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ABSTRACT

Al₂O₃ rear surface passivated ultra-thin Cu(In,Ga)Se₂ (CIGS) solar cells with Mo nano-particles (NPs) as local rear contacts are developed to demonstrate their potential to improve optical confinement in ultra-thin CIGS solar cells. The CIGS absorber layer is 380 nm thick and the Mo NPs are deposited uniformly by an up-scalable technique and have typical diameters of 150 to 200 nm. The Al₂O₃ layer passivates the CIGS rear surface between the Mo NPs, while the rear CIGS interface in contact with the Mo NP is passivated by [Ga]/([Ga] + [In]) (GGI) grading. It is shown that photon scattering due to the Mo NP contributes to an absolute increase in short circuit current density by 3.4 mA/cm², as compared to equivalent CIGS solar cells with a standard back contact.

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1. Introduction

One way to lower the cost of Cu(In,Ga)Se₂ (CIGS) solar cells is to reduce the thickness of the CIGS absorber layer (tₐ). First, this will cut material usage – critical feedstock materials are In and Ga [1] – and thus material cost. Furthermore, tₐ reduction has the potential to increase manufacturing output due to shortened deposition times. And, finally, using less absorber material might even lead to higher efficiencies thanks to the associated reduction in bulk defects (i.e. if optical confinement and rear surface passivation are kept satisfactory).

Recombination at the Mo/CIGS rear interface can be reduced by introduction of a rear surface passivation layer with nano-sized point openings [3,4]. This idea stems from the Si solar cell industry, where rear passivation layers are combined with micron-sized point openings to boost Voc. See e.g. Ref. [5]. The passivation layer is known to reduce interface recombination by chemical (equals a reduction in interface trap density at the rear CIGS surface) and field-effect passivation (equals a fixed charge density in the passivation layer that reduces the surface minority or majority charge carrier concentration), while the point openings allow for contacting. Such a typical Si surface passivation layer is Al₂O₃, as described in Ref. [6]. In Refs. [3,4,7], equivalent Al₂O₃ layers are used to passivate the rear CIGS surface and the formation of nano-sphere shaped precipitates in chemical bath deposition (CBD) of Cds to generate point contact openings. This way, an obvious increase in Voc is measured for the rear passivated CIGS solar cells with ultra-thin absorber layers compared to corresponding unpassivated standard cells, as is shown in Fig. 1(a). Moreover, using a solar cell capacitance simulator (SCAPS) to model the Al₂O₃ rear surface passivated cells, the minimal Sb has been estimated to be as low as 100 cm/s [3]. Note that comparing the Voc of rear surface passivated Si solar cells and unpassivated reference cells (see e.g. Fig. 4 in [5]) shows a very similar tendency as depicted in Fig. 1(a).

Additionally, also rear reflection can be enhanced by applying the same advanced rear contacting structure [7]. In Si solar cells, Rs is optimized applying rear surface passivation layer stacks with a total...
thickness of several hundreds of nanometers [8]. Equally, in Ref. [7] rear internal reflection is improved by increasing the thickness of the Al₂O₃ passivation layer, or stacking a thin Al₂O₃ interface passivation layer on top of another thick layer (e.g. MgF₂). Hence, JSC is enhanced substantially for the ultra-thin rear passivated solar cells compared to matching unpassivated standard cells, as shown in Fig. 1(b). Note that there is a practical limit to increasing the thickness of the rear surface passivation layer as the CIGS absorber layer itself is only a few hundreds of nanometers thick.

Due to reflection limitations of passivation layers, supplementary ways to optimize optical confinement in ultra-thin CIGS solar cells are needed. In Fig. 1(b), there is still a difference in JSC between rear passivated ultra-thin CIGS cells and standard thick cells, while JSC losses can be completely avoided for rear passivated Si solar cells with reduced Si thickness (see e.g. Fig. 3 in [8]). As this loss in JSC is mainly caused by rear reflected photons escaping at the front surface of the solar cell, additional methods to prolong the travel path of photons are sought for.

In this work, rear surface passivated CIGS solar cells with Mo nanoparticles (NPs) as local rear contacts are developed to demonstrate that these Mo NPs show potential to improve optical confinement of ultra-thin CIGS solar cells by increased scattering of photons.

2. Experimental details

The Mo NPs are deposited uniformly by an upscalable technique and have typical diameters of about 150 to 200 nm. Negatively charged Mo NPs are first grown in a highly ionized pulsed plasma and then – thanks to their electrostatic repulsion – evenly spread onto a Mo coated soda lime glass (SLG) substrate; as described in more depth in Refs. [9,10]. A top-view scanning electron microscopy picture of Mo NP on a SLG/Mo substrate is shown in Fig. 2. This Mo NP density has been chosen, as it is comparable to the density of the CdS rear passivated CIGS solar cells.

A summary of the applied cell processing steps is given in Table 1; a more detailed description of the fabricated 0.5 cm² SLG/Mo(Mo NP/Al₂O₃)/CIGS/CdS/ZnO/ZnO:Al/MgF₂ anti-reflective coating (ARC) solar cell devices with thin co-evaporated CIGS absorber layers, and the performed J–V and external quantum efficiency (EQE) measurements can be found elsewhere [3,4,7].

A cross section picture of an Al₂O₃ rear surface passivated CIGS solar cell with Mo NP contacts can be found in Fig. 3: (a) A transmission electron microscopy (TEM) cross section picture and (b) an energy-dispersive X-ray spectroscopy (EDS) map for the elements Cu, Al and Mo in such a cross section.

3. Results and discussion

3.1. Constant GGI

Introducing Mo NP at the Mo/CIGS rear interface increases photon scattering, but also recombination, which can be partly off-set by passivating the Mo/CIGS interface between the NPs with Al₂O₃. Table 2 gives an overview of average cell characterization results of unpassivated CIGS solar cells with and without Mo NP at the Mo/CIGS interface as well as Al₂O₃ rear surface passivated CIGS solar cells with Mo NP contacts. In all cases, the t_CIGS is 350 nm with the [Ga]/([Ga] + [In]) (GGI) ratio constant and equal to 30%. This table shows that introducing Mo NP at the rear interface of standard CIGS solar cells lowers V_OC and increases J_SC. This lower V_OC and higher J_SC can be explained by respectively the increase in Mo/CIGS interface area and the increase in photon scattering, both due to the Mo NP. However, direct current (DC) sputtering of a thin Al₂O₃ layer (10–15 nm, see Fig. 3(b)) on the 150–200 nm Mo NP before CIGS deposition passivates the Mo/CIGS interface between the NPs and reduces this loss in V_OC. Also, the reasonable fill factor (FF) of these Al₂O₃ rear passivated cells shows that – thanks to the characteristic directionality of sputtering processes – parts of the Mo NP remain uncovered and thus serve as rear contacting area, as
already seen in Fig. 3(b). However, there is a residual loss (relative loss = 11%) in $V_{OC}$ compared to the unpassivated standard cells without Mo NP, since the total unpassivated surface area of the Mo NP still remains large. A few notes: (i) a simple estimation indicates that the Mo/CIGS contacting area in the standard unpassivated cells and passivated cells with Mo NP is in the same order, if one takes into account that the particles are not completely spherical and that there is uncoated Mo/CIGS area around the Mo NP after Al$_2$O$_3$ sputtering (see Figs. 2 and 3); and (ii) the Mo NP contacts separate both contributions.

### 3.2. Single-graded GGI

Introducing a back surface field (BSF) in the CIGS absorber layer to passivate the Mo NP surface area in contact with this absorber layer lowers recombination even further. Table 2 gives an overview of standard cells with and without Mo NP and rear passivated cells with Mo NP contacts, but now GGI is single-graded (from 40% (rear) down to 20% (front)) and t$_{CIGS}$ equals 380 nm. Such a GGI gradient is known to create a BSF, which will reduce recombination in the rear part of the cell. However, this strategy also leads to another absorption problem in spite of the similar average GGI ratio as compared with the cells presented in Section 3.1. Also in the case of single-graded GGI, standard cells with Mo NP lose $V_{OC}$ and gain $J_{SC}$ compared to standard cells without Mo NP, and this loss in $V_{OC}$ is reduced by implementing an Al$_2$O$_3$ rear surface passivation layer. This time a relative loss in average $V_{OC}$ of 7% remains between rear passivated cells with Mo NP and standard cells (which is lower than when a uniform GGI is used, because of the BSF). Comparing the rear passivated cells with Mo NP to the standard cells in more detail, there is a small increase in average efficiency (0.4% absolute) thanks to a clear increase in $J_{SC}$ (3.4 mA/cm$^2$ absolute) but correlated to a decrease in $V_{OC}$. Representative J–V and EQE curves of all these cells can be found in Fig. 4. The J–V graph shows that the FF is low for the standard cells with Mo NP, due to an increase in series resistance ($R_s$) and shunt conductance ($G_{sh}$) compared with standard cells without Mo NP. $G_{sh}$ is increased due to an increase in rear surface recombination (more recombination current due to the large Mo/CIGS interface area); while $R_s$ is increased as the contact grid of Mo NP is only sub-optimized (the Mo NP process is highly randomized). For the rear passivated cells with Mo NP, $G_{sh}$ is at the same level as the standard cells without Mo NP (as the rear surface passivation is at the same level), and $R_s$ is still higher compared with these standard cells (also here, the contact grid of Mo NP is only sub-optimized). The EQE curves show increased photon absorption in a broad wavelength range for the (rear passivated) cells with Mo NP. Additionally, Fig 4(b) also shows that this increase in EQE is mainly caused by increased photon scattering due to the Mo NP as expected, since passivation layer reflection is negligible for such a thin Al$_2$O$_3$ layer [4]. However, a more detailed front scattering and back reflection study is needed to separate both contributions.

### Table 2

Overview of average cell characterization results (AM1.5 G) for 0.5 cm$^2$ unpassivated standard CIGS solar cells (with and without Mo NP at the Mo/CIGS interface) and Al$_2$O$_3$ rear surface passivated cells with Mo NP contacts. GGI is constant and equals 30%; and $t_{CIGS}$ is 380 nm. Note that these cells are without an anti-reflective coating.

<table>
<thead>
<tr>
<th>Cell description</th>
<th># cells</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>6</td>
<td>572 ± 07</td>
<td>20.4 ± 0.6</td>
<td>70 ± 2</td>
<td>8.2 ± 0.4</td>
</tr>
<tr>
<td>Standard + Mo NP</td>
<td>6</td>
<td>347 ± 10</td>
<td>21.7 ± 0.3</td>
<td>43 ± 3</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>Standard + Mo NP + Al$_2$O$_3$</td>
<td>6</td>
<td>508 ± 39</td>
<td>22.1 ± 0.4</td>
<td>57 ± 3</td>
<td>6.4 ± 0.9</td>
</tr>
</tbody>
</table>

### Table 3

Overview of average cell characterization results (AM1.5 G) for 0.5 cm$^2$ unpassivated standard CIGS solar cells (with and without Mo NP) and Al$_2$O$_3$ rear surface passivated cells with Mo NP contacts. GGI is single-graded: from 40% (rear) down to 20% (front); and $t_{CIGS}$ is 380 nm.

<table>
<thead>
<tr>
<th>Cell description</th>
<th># cells</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>6</td>
<td>568 ± 17</td>
<td>22.2 ± 0.4</td>
<td>67 ± 7</td>
<td>8.4 ± 1.3</td>
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<tr>
<td>Standard + Mo NP</td>
<td>6</td>
<td>463 ± 20</td>
<td>25.3 ± 0.5</td>
<td>49 ± 3</td>
<td>5.8 ± 0.7</td>
</tr>
<tr>
<td>Standard + Mo NP + Al$_2$O$_3$</td>
<td>6</td>
<td>530 ± 31</td>
<td>25.7 ± 0.4</td>
<td>65 ± 2</td>
<td>8.8 ± 0.8</td>
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</tbody>
</table>
4. Conclusions and outlook

Mo NP can potentially optimize light management in ultra-thin CIGS solar cells, if recombination at the large Mo/CIGS interface area is kept sufficiently low. Proof-of-principle ultra-thin ($t_{\text{CIGS}} = 380$ nm) Al$_2$O$_3$ rear surface passivated CIGS solar cells with Mo NPs as local rear contacts have been developed with an average efficiency of $8.8\%$. The Al$_2$O$_3$ layer passivates the CIGS rear surface between the Mo NPs, while the impact of the highly recombinative rear CIGS interface in contact with the Mo NP is reduced by GGI grading. It is shown that photon scattering due to the increased roughness of front and rear CIGS surfaces contributes to a clear increase in $J_{\text{SC}}$, as compared to corresponding ultra-thin standard CIGS solar cells.

There is still room to improve the suggested approach through e.g. (i) fine-tuning the shape, size and density of the Mo NP (to optimize scattering or obtain plasmonic light trapping), (ii) improvement of the passivation layer quality (thickness, alternative layers), (iii) reduction of the series resistance of the cells (adapted cell processing), and (iv) refinement of the GGI profile (double-grading).

Acknowledgments

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