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Innovative and industrially viable approach to fabricate AlO_x rear passivated ultra-thin Cu(In, Ga)Se₂ (CIGS) solar cells.

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15 <u>Abstract</u>

16

17 In this work, an industrially viable and novel rear surface passivation approach for Copper 18 Indium Gallium di-Selenide, Cu(In, Ga)Se₂, CIGS, ultra-thin (500nm) solar cells is developed. 19 The passivation layer was deposited by atomic layer deposition (ALD), and an alkali treatment 20 was applied via spin coating. It was observed that selenization of the samples is required to 21 create contact openings. The openings were visualized by SEM, and these results were 22 supported by EDS. The impact of the oxide layer's thickness, as well as the alkali solution's 23 molarity, was studied. Solar cells were produced for the optimal combination of these two 24 parameters. As a result, with a relative 13% increase, the highest V_{oc} of 623mV was achieved. 25 Hence, the efficiency of the passivated solar cell was relatively increased by one-third, by using 26 an industrially feasible, fast, and repeatable technique.

1. Introduction

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30 Today, one of the most efficient thin-film photovoltaic (PV) technology is CIGS multi-31 crystalline thin-film solar cells (Green et al., 2020). In order to compete with other solar cell 32 technologies, the production costs should be reduced, and the structure should be simplified. 33 To make cheaper solar cells, reducing the thickness of the absorber layer is one solution. 34 However, reducing the thickness of the absorber layer has drawbacks like incomplete 35 absorption and increased back-contact recombination, both resulting in power conversion 36 efficiency losses (Naghavi et al., 2016), (Umehara et al., 2016). One solution is to implement 37 a rear surface passivation layer, which has the potential to reduce rear surface recombination 38 velocity and increase rear internal reflection (Poncelet et al., 2018). However, CIGS solar cells 39 generally benefit from the sodium (Na) coming from the soda-lime glass substrate (Li et al., 40 2019), (Rudmann, 2004). Usage of a dielectric layer at the rear surface, such as alumina (Al₂O₃) 41 which is an ideal passivation layer (Groner et al., 2002), (Poncelet et al., 2017), unfortunately, 42 acts as an electron and diffusion barrier layer, and thus prevents current flow and the Na diffusion. In order to overcome these problems, there needs to be contact openings in this 43 44 passivation layer. In reference (Vermang et al., 2014b), the rear surface passivation technique 45 used for silicon (Si) solar cells was implemented to CIGS solar cells. In that study, Al₂O₃ was

used as the rear surface passivation layer, and nano-sized point contact openings were realized
via chemical bath deposited CdS nanoparticles (Vermang et al., 2014b). Over the years, many
research groups developed and applied different techniques to generate these openings in
various dielectric layers, see (Birant et al., 2019). Almost all of the proven methods – e.g.,
using nanoparticles, e-beam or nano-imprint lithography – are well controlled, but also
expensive, time-consuming or not applicable for larger areas, see (Necas and Klapetek, 2012),
(Vermang et al., 2015) and (Yin et al., 2017).

D. Ledinek et al. previously proposed using a very thin layer of Al₂O₃ as rear surface 53 54 passivation in combination with NaF evaporation to enhance the electrical characteristics of 55 CIGS solar cells. In their study, the surface passivation layer is claimed to have a porous 56 structure that allows direct contact between Mo and CIGS, and they supported their claims with 57 TEM and XPS analysis (Ledinek et al., 2018). The proposed method in our study is to spin-58 coat the NaF on top of the Al₂O₃ passivation layer, which will generate contact openings during 59 selenization. The generated contact openings were visualized by SEM prior to and after CIGS 60 deposition. The aim is to prove that by using a simple, cost-effective, and fast process, it is 61 possible to passivate the rear surface of ultra-thin CIGS solar cells, and hence, increase the 62 efficiency, i.e., make it cheaper and industrially feasible.

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2. Experimental details:

66 In this section, the implementation of the novel rear surface passivation approach into the 67 standard solar cell structure is explained. The proposed method is to spin-coat sodium fluoride 68 (NaF) on top of the Al₂O₃ passivation layer to generate the contact openings during 69 selenization. Al₂O₃ passivation layer was deposited through atomic layer deposition (ALD) at 70 300°C. During the depositions, trimethylaluminum (TMA) was used as the precursor, and H₂O 71 used as the reactant. The nm/cycle rate was calculated to be 0.17, by measuring the Al_2O_3 72 thickness on Mo with ellipsometry and assuming a constant growth rate with time. The 73 proposed rear surface passivation approach is integrated into the standard stack: 74 SLG/Mo/AlOx/CIGS/CdS/i-ZnO/ZnO:Al/Ni-Ag-Ni grids, where solar cell devices have 75 ultrathin (500 nm), single-stage and ungraded, i.e. without Ga-grading, CIGS absorber layers 76 with ([Cu]/([Ga] + [In]) = 0.83 and ([Ga]/([Ga] + [In]) = 0.33, with active area of 0.5cm². In 77 this study, a flat Ga profile was preferred to eliminate reciprocal rear surface passivation effects 78 of Ga-grading (Vermang et al., 2014b), (de Wild et al., 2019).

- 79
- **80 Table-1** Overview of all steps required to produce sample Set 1 and Set 2
- 81

Step	Sample Set 1	Sample Set 2			
1	Substrate cleaning	Substrate cleaning			
2	Al ₂ O ₃ passivation layer deposition	Al ₂ O ₃ passivation layer deposition			
	(2nm-10nm)	(6nm)			
3	NaF spin coating (0.4M)	NaF spin coating (0.2M-0.4M)			
4	Selenization	Selenization			

- 83 In order to identify the optimal parameters, two sets of samples were prepared: altering, first,
 84 the thickness of the dielectric layer (Set 1), and second the molarity of the alkali solution (Set
 85 2); see Table-1 and Figure-1. For both sets, and for each parameter, two different samples were
 86 produced: one for characterization and one for solar cell production. As the substrate, 3mm
 87 thick soda-lime glass (SLG) with Si(O, N) barrier layer, which has 300nm molybdenum (Mo)
- **88** as the rear contact, was used.



Figure 1 Sketch of the two sets of samples with altering i- Al₂O₃ thickness and ii- NaF
molarity; to investigate their effects on passivation characteristics and openings.

92

93 For Set 1, five different Al₂O₃ layer thicknesses were tested, starting from 2nm and ending with 94 10nm, by 2nm steps. Following the Al₂O₃ depositions, 0.4M NaF was spin-coated on those 95 layers. Characterization samples were selenized at 540°C, for 10 minutes, in order to mimic the absorber layer deposition environment. For selenization, a quad-elliptical radiant heating 96 97 chamber and pure selenium particles were used. This process has occurred under a vacuum. To 98 monitor the formation of the openings, characterization samples underwent several 99 characterization steps. As a first step, scanning electron microscopy (SEM) imaging and 100 energy-dispersive X-ray spectroscopy (EDS) analysis was done with a Tescan and Bruker 101 SEM. In order to calculate the density of the opening-like structures, a data analysis software 102 named Gwyddion was used. This software can analyze and compare the height difference 103 between the two layers by using SEM images (Necas and Klapetek, 2012). In our case, it spots 104 the height difference between the alumina layer and the molybdenum back contact and gives 105 the percentage of the contact openings. An example of the Gwyddion analysis is shown in 106 Figure-2-a. We used three different SEM pictures with varying magnifications for each sample, 107 and use the arithmetic average of those three images while calculating the surface coverage 108 (SC) ratios.

- **109** In order to decide the optimal thickness of the dielectric layer, samples that were completed as
- solar cells were used. According to the IV results, the optimal thickness was chosen as 6nm.Concerning the molarity of the NaF solution, i.e., Set 2, two different molarities were tested,
- 112 0.2M and 0.4M, with a 6nm Al_2O_3 layer. Also, regarding the necessity of this treatment,
- samples without any alkali treatment, i.e., 0 M condition, were prepared. Similar to Set 1, these
- samples also underwent the same characterization steps, and 0.4M was chosen as the optimal
- molarity for our approach. Exact reasons why we chose the thickness and the molarity as 6 nm
- 116 and 0.4M, respectively, will be shared in the following section.
- **117** Production steps of the reference and passivated solar cells are shared in Table-2. For the
- **118** passivated solar cell, the aforementioned optimal parameters were used, and the detailed
- **119** explanation of the steps for the reference sample can be found in (de Wild et al., 2019).

120 The completed solar cells were characterized by JV measurement under AM 1.5 illumination.

- 121 The Voc, Jsc, FF, and efficiency were derived from the JV curves. Twelve cells were measured
- 122 for reference and passivated samples, and the arithmetic average results are shared in Table-3.
- 123 The values for saturated current density (J_0) , shunt and series resistances (Rsh and Rs) are
- 124 calculated from the dark JV measurement using a MATLAB routine. J_0 values are extracted
- 125 from the JV curve, which is corrected for Rs and Rsh, with a 1-diode model.
- 126

127 Table-2 Overview of all steps required to produce reference Cu(In, Ga)Se₂ solar cells and
 128 Al₂O₃ rear surface passivated cells with contacts.

129

Step	Description					
	Reference	Passivated				
1	Substrate cleaning	Substrate cleaning				
2		Al ₂ O ₃ passivation layer deposition				
3	NaF spin coating	NaF spin coating				
4	1 stage ultra-thin (500 nm) CIGS	1 stage ultra-thin (500 nm) CIGS				
	absorber co-evaporation	absorber co-evaporation				
5	CBD CdS buffer deposition CBD CdS buffer deposition					
6	i-ZnO and ZnO:Al window sputtering	i-ZnO and ZnO:Al window sputtering				
7	Ni/Al/Ni front contact evaporation	Ni/Al/Ni front contact evaporation				

130

EQE was measured under dark conditions and scanned through the wavelength interval of 3501300nm in 5nm steps. For the passivated sample, Jsc values were extracted from the EQE, and
the efficiencies recalculated accordingly. PL and TRPL measurements were carried out in a
photo spectrometer from Picoquant with a TimeHarp 260 single-photon counter for the timeresolved measurements. The excitation intensity is approximately 0.2 W cm⁻², the repetition
rate is 3 MHz, and the wavelength is 532nm.

|37 |38

3. <u>Results and discussion:</u>

139

3.1 Creation of the contact openings:

In order to interpret the effect of NaF spin-coating on the alumina passivation layer during
selenization, two characterization sample sets were used as described above. To monitor the
results of this process, SEM imaging was done before and after this step, and results were
supported with EDS analysis, see Figure-2-b. In the end, it was experimentally proven that,
during the selenization, in certain cases, contact openings are formed in the passivation layer.

- 146 The impact of the thickness of the dielectric layer and the molarity of the alkali solution on the
- density and size of the contact openings was also investigated, see Figure-3-a. By considering
- 148 the change in the surface coverage ratios as well as the shape and the size of the openings,
- 149 samples that were finished as solar cells were used to assess the impact of this difference on
- **150** open-circuit voltage, Voc.
- 151



|52 |53

Figure 2 a-SEM picture of the optimal sample after selenization and b- EDS line scan to prove
the existence of the openings in the dielectric layer (inset SEM picture of the analyzed sample)
and c- example of Gwyddion analysis with calculated surface coverage ratio.

158 As can be seen from Fig.3-b, there is an inverse relation between Voc and the SC. The **159** discussion part for this graph is divided into two subsections: 3.1.1- effect of the thickness of **160** the Al₂O₃ layer and 3.1.2- effect of the molarity of the alkali solution. In the end, there is **161** section iii, which will contain the discussion associated with the solar cells prepared with the **162** optimal conditions decided according to subsections 3.1-a and 3.1-b.

163

164 3.1.1 Effect of the thickness of the alumina layer, Set 1:

165 For this set, in order to monitor the effect of the thickness of the Al₂O₃ layer, we kept the 166 molarity of the alkali solution as 0.4M for all of the samples. As can be seen from Fig.3-a, for 8nm and 10nm thick alumina layers, we could not detect any opening like structure. On the 167 other hand, for 2nm, 4nm, and 6nm thick alumina layers, we were able to observe openings in 168 the alumina layer. For those samples, the surface coverage ratios were calculated with the help 169 170 of Gwyddion software, as described in Fig.2-c. If Fig.3.b is investigated further in terms of the 171 thickness of the Al₂O₃ layer, it can be seen that until the 8nm thick dielectric layer, the Voc is 172 improved compared to the reference. However, for 8nm and 10nm thick Al₂O₃ layer, the Voc 173 is worse than the rest of the Set-1, including the reference. This information is vital for us to 174 understand that, with our novel contacting approach, thicknesses over 6nm is not suitable for 175 rear surface passivation.

176





Figure 3 a-Molarity vs. thickness of the aluminum oxide layer with insets of SEM images, 179 Gwyddion masks and surface coverage ratios of samples belongs to Set 1 and Set 2, and b-180 Open circuit voltage and surface coverage ratios vs. thickness of the aluminum oxide layer for 181 the same set of samples; box charts represents the Voc and boxes represents the SC (%). The 182 arrows are given to emphasize the inverse relation between Voc and SC in terms of Al₂O₃ thickness.

183 When we compare our surface coverage (SC) results with other groups, we realized a slight 184 difference. In (Casper et al., 2016), they studied rear surface passivation of ultra-thin CIGS solar cell, by using 25nm and 50nm thick Al₂O₃ as the passivation layer, and the contact 185 openings were realized by lithography, i.e., they had controlled size and distribution for the 186 187 openings. They experimentally proved that 90% surface coverage gave the best Voc. In 188 (Vermang et al., 2014a), on the other hand, it was mentioned that the 5% contact opening area, 189 i.e., 95% surface coverage, in 5nm thick Al2O₃ layer is sufficient for passivation. In our case, we got the best Voc from 6nm thick Al₂O₃, i.e., 83% SC (Fig.3-a). The reason for this 190 191 difference can be explained by our novel approach. Since the size and the distribution of the 192 openings are reasonably random, and not yet controllable, it is reasonable to have slightly 193 different results from the literature. The detailed solar cell results will be shared and discussed 194 in the following section. The JV results showed that for 2nm (95% SC) and 4nm (90% SC) 195 thick layers, there was a little enhancement in Voc values as compared to the reference, i.e., 196 unpassivated solar cell, but it was not as significant as a 6nm (83% SC) thick layer. Since the 197 effect of the rear surface passivation reveals itself as an increased diffusion length of the 198 minority carriers due to the created field effect, the difference in these results can be explained 199 by the insufficient thickness of the dielectric layer and the non-optimized contacting approach 200 (Kotipalli, 2016). For 8nm and 10nm thick layers, on the other hand, the current was almost 201 completely blocked, and the passivation layer acted as a barrier layer. The JV curves of those 202 samples showed us that the sample with an 8nm thick Al₂O₃ layer has suffered from low shunt 203 resistance, and the sample with a 10nm thick Al₂O₃ layer had high series resistance, both results 204 in low FF, hence low power conversion efficiency. (Supporting Figure 1) Therefore, we proved 205 that 8nm and 10nm are too thick for described alkali treatment to make sufficient openings 206 with our approach, and consequently, we decided to use a 6nm thick alumina layer for further 207 experiments.

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209

3.1.2 Effect of the molarity of the alkali solution, Set 2:

210 After optimizing the thickness of the passivation layer to 6nm, we investigated the necessity of 211 the alkali treatment. To do so, two samples were prepared, one without any alkali treatment 212 and one with a 0.2M NaF solution. As can be seen from Figure-3-a, if we do not use any alkali 213 solution, there will be no opening-like structures in the alumina layer. On the other hand, for 214 the 0.2M NaF solution, we were able to detect and analyze the openings. There is a slight 215 difference in SC ratios between 0.2M (86.5% SC) and 0.4M (83% SC) NaF solutions. 216 However, if the solar cell parameters, especially the Voc, are compared, it is safe to say that 217 0.4M NaF works better than 0.2M NaF, see Figure-3-b.

218 According to the JV measurement, it is clear that the alkali treatment is necessary since the 219 current is completely blocked, resulting in diode like response under illumination, for the solar 220 cell that has no alkali treatment. Besides, for 0.4M NaF, as told earlier, we achieved better solar 221 cell characteristics in comparison to 0.2M NaF. The FF, for instance, is noticeably lower for 222 0.2M NaF sample, 20% less than 0.4M NaF sample, which was resulting in lower power 223 conversion efficiency. (Supporting Figure 2) This can be explained by the lack of contact 224 openings due to less alkali salt crystal and/or lack of Na supply due to low concentration. 225 Hence, we decided to use a 0.4M NaF solution from this point forward.

226

227 *3.1.3* Solar cells prepared with optimal conditions:

228 After we validated our approach regarding the openings with the help of two sets of 229 characterization samples, the next step was to prove that our assumption is valid for finished 230 solar cells. We prepared a sample with the optimal conditions again. The first aim is to show 231 the process's repeatability, and the second aim is to use that sample for detailed electrical and 232 optical analysis. After completing the measurements, we picked the solar cell with the highest 233 efficiency, and then made a scratch with the help of a tweezer to remove the window layer and 234 the absorber layer. The aim is to prove that the contact openings are realized in the dielectric 235 layer during CIGS absorber layer deposition. Since we only mimicked the environment for 236 characterization samples, it is always possible that during the actual deposition, conditions can 237 slightly differ. After we made the scratch, we were able to prove that there were contact 238 openings created in the passivation layer for a finished solar cell as well, by using SEM and 239 EDS measurements. (Supporting Figure 3) As a result, we proved that with our novel approach, 240 contact openings could be realized in the dielectric passivation layer with a fast and cost-241 effective technique.

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3.2 Electrical and optical analysis of the solar cell devices produced with optimal parameters:

246 In this section, we present the results of the solar simulator, EQE, and TRPL. The results of247 these measurements will be shared and discussed in detail.

248 The arithmetic average of standard solar cell parameters for the 12 best cells for passivated and
249 reference samples is given in Table-3. Further, two passivated cells that have the best efficiency
250 and the best Voc when compared to the other cells are shared as well.

25 I The addition of the passivation layer with contact openings leads to an increase in nearly all 252 solar cell parameters compared to standard unpassivated solar cells. We extracted the Jsc values 253 from the EQE for the best two solar cells only, in order to avoid potential errors caused by the 254 grids or scribing. Then, the power conversion efficiency values for those two best cells are 255 recalculated (Table-3). If we compare the Jsc value for the average passivated solar cells and 256 Jsc value that is extracted from the EQE for the best cells, we noticed a 5mA difference between 257 those values, see Table-3. The probable cause for this difference is explained in detail in 258 (Scheer and Schock, 2011).

As shared in Table-3, by the addition of a passivation layer with contact openings through an easy and cost-effective way, we reached Voc of 623mV with ultra-thin single-stage CIGS solar cells. If we examined even further, due to the 14% relative increase in open-circuit voltage, i.e., from 536mV to 608mV, the power conversion efficiency of the passivated sample gained a 24% relative increase, i.e., from 5.2% to 7.2%, for the average of twelve cells. Furthermore, by using the extracted current values from EQE, i.e., corrected Jsc, we achieved 9.8% power conversion efficiency.

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Table-3 JV parameter comparison between reference (bare) and passivated ultrathin CIGS
solar cells. (average of 12 cells) Further, JV parameters of the cells that have the best efficiency
and open-circuit voltage values for passivated solar cells. **Jsc values extracted from EQE and the power conversion efficiencies recalculated accordingly.*

275

	Number of cells	Jsc (mA/cm ²)	Voc (mV)	FF (%)	Eta (%)
Reference- Average	12	20.9 ± 2.3	536 ± 28.1	51.8 ± 6.6	5.8 ± 1.1
Passivated- Average	12	19.9 ± 1.63	608 ± 8.9	59.6 ± 1.77	7.2 ± 0.7
Passivated- Best Eff.	1	25.1*	617.01	62.2	9.8 *
Passivated- Best Voc	1	23.6*	622.84	56.9	8.4*

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The rear surface passivation effect can easily be explored by examining the differences between
reference and passivated solar cells' Voc values. To this effect, the following simplified
equation is used:

- 280
- 281 282

 $V_{oc} \approx \frac{k_B T}{q} \ln \left(\frac{J_{ph}}{J_0} \right)$ Eq.1

where J_{ph} is equal to short circuit current in an ideal case. Since the variation in J_{ph} is generally limited, the key element that determines the change in Voc is the saturation current density. The change in saturation current density (J_0) can be in orders of magnitudes, and this change depends on the recombination in the solar cell (Smets et al., 2016). Hence, lower J_0 means lower recombination, and eventually higher Voc. The addition of the aluminum oxide dielectric layer in combination with sodium fluoride decreases the J_0 noticeably, and causes a significant increase in Voc, see Table-4.

290 For further investigation, we update the Eq.1 to calculate the open-circuit voltage difference **291** (ΔV_{oc}) between reference and passivated solar cells:

292

293 $\Delta V_{oc} \approx \frac{k_B T}{q} \ln \left(\frac{J_{0,passivated}}{J_{0,reference}} \right)$ Eq.2

295 A random cell for reference and passivated sample, and the best efficient passivated solar cell 296 are chosen and the measured J_0 and Voc values, ΔV_{oc} and calculated Voc values for those cells 297 are given in Table-4.

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302 Table 4- The saturated current density (J_0) , measured open-circuit voltage $(V_{oc}$ -m), the 303 difference in Voc (ΔV_{oc}) (calculated from Eq.2) and the calculated open-circuit voltage $(V_{oc}$ -c) 304 values are given for: the reference average, the passivated average, and the passivated-best 305 efficient solar cells.

	$J_0 (\mathrm{mA/cm^2})$	V_{oc} -m (mV)	V_{oc} -c (mV)	ΔV_{oc}
Reference- average cell	1.72E - 8	562	-	-
Passivated-average cell	5.63 <i>E</i> – 9	610	652.5	90.5
Passivated-best efficient cell	5.62 <i>E</i> – 10	617.1	711.9	149.9

According to the Table-4, the significant decrease in the Jo results in an increase in Voc values. 307 308 This increase implies that the reason for higher Voc is very likely due to reduced recombination 309 at the rear surface. The reduced rear surface recombination should show itself clearly as an improved FF, as well (Vermang et al., 2014b), (Leilaeioun, 2018). However, our contacting 310 311 approach is not optimized yet, so the increase in FF is somewhat limited. This limitation is due 312 to the high series resistance (Rs) values for passivated solar cells. (Fig.5 a) The Rs values for passivated solar cells are significantly higher than the reference solar cells. This increase means 313 314 that there is a lack of contact openings. Hence, our contacting approach needs further 315 optimizations. In fact, after further optimizations, the calculated Voc values could be reached. 316 If the TRPL and EQE results are investigated, it can be seen that the improvement in Voc is 317 not related to optical enhancements, see Figure-4. The 1-Reflectance (1-R), is also given in 318 Fig.4-b. Since the transmittance is nearly zero for our structure, 1-R can be accepted as the 319 absorption of our solar cells. The TRPL measurement was performed on the finished solar 320 cells. As can be seen from Fig.4-a, the passivated solar cell gave the slowest decay time. This 321 slow decay arguably implies the reduced recombination at the rear surface. However, even for 322 the passivated solar cell, the life-time is not at the same level as the state-of-the-art CIGS solar 323 cells. At this point, one needs to remember that our absorber layer is ultra-thin (500nm) and 324 non-graded. So, lower life-time values are expected.

325



Figure 4 a-TRPL and b-smoothened EQE and 1-R of reference (black) and passivated (red)solar cells.

326

330 For passivated solar cells, the EOE response is higher for long wavelengths. One known reason 331 for this increase is the optical enhancement due to the contact openings. The bump around 332 980nm for the passivated solar cell can be seen as an optical effect since a similar bump has 333 been explained in detail for 390nm thick CIGS solar cells before, as an optical effect, see 334 (Hegedus and Shafarman, 2004). On the other hand, the results coming from the reflectance 335 measurement (1-R) for passivated and reference solar cells are quite similar. Hence, the 336 increase in EQE can be associated with the rear-surface passivation effect rather than the optical 337 enhancement.







Figure 5 a- Distribution of the series resistance values for reference (black) and passivated
(red) solar cells and b- JV curve for the best efficient passivated solar cell with the shifted dark
curve. *Jsc and efficiency values were extracted from EQE, and the associated curves also adapted for this
change.

344

We also analyze the JV curve for the passivated sample to check if there are any anomalies,
see Figure 5-b. Our JV curve seems to suffer from two anomalies: i-violation of superposition
principle and ii-cross-over. In (Scheer and Schock, 2011), both of these anomalies and the

348 reasons for them were discussed in detail. In our case, the most probable reasons for (i) is that

a- the boundary condition for quasi-neutral region (QNR) recombination is changed by large
series resistance, or b- due to light modulated potential barrier, the change from interface
recombination to Shockley Read Hall (SRH) recombination. We shifted the dark curve by Jsc
and compared it with the light curve. The aim is to see the Voc without any light-induced defect
and/or recombination. (Fig. 5-b) Since the FF is increasing under light, the reason for this
anomaly, i.e., shifting violation, is most probably caused by high series resistance.

355 If we investigate the JV curve further, the second anomaly (ii) that we suffered from, the cross-356 over phenomenon, can be seen (Igalson et al., 2009). Several possible reasons can cause this 357 anomaly, but the exact reason is still unknown. However, if we will be able to solve our high 358 series resistance problem, and by doing so, overcome the violation of shifting anomaly, we will 359 also be able to overcome the cross over phenomenon. If the shifted dark curve, i.e., the dashed 360 curve, is followed, it is clear that it will not cross the dark curve. (Fig. 5-b) Hence, reducing 361 the series resistance by optimizing our contacting approach will help us to overcome those 362 anomalies in the future. As a result, we can reach higher efficiencies.

363 364

4. Conclusion and outlook:

365 In summary, we fabricated ultrathin rear surface passivated solar cells with an industrially 366 viable, fast and novel process. The novelty of our process is to create the contact openings by 367 adding NaF solution by spin coating it on the alumina passivation layer. In this way, we managed to detect the openings in the passivation layer by top-view SEM, even for the 368 369 complete solar cell. Even though we are still not able to thoroughly explain the origin of these 370 openings, it became clear that we need the alkali solution and the selenization at 540-degree 371 Celsius. After we were convinced that we managed to create the contact openings, we altered 372 the thickness of the passivation layer and the molarity of the alkali solution in pursuit of finding 373 the ultimate structure for best efficiency. As a result, we decided that 6nm alumina deposition 374 in combination with 0.4M NaF solution gives the best JV results. Hereby, we reached 623mV 375 Voc, and for the best cell, we gained a 43% relative increase in power conversion efficiency. 376 The main advantage of this structure is that it is easy, fast and applicable to larger areas. 377 Considering that spin-coating is not an industrially feasible technique, instead of this, other 378 industrially feasible coating techniques, for example, slot dye technique, could be used for 379 sodium fluoride deposition. Even though this process is not as controllable as more standard 380 techniques, upon the repetition of our experiment, we obtained very similar results. So, it is 381 safe to say that the alterations, i.e. non-controllable elements, do not affect the efficiency 382 significantly. Moreover, it is possible to apply this structure to the front surface of CIGS solar 383 cells. The next step is to investigate further the chemistry and physics behind the creation of 384 the openings, and then optimize the process. After that, we believe that the calculated Voc 385 values can be reached by reducing the series resistance.

386

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465 <u>Supporting Information:</u>



















476 Supported Figure 3: EDS analysis and SEM pictures of openings from the complete cell

477 structure. EDS measurement was done from layer and opening, and the atomic concentrations

478 are shared as a graph to emphasize the change. The arrows indicate the direction of the change.

479 As can be seen from the EDS graph, the Al signal drops nearly to zero, which means there is

480 no Al signal through the opening. On the other hand, the Na signal increases from layer to

481 openings. This indicates that aluminum oxide layer blocks the Na coming from the glass, and

482 hence, from the openings, we observed higher Na signal.

483 Window and absorber layers removed via tweezer.