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Authors

Elanzeery, Hossam
Babbe, Finn
Melchiorre, Michele
et al.

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Potassium Fluoride *Ex Situ* Treatment on Both Cu-Rich and Cu-Poor CuInSe₂ Thin Film Solar Cells

Hossam Elanzeery, Finn Babbe, Michele Melchiorre, Anastasiya Zelenina, and Susanne Siebentritt

Abstract—In this paper, we show that CuInSe₂ (CIS) absorbers grown under Cu-excess have better collection efficiencies compared to Cu-poor ones. We also show that an *ex situ* potassium fluoride postdeposition treatment leads to an improvement in V_{OC} for CIS absorbers grown under both Cu-excess and Cu-poor conditions. Additionally, for absorbers grown under Cu-excess, the junction breakdown, which is observed in reverse bias of untreated cells, is removed. This improvement is based mainly on improving the interface of the CIS absorber grown under Cu-excess to the cadmium sulphide buffer layer through moving the dominant recombination from the interface to the bulk. In contrast to observations in the literature, the treated surface is not completely Cu-free.

Index Terms—Cu-peak shift, Cu-rich CuInSe₂ (CIS), improve V_{OC} , interface enhancement, surface compounds.

I. INTRODUCTION

CHALCOPYRITE copper indium gallium di-selenide Cu(In,Ga)Se₂ or CIGS represents one of the most attractive absorber materials to thin film solar cells due to their high efficiencies reaching 22.6% for the laboratory scale [1] and 16.5% for the large module scale [2]. CuInSe₂ (CIS) is the ternary compound characterized by its simpler structure compared to CIGS but with lower bandgap and with lower efficiency (15%) [3]. CIS can be formed in a wide compositional range in the copper poor region ($[Cu]/[In] < 1$), whereas the stoichiometric composition is at $[Cu]/[In] = 1$. From the phase diagram [4], it can be realized that CIS absorber grown under Cu-excess; referred to as “Cu-rich” ($[Cu]/[In] > 1$) material is characterized by a stoichiometric chalcopyrite bulk with an additional copper selenide (Cu₂Se) secondary phase, which forms on the surface and can be etched [5]. The advantage of using “Cu-rich” absorbers is based mainly on their electronic properties that are superior to Cu-poor ones where “Cu-rich” absorbers are reported to exhibit higher mobility with larger grains and lower defect densities [6]–[7]. However, solar cells based on “Cu-rich” absorbers are still exhibiting lower efficiencies compared to Cu-poor ones

mainly due to a strong decrease in open-circuit voltage (V_{OC}) and fill factor (FF). This has been attributed to recombination at the interface between CIS absorber and cadmium sulphide (CdS) buffer layers [8]. “Cu-rich” absorbers with a Cu-poor surface have been fabricated by an In–Se surface treatment. These treated absorbers show the same efficiencies as Cu-poor ones due to an improved interface and higher V_{OC} , as in Cu-poor cells [9]–[10]. Another technique to improve the surface of the absorber and increase both V_{OC} and FF is through the addition of an alkali treatment on the absorber surface and prior to the deposition of the buffer layer. Potassium fluoride (KF) is used for those postdeposition treatments (PDT) improving both V_{OC} and FF and, consequently, the efficiency [11]. The enhancement is reported to be due to a completely Cu-depleted surface of the absorber resulting in an improved absorber/buffer heterojunction quality [12]. KF PDTs have been used as *in situ* treatments for CIGS solar cells [11], [13]. Only few reports have been published on the *ex situ* treatment [14]–[15] showing an increase in V_{OC} values by 30–60 mV. In this paper, *in situ* treatment means that KF PDT treatments are deposited on the absorber layer in the same deposition chamber during the same deposition process, while *ex situ* treatment means getting the samples out of the deposition chamber, in our process etching the absorbers layers using potassium cyanide (KCN) and then adding the KF externally using electron-beam evaporation followed by an annealing process. The main purpose of this work is to investigate the effect of adding an *ex situ* KF PDT step on both “Cu-rich” and Cu-poor CIS thin film solar cells. The questions to answer here is the following: Does the KF treatment have any positive effect on “Cu-rich” absorbers, can KF *ex situ* treatment create a Cu-poor surface on “Cu-rich” CIS, does the KF *ex situ* PDT treatment behave in the same way for “Cu-rich” and Cu-poor cells, and can we use *ex situ* treatment as an alternative to the established *in situ* treatment?

II. EXPERIMENTAL

A. Synthesis of CuInSe₂ Solar Cells

CIS solar cells have been fabricated on molybdenum-coated soda lime glass substrates. Cu, In, and Se are deposited in a Veeco molecular beam epitaxy system through a one-stage evaporation process at a nominal temperature of 590 °C with either Cu/In ratio lower than one leading to Cu-poor absorbers or Cu/In ratio higher than one leading to “Cu-rich” ones. The formed “Cu-rich” CIS absorbers are then etched using a 10% aqueous KCN solution for 5 min to remove excess Cu₂Se secondary phases,

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The authors are with the Laboratory for Photovoltaics, Physics and Materials Science Research Unit, University of Luxembourg, Belvaux L-4422, Luxembourg (e-mail: hossam.elanzeery@gmail.com; finn.babbe@uni.lu; michele.melchiorre@uni.lu; anastasiya.zelenina@uni.lu; susanne.siebentritt@uni.lu).

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whereas the Cu-poor ones are etched in 5% aqueous KCN solution for 30 s to remove surface oxide layers [16]–[17]. A PDT step is then performed on the etched absorbers. KF is evaporated using a Ferrotec electron-beam deposition tool targeting thicknesses between 5 and 30 nm followed by an annealing step in a Carbolite tube furnace at 100–400 °C with a graphite box for 10–60 min under different environmental gas conditions. The treatment conditions were optimized for Cu-rich CIS absorbers and then the same conditions were used for Cu-poor ones. The optimum condition for the KF PDT was achieved by depositing a KF thickness in the range of 5–20 nm followed by an annealing step at 300–350 °C for durations less than 20 min in the presence of 40 mg Se. The *ex situ* method for KF treatment remained problematic due to the hygroscopic behavior of KF. The treated CIS absorbers are then rinsed in de-ionized water to remove remaining fluorides. After that, a CdS buffer layer is deposited using chemical bath deposition (CBD) followed by sputtering of zinc oxide (ZnO) and aluminum-doped ZnO window layers using an Aja Orion 8 sputtering tool. Finally, nickel–aluminum contact grids are deposited by electron-beam evaporation on top of the window layers.

B. Characterization

Finished solar cells were characterized by current–voltage (*IV*) measurements using a Keithley current–voltage (*IV*) source. Cells are illuminated by a cold mirror halogen lamp with an intensity of 100 mW/cm² calibrated by a silicon reference solar cell. Moreover, current–voltage at low temperatures (*IVT*) characteristics were performed using also a cold-mirror halogen lamp in order to extract the activation energy of the dominant recombination path. The *IVT* measurements were performed using a CTI-cryogenic closed cycle helium cryostat with a temperature range of 320–20 K. The illumination intensity was calibrated to the short-circuit current density (J_{SC}) obtained by *IV* measurements. The sample temperature was determined using a calibrated Si diode mounted on a glass substrate identical to the glass substrates used for the absorber growth. External quantum efficiency (EQE) measurements were performed at room temperature using a Bentham grating monochromator based setup, under chopped light of halogen and xenon lamps and a Stanford Research Systems Lock-in amplifier. Structural analyses of treated absorbers were characterized by X-ray photoemission spectroscopy (XPS) measurements using a Kratos Axis spectrometer and a monochromatic Al K α radiation (1486.6 eV). Photoelectrons were detected parallel to the normal to the surface with a pass energy of 20 eV for the narrow scans. Atomic concentration calculations and peak fitting were carried out after removing a Shirley-type background and by using the relative sensitivity factors provided by the spectrometer manufacturer. The sputtering of the samples was performed with Ar⁺ ions ($E = 4$ kV) and with an angle of 45°. The over-all Cu/In ratio was determined by an Oxford instrument energy dispersive X-ray spectrometer (EDX), using an electron acceleration voltage of 20 kV. The obtained Cu/In ratio by EDX represents the averaged overall composition of the absorber, including the surface Cu_xSe layer, where present.

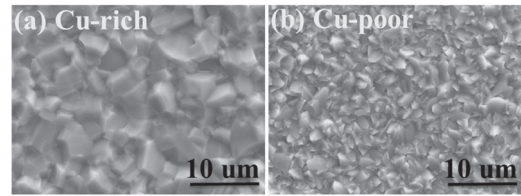


Fig. 1. Top-view SEM micrograph for (a) “Cu-rich” and (b) Cu-poor CIS absorbers before etching.

TABLE I
EDX FOR “CU-RICH” AND CU-POOR CIS ABSORBERS BEFORE AND AFTER KCN ETCHING

Sample	Cu (at%)	In (at%)	Se (at%)	Cu/In
“Cu-rich” before etching	29.5	22.1	48.4	1.30
“Cu-rich” after etching	25.8	24.5	49.7	1.05
Cu-poor before etching	22.8	25.5	51.7	0.89
Cu-poor after etching	23.4	25.8	50.7	0.91

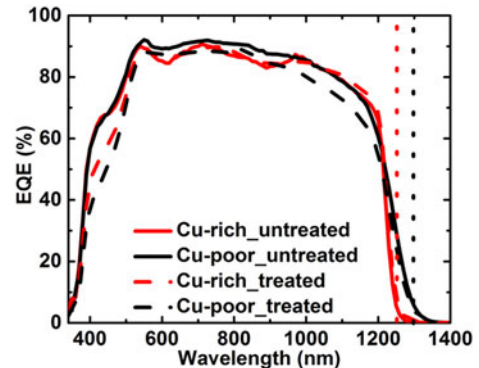


Fig. 2. EQE measurements for “Cu-rich” and Cu-poor CIS solar cells before and after the *ex situ* KF treatment. Dotted lines represent the extrapolated band gap for both “Cu-rich” (red) and Cu-poor (black) CIS absorbers.

III. RESULTS AND DISCUSSION

“Cu-rich” CIS absorbers are characterized by their large grains compared to Cu-poor ones as indicated in Fig. 1, which represents the top-view scanning electron microscope (SEM) micrograph for “Cu-rich” and Cu-poor CIS absorbers before etching. After etching, the Cu/In ratio is stoichiometric as presented in Table I where the EDX values for Cu/In ratio decreased from 1.3 to 1.05 indicating the removal of Cu₂Se secondary phases. The composition of Cu-poor absorbers remained the same within error before and after etching [5]. Each value of Cu/In ratio in Table I represents the average of four absorbers.

In EQE measurements, depicted in Fig. 2, “Cu-rich” CIS cells show somewhat higher EQE values compared to Cu-poor ones at longer wavelengths (1100–1200 nm) indicating a better carrier collection near the absorber band gap. To compare carrier collection efficiency for both “Cu-rich” and Cu-poor cells, we need the optical bandgap, which was determined by linear extrapolation around the minimum point in the derivative of the EQE measurements.

TABLE II
CARRIER COLLECTION EFFICIENCY CALCULATIONS FOR “CU-RICH” AND CU-POOR CIS SOLAR CELLS BEFORE AND AFTER KF PDT EXTRAPOLATED FROM EQE MEASUREMENTS

Sample	Optical band gap (eV)	J_{SC_EQE} ($\text{mA}\cdot\text{cm}^{-2}$)	J_{SC_MAX} ($\text{mA}\cdot\text{cm}^{-2}$)	Carrier collection efficiency (%)
“Cu-rich”	0.995	37.9	48.2	78.6
Cu-poor	0.957	38.8	50.3	77.1
“Cu-rich” treated	0.994	37.4	48.3	77.4
Cu-poor treated	0.959	36.3	50.2	72.3

TABLE III
ELECTRICAL PARAMETERS FOR “CU-RICH” AND CU-POOR CIS SOLAR CELLS BEFORE AND AFTER KF TREATMENT, MEASURED UNDER DARK CONDITIONS

Sample	Efficiency (%)	FF (%)	V_{OC} (mV)	J_{SC} ($\text{mA}\cdot\text{cm}^{-2}$)	R_S ($\Omega\cdot\text{cm}^{-2}$)	A A	J_0 ($\text{A}\cdot\text{cm}^{-2}$)
“Cu-rich”	7.4	57	336	38.9	0.5	1.4	1.4E-06
“Cu-rich” treated	7.0	49	372	37.8	0.9	1.8	5.0E-06
Cu-poor	12.8	68	446	42.0	0.6	1.3	4.8E-08
Cu-poor treated	9.9	54	458	40.3	1.2	2.0	1.6E-06

The band gap of “Cu-rich” CIS absorber shows higher values (0.995 eV) compared to the band gap of Cu-poor ones (0.957 eV) as reported in [18] and indicated by the dotted lines in Fig. 2. Based on the EQE measurements in Fig. 2, J_{SC} was determined by integrating the EQE spectrum multiplied with the AM1.5 spectrum [19]. J_{SC} extrapolated from the EQE spectrum (J_{SC_EQE}) for “Cu-rich” CIS cell indicated a value of $37.9 \text{ mA}\cdot\text{cm}^{-2}$ compared to $38.8 \text{ mA}\cdot\text{cm}^{-2}$ for Cu-poor ones. After that, the maximum J_{SC} (J_{SC_MAX}) values that could be achieved for those two band gaps were calculated by integrating the AM1.5 spectrum until the specified band gap resulting in J_{SC_MAX} of $48.2 \text{ mA}\cdot\text{cm}^{-2}$ for “Cu-rich” (band gap of 0.995 eV) compared to $50.3 \text{ mA}\cdot\text{cm}^{-2}$ for Cu-poor (band gap of 0.957 eV). Finally, the carrier collection efficiency was calculated as reported in [20] based on

$$\text{Carrier collection efficiency} = \frac{J_{SC_EQE}}{J_{SC_MAX}} \times 100\%. \quad (1)$$

Based on these calculations, “Cu-rich” CIS solar cells show superior carrier collection efficiency with 78.6% compared to Cu-poor cells with 77.1% as summarized in Table II.

Despite these superior properties of “Cu-rich” over Cu-poor CIS absorbers, the electrical characteristics show a worse behavior for “Cu-rich” CIS cells for almost all parameters as summarized in Table III. The drop in the efficiency from 12.8% for the Cu-poor cell to 7.4% for “Cu-rich” one is mainly due to the losses in V_{OC} and FF. To tackle this deficiency in the electrical behavior, KF PDT was used.

Different conditions have been tested to analyze the effect of the *ex situ* KF treatment. From these, we can draw several conclusions on the necessary conditions for the PDT process, which consists of the deposition of a KF layer and subsequent annealing. First, the presence of Se during the annealing step is necessary to maintain the quality of the formed absorber layer.

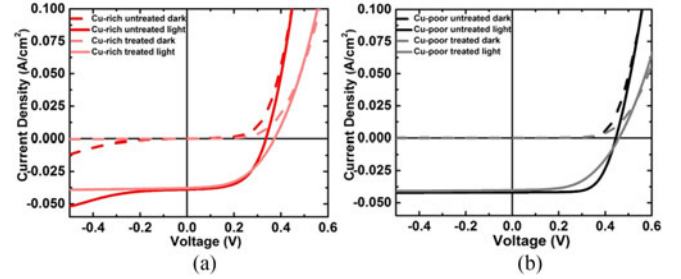


Fig. 3. IV Characteristics for (a) “Cu-rich” and (b) Cu-poor CIS solar cells before and after the *ex situ* KF treatment.

Second, a high amount of Se (40 mg for our experiments) needs to be provided as less Se deteriorates the electrical performance of the solar cell. Third, the most preferable temperatures are between 300 and 350 °C. Temperatures below this range deteriorate the V_{OC} and FF values significantly while those above this range deteriorates the absorber layer and form excess secondary phases such as Cu_2Se , CuSe_2 , and InSe_2 . Fourth, the annealing duration should not exceed 20 min to avoid shunting the solar cell. Finally, the thickness of the KF layer needs to be thin enough (nominally 5–20 nm) where excess KF has shown a negative impact on the V_{OC} and FF values.

EQE measurements in Fig. 2 show a decrease in the short wavelength region (350–550 nm) for both “Cu-rich” and Cu-poor cells after the *ex situ* KF treatment, referred to as “Cu-rich treated” and “Cu-poor treated.” Knowing that the yellow turbidity in the CdS CBD of the treated absorbers appeared later than our standard CBD process, this decrease in EQE values at short wavelengths can be attributed to an increased absorption in a thicker CdS buffer layer, since the treatment makes the buffer layer grow faster as reported in [11]. While the EQE values for Cu-poor treated cells also decreased for longer wavelengths, the behavior for “Cu-rich” treated cells was different. Similar EQE values for “Cu-rich” cells before and after the treatment were recorded with even higher values for treated “Cu-rich” samples near the band gap (1100–1200 nm). “Cu-rich” treated samples show the highest EQE response among all four cells in this wavelength range. In accordance, the extrapolated J_{SC} (J_{SC_EQE}) did not suffer the same drop for “Cu-rich” cells ($\Delta J_{SC_EQE} = -0.5 \text{ mA}\cdot\text{cm}^{-2}$) compared to Cu-poor ones ($\Delta J_{SC_EQE} = -2.5 \text{ mA}\cdot\text{cm}^{-2}$). The calculated carrier collection efficiency for “Cu-rich” cells after treatment indicated 77.4% similar to untreated Cu-poor ones (77.1%). This decrease in carrier collection efficiency for both “Cu-rich” and Cu-poor cells after the treatment is reflected in the J_{SC} values from the IV measurements presented in Table III and shown in Fig. 3. On the other side, the V_{OC} values increased for both “Cu-rich” ($\Delta V_{OC} = +36.6 \text{ mV}$) and Cu-poor ($\Delta V_{OC} = +12.9 \text{ mV}$) cells after treatment with more pronounced improvement for “Cu-rich” ones. An additional effect is observed in Fig. 3(a). Untreated “Cu-rich” cells show a reverse breakdown behavior with a strong increase of the current which already starts at reverse voltages below 0.3 V. This breakdown is not observed within the measured voltage range for treated “Cu-rich” cells. The drop in efficiency for both

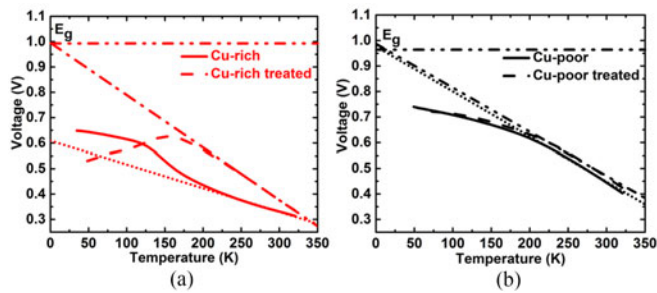


Fig. 4. Temperature dependence of voltage measured by *IVT* measurements for (a) “Cu-rich” and (b) Cu-poor CIS solar cells before and after the *ex situ* KF treatment. Dashed, dotted lines represent the extrapolated activation energy. Dashed-double dotted lines represent the band gap energy (E_g).

“Cu-rich” and Cu-poor cells is mostly due to the decrease in FF values. This decrease in FF is a result of an increase in the series resistance (R_S) from 0.5 to 0.9 $\Omega \cdot \text{cm}^{-2}$ for “Cu-rich” cells and from 0.6 to 1.2 $\Omega \cdot \text{cm}^{-2}$ for Cu-poor ones accompanied by an increase in the ideality factor (A) from 1.4 to 1.8 in the case of “Cu-rich” samples and from 1.3 to 2.0 for Cu-poor ones. The values of R_S , A , and the saturation current (J_0) presented in Table III were obtained by fitting the dark *IV* curve with the single diode model of the ECN *IV* curve fitting program *ivfit*. The program and the methods used are described in [21]. The values presented in Table III represent the electrical performance of the best cells with other cells behaving in a similar manner. We believe that the increase in series resistance is due to the formation of an additional layer at the surface of the absorbers, as discussed below. The influence of this layer on the diode factor is difficult to describe at the moment.

As the KF PDT succeeded in increasing the V_{OC} values for both “Cu-rich” and Cu-poor CIS cells, we would like to understand the mechanism of the improvement. In order to analyze the treatment’s impact on the interface between the absorber and the buffer layers, *IVT* measurements were performed. The linear extrapolation of the open-circuit voltage toward 0 K gives the activation energy of the dominant recombination path [22]. Untreated “Cu-rich” cells exhibit an extrapolated activation energy (0.62 eV) lower than the band gap (0.996 eV), as indicated in Fig. 4. This implies that the dominant recombination is at or near the interface. However, after the KF treatment, the extrapolated activation energy shows values close to the band gap indicating an improvement in the interface moving the dominant recombination from the interface to the bulk. For Cu-poor CIS cells, the *ex situ* treatment did not imply a negative effect to the interface surface from the point of view of extrapolated activation energy, where the extrapolated values before and after the treatment are close to each other and close to the band gap.

With the aim to understand the chemical changes at the surface due to the treatment we performed an XPS study on treated absorbers, both “Cu-rich” and Cu-poor. XPS measurements were performed at the surface (0 s) and after a series of sputtering steps with a total duration of 120, 240, and 720 s. After the last step, we sputtered about 50 nm deep into the absorber; thus, we can expect that the last spectrum shows the

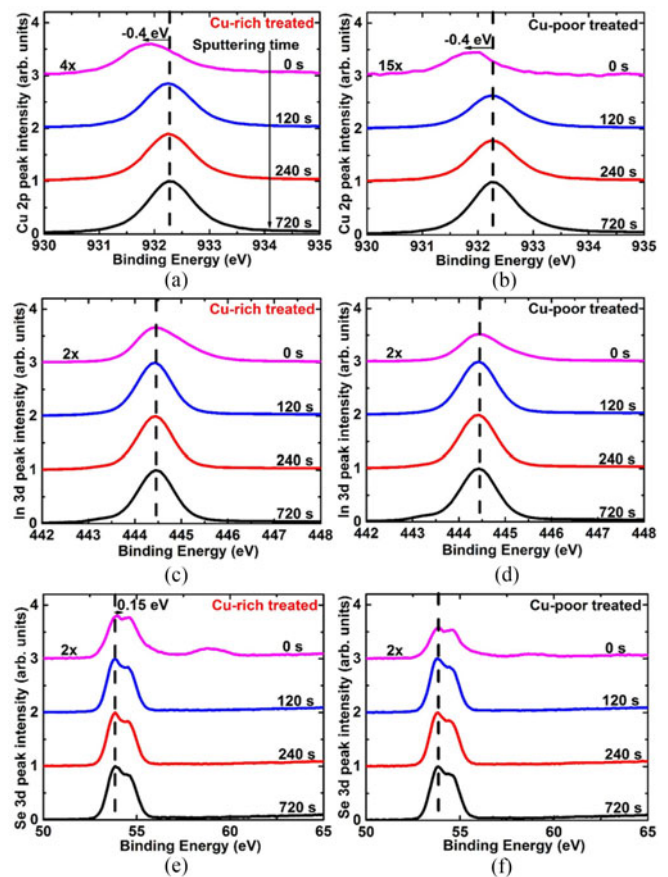


Fig. 5. XPS measurements for (a) Cu 2p peak for “Cu-rich,” (b) Cu 2p peak for Cu-poor, (c) In 3d peak for “Cu-rich,” (d) In 3d peak for Cu-poor, (e) Se 3d peak for “Cu-rich,” and (f) Se 3d peak for Cu-poor CIS absorbers after the *ex situ* KF treatment.

bulk properties. The first observation from Fig. 5 is that the spectra and their development with depth are very similar between “Cu-rich” and Cu-poor CIS. The second observation is that the spectra after 120, 240, and 720 s of sputtering are the same. Thus, only the unsputtered surface shows the features of the surface layer. All unsputtered spectra for the Cu, In, and Se peaks show lower intensity at the surface than in the bulk (note the multiplication factors in Fig. 5). This is expected since the samples were transferred through ambient air to the XPS system and were contaminated. The most important observation, however, is that we observe a Cu peak at the treated surface. This is opposed to the findings in the literature [11], [14], [23] where the K-treatment was observed to result in a completely Cu-depleted surface. We find a reduction of the Cu signal: Cu/In ratio is reduced by a factor of 2 with respect to the bulk in the case of “Cu-rich” CIS and by a factor of 8 in the Cu-poor case—but there is still Cu at the surface. This can have two reasons: the surface treatment leads to a noncontinuous surface layer, as observed in [24], or our treatment leads to a different surface layer which still contains Cu. We find the energy of the Cu peak at the surface shifted with respect to the bulk by 0.4 eV toward lower binding energy. This shift is not due to an oxidation of Cu at the surface, since Cu oxides would move the Cu peak toward higher

energies [25]. It is also not simply a Cu_xSe compound, since it is present at the Cu-poor surface as well and the surface was etched by KCN before the measurement. This Cu peak shifted in binding energy indicates that the surface layer does contain Cu in a different chemical environment than in the bulk. Other chemical changes at the surface are observed by a broadening of the In peak toward higher binding energies. The Se spectra show an additional peak doublet at the surface. This additional peak can be due to Se oxides [26]. It is at the moment, not possible to make a conclusion about the detailed chemical nature of the surface layer, except that it does contain Cu, in contrast to what has been observed in the literature.

IV. CONCLUSION

“Cu-rich” CIS absorbers have better carrier collection efficiencies compared to Cu-poor ones. However, the main drawback in “Cu-rich” CIS cells compared to Cu-poor ones is the decrease in V_{OC} and FF values. *Ex situ* KF treatment has been implemented on “Cu-rich” and Cu-poor CIS thin film solar cells showing improved values of V_{OC} for both “Cu-rich” and Cu-poor CIS cells. The breakdown at reverse bias observed for “Cu-rich” cells was also removed by the treatment. On the other side, the FF values decreased as a consequence of increasing the series resistance and ideality factor values after the treatment. By the *ex situ* KF treatment, we succeeded to remove one of the main drawbacks in “Cu-rich” CIS cells related to its interface with the buffer layer: the KF PDT moves the dominant recombination from the interface to the bulk. In terms of chemical changes at the surface, a shifted XPS Cu 2p peak toward lower binding energy is observed at the surface of both “Cu-rich” and Cu-poor treated absorbers as well as a broadening of the In peak toward higher binding energies and an additional Se peak doublet at the surface. This suggests the formation of new compounds containing Cu and Se in a different chemical structure than CIS or Cu–Se secondary phases. Although the improvement in electrical parameters is not yet comparable to the one obtained from the In–Se treatment [10], this paper shows that KF *ex situ* treatment has a positive influence on the surface of the absorbers grown under Cu-excess. The KF *ex situ* treatment also improves V_{OC} of Cu-poor CIS solar cells.

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Hossam Elanzeery was born in Cairo, Egypt, in 1987. He received the B.S. degree in instrumentation and control from the University of Technology Petronas, Tronoh, Malaysia, in 2010 and the M.Sc. degree in microelectronics system design from Nile University, Cairo, Egypt, in 2014. He is currently working toward the Ph.D. degree with the Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg, in the alkali treatment of “Cu-rich” CuInSe_2 .

His Master’s thesis was completed at IMEC, Belgium, where he was a Researcher with the alternative thin film photovoltaic team working on the optical characterization and optimization of thin-film absorber materials, as well as the fabrication of high band gap absorbers. He had worked with $\text{Cu}_2\text{ZnSnSe}_4$, $\text{Cu}_2\text{ZnGe}(\text{S},\text{Se})_4$, $\text{Cu}_2\text{ZnSiSe}_4$, and $\text{Cu}_2\text{Si}(\text{S},\text{Se})_3$ absorbers. He has more than 10 publications, two patents, and one book on thin film solar cells. His current research interests include physics and electrical characterization of solar cells.



Finn Babbe was born in Husum, Germany, in 1989. He received the B.S. and M.S. degrees in physics from the Carl von Ossietzky University, Oldenburg, Germany, in 2012 and 2014, respectively. During his Master’s thesis, he worked on the preparation methods to introduce artificial shunts into thin film $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ solar cells via focused ion beam milling. Following the scientific career path, he moved to Luxembourg, where he is currently working toward the Ph.D. degree in optical characterization of alkali-treated $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ layers.

He has a handful of publications. His research interests include high-vacuum thin film solar cell growth and optical characterization.

Mr. Babbe received a prize at a national competition regarding environmental issues (BundesUmweltWettbewerb II).



Michele Melchiorre received the M.Sc. degree in chemistry and pharmaceutical technologies from the Alma Mater Studiorum, University of Bologna, Bologna, Italy, in 2006 and the Ph.D. degree in medicinal chemistry in 2010 from the University of Florence, Florence, Italy.

His scientific background lies in the life science field, mainly in the interconnection between chemistry and biology. In 2009, he spent 10 months at Harvard University, Cambridge, MA, USA, as a visiting Ph.D. student in chemical biology. After several postdoctoral positions (first at the Italian Institute of Technology and then at ISOF-CNR Bologna), he gained experience as a Researcher with Lipinutragen Srl, which is spin-off of the CNR Bologna. In 2015, he completely changed subject by switching from chemical biology to material chemistry. Currently, he is with the Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg, where he is taking care of the whole baseline process that leads to the formation of semiconductor photovoltaic devices, and he is developing new buffer layers to be implemented in the process.



Anastasiya Zelenina received the Ph.D. degree in physics from the University of Freiburg, Freiburg, Germany, in 2016.

She is currently a Postdoctoral Researcher with the Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg. Her background includes thin film preparation and characterization. Her previous experience includes research on silicon nanocrystals in various dielectric matrices. Currently, her major research focus is the fundamental understanding of “Cu-rich” chalcopyrite absorbers.



Susanne Siebentritt studied physics in Erlangen, Germany, and received the Doctoral degree in physics from the University of Hannover, Hannover, Germany.

She has been a Physics Professor and has headed the Laboratory for Photovoltaics, University of Luxembourg, Belvaux, Luxembourg, since 2007. Her research interest is twofold: the development of new thin film solar cells and the semiconductor physics of the materials used in these cells. Her group’s research focuses on chalcopyrites and related materials. After several postdoc positions in Los Angeles, CA, USA, and Berlin, Germany, she became a Group Leader at Helmholtz-Zentrum Berlin, before moving to Luxembourg to build up the Laboratory for Photovoltaics. She is the author of more than 160 peer reviewed publications, with more than 3000 independent citations.

Dr. Siebentritt received the FNR Outstanding Publication Award, together with three co-authors in 2014. In 2015, she received the “Grand Prix en Sciences Physique–Prix Paul Wurth” of the Luxembourgish Institute Grand Ducal. She is a regular topical organizer at the international photovoltaics conferences in Europe and the United States. She is a member and the Vice Chair of the scientific council of Science Europe. Since 2016, she is a board member for the Kopernikus programme of the German Ministry of Education and Research.