorber and the CdS buffer layer is measured, as depicted in Fig. 2. However, in this case the previously described Na barrier effect of Al₂O₃ passivation layers most likely slows down the degradation process.

Accelerating the recovery of both cell types for 186 h brings the reference cells to a similar level as before PID, but improves the average \( V_{OC} \) (+25 mV), \( J_{SC} \) (+2.3 mA/cm²) and FF (+13.5% absolute) of the rear passivated cells due to Na profile optimization in the absorber layer. In [13], recovery of unpassivated reference cells degraded by PID has been correlated to Na migrating out of the CIGS absorber and CdS buffer layer; so part of the Na concentration added during PID is again removed during recovery. This way, solar cell characteristics can be restored, as shown in [13] and Table 2. However, in this work small changes in \( V_{OC} \) and FF are measured after re-
covery of the unpassivated reference cells, which might be
due to the fact that ultra-thin CIGS absorber layers are used.
Contrarily, large increases in $V_{OC}$, $J_{SC}$ and FF are measured
after accelerated recovery of the rear passivated cells, as
also listed in Table 2. Also in this situation, only part of the
Na concentration added during PID is removed during re-
covery (Fig. 2). Moreover, the $J$–$V$ curve roll-over of the
initial Al$_2$O$_3$ rear passivated cell disappeared after PID and
subsequent recovery (Fig. 1(b)), which leads to increased
FF and thus also $V_{OC}$ and $J_{SC}$. Hence, this indicates that PID
followed by accelerated recovery can be applied to optimize Na
profiles in CIGS absorber layers of these rear passivated
solar cells. Note that: (i) the Na profile after recovery is
shown before and after potential induced degradation, and after accelerated recovery. A
transmission electron microscopy cross-section picture is used as background, a guide to the eye.

5 Conclusions
In this work, electrical fields between the backside of the SLG substrate and the SLG/Mo interface have been used to optimize the Na concentration in Al$_2$O$_3$ rear surface passivated CIGS solar cells. These Al$_2$O$_3$ films are excellent diffusion barriers, which occasionally leads to underperforming rear surface passivated CIGS solar cells due to insufficient Na diffusion from the SLG during CIGS absorber layer growth. This Na deficiency is apparent in the solar cell $J$–$V$ curve by a characteristic “roll-over” effect; and PID followed by accelerated recovery has been used to optimize the Na concentration of such Na-deficient solar cells. This way, Al$_2$O$_3$ rear surface passivated CIGS solar cells are optimized, leading to higher $V_{OC}$ (+42 mV), $J_{SC}$ (+7.4 mA/cm$^2$) and similar FF compared to the corresponding unpassivated reference cells. This increase in $V_{OC}$ and $J_{SC}$ can be explained by enhanced rear surface passivation and rear internal reflectance due to the Al$_2$O$_3$ passivation layer, as previously discussed in [6].

Although the applied method appears to be a very interesting approach to improve the quality of CIGS absorber layers, the method seems to be too lengthy to be viable for actual photovoltaic production and many questions about its fundamental nature and long-term stability are fuel for future research.

Nevertheless, it is a great novel technique to acquire more insight into the role of alkali metals (Na, K, ...) in thin-film solar cells, and it will also be interesting to test this methodology on other thin-film solar cell technologies.

Acknowledgements B. Vermang acknowledges the financial support of the European Commission (via FP7 Marie Curie IEF 2011 Action No. 300998), the Swedish Science Foundation (VR), and the Swedish Energy Agency.

References