Short communication

Prediction of photovoltaic p–n device short circuit current by photoelectrochemical analysis of p-type CIGSe films

Diego Colombara [a,*], Alexandre Crossay [a], David Regesch [a], Cedric Broussillou [b], Thomas Goislard de Monsabert [b], Pierre-Philippe Grand [b], Phillip J. Dale [a]

[a] Physics and Materials Research Unit, Université du Luxembourg, 41, rue du Brill, L-4422 Belvaux, Luxembourg
[b] Nexcis, 190 av. Célestin Coq, Zone Industrielle, 13790 Rousset, France

ARTICLE INFO

ABSTRACT

The quality control of individual semiconductor thin films during fabrication of multiple layers is important for industry and academia. The ultimate aim of this research is to predict the efficiency of p–n junction solar cells by photoelectrochemical analysis of the bare p-type semiconductor. A linear correlation between the photocurrent measured electrochemically on Cu(In,Ga)Se$_2$ absorber layers through a Eu^{3+} electrolyte junction and short circuit current and efficiency of the corresponding solid state devices is found. However, the correlation is complicated by pronounced recombination at the semiconductor/electrolyte interface, while the solid state interface behaves more ideally.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Being able to predict the final efficiency or photovoltaic (PV) properties of a p–n junction solar cell from analysis of just the p-type semiconductor film before the addition of the four subsequent layers required to complete the device would allow a cost effective control of the production line (Fig. 1). Besides suggesting if device completion is worthwhile, accurately assessing PV potential would also provide academic groups without device completion facilities the means of estimating potential conversion efficiencies. Hence, the goal of this research is to develop a photoelectrochemical (PEC) method to test the PV potential of p-type semiconductor thin films on conductive substrates.

The underlying assumption of this work is that overall device efficiency is dominated by the quality of the p-type semiconductor layer. The hypothesis is that a measurable PEC parameter can be correlated to the PV device efficiency. Device efficiency is proportional to the product of the short circuit current density (J_{SC}) and the open circuit voltage. J_{SC} is proportional to the collection length of excited charge carriers, and if single-junction devices with same band-gap semiconductors are considered [1], it is a reasonable predictor of efficiency (Fig. 1). If a PEC parameter could be correlated to J_{SC}, a relationship with the final device efficiency would be established.

In a very close similarity with p–n junctions, the electrical behavior of p-semiconductor/electrolyte junctions as a function of the applied

bias can be expressed by the diode equation [2], and is shown schematically in Fig. 1. The theory of semiconductor electrochemistry has been extensively reviewed by Memming, to whom the reader is referred [3].

This similarity with the p–n junction made possible the design of a number of PEC solar cells [12–15] that in the case of n-type semiconductors have achieved power conversion efficiencies as high as 15% [16]. Issues of semiconductor photocorrosion, as well as surface instability under prolonged operation have somehow discouraged their further development. Nevertheless, optically transparent semiconductor/electrolyte junctions, with their near-reversibility and fast implementation, have been viably and widely employed [17] to characterize single [18–20] and polycrystalline [21–33] semiconductor materials. Information such as conductivity type [29,30], band-gap and flat-band potential [31], doping density [25,33], as well as insights on the presence of optically absorbing phases on the film surface [32] have been obtained.

This versatility is appealing for the development of a method aimed at screening PV semiconductor properties. Perhaps due to its relationship with J_{SC} and to the simplicity of the measurement, photocurrent density (J_{Ph}) remains the most reported PEC parameter. However, it is known that the theoretical correlations between solid state and PEC solar cells are complicated by experimental issues including the nonideality of surface structures and current collection at the semiconductor/electrolyte interface [34].

In this sense, the present work aims at explicitly testing if the correlation between J_{SC} and J_{Ph} holds satisfactorily, and thus if J_{Ph} can be considered a suitable indicator for the quality assessment of thin films for PV applications. This is an important research question that has never

* Corresponding author.
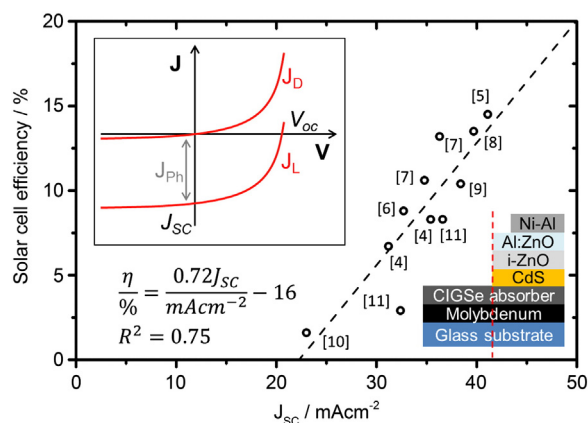E-mail address: diego.colombara@uni.lu (D. Colombara).

Fig. 1. Correlation between J_{SC} and solar cell power conversion efficiency for a number of CuInSe$_2$-based devices with equation and coefficient of determination R^2 [4–11]. Left inset: ideal current-voltage characteristics of a p-semiconductor/electrolyte junction in the dark (J_D) and under illumination (J_L). J_{Ph} is the intercept of J_L on the y axis and is negative for p-semiconductors. The similarity with solid state p–n junctions is emphasized by the corresponding solar cell parameter (J_{SC}). Right inset: schematic structures of bare CIGSe photoelectrode on conductive substrate and full solar cell device.

been explored in the literature. This work provides an idea of how much J_{Ph} can be related to J_{SC} and therefore if comparative assessments of semiconductors based simply on J_{Ph} are reliable.

2. Experimental

Six Cu(In,Ga)Se$_2$ (CIGSe) absorber layers with strikingly diverse properties were intentionally produced for this study by deliberate deviation from the baseline procedure which consists of electrodeposition of metal precursors followed by selenization. Each absorber layer was split into two, with half completed into solar cell devices and the other half tested photoelectrochemically with a statistics of eight samples for each absorber and each technique in order to obtain a meaningful data distribution (total of 96 samples). The cell finishing procedure consisted of 30 s etching in 5 wt.% KCN aqueous solution followed by chemical bath deposition of CdS, RF-magnetron sputtering of i-ZnO and Al:ZnO and e-beam evaporation of Ni–Al front contact grids. Importantly, the cell finishing procedure of the samples was carried out in the same deposition batches, ensuring similar properties of buffer and window layers. The power conversion efficiencies of the solar cells were measured with a current-voltage setup (with a halogen lamp of AM1.5 intensity equivalent) and ranged between 2 and 11%. The PEC experiments were performed with a three electrode setup (Ag/AgCl reference, Pt wire counter electrodes) in a 0.2 M aqueous solution of EuCl$_3$ and consisted of chronoamperometric analyses in reverse bias (−0.5 V vs Ag/AgCl) under pulsed illumination from a white light emitting diode (LED) source with light intensity corresponding to approximately 1‰ of AM1.5. The series of CIGSe photoelectrodes displayed very similar open circuit potentials around −0.1 V vs Ag/AgCl when immersed in the Eu^{3+} solution. The potential of −0.5 V vs Ag/AgCl was chosen because it corresponds to a similar band bending as per the solid state devices. A 530 nm LED source was also employed to perform light intensity dependence measurements. The majority of the LEDs output power lies at photon energies well above the CIGSe band-gap, thus any slight variations among the CIGSe films can be neglected. Apparent quantum efficiency (AQE — aka incident photon to current conversion efficiency, IPCE) is calculated from a calibrated Si photodiode. The PEC tests were performed on absorbers of 0.2 cm^2 masked area immediately after 30 s etching in 5 wt.% KCN aqueous solution. All data were area corrected.

3. Results and discussion

3.1. Choice of the measurement conditions

The importance of employing intentional redox species for reliable PEC measurements, besides the naturally occurring hydrated protons in deionized water is investigated. Fig. 2 shows the chronoamperometric analyses of a CIGSe film measured in the absence (solid line) and presence (dotted line) of 0.2 M Eu^{3+} at pH = 3.6 under the pulsed illumination of a white LED. In both cases a negative photocurrent is recorded when the light is turned on, as expected for a p-type semiconductor. However, it is very clear that in the absence of Eu^{3+} J_{Ph} is not reproducible; during the illumination the photocurrent decreases and the rate of decrease increases after each LED pulse.

This behavior points to some sort of light-induced surface degradation of the semiconductor. Due to the absence of electron scavengers in the electrolyte, it is likely that the photogenerated electrons cause photoreduction of the CIGSe surface, with formation of surface copper adatoms acting as recombination centers. Contrarily, the measurement performed in the presence of Eu^{3+} proved reasonably reproducible.

This result suggests that even though it is possible to measure J_{Ph} in inert electrolytes, as also reported in the literature [22,23,25], intentional redox species with suitable reduction potential are needed if the reproducibility of the measurement and semiconductor surface preservation are considered.

J_{Ph} was determined as the difference between the current density measured in the dark and under illumination at the steady-state value (Fig. 2).

3.2. Correlation between J_{Ph} and J_{SC} of CIGSe films

Fig. 3a shows that linear correlations hold between the PEC-assessed photocurrent density (J_{Ph}) of the series of CIGSe layers and short circuit current density (J_{SC}) and efficiency (η) of the solid state solar cell devices (R^2 ~ 0.9). Since the correlations are composed of two independent data sets, the graph is obtained by plotting the average values and the standard deviations (8 + 8 measurements/sample). Although the data distribution associated with J_{Ph} is broader compared to J_{SC} and η, the correlations indicate that J_{Ph} is a reasonable predictor of J_{SC} and η and may serve as a quality control indicator for CIGSe absorber layers. Differences in J_{SC} could have simply been caused by different surface band-gaps; however, it is estimated that the measured band-gap variations account for less than 4% of the variation of J_{SC} based on the AM1.5 spectrum.
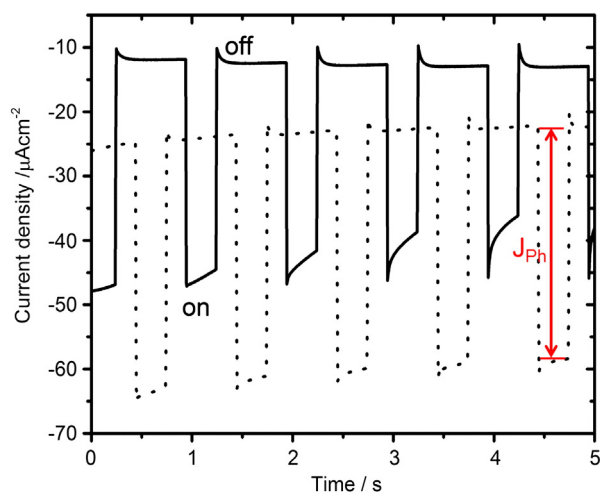

Fig. 2. Chronoamperometric analysis of a CIGSe film performed in KCl 0.6 M (solid line) and EuCl$_3$ 0.2 M (dotted line) at −0.5 V vs Ag/AgCl. The LED light source is pulsed as indicated.

It is interesting to note that the least-squares fitting line (dashed) has a positive intercept on the J_{SC} axis, while one would expect the line to pass through the origin. This behavior may be associated with the difference in the light intensities employed for the two kinds of measurements (AM1.5 for J_{SC} and 1‰ of AM1.5 for J_{Ph}). Therefore, in order to gain insights into the light intensity dependence of J_{Ph}, PEC measurements were performed by varying the 530 nm LED output power (Fig. 3b).

The upper inset in Fig. 3b shows the apparent quantum efficiency (AQE) of two CIGSe films: a "good performing" photoelectrode and a "bad performing" one taken from samples (e) and (b), respectively. For both films, AQE increases with increased light intensities until a seeming plateau is reached. This dependence suggests the existence of a light intensity threshold below which photogenerated electrons are poorly collected (Fig. 3b). The reason for this phenomenon may be attributed to the existence of trap states on the semiconductor surface, inducing recombination of the photogenerated electrons with a relatively slow kinetics [35]. This mechanism is thought to be responsible for the reduction of the current collection to the steady state photocurrent observed with Eu^{3+}. The use of an intentional electron scavenger ensures that these trap states are not self-inflicted (Fig. 2). On the other hand, the fact that J_{Ph} does not saturate at very high light intensity signifies that there is no shortage of Eu^{3+} at the interface. Due to the relatively slow kinetics of recombination via trapped states, the proportion of trapped photocurrent decreases with the increase of the light intensity (Fig. 3b lower inset), hence the increase of AQE until the plateau is reached.

Since the maximum AQEs measured under high illumination intensity (plateau) are still well below the EQEs of the devices, it is assumed that other interface recombination phenomena are taking place, the kinetics of which is much faster and cannot be detected with the employed instrumentation.

The presence of bulk and surface recombination is well known in the literature for semiconductor single crystals [36], and it seems likely that recombination for polycrystalline films is exacerbated by the additional presence of grain boundaries. In this sense, the grain size may play a decisive role in defining the efficiency of carrier collection. Surface recombination may dominate if the crystallite size is smaller than the effective diffusion length (L_{eff}) of the minority carriers, which is seldom the case for single crystals. Intensity modulated photocurrent spectroscopy (IMPS) may prove useful to discriminate the different kinds of recombination mechanisms taking place [37].

Photoluminescence spectroscopy has shown that CdS exerts a passivating effect on the CIGSe surface structure [38]. Therefore, it is possible that, due to the addition of CdS and i-ZnO, the charge carrier recombination at the solid state interface is lower compared to the CIGSe/electrolyte case. This may translate into a comparatively high J_{SC}, even for samples that display reduced values of J_{ph}, and may therefore account for the oversensitivity of J_{ph} to surface defects on the bare p-type film, making this parameter unreliable for a sound prediction of PV property, especially for "bad performing" photoelectrodes.
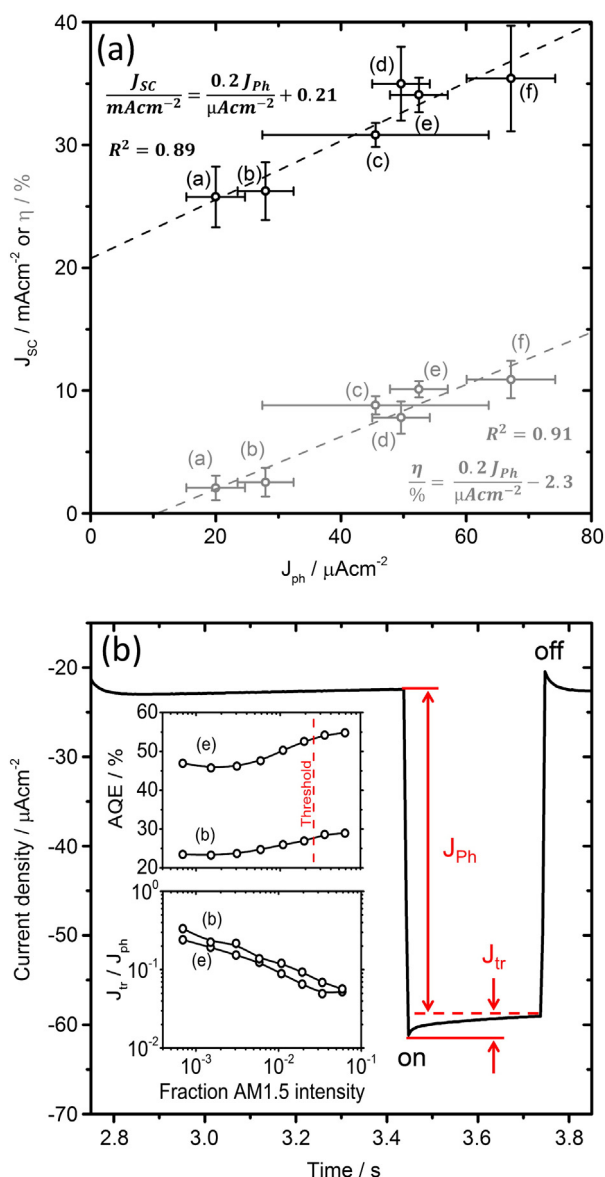
4. Conclusions

This work shows that the photoelectrochemically assessed photocurrent of the bare CIGSe absorbers (J_{ph}) can be correlated to short circuit current density (J_{SC}) and efficiency (η) of CIGSe solar cells ($R^2 \sim 0.9$, statistics of 48 + 48 samples). However, such correlations are not trivial. Recombination of photogenerated electrons at the absorber/electrolyte interface can be dominant in polycrystalline materials and can vary substantially from sample to sample and also as a function of the illumination intensity. Such a variation is much reduced in solid state devices because CdS and i-ZnO layers seem to passivate the surface states reducing interface recombination. As such, although they provide reasonable qualitative guidance, these correlations cannot be easily employed to provide quantitative assessment for the control of CIGSe quality at an industrial level. In this sense, a range of analytical techniques such as: electroluminescence imaging, photoluminescence and Raman spectroscopies may prove useful. Nevertheless, in view of the simplicity offered by PEC, further studies may be able to disentangle the problems raised by this work or propose an alternative PEC parameter for which surface recombination does not pose a serious hindrance.

Conflict of interest

Phillip J. Dale is co–inventor of international patent application WO 2010/125078 A1 relating to the electrical and opto-electrical characterisation of large-area semiconductors devices.

Fig. 3. a) Correlation plot of J_{Ph} versus solid state solar cell J_{SC} (black) and efficiency η (gray) for the series of CIGSe layers with corresponding least square fitting lines, equations and coefficients of determination R^2. b) Analysis of a typical photocurrent transient with the decay of photocurrent attributed to a slow recombination kinetics induced by the presence of trap states. Insets: apparent quantum efficiency (AQE, upper) acquired at −0.8 V vs Ag/AgCl and proportion of trapped photocurrent expressed as the J_{tr}/J_{Ph} dimensionless ratio (lower) of two CIGSe films from samples (b) and (e) as a function of the 530 nm LED light intensity expressed as AM1.5 equivalent intensity, as measured with a Si photodiode (the solid lines are guides to the eye).

Acknowledgments

References

[1] J.J. Loferski, Theoretical considerations governing the choice of the optimum semiconductor for photovoltaic solar energy conversion, J. Appl. Phys. 27 (1956) 777–784.

[2] W. Shockley, The theory of p–n junctions in semiconductor and p–n junction transistors, Bell Syst. Tech. J. 28 (1949) 435–489.

[3] R. Memming, Semiconductor Electrochemistry, Wiley, 2001.

[4] P.J. Dale, A.P. Samantilleke, G. Zoppi, I. Forbes, L.M. Peter, Characterization of CuInSe$_2$ material and devices: comparison of thermal and electrochemically prepared absorber layers, J. Phys. D. Appl. Phys. 41 (2008) 085105.

[5] J.A.M. AbuShama, S. Johnston, T. Moriarty, G. Teeter, K. Ramanathan, R. Noufi, Properties of ZnO/CdS/CuInSe$_2$ solar cells with improved performance, Prog. Photovolt. Res. Appl. 12 (2004) 39–45.

[6] D. Guimard, P.P. Grand, N. Bodereau, P. Cowache, J.F. Guillemoles, D. Lincot, S. Taunier, M. Ben Farah, P. Mogensen, Copper indium diselenide solar cells prepared by electrodeposition, Photovoltaic Specialists Conference, Conference Record of the Twenty-Ninth IEEE, 2002, pp. 692–695.

[7] M.A. Contreras, J. Tuttle, A. Gabor, A. Tennant, K. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, J. Scofield, R. Noufi, High efficiency Cu(In, Ga)Se2-based solar cells: processing of novel absorber structures, Photovoltaic Energy Conversion, 1994, Conference Record of the Twenty Fourth, IEEE Photovoltaic Specialists Conference — 1994, 1994 IEEE First World Conference on, vol. 1vol. 61, 1994, pp. 68–75.

[8] Y. Aida, V. Depredurand, J.K. Larsen, H. Arai, D. Tanaka, M. Kurihara, S. Siebentritt, Cu-rich CuInSe$_2$ solar cells with a Cu-poor surface, Progress in Photovoltaics: Research and Applications2014. (n/a-n/a).

[9] F. Karg, V. Probst, H. Harms, J. Rimmasch, W. Riedl, J. Kotschy, J. Holt, R. Treichler, O. Eibl, A. Mitwalsky, A. Kiendl, Novel rapid-thermal-processing for CIS thin-film solar cells, Photovoltaic Specialists Conference, Conference Record of the Twenty Third IEEE, 1993, pp. 441–446.

[10] H.J. Meadows, A. Bhatia, V. Depredurand, J. Guillot, D. Regesch, A. Malyeyev, D. Colombara, M.A. Scarpulla, S. Siebentritt, P.J. Dale, Single second laser annealed CuInSe$_2$ semiconductors from electrodeposited precursors as absorber layers for solar cells, J. Phys. Chem. C 118 (2014) 1451–1460.

[11] Y.S. Lim, H.-S. Kwon, J. Jeong, J.Y. Kim, H. Kim, M.J. Ko, U. Jeong, D.-K. Lee, Colloidal solution-processed CuInSe$_2$ solar cells with significantly improved efficiency up to 9% by morphological improvement, ACS Appl. Mater. Interfaces 6 (2013) 259–267.

[12] A. Heller, B. Miller, F.A. Thiel, 11.5% solar conversion efficiency in the photocathodically protected p-InP/V^{3+}-V^{2+}-HCl/C semiconductor liquid junction cell, Appl. Phys. Lett. 38 (1981) 282–284.

[13] M.L. Rosenbluth, C.M. Lieber, N.S. Lewis, 630-mV open circuit voltage, 12% efficient n-Si liquid junction, Appl. Phys. Lett. 45 (1984) 423–425.

[14] F.R.F. Fan, A.J. Bard, Semiconductor electrodes. 24. Behavior of photoelectrochemical cells based on p-type gallium arsenide in aqueous solutions, J. Am. Chem. Soc. 102 (1980) 3677–3683.

[15] K. Nakatani, S. Matsudaira, H. Tsubomura, Photoanodic behavior of n-type cadmium sulfide in acetonitrile solutions containing iodide ion, J. Electrochem. Soc. 125 (1978) 406–409.

[16] B.J. Tufts, I.L. Abrahams, P.G. Santangelo, G.N. Ryba, L.G. Casagrande, N.S. Lewis, Chemical modification of n-GaAs electrodes with Os3+ gives a 15% efficient solar cell, Nature 326 (1987) 861–863.

[17] L.M. Peter, Semiconductor electrochemistry, in: J.M. Feliu-Martinez, V.C. Paya (Eds.), Electrochemistry, Encyclopedia of Life Support Systems, Oxford, 2010.

[18] H.S. White, A.J. Ricco, M.S. Wrighton, Characterization of p-type cadmium telluride electrodes in acetonitrile/electrolyte solutions. Nearly ideal behavior from reductive surface pretreatments, J. Phys. Chem. 87 (1983) 5140–5150.

[19] A.B. Bocarsly, D.C. Bookbinder, R.N. Dominey, N.S. Lewis, M.S. Wrighton, Photoreduction at illuminated p-type semiconducting silicon photoelectrodes. Evidence for Fermi level pinning, J. Am. Chem. Soc. 102 (1980) 3683–3688.

[20] B.P. Minks, N.A.M. Verhaegh, J.J. Kelly, J. Stumper, L.M. Peter, High quantum yield photoreduction of iodate in basic solution at p-GaAs, J. Electroanal. Chem. 303 (1991) 277–282.

[21] A. Kampmann, D. Lincot, Photoelectrochemical study of thin film semiconductor heterostructures: junction formation processes in CdS, J. Electroanal. Chem. 418 (1996) 73–81.

[22] O. Solorza-Feria, R. Rivera-Noriega, Photoelectrochemical response and characterization of p-CuInSe$_2$ electrodeposited with different citrate ion concentrations, J. Mater. Sci. 30 (1995) 2616–2619.

[23] C. Guillen, J. Herrero, D. Lincot, Photovoltaic activity of electrodeposited p-CuInSe$_2$/electrolyte junction, J. Appl. Phys. 76 (1994) 359–362.

[24] J. Kessler, D. Lincot, J. Vedel, B. Dimmler, H.W. Schock, Photoelectrochemical studies of copper gallium diselenide films, Sol. Cells 29 (1990) 267–281.

[25] D. Lincot, H. Gomez Meier, J. Kessler, J. Vedel, B. Dimmler, H.W. Schock, Photoelectrochemical study of p-type copper indium diselenide thin films for photovoltaic applications, Sol. Energy Mater. 20 (1990) 67–79.

[26] Y.W. Chen, D. Cahen, R. Noufi, J.A. Turner, Photoelectrochemical test for photovoltaic activity of p-CuInSe$_2$ films, Sol. Cells 14 (1985) 109–121.

[27] S.C. Riha, S.J. Fredrick, J.B. Sambur, Y. Liu, A.L. Prieto, B.A. Parkinson, Photoelectrochemical characterization of nanocrystalline thin-film Cu$_2$ZnSnS$_4$ photocathodes, ACS Appl. Mater. Interfaces 3 (2010) 58–66.

[28] S.D. Kharade, N.B. Pawar, V.B. Ghanwat, S.S. Mali, W.R. Bae, P.S. Patil, C.K. Hong, J.-H. Kim, P.N. Bhosale, Room temperature deposition of nanostructured Bi$_2$Se$_3$ thin films for photoelectrochemical application: effect of chelating agents, New J. Chem. 37 (2013) 2821–2828.

[29] P. Dale, A. Samantilleke, G. Zoppi, I. Forbes, S. Roncallo, L. Peter, Deposition and characterization of copper chalcopyrite based solar cells using electrochemical techniques, Electrochem. Soc. Trans. 6 (2007) 535–546.

[30] J. Kessler, D. Schmid, R. Schaffler, H.W. Schock, S. Menezes, Electro-optical and photoelectrochemical studies of CuIn$_3$Se$_5$ chalcopyrite films, Photovoltaic Specialists Conference (PVSC), 1993 23rd IEEE, 1993, pp. 549–555.

[31] J.J. Scragg, P.J. Dale, L.M. Peter, Towards sustainable materials for solar energy conversion: preparation and photoelectrochemical characterization of Cu$_2$ZnSnS$_4$, Electrochem. Commun. 10 (2008) 639–642.

[32] D. Colombara, L.M. Peter, K.D. Rogers, J.D. Painter, S. Roncallo, Formation of CuSbS$_2$ and CuSbSe$_2$ thin films via chalcogenisation of Sb–Cu metal precursors, Thin Solid Films 519 (2011) 7438–7443.

[33] D. Colombara, L.M. Peter, K. Hutchings, K.D. Rogers, S. Schäfer, J.T.R. Dufton, M.S. Islam, Formation of Cu$_3$BiS$_3$ thin films via sulfurization of Bi–Cu metal precursors, Thin Solid Films 520 (2012) 5165–5171.

[34] H. Gerischer, The role of semiconductor structure and surface properties in photoelectrochemical processes, J. Electroanal. Chem. Interfacial Electrochem. 150 (1983) 553–569.

[35] L.M. Peter, J. Li, R. Peat, Surface recombination at semiconductor electrodes: part I. Transient and steady-state photocurrents, J. Electroanal. Chem. Interfacial Electrochem. 165 (1984) 29–40.

[36] L.M. Peter, Dynamic aspects of semiconductor photoelectrochemistry, Chem. Rev. 90 (1990) 753–769.

[37] J. Li, L.M. Peter, Surface recombination at semiconductor electrodes: part IV. Steady-state and intensity modulated photocurrents at n-GaAs electrodes, J. Electroanal. Chem. Interfacial Electrochem. 199 (1986) 1–26.

[38] D. Regesch, L. Gütay, J.K. Larsen, V. Depredurand, D. Tanaka, Y. Aida, S. Siebentritt, Degradation and passivation of CuInSe$_2$, Appl. Phys. Lett. 101 (2012) 112108.