



Long term stability and recovery of 3 MeV proton irradiated Cu(In,Ga)Se₂ and Cu₂(Zn,Sn)(S,Se)₄ thin film solar cells

Patrick Pearson^{a,*}, Jan Keller^a, Jes Larsen^a, Volodymyr Kosyak^b, Charlotte Platzter-Björkman^a

^a Division of Solar Cell Technology, Department of Materials Science and Engineering, Uppsala University, Box 35, Ångströmlaboratoriet, Lägerhyddsvägen 1 75121, Uppsala 751 03, Sweden

^b Midsummer AB, Elektronikhöjden 6, Järfälla 175 43, Sweden

ARTICLE INFO

Keywords:

Copper indium gallium diselenide
Copper zinc tin sulfide
Copper zinc tin sulphide selenide
Proton irradiation
Radiation hardness
Stability

ABSTRACT

In 2017, Cu(In,Ga)Se₂ (CIGS), Cu₂(Zn,Sn)S₄ (CZTS) and Cu₂(Zn,Sn)(S,Se)₄ (CZTSSe) thin film solar cells were irradiated by our group using 3 MeV protons to investigate the materials' radiation hardness and subsequent recovery following dark storage. It was observed that the primary losses were in open-circuit voltage (V_{OC}), with the CZTS and CZTSSe being more resistant than the CIGS, also recovering to $\sim 95\%$ of initial performance, compared to $\sim 70\%$ for CIGS after two months dark storage. In 2021 the cells were investigated by external quantum efficiency and current-voltage measurements once again, to investigate further recovery. The CIGS cells had continued to recover, whilst the CZTSSe devices appear to have fully recovered from radiation induced damage, but now suffer from aging-related degradation and exhibit slight bandgap widening over time. The CZTS cells were observed to recover fully from the radiation induced damage, whilst also showing gains in V_{OC} .

1. Introduction

One of the first serious commercial applications of solar cells was for use in space. Although the solar energy industry has advanced considerably since this time, space applications are still highly relevant and bring additional challenges that terrestrial installations need not face. Due to their low mass and potential for flexibility, thin film solar cells are highly desirable for use in space, though at present extra-terrestrial solar technology is still limited to Si and GaAs, motivating our interest in investigating the effects of radiation on two key thin-film technologies: the established Cu(In,Ga)Se₂ (CIGS) and emerging Cu₂(Zn,Sn)(S,Se)₄ (CZTS(Se)). It is also hoped that by investigating long-term recovery, further light can be shed on the internal mechanisms of the three materials. It is known that CIGS, CZTS and CZTSSe are considerably more radiation hard than Si or GaAs [1]. There are many reports on the effects of radiation on CIGS (key references being [2–4]), but only very few on CZTS and CZTSSe ([5–7]). One of these, a work by Suvanam, et al. [5] is the predecessor to this study. In this initial work CIGS, CZTS and CZTSSe thin film solar cells were irradiated by 3 MeV protons in an attempt to quantify the radiation hardness of CZTS and CZTSSe and compare them to CIGS when irradiated. The samples were additionally kept in dark conditions for two months, such that the materials' self-recovery

processes could be investigated. It was observed that the primary losses were in open-circuit voltage (V_{OC}), with CZTS and CZTSSe being more resilient than CIGS and recovering to $\sim 95\%$ of initial performance, compared to $\sim 70\%$ for CIGS after the dark storage. After the initial study, the cells were placed in dark storage until 2021, when current-voltage (IV) and external quantum efficiency (EQE) measurements were used to investigate any further recovery, as we report on here.

2. Experimental details

The CIGS absorbers were provided by Solibro AB and grown via a three-stage co-evaporation process. The CZTS and CZTSSe samples were grown as described in [5], with 1100 nm thick CZTS absorber layer and 1250 nm thick CZTSSe absorber. All cells were deposited on 300 nm Mo on soda-lime glass substrates. The CZTS and CZTSSe samples were slightly Cu-poor and Sn-rich ($\text{Cu}/(\text{Zn}+\text{Sn}) = 0.94$ and $\text{Zn}/\text{Sn} = 0.97$). The CZTSSe samples had a bandgap of just over 1.2 eV, corresponding to a sulphur to sulphur-selenium ratio of around 0.4. A 70 nm CdS buffer was applied to all samples via chemical bath deposition, followed by sputtering of a window layer consisting of an 80 nm intrinsic ZnO layer and 210 nm ZnO:Al transparent conducting oxide. The devices were

* Corresponding author.

E-mail address: patrick.pearson@angstrom.uu.se (P. Pearson).

<https://doi.org/10.1016/j.tsf.2021.139023>

Received 17 June 2021; Received in revised form 22 November 2021; Accepted 22 November 2021

Available online 26 November 2021

0040-6090/© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

irradiated by 3 MeV protons at fluences of $\Phi = 10^{10}$, 10^{11} , 10^{12} and 10^{13} cm^{-2} at the Tandem Lab, Uppsala University (a constant proton flux was maintained with samples irradiated for a time sufficient to reach the specified fluence, this was in the order of ten minutes). This energy was chosen to ensure reasonably uniform absorption throughout the device and avoid localised damage, based on the knowledge that ~ 0.4 MeV is sufficient to penetrate to the rear surface [8]. The irradiation procedure followed the AIAA S-111-2005 "Qualification and Quality Requirements for Space Solar Cells" test standards [9]. In order to investigate the radiation induced effects and long-term recovery, the devices were characterised by IV and EQE measurements. Some devices were also characterised using capacitance-voltage (CV) measurements with an Agilent 4284A Precision LCR Meter and Keithley 2401 Source Meter. Sweep frequency was determined via admittance measurements, using the frequency that brought the phase angle closest to 90° (~ 40 kHz for CIGS samples, ~ 95 kHz for CZTSSe samples and 15–20 kHz for CZTS samples). Measurements were performed in January 2021 and related to measurements performed in November 2017 (prior to irradiation) and January 2018 (immediately after irradiation) [5]. The devices were stored in dark conditions at room temperature. When IV measurements were first performed in 2017, all cells were measured on each sample, with one representative cell chosen for each sample. Only the representative cells went on to have EQE measurements. At all later stages, it was the same representative cells that were characterised by EQE and, in 2021, CV measurements. The IV graphs presented in this work are those of the representative cells. Those measurements taken to evaluate the irradiated state of the samples were performed within an hour of irradiation.

3. Results and discussion

3.1. CIGS

A clear increase in current density-voltage (JV) degradation can be observed as proton fluence increases (Fig. 1), with V_{OC} decreasing by ~ 155 mV for maximum irradiation, from 670 mV to 515 mV (Fig. 1c). A clear recovery in V_{OC} can be observed over the three year extended dark recovery period for the maximally irradiated sample, reaching 575 mV (86% of the as grown value, Fig. 1c). The sample irradiated with a fluence of 10^{12} cm^{-2} also exhibited partial recovery, gaining 10 mV (from 610 mV to 620 mV) and reaching 93% of the as grown value (660 mV, Fig. 1b). The 10^{11} cm^{-2} sample was observed to have suffered only very minimal degradation and no significant gains were measured over the recovery period (Fig. 1a). No irradiation damage was observed for the sample receiving a fluence of 10^{10} cm^{-2} . There is no variation in bandgap after irradiation, so it is to be concluded that irradiation either reduces net doping or increases recombination centre concentration. The EQE response of the sample under maximal irradiation (Fig. 2c) indicates a significant increase in recombination immediately after irradiation, leading to speculation of radiation-induced recombination

centres. However, it is also noted that the EQE response of the 10^{11} cm^{-2} fluence sample was unchanged by irradiation, whilst the 10^{12} cm^{-2} fluence sample suffered only minimal losses (Fig. 2a and b), suggesting that recombination centre creation is at a significantly lower level below a fluence of 10^{13} cm^{-2} . Moreover, it is seen that though the EQE response of the maximally irradiated CIGS sample recovers almost completely after extended dark storage, the V_{OC} recovery remains incomplete, indicating that there is potentially an additional mechanism acting. Indeed, a review of the literature suggests that there is a proton fluence threshold separating a lower and higher damage regime: A study by Kawakita also observed a significant increase in degradation above proton fluences of 10^{12} cm^{-2} , observing significant reductions in net doping. A defect level suspected to correspond to the donor-like In_{Cu} antisite defect was also seen to emerge with irradiation [3]. Similarly, a fluence threshold for increased damage via a transition from shallow compensating defect generation to deep trap state generation was reported by Khatri, et al. [10]. Lee, et al. utilised THz spectroscopy to complement photoluminescence (PL) measurements to investigate the effects of H^+ radiation on CIGS, observing remarkable reductions in minority-carrier bulk lifetime, pointing towards the generation of non-radiative recombination centres. From Hall measurements they also observed a decrease in both carrier concentration and carrier mobility with irradiation. Surface conversion from p - to n -type CIGS was also seen [11]. PL studies by Yoshida and Hirose also follow this trend [12,13]. We cannot add evidence to speculation, as no PL or CV measurements were taken in the initial study to allow comparison, though CV profiling performed in 2021 shows only small variations between samples, with net-doping in the region of $0.8\text{--}1.1 \times 10^{16}$ cm^{-3} which is not unusually low [14,15]. Considering that the maximally irradiated sample still exhibits clear V_{OC} degradation, it seems unlikely that reduced carrier concentration is the primary mechanism at play here. It seems most likely that the cause for the observed degradation is an increased density of deep recombination centres.

3.2. CZTSSe

CZTSSe was observed to be much more radiation hard than CIGS, showing minimal degradation, even at the highest level of irradiation (Fig. 3c), losing 8% of V_{OC} compared to 22% (lower fluences caused no V_{OC} degradation for CZTSSe (Fig. 3a)). After extended dark storage, V_{OC} recovery has continued minimally since the initial two month recovery period, remaining around 95% for the 10^{12} cm^{-2} and 10^{13} cm^{-2} fluence levels, though the 10^{11} cm^{-2} irradiated sample now measures an improvement of 5% beyond pre-irradiation V_{OC} . Due to the significant and rapid recovery of radiation damage and the consistent and similar fill-factor (FF) degradation observed across all CZTSSe samples, we speculate that a full recovery from radiation damage has in fact been made, however age-related degradation is now evident in the materials. The sample irradiated with a fluence of 10^{10} cm^{-2} showed no changes immediately after irradiation, however FF degradation similar to the

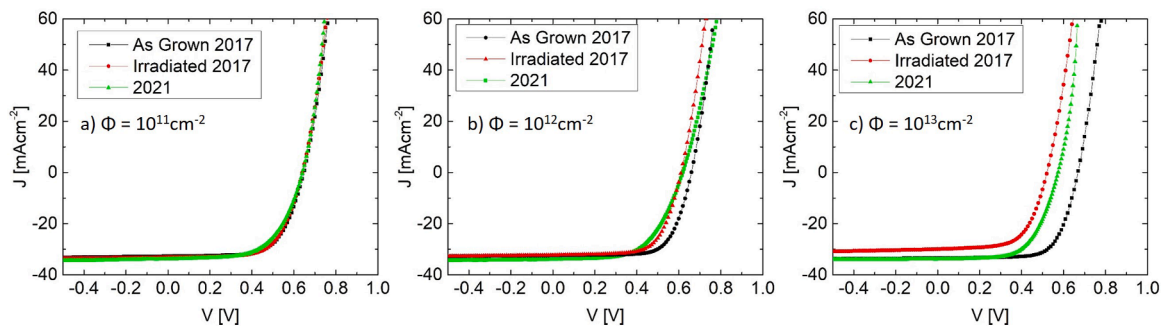


Fig. 1. Light JV curves for each of the CIGS samples, showing clear initial V_{OC} losses, increasing with proton fluence, with subsequent partial recovery. Figure 1c is recreated and extended through addition of new data with the permission of the authors of the initial study [5].

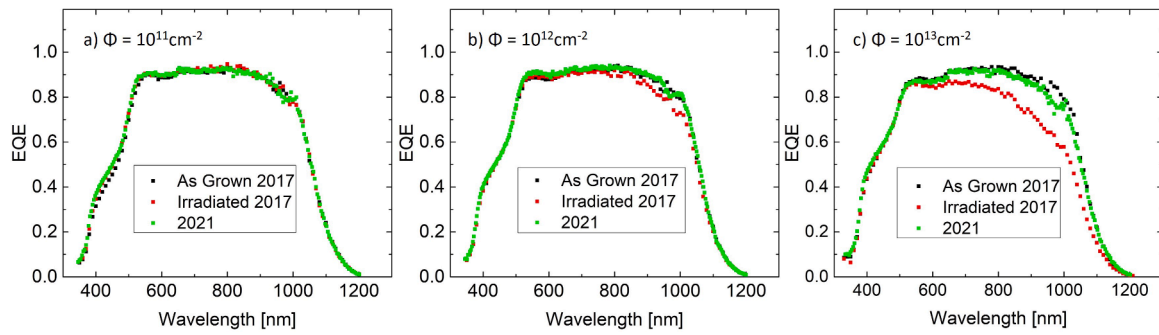


Fig. 2. The EQE response for each of the CIGS samples, showing significant degradation at $\Phi = 10^{13} \text{ cm}^{-2}$, indicating a strong increase in recombination compared to lower fluences. Figure 2c is recreated and extended through addition of new data with the permission of the authors of the initial study [5].

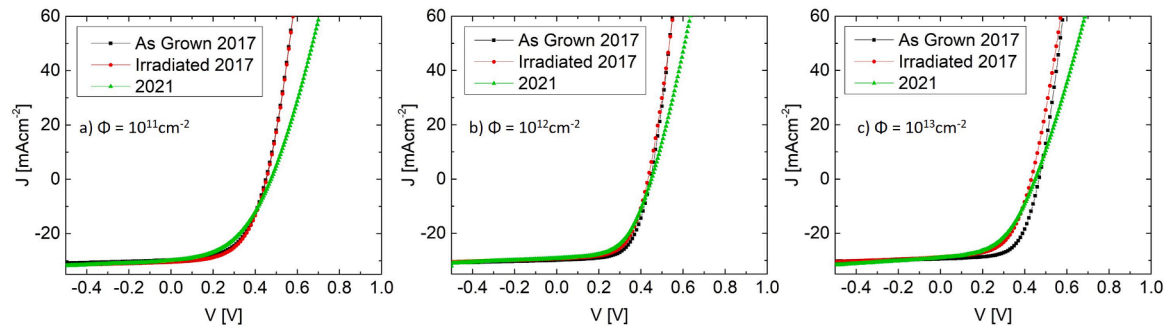


Fig. 3. Light JV curves for each of the CZTSSe samples, showing high levels of radiation hardness and requiring an order of magnitude greater proton fluence to induce damage comparable to the CIGS cells. Near full V_{OC} recovery is observed, but fluence-independent FF degradation is also seen. Figure 3c is recreated and extended through addition of new data with the permission of the authors of the initial study [5].

other samples was observed. A PL study by Sulimov, et al. irradiating CZTSe with high energy electrons (which seem to have similar effects to protons, for CIGS) reported an overall decrease in PL peak intensity and a red-shifting of peak position, consistent with the formation of deep non-radiative recombination centres [7]. This is supported by another work undertaken at Uppsala [16] using similar samples, irradiated with 0.25 MeV protons, and incorporating CV profiling. It was noted that though net doping did decrease upon sample irradiation, the extent to which doping was reduced was insufficient to explain the severe V_{OC} degradation, leading to the conclusion that recombination centres,

rather than doping compensation is responsible for the observed effects. Performing CV profiling on these 0.25 MeV samples now, in 2021, revealed an almost complete recovery of doping levels, CV profiling of the 3 MeV samples reveals small differences in net-doping (of the order $2 \times 10^{15} \text{ cm}^{-3}$). An interesting and unexpected observation from EQE measurements on the CZTSSe samples (Fig. 4) is an apparent increase in bandgap over time for the 10^{12} cm^{-2} fluence sample (Fig. 4a). No changes in EQE were observed immediately after irradiation for this sample (Fig. 4a), but for the 10^{13} cm^{-2} fluence sample, a decrease in the signal for longer wavelengths is observed in addition to a bandgap

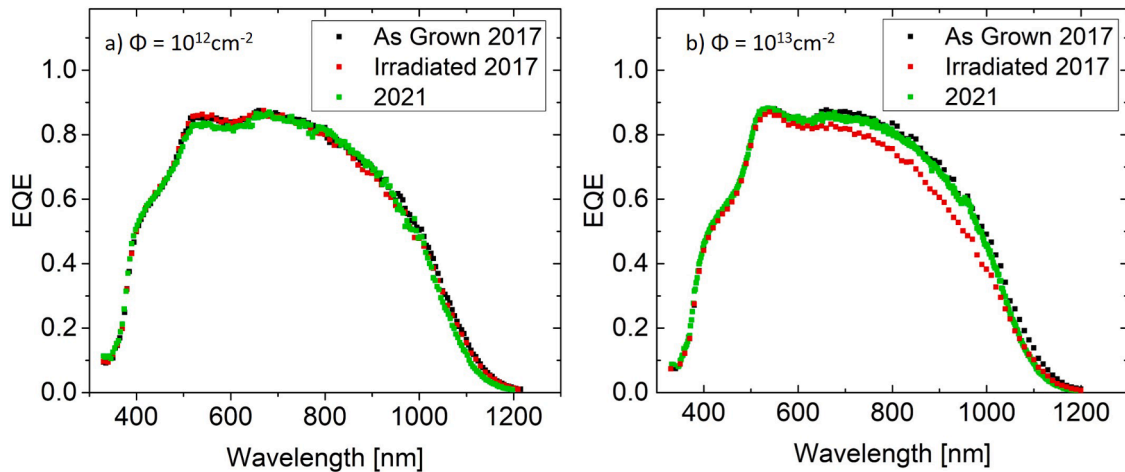


Fig. 4. The EQE response of the CZTSSe samples irradiated with proton fluences of 10^{12} cm^{-2} and 10^{13} cm^{-2} , showing no signs of significant recombination increase, or irradiation induced bandgap shift after a fluence of 10^{12} cm^{-2} , but exhibiting losses for the 10^{13} cm^{-2} case, which are subsequently recovered over time. The 2021 measurements indicate a slight widening of the bandgap compared to the as-grown samples. Figure 4b is recreated and extended through addition of new data with the permission of the authors of the initial study [5].

widening of 0.04 eV, both of which are mostly recovered over time (Fig. 4b). This appears to correspond closely to the JV curves in Fig. 3. Cu-Zn ordering is a known source of bandgap variation within CZTS(Se), however storage at room temperature seems unlikely to provide sufficient energy to induce a change in ordering of the sample that received an intermediate proton fluence, though the long time scale may play a role.

3.3. CZTS

The JV curves of the CZTS samples indicate significant radiation hardness, similar to that of CZTSSe and in fact showing a reduced V_{OC} degradation for the highest proton fluence (Fig. 5d). It is also seen that over the extended recovery period, the degradation observed in the EQE and JV of the highest fluence sample after irradiation is fully recovered, with a very slight improvement observed in the sample's EQE response (Fig. 6b). The sample irradiated with a low fluence of 10^{10} cm^{-2} was observed to show no measurable degradation for any performance parameter.

With the exception of the sample receiving a proton fluence of 10^{12} cm^{-2} it can be seen that each sample shows a gain in V_{OC} over time. No increases in the samples' bandgaps were observed and neither was a significant improvement in the EQE response (Fig. 6). An accelerated aging investigation by Neubauer, et al. [17] using 100°C air anneal also observed an increase in the V_{OC} of CZTS samples. At present, we cannot

offer an explanation for this observed increase. A PL and JV study by Sugiyama et al. reported V_{OC} degradation for proton fluences in excess of 10^{13} cm^{-2} and a considerable reduction in the intensity of the primary PL peak [6] (attributed by the authors to Cu_{Zn} , which is calculated to be the dominant p-dopant in CZTS [18]). Though no CV data from 2017 exists for the samples, measurements performed in 2021 display minimal differences in net doping between the samples (approximately $0.2 \times 10^{15} \text{ cm}^{-3}$) and each sample has a value in the range $1.0\text{--}1.5 \times 10^{16} \text{ cm}^{-3}$ which is within the regular range of expected values [19,20].

4. Summary

The long-term recovery of thin-film CIGS, CZTS and CZTSSe solar cells irradiated by 3 MeV protons was investigated through IV and EQE characterisation. It was observed that the CIGS cells recovered a significant proportion of V_{OC} which was highly degraded by irradiation (99%, 94% and 86% in order of increasing dose), whilst CZTS and CZTSSe samples retained similar V_{OC} values as were observed after two months of dark storage (in the region of 95%). Moreover, it was seen that the maximally irradiated CIGS cells exhibited much greater recombination losses than the lesser irradiated samples, showing significant EQE response degradation. This degradation in the EQE was nearly fully recovered after the extended dark storage period, however considerable V_{OC} degradation is still present. It is speculated that the V_{OC} losses are caused by deep defect states created by the irradiation and that the

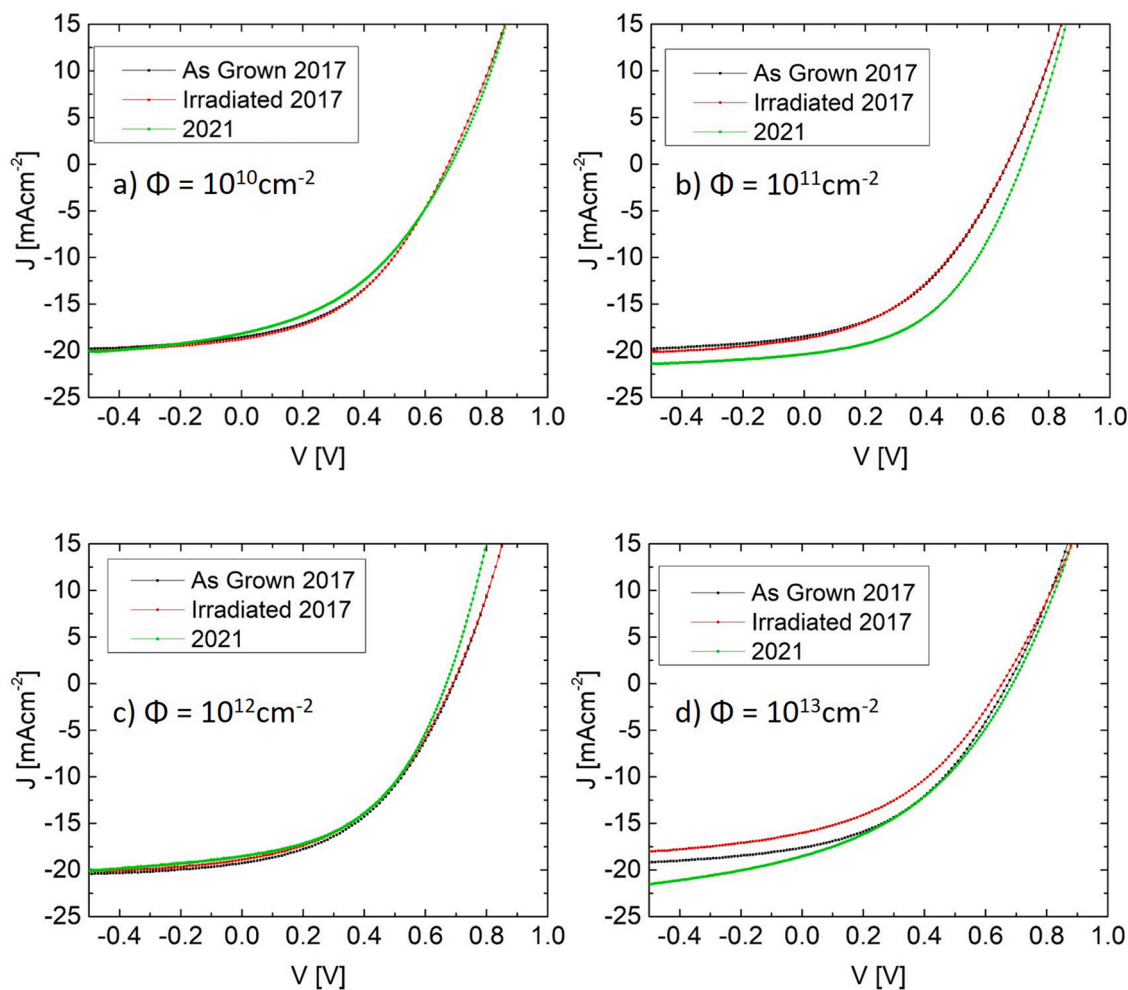


Fig. 5. JV curves of the CZTS samples, also including a sample irradiated with a proton fluence of 10^{10} cm^{-2} . The samples exhibit significant radiation hardness similar to, if not in excess of, that of CZTSSe, with no significant degradation observed for proton fluences below 10^{13} cm^{-2} and only a minor reduction in V_{OC} for this highest fluence. Figure 5d is recreated and extended through addition of new data with the permission of the authors of the initial study [5].

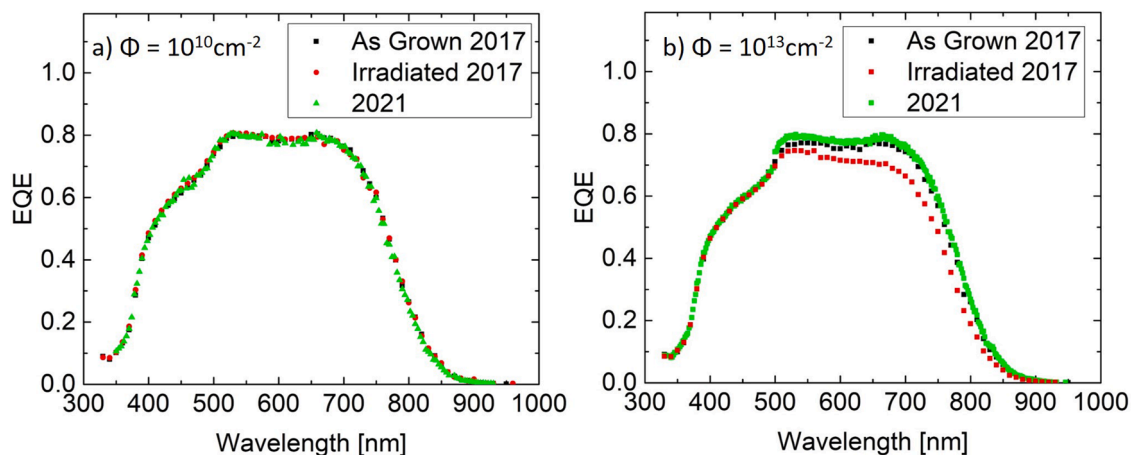


Fig. 6. The EQE response of the CZTS samples for $\Phi = 10^{10} \text{ cm}^{-2}$ and $\Phi = 10^{13} \text{ cm}^{-2}$, showing no evidence of significant radiation-induced recombination or bandgap shifting for the low fluence sample, and a full recovery of irradiation induced degradation over time for the high fluence sample. Figure 6b is recreated and extended through addition of new data with the permission of the authors of the initial study [5].

density of such defects increases significantly for high proton fluence. It is also possible that additional mechanisms could be at work, with literature sources suggesting that net doping is decreased by irradiation. It is further speculated that the CZTS and CZTSSe samples have recovered fully from the radiation induced degradation, with aging-related degradation now impacting key electrical characteristics of the CZTSSe samples. The EQE cut-off wavelength of all CZTSSe samples was observed to decrease, whilst three of the four CZTS samples were observed to gain in V_{OC} after extended dark storage. Further work is planned to investigate the observed phenomena, using photoluminescence and thermal admittance spectroscopy techniques to learn more about the radiation-induced defects, in addition to using a broader range of proton fluences to investigate the possibility of a high-damage regime fluence threshold for CZTS and CZTSSe, as was observed in the CIGS. Raman spectroscopy is also planned to be used, to investigate whether Cu-Zn ordering is responsible for the bandgap widening of CZTSSe over time.

CRediT authorship contribution statement

Patrick Pearson: Investigation, Writing – original draft, Writing – review & editing, Visualization. **Jan Keller:** Conceptualization, Writing – review & editing. **Jes Larsen:** Conceptualization, Writing – review & editing. **Volodymyr Kosyak:** Methodology, Resources, Writing – review & editing. **Charlotte Platzer-Björkman:** Resources, Writing – review & editing, Supervision.

CRediT authorship contribution statement

Patrick Pearson: Investigation, Writing – original draft, Writing – review & editing, Visualization. **Jan Keller:** Conceptualization, Writing – review & editing. **Jes Larsen:** Conceptualization, Writing – review & editing. **Volodymyr Kosyak:** Methodology, Resources, Writing – review & editing. **Charlotte Platzer-Björkman:** Resources, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank Solibro AB for providing the CIGS absorber

material. Thanks are also given to Sethu Saveda Suvanam for performing initial measurements and Nils Ross for fabrication of the CZTSSe samples. There are no competing interests to declare. This work was supported by the Swedish Research Council, (grant number 2019-04793) and Swedish Energy Agency, (grant number 48479-1).

References

- [1] R.M. Burgess, W.S. Chen, W.E. Devaney, D.H. Doyle, N.P. Kim, B.J. Stanbery, Electron and proton radiation effects on GaAs and CuInSe₂ thin film solar cells, in: *Proceedings of the Photovoltaic Specialists Conference, Record of the Twentieth IEEE*, 1988.
- [2] A. Jasenek, U. Rau, Defect generation in Cu(In,Ga)Se₂ heterojunction solar cells by high-energy electron and proton irradiation, *J. Appl. Phys.* 90 (2001) 650–658.
- [3] S. Kawakita, M. Imaizumi, T. Sumita, K. Kushiya, T. Ohshima, M. Yamaguchi, S. Matsuda, S. Yoda, T. Kamiya, Super radiation tolerance of CIGS solar cells demonstrated in space by MDS-1 satellite, in: *Proceedings of the 3rd World Conference on Photovoltaic Energy Conversion* 1, 2003, pp. 693–696.
- [4] S. Kawakita, M. Imaizumi, K. Kibe, T. Ohshima, H. Itoh, S. Yoda, O. Odawara, Analysis of anomalous degradation of Cu(In,Ga)Se₂ thin-film solar cells irradiated with protons, *Jpn. J. Appl. Phys.* 46 (2007) 670.
- [5] S. Suvanam, J. Larsen, N. Ross, V. Kosyak, A. Hallen, C. Platzer Björkman, Extreme radiation hard thin film CZTSSe solar cell, *Sol. Energy Mater. Sol. Cells* 185 (2018) 16–20.
- [6] M. Sugiyama, S. Aihara, Y. Shimamune, H. Katagiri, Influence of electron and proton irradiation on the soaking and degradation of Cu₂ZnSnS₄ solar cells, *Thin Solid Films* 642 (2017) 311–315.
- [7] M.A. Sulimov, M.N. Sarychev, M.V. Yakushev, J. Marquez-Prieto, I. Forbes, V. Yu Ivanov, P.R. Edwards, A.V. Mudryi, J. Krustok, R.W. Martin, Effects of Irradiation of ZnO/CdS/Cu₂ZnSnSe₄/Mo/glass solar cells by 10 MeV electrons on photoluminescence spectra, *Mater. Sci. Semicond. Process.* 121 (2021), 105301.
- [8] J.F. Ziegler, SRIM-2003, *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* 219–220 (2004) 1027–1036.
- [9] American Institute of Aeronautics and Astronautics, Inc., Standard, Qualification and Quality Requirements for Space Solar Cells (AIAAS111A–2014), American Institute of Aeronautics and Astronautics, Inc., Washington, DC, 2014.
- [10] I. Khatri, T.Y. Lin, T. Nakada, M. Sugiyama, Proton irradiation on cesium-fluoride-free and cesium fluoride-treated Cu(In,Ga)Se₂ solar cells and annealing effects under illumination, *Phys. Status Solidi Rapid Res. Lett.* 13 (2019), 1900519.
- [11] W.J. Lee, G. Lee, D.H. Cho, C. Kang, N. Myoung, C.S. Kee, Y.D. Chung, Ultrafast photoexcited-carrier behavior induced by hydrogen ion irradiation of a Cu(In,Ga)Se₂ thin film in the terahertz region, *IEEE Trans. Terahertz Sci. Technol.* 11 (2021).
- [12] K. Yoshida, M. Tajima, S. Kawakita, K. Sakurai, S. Niki, K. Hirose, Photoluminescence analysis of proton irradiation effects in Cu(In,Ga)Se₂ solar cells, *Jpn. J. Appl. Phys.* 47 (2008) 857.
- [13] Y. Hirose, M. Warasawa, I. Tsunoda, K. Takakura, M. Sugiyama, Effects of proton irradiation on optical and electrical properties of Cu(In,Ga)Se₂ solar cells, *Jpn. J. Appl. Phys.* 51 (2012), 111802.
- [14] J.T. Heath, J.D. Cohen, W.N. Shafarman, Bulk and metastable defects in CuIn_{1-x}Ga_xSe₂ thin films using drive-level capacitance profiling, *J. Appl. Phys.* 95 (2004) 1000.
- [15] M. Cwil, M. Igalson, P. Zabierowski, S. Siebentritt, Charge and doping distributions by capacitance profiling in solar cells, *J Appl Phys* 103 (2008), 063701.
- [16] Danaki P. Radiation hardness of thin film solar cells Dissertation, 2019.

- [17] C. Neubauer, A. Samiepour, S. Oueslati, M. Danilson, D. Meissner, Ageing of kesterite solar cells 1: degradation processes and their influence on solar cell parameters, *Thin Solid Films* 669 (2019) 595–599.
- [18] S. Chen, J.H. Yang, X.G. Gong, A. Walsh, S.H. Wei, Intrinsic point defects and complexes in the quaternary kesterite semiconductor $\text{Cu}_2\text{ZnSnS}_4$, *Phys. Rev. B* 81 (2010), 245204.
- [19] M. Grossberg, J. Krustok, C.J. Hages, D.M. Bishop, O. Gunawan, R. Scheer, S. M. Lyam, H. Hempel, S. Levenco, T. Unold, The electrical and optical properties of kesterites, *J. Phys. Energy* 1 (2019), 044002.
- [20] C. Frisk, T. Ericson, S.Y. Li, P. Szaniawski, J. Olsson, C. Platzer-Björkman, Combining strong interface recombination with bandgap narrowing and short diffusion length in $\text{Cu}_2\text{ZnSnS}_4$ device modeling, *Sol. Energy Mater. Sol. Cells* 144 (2016) 364–370.