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1 **Development of reflective back contacts for high-efficiency ultrathin Cu(In,Ga)Se<sub>2</sub> solar**  
2 **cells**

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## 14 **Abstract**

15 Because of poor light absorption, Cu(In,Ga)Se<sub>2</sub>-based (CIGS) solar cells with an ultrathin  
16 absorber layer (<500 nm) require the development of reflective back contacts. To enhance  
17 rear reflectance in CIGS ultrathin devices, we investigate novel back contact architectures  
18 based on a silver metallic mirror covered with a thin layer of In<sub>2</sub>O<sub>3</sub>:Sn (ITO), which is fully  
19 compatible with nanopatterning for further light trapping improvements. First, numerical  
20 electromagnetic simulations of complete solar cells have been performed for a 490 nm thick  
21 CIGS absorber with various back contacts. We predict a short-circuit current density of  $J_{SC} =$   
22  $34.0 \text{ mA/cm}^2$  for a 490 nm thick CIGS absorber with a silver nanostructured mirror. Second,  
23 we have fabricated and characterized 490 nm thick CIGS solar cells with transparent back  
24 contacts made of ITO, and reflective back contacts made of silver covered with ITO. Solar  
25 cells with a transparent ITO back contact exhibit an average efficiency of 10.0 %, compared  
26 to 9.3 % for standard molybdenum back contacts. A 5 nm thick Ga<sub>2</sub>O<sub>3</sub> layer is revealed at the  
27 ITO/CIGS interface by transmission electron microscopy and energy dispersive X-ray  
28 spectroscopy. When silver is added, the reflective back mirror leads to a  $J_{SC}$  improvement of  
29  $4.6 \text{ mA/cm}^2$  (from 22.4 to 27.0  $\text{mA/cm}^2$ ). These results pave the way for efficient ultrathin  
30 CIGS solar cells on reflective back contacts.

## 31 **Keywords**

32 Solar cells, Copper indium gallium selenide, Ultrathin films, Transparent back contact,  
33 Reflective back contact, Nanostructured back mirror

## 34 **1. Introduction**

35 Cu(In,Ga)Se<sub>2</sub>-based (CIGS) solar cells are one of the most promising thin-film technologies,  
36 with a record efficiency of 22.9 % achieved with a 2–3  $\mu\text{m}$  thick absorber [1], [2]. However,  
37 the scarcity and high cost of Indium are a drawback for industrial production of competitive  
38 modules. With a CIGS absorber thickness lower than 500 nm it is possible to reduce  
39 deposition time and materials consumption, resulting in a decreased manufacturing cost [3],  
40 [4].

41 Ultrathin CIGS-based solar cells exhibit lower short-circuit current densities ( $J_{SC}$ ) and  
42 efficiencies mainly due to lower light absorption, enhanced recombination [5] and low  
43 reflectivity of the conventional Mo back contact [6], [7]. These loss mechanisms can be  
44 overcome by substituting the Mo back contact with passivating and more reflective back

45 contact. Up to now, there are few studies of reflective back contacts for CIGS solar cells, such  
46 as: direct use of reflective or metallic back contacts [8]–[10], a combination of transparent  
47 conducting oxide and metallic reflector [7], passivating reflective back contact [11], or  
48 nanostructured back contacts [12], [13]. Nanostructured back reflectors are a promising  
49 strategy for enhanced absorption in ultrathin CIGS layers, as they lead to calculated  $J_{SC}$  up to  
50  $36.3 \text{ mA/cm}^2$  in a 150 nm thick CIGS layer compared to  $23.5 \text{ mA/cm}^2$  with a standard Mo  
51 back contact [12]. Nanostructured mirrors have also yielded significant  $J_{SC}$  improvements in  
52 other types of solar cells such as amorphous Si:H [14] and ultrathin GaAs [15], [16].

53 In this paper we present the first steps towards the development of a reflective back contact  
54 based on a silver metallic mirror encapsulated with a thin layer of  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO). Reflective  
55 back contacts for CIGS solar cells need not only to provide enhanced rear reflectance but also  
56 to form an ohmic contact with the absorber. Several studies report on the formation of a  
57 resistive interfacial layer of  $\text{Ga}_2\text{O}_3$  after CIGS deposition on oxide layers such as hydrogen-  
58 doped  $\text{In}_2\text{O}_3$ , ITO,  $\text{MoO}_3$ ,  $\text{SnO}_2:\text{F}$ , ZnO or ZnO:Al [17]–[22]. In particular, ITO is known to  
59 prevent Na diffusion from the glass to the CIGS absorber and to form a detrimental layer of  
60  $\text{Ga}_2\text{O}_3$  for CIGS deposition temperatures above  $520 \text{ }^\circ\text{C}$  [22], [23]. As a result, the stability and  
61 electrical properties of ultrathin devices on transparent ITO-based substrates were first  
62 investigated by co-evaporation of CIGS at low temperature ( $450^\circ\text{C}$ ) with incorporation of Na  
63 from a NaF post-deposition treatment.

64 In this study, the improvement of light absorption in a 490 nm thick CIGS absorber is first  
65 simulated using a nanostructured and a flat mirror encapsulated in transparent conducting  
66 oxides such as ITO. Then, the optical properties of glass substrates covered with Mo, Ag and  
67 Ag/ITO are determined and compared. 490 nm thick CIGS solar cells are fabricated on ITO  
68 back contacts, and the ITO/CIGS interface is studied in-depth with transmission electron  
69 microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). The performances of  
70 cells on ITO and Mo back contacts are compared and discussed, and preliminary results on  
71 Ag/ITO back contacts are presented.

## 72 **2. Experimental methods**

73 CIGS solar cells were fabricated on soda-lime glass (SLG) substrates with three different  
74 back contacts. The first stack is made of a conventional 800 nm thick molybdenum (Mo) back  
75 contact deposited on a 300 nm  $\text{Al}_2\text{O}_3$  layer that acts as a diffusion barrier for alkali elements  
76 present in SLG.  $\text{Al}_2\text{O}_3$  is deposited by atomic layer deposition. The second stack is based on a

77 transparent 300 nm thick ITO layer sputtered on SLG. The third stack contains a 30 nm thick  
78 ITO sputtered on a 150 nm thick Ag layer deposited by electron beam evaporation. A 490 nm  
79 thick CIGS layer was deposited by thermal co-evaporation in a one-stage process, at a fixed  
80 substrate temperature of 450 °C. This substrate temperature was calibrated in a previous  
81 work, using an infrared camera [24]. Average composition of absorbers was determined from  
82 X-Ray Fluorescence (XRF) signal of CIGS deposited on Mo, leading to atomic ratios of  
83  $[Cu]/([In]+[Ga]) = 0.81 \pm 0.01$  (CGI) and  $[Ga]/([Ga]+[In]) = 0.32 \pm 0.01$  (GGI). A NaF post-  
84 deposition treatment was applied with an evaporation rate of 1 nm/min under Se flux and at  
85 fixed substrate temperature of 350 °C. Solar cells were completed with the standard front  
86 layer stack consisting in a chemical bath deposited CdS/rf-sputtered ZnO/rf-sputtered ZnO:Al  
87 with respective thicknesses 50nm/50nm/400nm determined by XRF analysis on control  
88 samples.

89 Opto-electrical properties of ITO were determined from a 200 nm thick ITO layer sputtered  
90 on SLG. As annealing of ITO improves its optical transparency and carrier mobility, its  
91 optical indices and resistivity were measured before and after a 10-minute-annealing  
92 performed in air on a hotplate set at 540 °C. Refractive index  $n$  and extinction coefficient  $k$   
93 were extracted from ellipsometric measurements on a UVISEL ellipsometer from Horiba  
94 Jobin-Yvon. The ITO resistivity was measured with a four-point probe system before ( $\rho =$   
95  $9.0 \times 10^{-4} \Omega \cdot \text{cm}$ ) and after annealing ( $\rho = 7.0 \times 10^{-4} \Omega \cdot \text{cm}$ ). Finally, a Sentech reflectometer was  
96 used to determine the spectral reflectance of four different substrates: SLG/600-nm-Mo,  
97 SLG/150-nm-Ag, SLG/150-nm-Ag/30-nm-ITO and SLG/150-nm-Ag/200-nm-ITO substrates.

98 Current-voltage I(V) measurements of 0.1 cm<sup>2</sup> solar cells were carried out with a Newport  
99 class AAA solar simulator under AM1.5G illumination and in the dark. Devices on  
100 transparent substrates were placed on a black paper before light I(V) measurements to avoid  
101 additional rear-reflection from the substrate holder. External Quantum Efficiency (EQE)  
102 measurements were performed with a IQE200 Newport Instrument. A slab of a 490 nm thick  
103 CIGS layer deposited on an ITO-based transparent back contact was prepared by a focused  
104 ion beam, and analysed with TEM in a FEI Titan Themis XFEG instrument at an acceleration  
105 voltage of 200 kV. Composition mappings were determined by EDX.

## 106 3. Results and discussion

### 107 3.1 Absorption simulation

108 We first investigate numerically the optical effects of a nanostructured back mirror, a flat back  
109 mirror, and a transparent back contact as compared to a conventional Mo back contact. The  
110 spectral absorption is simulated with a rigorous coupled wave analysis method, and the  
111 optical indices are calculated from ellipsometric measurements for CIGS and annealed ITO,  
112 and taken from the literature for other materials. More details can be found in reference [12].  
113 The architecture of flat ultrathin devices is sketched in Fig. 1a), while the optimized geometry  
114 of a complete device including a nanostructured back mirror is presented in Fig. 1b) and c).  
115 This simulated nanostructured back mirror consists of square-shaped dielectric nanogrid on  
116 top of a flat ITO-coated Ag stack. The dielectric nanogrid has a refractive index of  $n = 1.5$ , a  
117 height of 200 nm, a period of 600 nm and hole width of 350 nm. The experimental fabrication  
118 of such a dielectric nanogrid is under development, using a scalable process based on direct  
119 nanoimprint of a sol-gel derived metal oxide [25], [26]. The simulated absorptions of CIGS  
120 devices on Mo, ITO, as well as flat and nanostructured reflective back contacts are plotted in  
121 Fig. 2.

122 As shown in Fig. 2a, using a standard Mo back contact leads to substantial absorption losses  
123 for long wavelengths ( $> 600$  nm), because of the low reflectivity at CIGS/Mo interface.  
124 Moreover, optical losses are also observed at short wavelengths ( $< 500$  nm) due to the low  
125 bandgap of CdS (2.4 eV) buffer layer. Assuming a perfect collection of photogenerated  
126 carriers, a theoretical short-circuit current density  $J_{SC}$  can be deduced from the simulated  
127 CIGS absorption [12]. It is limited to  $28.8 \text{ mA/cm}^2$  with a Mo back contact. When Mo is  
128 replaced by ITO (Fig. 2b) a similar spectral absorption with a  $J_{SC}$  of  $28.5 \text{ mA/cm}^2$  is  
129 calculated. The introduction of an Ag layer results in enhanced back reflectance and  
130 significant improvement of CIGS light absorption at long wavelengths ( $> 800$  nm), (Fig. 2c),  
131 which leads to an increased  $J_{SC}$  of  $32.2 \text{ mA/cm}^2$ . Finally, if the flat mirror is replaced by an  
132 optimised nanostructured back mirror made of a nanogrid, additional absorption resonances  
133 occur close to the bandgap (Fig. 2d). Multi-resonant absorption in the thin CIGS layer leads to  
134 a  $J_{SC}$  of  $34.0 \text{ mA/cm}^2$ , which represents an additional  $1.8 \text{ mA/cm}^2$  gain as compared to the flat  
135 back mirror.

### 136 3.2 Optical characterization of back contacts

137 Before deposition of CIGS on transparent and reflective back contacts, the spectral reflectance  
138 of 4 different back contacts deposited on SLG were first measured and compared: a 600 nm  
139 thick Mo, a 150 nm thick Ag layer, and 150 nm thick Ag layers with 30 nm and 200 nm ITO  
140 coatings (Fig. 3a). As expected, Mo has a low reflectivity and cannot act as a back mirror,  
141 resulting in low CIGS absorption for ultrathin CIGS solar cells (Fig. 2a). On the contrary, the  
142 silver layer provides a high reflectivity ( $R > 90\%$  for  $\lambda > 500$  nm), but it cannot be used as a  
143 back contact due to diffusion of Ag in CIGS during the growth. When the silver layer is  
144 covered with ITO coatings, the reflectivity is significantly reduced due to parasitic absorption.  
145 Reflectivity dips are attributed to Fabry-Perot resonances in the ITO layer. After a 10-minute-  
146 annealing in air at 540 °C, the reflectivity is strongly enhanced and exceeds 90 % for  
147 wavelengths above 550 nm. This annealing experiment performed in air proves that the ITO  
148 layer efficiently encapsulates the Ag mirror, preventing its oxidation and morphological  
149 changes that negatively impact its reflectivity; the stability of such reflective back contact  
150 under CIGS deposition was only tested after the complete solar cell fabrication. To determine  
151 the origin of the enhanced reflectivity of Ag/ITO stacks after annealing, ellipsometric  
152 measurements were carried out on a 200 nm thick ITO layer sputtered on SLG before and  
153 after annealing in air at 540 °C during 10 minutes. The refractive index  $n$  and extinction  
154 coefficient  $k$  are displayed in Fig. 3b). The annealing results in an increase of  $n$  and a decrease  
155 of  $k$  in the visible and infrared domains ( $\lambda > 500$  nm). The origin of these effects was not  
156 investigated in detail, though it is commonly accepted that annealing of amorphous ITO  
157 generally results in an increased layer density, an improved carrier mobility and a reduced  
158 free-carrier absorption. It leads to a significant improvement of the Ag/ITO reflectivity and a  
159 spectral shift of the reflectivity dips toward shorter wavelengths (Fig. 3a).

### 160 3.3 TEM-EDX back contact characterization

161 A TEM-EDX analysis was performed in order to investigate the ITO/CIGS interface. Fig. 4a)  
162 and b) show a TEM image of an ultrathin 490-nm-CIGS layer deposited on an ITO back  
163 contact along with the average composition profile of absorber elements deduced from EDX  
164 analysis. An average GGI of 0.28 was calculated from the average EDX signal of the CIGS  
165 layer, which is close to the GGI value of 0.32 determined by XRF. It is worth mentioning that  
166 the EDX signal of Cu is overestimated as Cu from the substrate holder is also detected. Hence  
167 CGI cannot be deduced from this analysis.

168 This EDX analysis confirms that the CIGS composition is homogeneous from the front to the  
169 back interface, as expected from a one-stage CIGS deposition process. Moreover it reveals  
170 that Ga segregates at the back contact.

171 Closer views are shown in Fig. 4. with (c) an additional dark field TEM image and its  
172 corresponding compositional EDX mappings of O, Ga, In, and Se elements. They reveal a  
173 segregation of both Ga and O elements at the ITO/CIGS interface, which suggests that a thin  
174  $\text{Ga}_2\text{O}_3$  layer is formed during CIGS deposition. This layer should be highly resistive and  
175 possibly n-doped [17]. However, in this study the low substrate temperature ( $450\text{ }^\circ\text{C}$ ) during  
176 CIGS deposition results in a very thin  $\text{Ga}_2\text{O}_3$  layer of only 5 nm that does not seem to  
177 deteriorate solar cell performances.

### 178 3.4 Solar cell performances

179 The performances of ultrathin CIGS solar cells are summarized in Table 1 for Mo and ITO  
180 back contacts. Best efficiencies are given together with average I(V) parameters and standard  
181 deviation for the 10 best cells. Dark I(V) parameters are extracted from the fit of a 2-diode  
182 model: saturation currents for diodes with ideality factors of 1 ( $J_{01}$ ) and 2 ( $J_{02}$ ), shunt  
183 resistance ( $R_{\text{SH}}$ ) and series resistance ( $R_{\text{S}}$ ). I(V) and EQE curves of best cells are displayed on  
184 Fig. 5, together with the experimental EQE of a 490 nm thick CIGS cell on a reflective back  
185 contact (Ag). The reference solar cells on a SLG/ $\text{Al}_2\text{O}_3$ /Mo substrate exhibit an average  
186 efficiency of 9.3 %.

187 Ultrathin CIGS solar cells with an ITO back contact present an average efficiency of 10.0 %.  
188 Mo and ITO-based substrates lead to very close dark currents ( $J_{01}$ ,  $J_{02}$ ),  $R_{\text{SH}}$  and fill factors  
189 (FF). A slight increase of  $R_{\text{S}}$  is observed with an ITO back contact, from 0.1 for Mo to 1.2  
190  $\Omega\cdot\text{cm}^2$ . Importantly, the increase of both open-circuit voltage and  $J_{\text{SC}}$  results in an absolute  
191 efficiency enhancement of 0.7 %. It indicates that ITO has suitable electrical properties to be  
192 used as a back contact in CIGS solar cells. Ultrathin CIGS devices on transparent SLG/ITO  
193 substrates could be used for bifacial solar cells. Alternatively, solar cell efficiency could be  
194 enhanced by adding a mirror on the backside of the glass substrate.

195 According to simulation results (Fig. 2), the short-circuit current could also be increased by  
196 adding a flat silver back mirror between the ITO layer and the glass substrate, with an  
197 expected gain of  $4.6\text{ mA/cm}^2$  over the Mo reference. We have performed preliminary  
198 experiments of 490 nm thick CIGS solar cells deposited on reflective multilayer stacks (MLS)  
199 based on silver covered by ITO. They led to poor electrical performances due to process

200 issues that should be overcome by further optimizations. However, the reflective MLS  
201 resulted in a strong EQE enhancement. The EQE of ultrathin solar cells with a Mo back  
202 contact, an ITO back contact, and a reflective MLS are plotted and compared in Fig. 5b. The  
203 reflective back contact leads to an improvement for wavelengths above 500 nm and results in  
204 a promising  $J_{SC} = 27.0 \text{ mA/cm}^2$ . The same EQE measurements are also plotted and compared  
205 to numerical simulation in Fig. 2. A very good agreement between experiments and  
206 simulations is obtained.

## 207 **5. Conclusion**

208 Ultrathin CIGS solar cells with transparent and reflective back contacts were first numerically  
209 investigated. A  $J_{SC}$  of  $32.2 \text{ mA/cm}^2$  is calculated for 490 nm thick CIGS solar cells with a flat  
210 back mirror, corresponding to a  $3.4 \text{ mA/cm}^2$  gain as compared to standard molybdenum back  
211 contacts. An additional optical gain is predicted with a nanostructured reflective back contact,  
212 leading to a  $J_{SC}$  of  $34.0 \text{ mA/cm}^2$ . Flat reflective stacks of Ag/ITO were fabricated and are  
213 stable under a 10-minute-annealing in air at  $540 \text{ }^\circ\text{C}$ . Their spectral reflectance is over 90 %  
214 for wavelengths above 550 nm, which should substantially increase absorption in ultrathin  
215 CIGS absorbers. Complete ultrathin CIGS solar cells were fabricated on molybdenum and  
216 transparent ITO back contacts, with respective average efficiencies of 9.3 % and 10.0 %. ITO  
217 forms an ohmic back contact with CIGS, as confirmed by an average FF of 70.3 %. A TEM-  
218 EDX investigation shows that the thickness of the  $\text{Ga}_2\text{O}_3$  formed at ITO/CIGS interface  
219 during CIGS deposition is limited to 5 nm and has no impact on solar cell performances.  
220 Preliminary experiments on reflective back contacts made of Ag and ITO led to a  $J_{SC} = 27.0$   
221  $\text{mA/cm}^2$ . These results provide a promising route toward efficient, ultrathin CIGS solar cells  
222 deposited on reflective back contacts.

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## 226 **References**

- 227 [1] "Solar Frontier press release dated December 20, 2017." [Online]. Available:  
228 [http://www.solar-frontier.com/eng/news/2017/1220\\_press.html](http://www.solar-frontier.com/eng/news/2017/1220_press.html). [Accessed: 11-Jun-  
229 2018].
- 230 [2] P. Jackson, R. Wuerz, D. Hariskos, E. Lotter, W. Witte, M. Powalla, Effects of heavy  
231 alkali elements in  $\text{Cu}(\text{In,Ga})\text{Se}_2$  solar cells with efficiencies up to 22.6%, *Phys. Status*  
232 *Solidi RRL - Rapid Res. Lett.* (2016).

- 233 [3] M. Edoff, S. Schleussner, E. Wallin, O. Lundberg, Technological and economical  
234 aspects on the influence of reduced Cu(In,Ga)Se<sub>2</sub> thickness and Ga grading for co-  
235 evaporated Cu(In,Ga)Se<sub>2</sub> modules, *Thin Solid Films* 519, 21 (2011).
- 236 [4] K. A. W. Horowitz, M. Woodhouse, Cost and potential of monolithic CIGS photovoltaic  
237 modules, *Photovolt. Spec. Conf. PVSC, 2015 IEEE 42nd* (2015) 1-6.
- 238 [5] B. Vermang, J. T. Wätjen, C. Frisk, V. Fjällström, F. Rostvall, M. Edoff, P. Salomé, J.  
239 Borme, N. Nicoara, S. Sadewasser, Introduction of Si PERC Rear Contacting Design to  
240 Boost Efficiency of Cu(In,Ga)Se Solar Cells, *IEEE J. Photovolt.* 4, 6 (2014).
- 241 [6] Z. Jehl, F. Erfurth, N. Naghavi, L. Lombez, I. Gerard, M. Bouttemy, P. Tran-Van, A.  
242 Etcheberry, G. Voorwinden, B. Dimmler, W. Wischmann, M. Powalla, J. F.  
243 Guillemoles, D. Lincot, Thinning of CIGS solar cells: Part II: Cell characterizations,  
244 *Thin Solid Films* 519, 21 (2011).
- 245 [7] F. Mollica, M. Jubault, F. Donsanti, A. Loubat, M. Bouttemy, A. Etcheberry, N.  
246 Naghavi, Light absorption enhancement in ultra-thin Cu(In,Ga)Se<sub>2</sub> solar cells by  
247 substituting the back-contact with a transparent conducting oxide based reflector, *Thin*  
248 *Solid Films* 633 (2017) 202–207.
- 249 [8] K. Orgassa, H. W. Schock, J. H. Werner, Alternative back contact materials for thin film  
250 Cu(In,Ga)Se<sub>2</sub> solar cells, *Thin Solid Films* 431–432 (2003) 387–391.
- 251 [9] Z. J. Li-Kao, N. Naghavi, F. Erfurth, J. F. Guillemoles, I. Gérard, A. Etcheberry, J. L.  
252 Pelouard, S. Collin, G. Voorwinden, D. Lincot, Towards ultrathin copper indium gallium  
253 diselenide solar cells: proof of concept study by chemical etching and gold back contact  
254 engineering: CIGSe: chemical etching and gold back contact engineering, *Prog.*  
255 *Photovolt. Res. Appl.* 20, 5 (2012).
- 256 [10] S. Schleussner, T. Kubart, T. Törndahl, M. Edoff, Reactively sputtered ZrN for  
257 application as reflecting back contact in Cu(In,Ga)Se<sub>2</sub> solar cells, *Thin Solid Films* 517,  
258 18 (2009).
- 259 [11] B. Vermang, J. T. Wätjen, V. Fjällström, F. Rostvall, M. Edoff, R. Gunnarsson, I. Pilch,  
260 U. Helmersson, R. Kotipalli, F. Henry, D. Flandre, Highly reflective rear surface  
261 passivation design for ultra-thin Cu(In,Ga)Se<sub>2</sub> solar cells, *Thin Solid Films* 582 (2015)  
262 300–303.
- 263 [12] J. Goffard, C. Colin, F. Mollica, A. Cattoni, C. Sauvan, P. Lalanne, J. F. Guillemoles, N.  
264 Naghavi, S. Collin, Light Trapping in Ultrathin CIGS Solar Cells with Nanostructured  
265 Back Mirrors, *IEEE J. Photovolt.* 7, 5 (2017).
- 266 [13] G. Yin, M. W. Knight, M.-C. van Lare, M. M. Solà Garcia, A. Polman, M. Schmid,  
267 Optoelectronic Enhancement of Ultrathin CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> Solar Cells by Nanophotonic  
268 Contacts, *Adv. Opt. Mater.* 5, 5 (2017).
- 269 [14] V. E. Ferry, M. A. Verschuuren, M. C. van Lare, R. E. I. Schropp, H. A. Atwater, A.  
270 Polman, Optimized Spatial Correlations for Broadband Light Trapping Nanopatterns in  
271 High Efficiency Ultrathin Film a-Si:H Solar Cells, *Nano Lett.* 11, 10 (2011).
- 272 [15] W. Yang, J. Becker, S. Liu, Y. S. Kuo, J. J. Li, B. Landini, K. Campman, Y. H. Zhang,  
273 Ultra-thin GaAs single-junction solar cells integrated with a reflective back scattering  
274 layer, *J. Appl. Phys.* 115, 20, (2014).
- 275 [16] H.-L. Chen, A. Cattoni, N. Vandamme, J. Goffard, A. Lemaitre, A. Delamarre, B.  
276 Behaghel, K. Watanabe, M. Sugiyama, J. F. Guillemoles, S. Collin, 200nm-thick GaAs  
277 solar cells with a nanostructured silver mirror, *Photovolt. Spec. Conf. PVSC, 2016 IEEE*  
278 *43rd* (2016) 3506-3509.
- 279 [17] J. Keller, W.-C. Chen, L. Riekehr, T. Kubart, T. Törndahl, M. Edoff, Bifacial  
280 Cu(In,Ga)Se<sub>2</sub> solar cells using hydrogen-doped In<sub>2</sub>O<sub>3</sub> films as a transparent back contact,  
281 *Prog. Photovolt. Res. Appl.* 26, 10 (2018).

- 282 [18] H. Simchi, J. Larsen, K. Kim, W. Shafarman, Improved Performance of Ultrathin  
283 Cu(In,Ga)Se<sub>2</sub> Solar Cells With a Backwall Superstrate Configuration, *IEEE J. Photovolt.*  
284 4, 6 (2014).
- 285 [19] W. Ohm, W. Riedel, Ü. Aksünger, D. Greiner, C. A. Kaufmann, M. C. Lux-Steiner, S.  
286 Gledhill, Bifacial Cu(In,Ga)Se<sub>2</sub> solar cells with submicron absorber thickness: back-  
287 contact passivation and light management, *Photovolt. Spec. Conf. PVSC, 2015 IEEE*  
288 42nd (2015) 1-5.
- 289 [20] M. Terheggen, H. Heinrich, G. Kostorz, F.-J. Haug, H. Zogg, A. N. Tiwari, Ga<sub>2</sub>O<sub>3</sub>  
290 segregation in Cu(In,Ga)Se<sub>2</sub>/ZnO superstrate solar cells and its impact on their  
291 photovoltaic properties, *Thin Solid Films* 403–404 (2002) 212-215
- 292 [21] M. D. Heinemann, F. Ruske, D. Greiner, A. R. Jeong, M. Rusu, B. Rech, R. Schlatmann,  
293 C. A. Kaufmann, Advantageous light management in Cu(In,Ga)Se<sub>2</sub> superstrate solar  
294 cells, *Sol. Energy Mater. Sol. Cells* 150 (2016) 76-81.
- 295 [22] T. Nakada, Microstructural and diffusion properties of CIGS thin film solar cells  
296 fabricated using transparent conducting oxide back contacts, *Thin Solid Films* 480–481  
297 (2005) 419-425.
- 298 [23] T. Nakada, Y. Hirabayashi, T. Tokado, D. Ohmori, T. Mise, Novel device structure for  
299 Cu(In,Ga)Se<sub>2</sub> thin film solar cells using transparent conducting oxide back and front  
300 contacts, *Sol. Energy* 77, 6 (2004).
- 301 [24] T. Klinkert, M. Jubault, F. Donsanti, D. Lincot, J.-F. Guillemoles, Ga gradients in  
302 Cu(In,Ga)Se<sub>2</sub>: Formation, characterization, and consequences, *J. Renew. Sustain.*  
303 *Energy* 6, 1 (2014).
- 304 [25] T. Bottein, O. Dalstein, M. Putero, A. Cattoni, M. Faustini, M. Abbarchia, D. Grosso,  
305 Environment-controlled sol–gel soft-NIL processing for optimized titania, alumina,  
306 silica and yttria-zirconia imprinting at sub-micron dimensions, *Nanoscale* 10, 3 (2018).
- 307 [26] O. Dalstein, D. R. Ceratti, C. Boissière, D. Grosso, A. Cattoni, M. Faustini,  
308 Nanoimprinted, Submicrometric, MOF-Based 2D Photonic Structures: Toward Easy  
309 Selective Vapors Sensing by a Smartphone Camera, *Adv. Funct. Mater.* 26 (2016) 81-  
310 90.

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## 312 List of figures

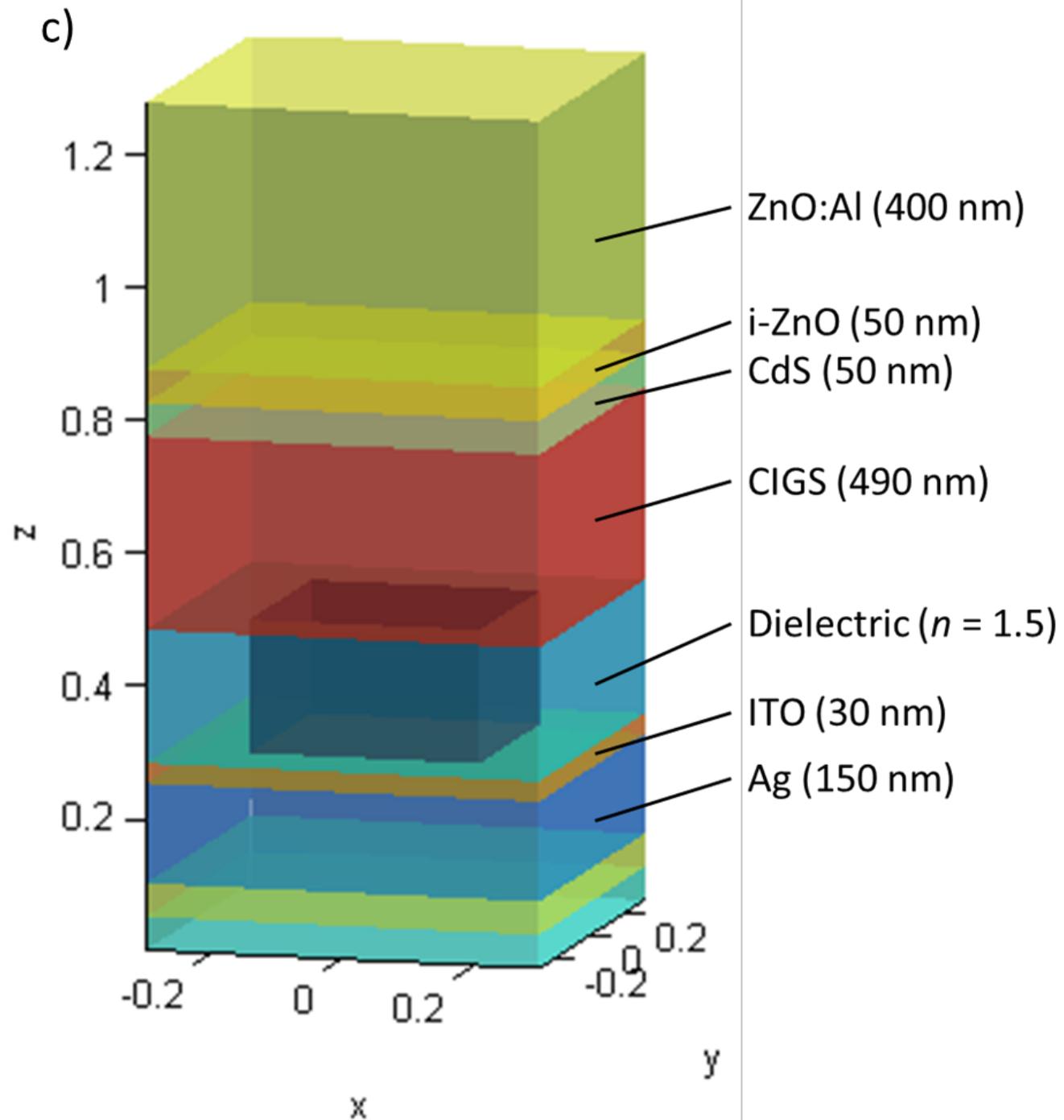
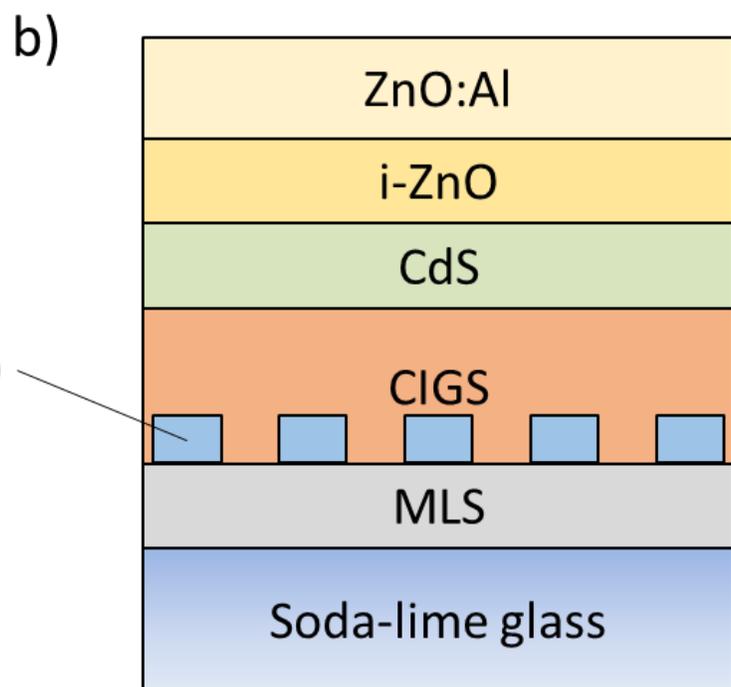
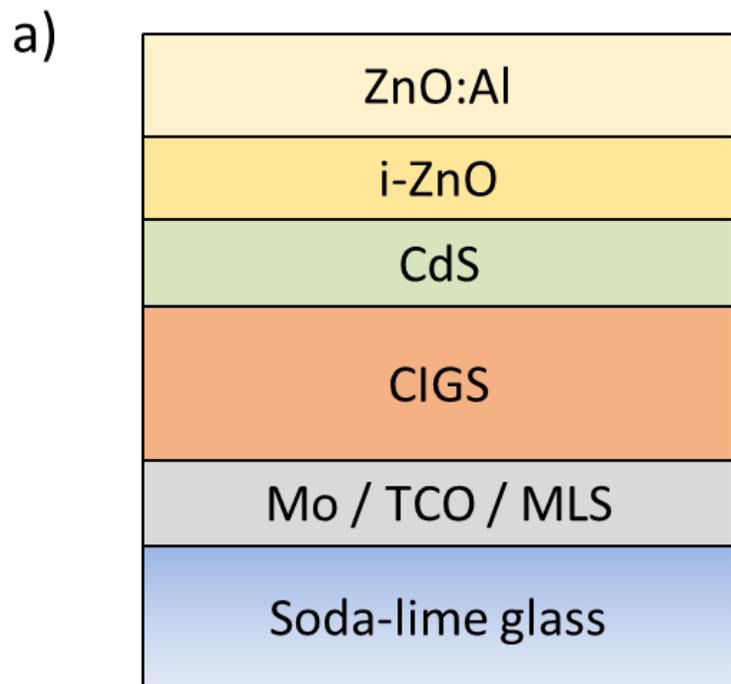
313 Fig. 1 Sketch of an ultrathin CIGS solar cell a) on planar back contacts such as  
314 molybdenum, TCO, or reflective multi-layer stack (MLS) and b) on a  
315 nanostructured back mirror consisting of a periodically patterned dielectric on top  
316 of reflective MLS. c) Three dimensional view of the ultrathin device on a  
317 nanostructured back mirror with optimized geometry. CIGS is deposited on top of  
318 a square-shaped dielectric nanogrid with a height of 200 nm, a period of 600 nm  
319 and hole width of 350 nm.

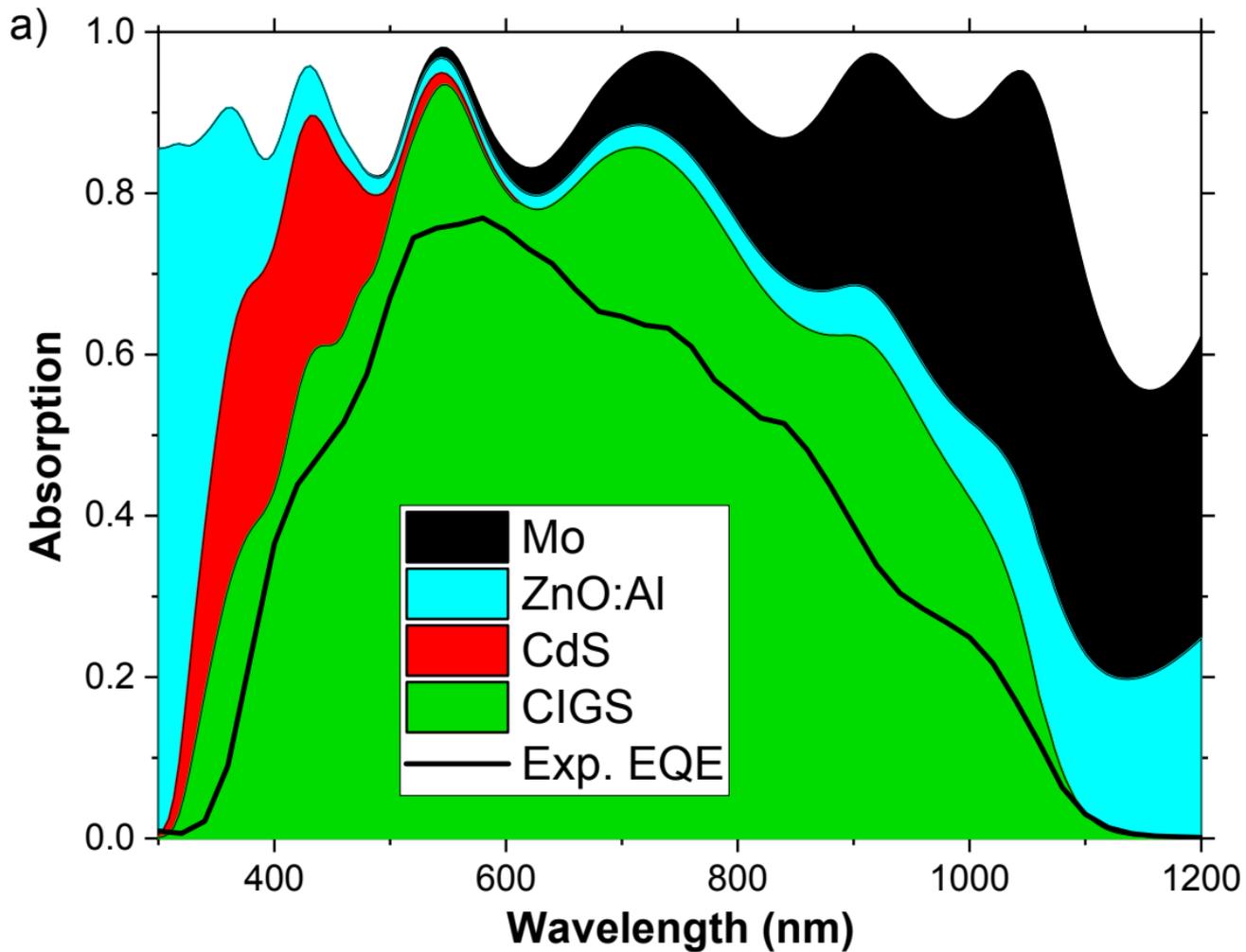
320 Fig. 2 Simulated absorption within each layer of 490 nm thick CIGS solar cells under  
321 AM1.5G illumination, with back contacts made of a) molybdenum, b) ITO, c)  
322 reflective multi-layer stack (MLS) and d) reflective MLS with nanopatterns.  
323 Respective experimental EQEs are given in a), b) and c) for comparison.

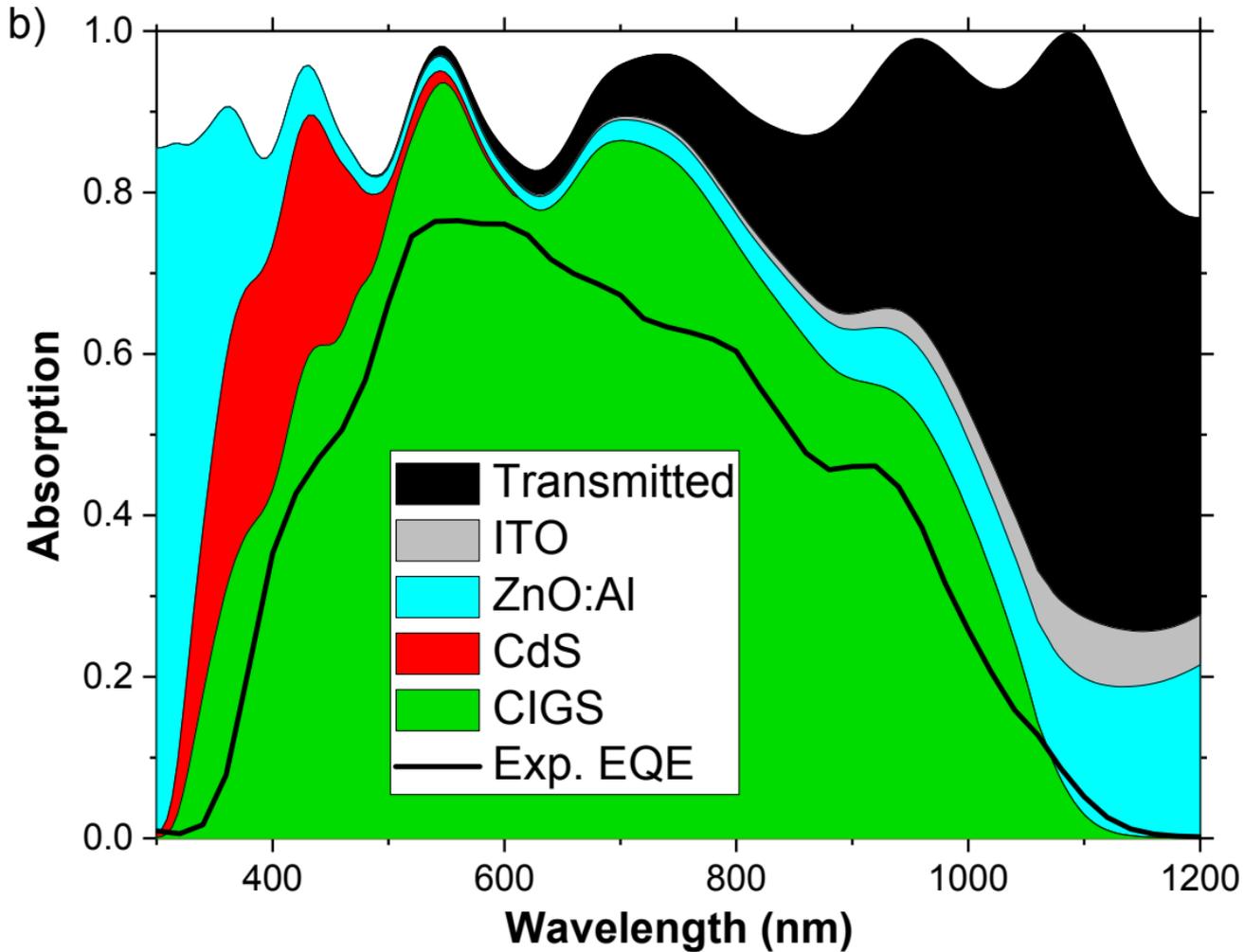
- 324 Fig. 3. a) Reflectance of 600 nm thick molybdenum (grey), 150 nm thick silver (black)  
325 and stacks of 30 nm thick (red) and 200 nm thick (blue) ITO on silver before and  
326 after annealing in air at 540 °C for 10 minutes (dashed and solid lines,  
327 respectively). b) Refractive index  $n$  (solid lines) and extinction coefficient  $k$   
328 (dashed lines) of a 200 nm thick sputtered ITO layer measured by ellipsometry  
329 before (black) and after (red) annealing.
- 330 Fig. 4 a) TEM dark field image of ultrathin CIGS layer deposited on ITO back contact  
331 with b) corresponding composition profile from average EDX signal, c) TEM dark  
332 field image of ultrathin CIGS layer close to the ITO back contact with associated  
333 EDX mappings of O, Ga, In, and Se elements.
- 334 Fig. 5 Experimental I(V) and External Quantum Efficiency (EQE) curves of 490 nm  
335 thick CIGS solar cells on molybdenum (black), ITO (red) and reflective multi-  
336 layer stack (blue) back contacts.

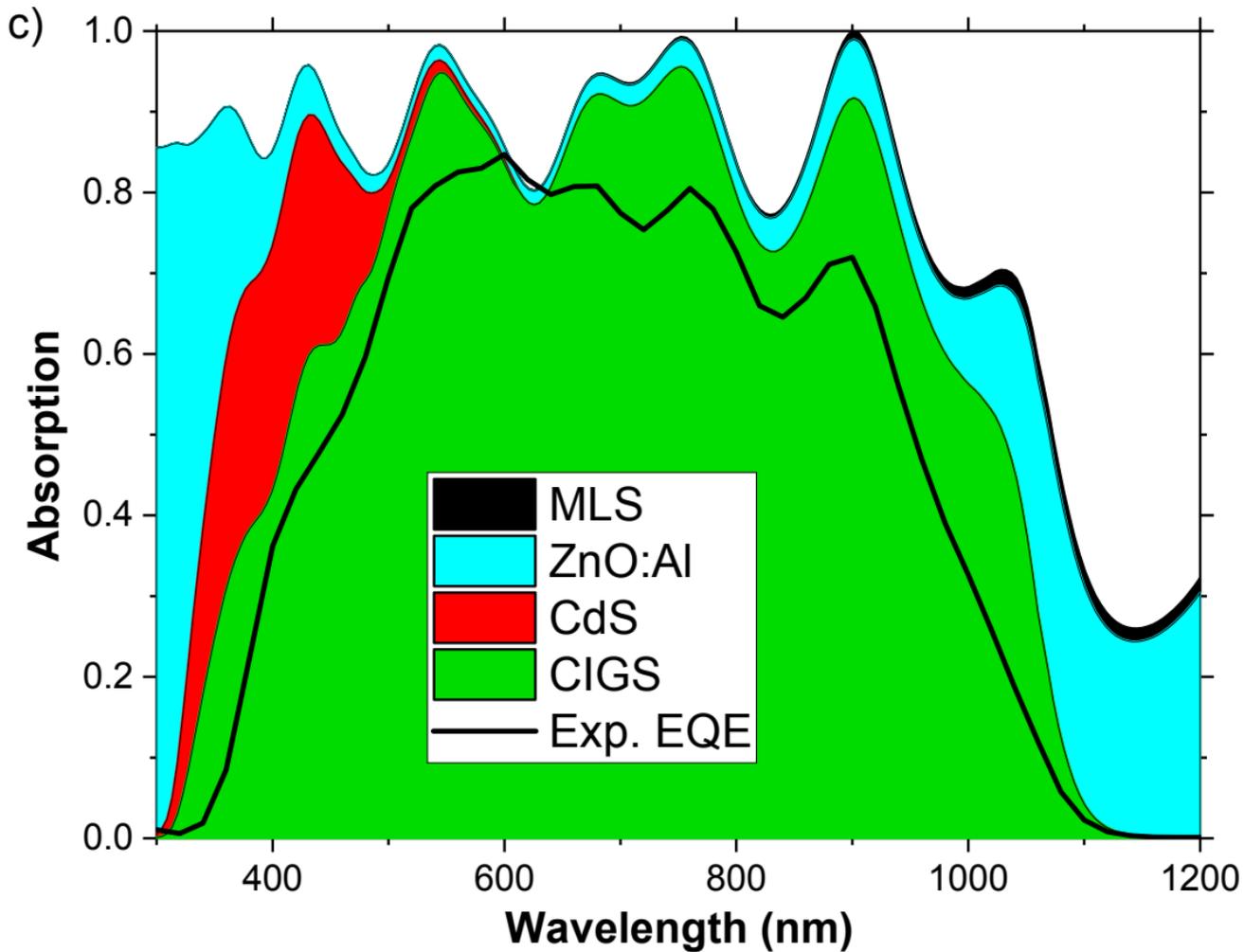
### 337 **Table captions**

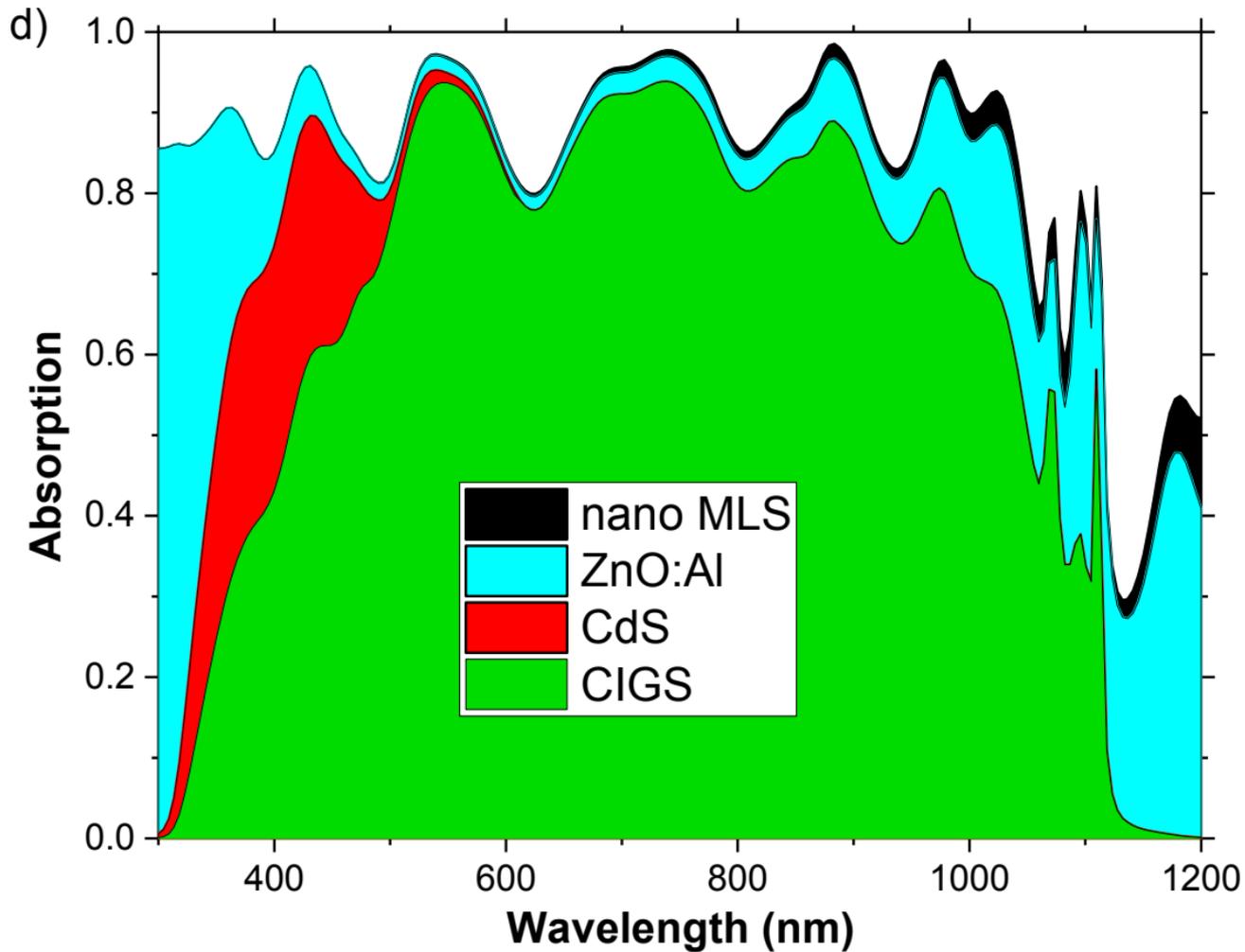
- 338 Table 1. Summary of I(V) parameters for 490 nm thick CIGS solar cells with various back  
339 contacts. A two-diode model is used to fit dark I(V) curves ( $J_{01}$  and  $J_{02}$ : saturation  
340 currents for respective ideality factors of 1 and 2,  $R_{SH}$ : shunt resistance,  $R_S$ : series  
341 resistance).

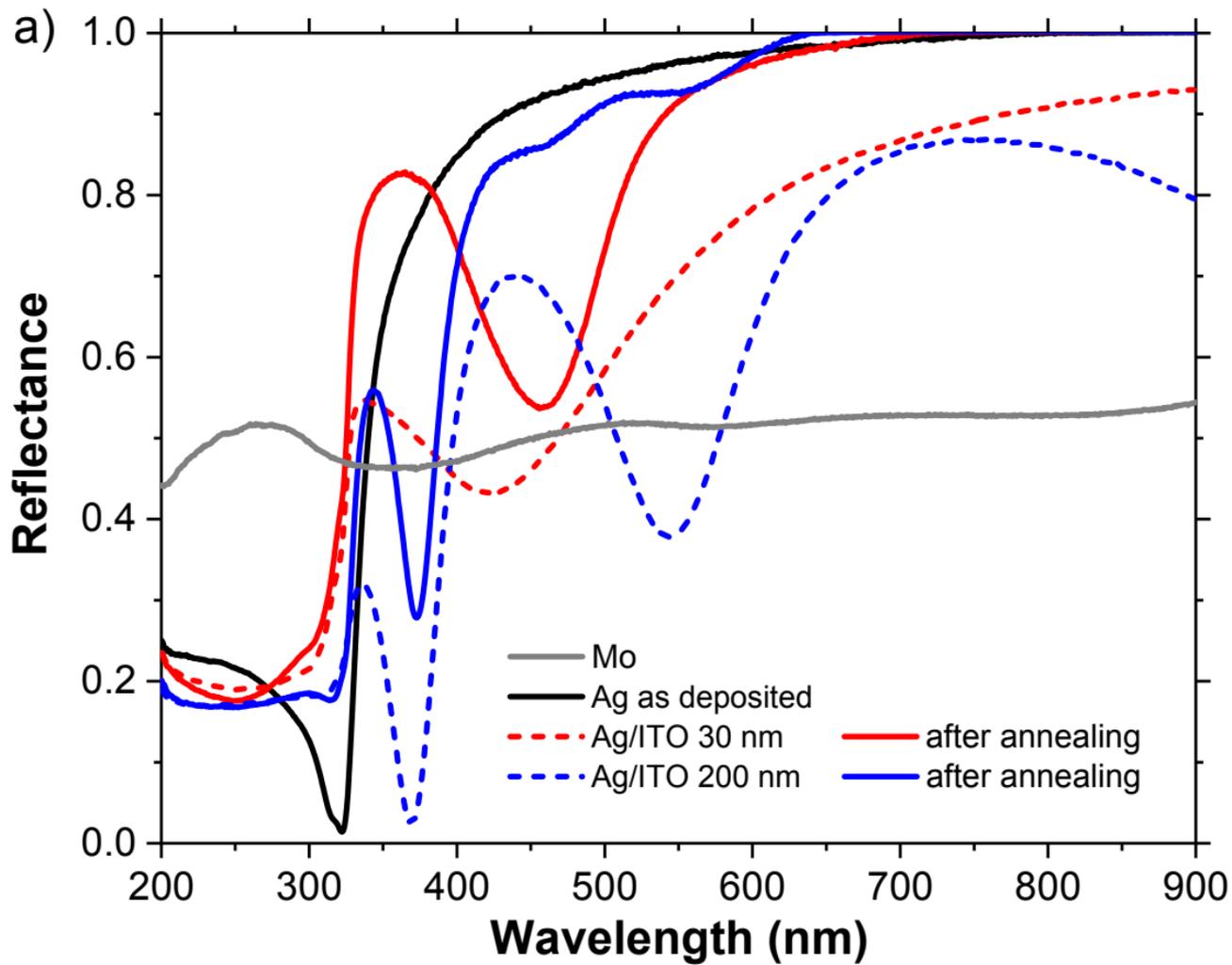


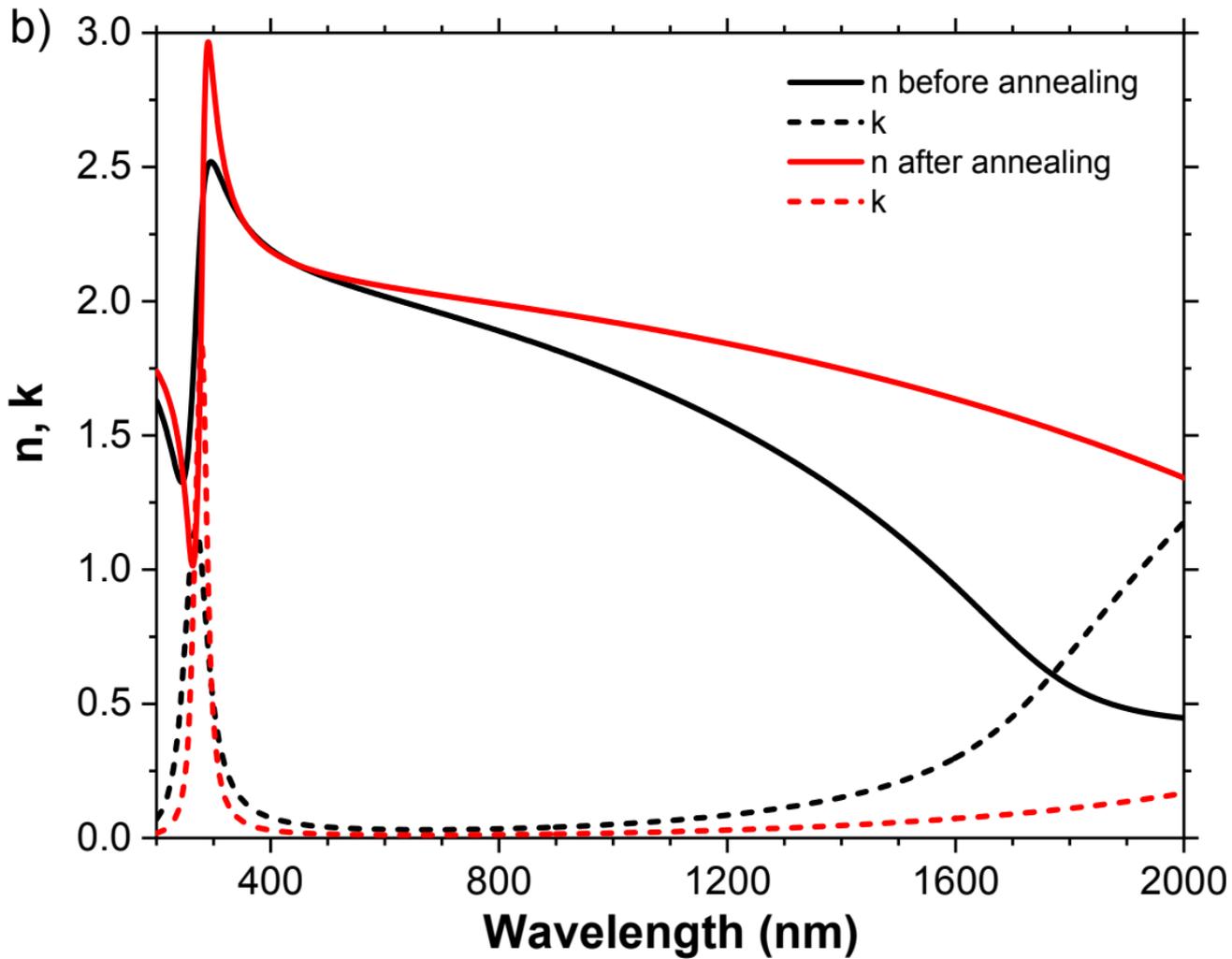








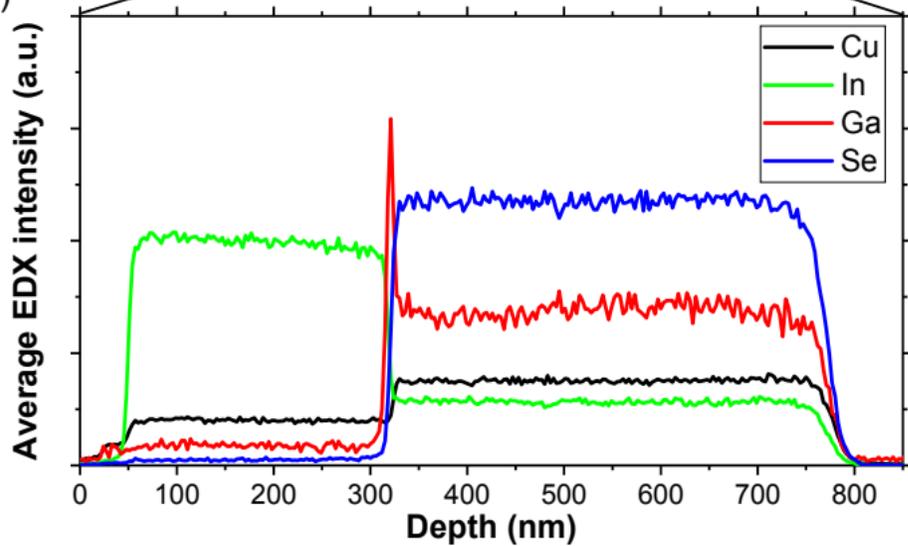




a)



b)



c)

