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Paper:

Barbé, J., Hughes, D., Wei, Z., Pockett, A., Lee, H., Heasman, K., Carnie, M., Watson, T. & Tsoi, W. (2019). Radiation Hardness of Perovskite Solar Cells Based on AluminumDoped Zinc Oxide Electrode under Proton irradiation. *Solar RRL*

<http://dx.doi.org/10.1002/solr.201900219>

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1 Radiation Hardness of Perovskite Solar Cells Based 2 on Aluminum-Doped Zinc Oxide Electrode under 3 Proton irradiation

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11 ABSTRACT

12 Due to their high specific power and potential to save both weight and stow volume, perovskite
13 solar cells have gained increasing interest to be used for space applications. However, before they
14 can be deployed into space, their resistance to ionizing radiations such as high-energy protons must
15 be demonstrated. In this report, we investigate the effect of 150 keV protons on the performance
16 of perovskite solar cells based on aluminium-doped zinc oxide (AZO) transparent conducting
17 oxide (TCO). Record power conversion efficiency of 15% and 13.6% were obtained for cells based
18 on AZO under AM1.5G and AM0 illumination, respectively. We demonstrate that perovskite solar
19 cells can withstand proton irradiation up to 10^{13} protons.cm⁻² without significant loss in efficiency.
20 At this irradiation dose, Si or GaAs solar cells would be completely or severely degraded when

1 exposed to 150 keV protons. From 10^{14} protons.cm⁻², a decrease in short-circuit current of the
2 perovskite cells is observed, which is consistent with interfacial degradation due to deterioration
3 of the Spiro-OMeTAD HTL during proton irradiation. Using a combination of non-destructive
4 characterization techniques, results suggest that the structural and optical properties of perovskite
5 remain intact up to high fluence levels. Although shallow trap states are induced by proton
6 irradiation in perovskite bulk at low fluence levels, they can release charges efficiently and are not
7 detrimental to the cell's performance. This work highlights the potential of perovskite solar cells
8 based on AZO TCO to be used for space applications and give a deeper understanding of interfacial
9 degradation due to proton irradiation.

10

11 **KEYWORDS:** Perovskite solar cells, proton irradiation, space, aluminium-doped zinc oxide

12 **INTRODUCTION**

13 Perovskite solar cells have recently attracted lots of attention in the scientific community due to
14 their rapid progress in efficiency and potentially low manufacturing costs^[1]. Using solution-based
15 processes, perovskite materials can be fully printed at low temperature on light-weight flexible
16 substrates^{[2][3][4]}, which has an enormous potential for a wide range of applications. Among them,
17 researchers have only recently considered the use of perovskite for aerospace and space
18 applications. Today, it costs around \$20,000 to put a kilogram of payload in earth orbit^[5]
19 (destinations beyond geosynchronous orbits require significantly higher launch costs) and solar
20 panels can represent a large fraction of satellites or probes total weight. In 2015, a single-junction
21 perovskite solar cell with super high specific power (power-per-weight) of 23 W.g⁻¹ under Air
22 Mass 1.5 Global (AM1.5G) illumination has been demonstrated^[6]. In comparison, commercial
23 triple junction solar cells based on GaAs developed by Azur Space® have much lower specific
24 power of 0.5 W.g⁻¹ under AM0 (zero air mass) illumination^[7]. Besides, flexible solar panels such
25 as roll-out solar arrays (ROSA) deployed in space by NASA in 2017 can be very compact in size
26 and have the potential to save stow volume during launch^[5]. Hence, perovskite solar cells have

1 key advantages to be used in space missions for which payload control is crucial. Besides,
2 perovskite solar cells limitations on earth such as lead toxicity and degradation due to humidity
3 and oxygen molecules are no longer an issue in space.

4 However, outer space is flooded with radiations such as electrons, protons, neutrons, X-rays or
5 gamma rays which can have dramatic consequences on microelectronic components. These high-
6 energy particles are known to cause damages in semiconductors through ionization and
7 displacement^[8]. For example, although GaAs solar cells are the most prominent solar technology
8 used in space due to their high efficiency, they are particularly sensitive to radiation and can
9 undergo more than 80% decrease in output power after irradiation with 150 keV protons at 10^{12}
10 particles.cm⁻² fluence^[9] or with 1 MeV protons at 10^{13} particles.cm⁻² fluence^[10]. The radiation
11 hardness of perovskite solar cells has been little investigated and is the subject of a few publications
12 only^{[11][12][13][14][15][16][17]}. In 2018, Miyasaka *et al.* studied the radiation tolerance of perovskite
13 solar cells composed of a mesoporous TiO₂ electrons transport layer (ETL) and P3HT holes
14 transport layer (HTL) to 1 MeV electrons and 50 keV protons and found that cells can survive to
15 accumulated dose of 10^{16} electrons.cm⁻² and 10^{15} protons.cm⁻², respectively^[14]. For this study,
16 P3HT was chosen as a HTL for its better thermal resistance as compared to Spiro-OMeTAD, which
17 is known to degrade at 80-100°C. P3HT showed robust radiation stability but the power conversion
18 efficiency (PCE) was rather low (4 to 5%) compared to state-of-the-art perovskite solar cells with
19 Spiro-OMeTAD HTL (>20%). The radiation hardness of p-i-n MAPbI₃ (inverted-type) solar cells
20 to protons irradiation was also investigated by two other groups^{[13][11][17]}. Huang et al. showed that
21 50 keV protons with fluence 10^{12} cm⁻² cause significant degradation of the performance of inverted
22 perovskite cells, but these cells can be restored with a vacuum annealing process. Lang et al.
23 showed that the cells exposed to 20 MeV and 68 MeV proton irradiation from the substrate side
24 could withstand protons dose up to 10^{12} protons.cm⁻² without significant damages. While
25 experiments such as these, with high energy protons, are useful in looking at extreme cases of
26 radiation bombardment and associated degradation, the realistic energy levels of protons in space
27 are, statistically, much lower. Proton's with energy between 50 and 200 keV occur at a flux of
28 $\sim 1E7$ higher than protons at >20 MeV and are therefore a more relevant energy range to
29 investigate.

1 In this work, we present a detailed study on the effect of 150 keV protons on the performance of
2 perovskite solar cells fabricated on quartz substrates coated with aluminium-doped zinc oxide
3 (AZO) transparent conducting oxide (TCO). Owing to the low-cost, nontoxicity and abundance,
4 AZO thin films could be a better alternative to ITO and FTO films^[18]. Besides, AZO is radio-
5 frequency (RF) sputtered at room temperature and can be deposited on flexible substrates.
6 Although room-temperature processed AZO is known for its relative poor resistance to
7 moisture^{[19][20]}, this issue could be mitigated for use in space where moisture is absent and by
8 encapsulation. Here, record AM1.5G PCE up to 15% was obtained with AZO TCO, SnO₂ ETL,
9 triple cation perovskite and Spiro-OMeTAD HTL. We also report the AM0 efficiency with a
10 champion cell having up to 13.6% PCE. Although Spiro-OMeTAD is not thermally stable, it could
11 be used for space missions to the outer regions of the solar system which wouldn't require solar
12 cells to be exposed to high temperature. Besides, it could be used on earth in regions with
13 radioactive pollution like damaged nuclear power plants, which were proposed to be rehabilitated
14 as solar plants, providing that solar cells have a high radiation hardness^[16]. Besides, SnO₂ was used
15 here as an ETL instead of mp-TiO₂. Indeed, mp-TiO₂ is known to be highly sensitive to UV light
16 and acts as a catalyst to the degradation of the perovskite layer. On the contrary, SnO₂ has been
17 shown to have much higher stability against UV irradiation^[21], which is particularly important in
18 space as the AM0 spectrum contains a higher level of UV radiation.

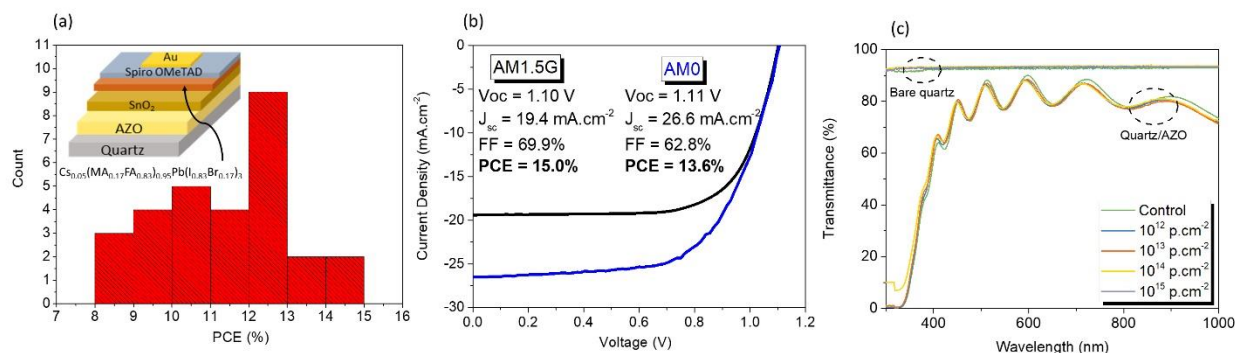
19 These devices were exposed to 150 keV proton irradiation from 10¹² to 10¹⁵ protons.cm⁻². We
20 demonstrate that the cells can withstand proton irradiation up to 10¹³ protons.cm⁻² without
21 significant loss in efficiency. The optical and structural properties of individual layers in the device
22 stack were measured by X-ray diffraction (XRD), UV-Vis, Raman and photoluminescence
23 spectroscopy, and the impact of proton irradiation on recombination within the devices was
24 measured by transient photovoltage (TPV). It was shown that the efficiency loss observed starting
25 from 10¹⁴ protons.cm⁻² can be ascribed to the degradation of the Spiro-OMeTAD HTL.

26 **RESULTS AND DISCUSSION**

27 Figure 1(a) shows the histogram of perovskite solar cells efficiencies fabricated on quartz/AZO
28 substrates before proton irradiation. Quartz was used instead of soda-lime glass which can be
29 darkened by radiations^[15]. Glass darkening is a well-known effect of ionizing radiations and space-

1 qualified glass made of ultra-thin cerium doped glass is usually used to prevent this effect for
2 satellites and other space applications. Quartz is used here to avoid any parasitic effect due to the
3 substrate and assess the effect of radiations on the layer stack only. As observed in figure 1(a), the
4 performances of the cells under AM1.5G illumination vary between 8% and 15%, mostly due to
5 variations in J_{sc} and FF (not shown). To the best of our knowledge, the champion cell with PCE of
6 14.95% outperforms previous works on perovskite solar cells fabricated on AZO by almost 3%
7 increase in absolute efficiency^{[22][23][24][25]}. We have also measured the efficiency under AM0
8 illumination, which reached up to 13.6% PCE with J_{sc} of 26.6 mA.cm⁻². The J-V curves under
9 AM1.5G and AM0 illumination for the champion cell are shown in figure 1(b). Due to the rather
10 large range of PCEs obtained, it was decided to select one sample with PCEs < 11% and one
11 sample with PCEs >11% to be exposed to each protons fluence (as well as for the control samples
12 not exposed to proton irradiations).

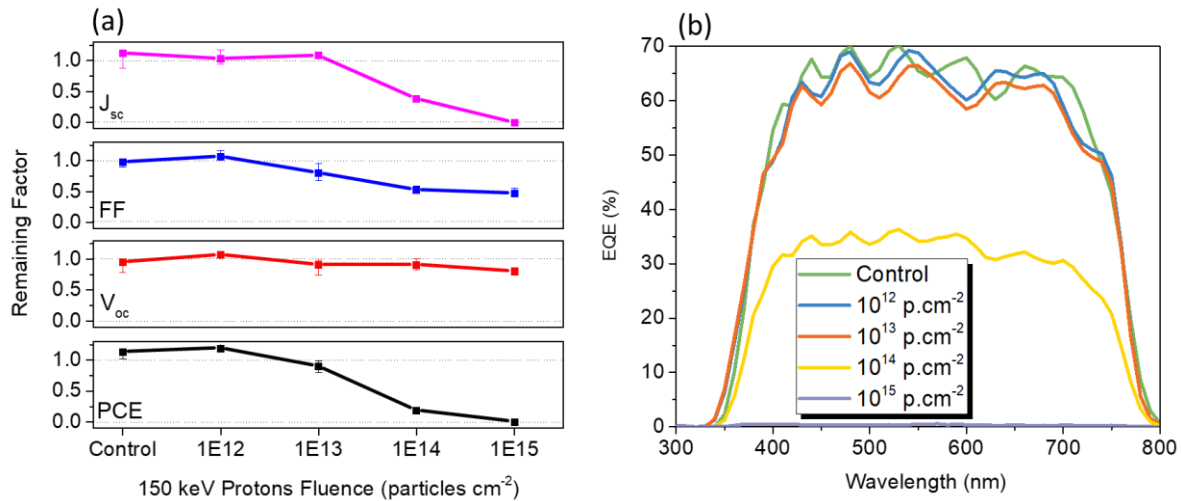
13 Then, the samples were irradiated with 150 keV protons with fluence ranging from 10¹² to 10¹⁵
14 protons.cm⁻². Some devices were not exposed to proton irradiation but subjected to the same
15 atmospheric conditions to serve as a reference. The value of 150 keV for the energy of protons is
16 commonly used for other types of PV such as Si or GaAs^{[26][9]}. We have performed simulations
17 using the program SRIM/TRIM to assess the effect of 150 keV protons on planar solar cells with
18 AZO/quartz substrates. In figure S1, it can be seen when samples are irradiated from the gold side,
19 collisions take place in all layers from the top contact (gold) to the bottom contact (AZO). This is
20 thus a good energy to probe the radiation hardness of perovskite solar cells. SRIM/TRIM
21 simulation were also performed from the quartz side (figure S2) and indicate that in this case all
22 protons are stopped in the first 230 nm of the quartz, never reaching the perovskite stack. Hence,
23 the cells were implanted from the gold side to directly probe the effect of 150 keV protons on the
24 perovskite stability. In figure S1, it can be seen that many protons collisions take place in the AZO
25 layer. Therefore, the TCO is also critical to the stability of the perovskite solar cells. As shown in
26 figure 1(c), the optical properties of AZO/quartz are unchanged after proton irradiation up to a
27 fluence of 10¹⁵ protons.cm⁻², which is a clear indication that AZO can withstand very high proton
28 irradiation without being damaged. Besides, a significant fraction of protons collide atoms in the
29 perovskite layer near the SnO₂ interface, as well as in the Spiro HTL. This allows to investigate
30 the effect of proton irradiation not only in the TCO, but in the active layer and extraction layers as
31 well.



1
2
3 **Figure. 1** (a) Histogram of power conversion efficiency (PCE) for perovskite solar cells with structure
4 quartz/AZO/SnO₂/Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃/Spiro/Au. (b) J-V curves under AM1.5G and AM0
5 illumination for champion cell. (c) Transmittance spectra of bare quartz and quartz/AZO substrates after protons
6 bombardment with various fluences.

7 The changes in PV parameters (J_{sc} , FF, V_{oc} and PCE) after proton irradiation are shown in Figure
8 2(a). The remaining factor was calculated by dividing the PV parameters after proton irradiation
9 by the PV parameters for the same set of cells (ie. for each fluence) before proton irradiation.
10 Interestingly, the PCE slightly improved for the control sample, which travelled to the Ion Beam
11 Center in Surrey with the other samples but was not irradiated. All samples were kept under N₂ in
12 the dark before the irradiation was carried out, and then kept for a week under dark air before they
13 could be measured after irradiation. The PCE is slightly improved at 10¹² cm⁻² fluence and slightly
14 decreased at 10¹³ cm⁻² fluence, as compared to the control sample. At 10¹⁴ cm⁻² fluence, a
15 prominent decrease is observed, and the PCE remaining factor is reduced to 0.2, which is due to a
16 decrease in J_{sc} and FF, while the V_{oc} remains almost constant. At 10¹⁵ cm⁻² fluence, a very low
17 current was measured as the cells were highly degraded, but the cells still had a non-negligible V_{oc}
18 of 0.8 V. The fact that the V_{oc} remains high until 10¹⁵ cm⁻² proton fluence suggests that the
19 perovskite layer itself is not significantly degraded, while the decrease in FF and J_{sc} can be
20 explained by a deterioration of charge extraction properties due to the degradation of spiro-
21 OMeTAD or SnO₂ interlayers^[27]. The remaining factors were also measured under AM0
22 illumination and are shown in figure S3, indicating similar trend as under AM1.5G illumination.
23 The external quantum efficiency (EQE) for representative cells at each protons fluence is shown
24 in Figure 2(b). The results are in good agreement with the J_{sc} trend obtained from current-voltage
25 measurements, showing a stable EQE up to 10¹³ protons.cm⁻² (interferences are due to the 700 nm-

1 thick AZO layer) and then significant decrease at 10^{14} protons.cm⁻². The decrease in EQE is
 2 uniform across the whole spectrum range and affects equally the UV and visible parts. On the
 3 contrary, Miyasawa et al. measured a non-uniform spectral response of photocurrent of
 4 FAMAPb(IBr)₃ cells after proton irradiation at fluence 10^{14} protons.cm⁻¹,^[14] which was ascribed to
 5 degradation of the active layer. Here, the uniform decrease of the EQE spectrum could be
 6 indicative of a deterioration of the charge extraction properties rather than charge generation
 7 properties and points out the role of charge extraction layers in the degradation of the solar cells
 8 during irradiation. At 10^{15} protons.cm⁻², the EQE is almost null and barely visible on the figure.
 9 Hence, from these measurements it is clear that perovskite solar cells with Spiro OMeTAD HTL
 10 can be exposed to a radiation level up to 10^{13} protons.cm⁻² without being significantly degraded.
 11 By comparison, the V_{oc} and J_{sc} of Si solar cells exposed to 150 keV protons decrease by more than
 12 40% and 10%, respectively, at 10^{13} protons.cm⁻²^[26]. Besides, it was demonstrated that GaAs solar
 13 cells exposed to 150 keV protons start to degrade at a radiation dose as low as 10^{10} protons.cm⁻²
 14 and the remaining factor for P_{max} is decreased to 0.2 at 10^{12} protons.cm⁻²^[9]. In our case, a P_{max}
 15 remaining factor of 0.2 is reached only at 10^{14} protons.cm⁻², which means that perovskite solar
 16 cells have at least two orders of magnitude higher tolerance to proton irradiation than GaAs solar
 17 cells.



18
 19 **Figure. 2** (a) Changes of photovoltaic characteristics (J_{sc} , FF, V_{oc} , and PCE) of perovskite solar cells under AM1.5G
 20 illumination as a function of protons fluence. Averaged values measured for a total of 6 different cells for each
 21 fluence. (b) External quantum efficiency for representative devices as a function of protons fluence.

1 Next, we used a combination of non-destructive techniques to investigate the degradation
2 mechanisms in perovskite solar cells and perovskite films after proton irradiation and have a better
3 understanding of the degradation of individual layers in the device stack.

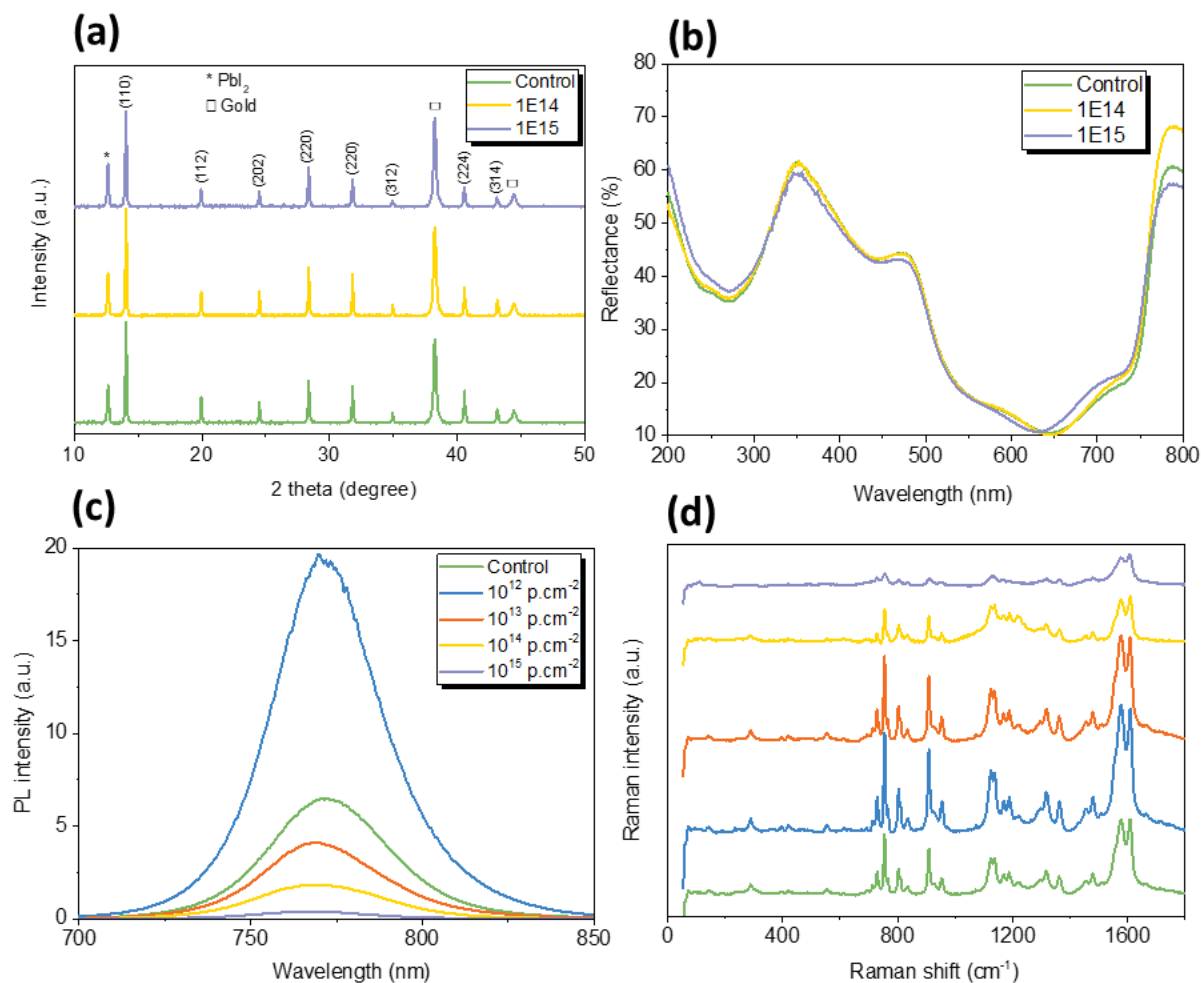
4 The X-ray diffraction (XRD) spectra of perovskite films deposited on quartz and exposed to
5 irradiation with 10^{14} and 10^{15} protons.cm⁻² are shown in figure 3(a) and compared to a non-
6 irradiated control sample. For all samples, a PbI₂ peak can be observed at 12.7°, which is ascribed
7 to the 5% PbI₂ excess used in the precursor solution and/or to environmental degradation (samples
8 were measured more than 40 days after fabrication). However, all samples have similar spectra.
9 The normalized spectra (figure S4) show perfect overlap of the (110) perovskite peak for the three
10 samples and similar intensity ratio between PbI₂ and perovskite peaks. This indicates no
11 degradation of the crystalline structure of the triple cation perovskite film due to protons
12 irradiation.

13 Reflectance spectra of perovskite films on quartz with gold electrode are shown in figure 3(b).
14 Any changes in perovskite absorbance would appear on the reflectance spectra (measured from
15 quartz side). The perovskite band edge is clearly visible at 740-775 nm for all three samples and
16 all spectra in the range 200-775 nm are very similar (intensity differences above 775 nm is not
17 related to perovskite and can be ascribed to gold thickness variations). We note however that the
18 sample irradiated with 10^{15} protons.cm⁻² has a slightly different spectral shape in the range 650-
19 700 nm and 200-300 nm. This could suggest that perovskite has undergone some degradation for
20 the highest proton fluence, although it may not fully explain the strong PCE drop measured for
21 this sample.

22 The photoluminescence (PL) intensity of the full device stack after proton irradiation is shown in
23 Figure 3(a). The PL intensity undergoes almost three folds increase in magnitude after irradiation
24 with 10^{12} protons.cm⁻² as compared to the reference sample. This can be correlated with the slight
25 increase in PCE after irradiation with 10^{12} protons.cm⁻² and suggests that the performance of
26 perovskite solar cells could be improved after 150 keV proton irradiation with mild fluence.
27 However, from 10^{13} protons.cm⁻² onwards, we observe a constant decrease of the PL intensity, in
28 good agreement with the decrease in PV performance. The PL intensity is indicative of the quality
29 of the perovskite bulk or interfaces. Deep trap states formed in the perovskite bulk can induce non-
30 radiative recombination and quench the PL^{[28][29]}. However, in a full device stack, a defective
31 interface due to degradation of the electrons or holes extraction layers can also quench the PL if

1 carriers are lost to nonradiative recombination in the contact and no longer return to the
2 perovskite^[30]. Hence, these results show that the PL intensity follows the same trend as the power
3 conversion efficiency after proton irradiation, but at this stage it cannot be clearly attributed to
4 specific damage in the perovskite bulk or in the electron/hole transport layers.

5 The Raman spectra of Spiro-OMeTAD after irradiation are shown in figure 3(b). The results were
6 averaged over 100 spectra measured for each sample to account for local non-uniformities.
7 Besides, at least two samples were measured for each fluence to confirm the results. The integrity
8 of Spiro-OMeTAD is clearly maintained up to 10^{13} protons.cm⁻² as the spectra remain unchanged,
9 showing sharp and intense signal from Spiro-OMeTAD^[32]. However, some degradation is
10 observed at 10^{14} protons.cm⁻² where the peaks intensity starts to decrease, and even stronger
11 degradation of the spiro-OMeTAD is observed at 10^{15} protons.cm⁻². As the Raman intensity can
12 be sensitive to measurement conditions (especially to the focus), normalized spectra are also
13 shown in figure S5 in SI. After normalization, all spectra up to 10^{13} protons.cm⁻² overlap each
14 other perfectly, indicating no change in spiro-OMeTAD chemical structure. However, at 10^{14} and
15 10^{15} protons.cm⁻², it is clear that some modes are attenuated such as 755 cm^{-1} or 914 cm^{-1} peaks,
16 and the shape of the spectrum is significantly different. This correlates well with the degradation
17 of cells performance after proton irradiation and indicates that the loss in PCE at 10^{14} and 10^{15}
18 protons.cm⁻² is likely due to degradation of the Spiro-OMeTAD HTL. It has been shown that Spiro-
19 OMeTAD is sensitive to temperature and can undergo strong thermal degradation at 100°C ^[14].
20 However, this is very unlikely that the temperature raised to such high temperature during the
21 implantation, even for the highest protons fluence. A low power density of 15 mW.cm^{-2} for the
22 proton beam was used, and the samples were clipped down onto a heat sink which should have
23 enough thermal mass to limit the temperature rise. Unfortunately, it was not possible to measure
24 any potential degradation of the SnO₂ ETL after proton irradiation as the techniques used in this
25 work are not sensitive to such a thin and transparent layer (besides SnO₂ nanoparticles don't have
26 measurable PL or Raman signal). Future work will be necessary to determine the role of SnO₂
27 ETL in the performance loss due to proton irradiation.

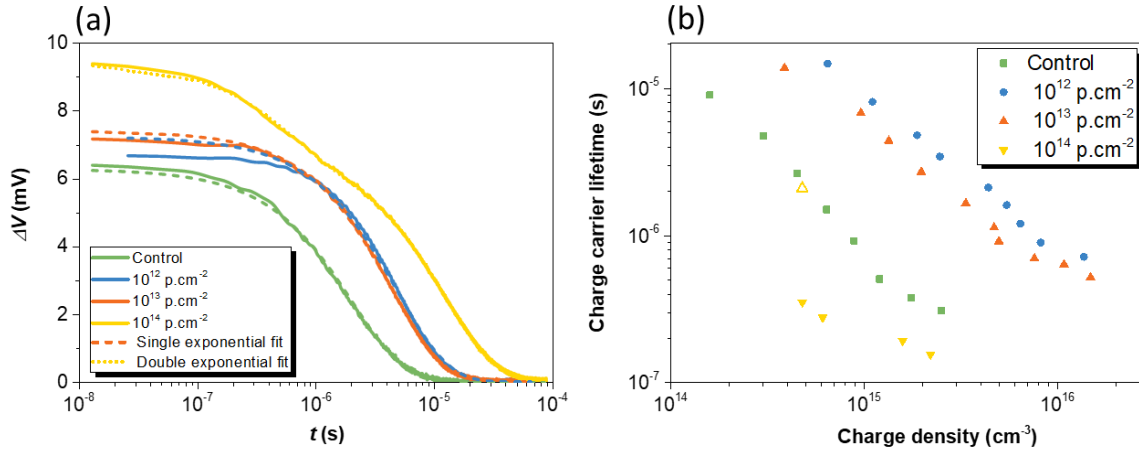


1
 2 **Figure 3.** (a) X-ray diffraction spectra of perovskite films deposited on quartz (+ gold electrode) without irradiation
 3 and after irradiation with fluences 10^{14} and 10^{15} protons.cm⁻². (b) Diffuse reflectance spectra measured with an
 4 integrating sphere for perovskite films deposited on quartz (+ gold electrode) without irradiation and after irradiation
 5 with fluences 10^{14} and 10^{15} protons.cm⁻². (c) Full perovskite solar cells PL intensity as a function of protons fluence.
 6 Inset: normalized PL intensity. (d) Raman spectra of perovskite solar cells measured between 0 and 1800 cm⁻¹ on top
 7 of Spiro-OMeTAD (outside gold electrodes) as a function of protons fluence.

8
 9 At this stage, we have shown that the Spiro-OMeTAD HTL starts to degrade at 10^{14} protons.cm⁻².
 10 The crystalline structure and optical properties of the perovskite film remain unchanged up to 10^{14}
 11 protons.cm⁻², but signs of minor degradation are observed at 10^{15} protons.cm⁻² from diffuse
 12 reflectance measurements. However, these measurements cannot account for local defects created
 13 in the perovskite by proton irradiation, such as trap states caused by atomic displacement. In order
 14 to study the impact of proton irradiation on recombination within the devices, transient

1 photovoltage (TPV) measurements were performed. For devices with one dominant recombination
2 mechanism, the perturbed V_{oc} decays back to the steady state with a single exponential time
3 constant^{[33][34]}. This behavior was observed for fluences up to 10^{13} protons.cm⁻², indicating that
4 bulk recombination in the perovskite layer is dominating for low proton doses, as shown in Figure
5 4(a). At 10^{14} protons.cm⁻², the TPV decays show clear double exponential behavior at light
6 intensities below 0.25 sun. At higher intensities it is not possible to resolve the additional faster
7 process. Indeed, it is often observed in perovskite cells that bulk recombination is dominant at the
8 highest light intensities, and that underlying mechanisms are only apparent when studied over a
9 range of conditions^{[34][35][36][37]}. This double exponential behavior has been linked to the presence
10 of interfacial recombination, either at the ETL or HTL contacts^{[38][39][40]}. From the observations of
11 Spiro-OMeTAD degradation in the Raman studies, the faster time constant can therefore be
12 attributed to recombination at the perovskite/Spiro interface for this device. It was not possible to
13 study the 10^{15} protons.cm⁻² device using the standard TPV technique as a stable V_{oc} could not be
14 obtained for this highly degraded device. However, evidence of fast interfacial recombination was
15 observed in the form of a negative transient deflection in response to the laser pulse, as studied in
16 other work (see Figure S6 in SI)^{[41][42][43]}.

17 The charge density in the devices was calculated using the differential capacitance method^[44].
18 Bombardment with 10^{12} and 10^{13} protons.cm⁻² resulted in a significant increase in charge density
19 as a result of trap formation, as shown in Figure 4(b). A corresponding increase in carrier lifetime
20 suggests that charges spend time in these shallow traps before being released (deeper traps would
21 likely act as recombination centres and cause a decrease in carrier lifetime). Lang et al. have also
22 observed this apparent decrease in the rate of recombination as a result of proton bombardment
23 induced defect formation^[11]. This was explained by an efficient trapping/detrapping of minority
24 charge carriers in radiation-induced trap states without major impact on device performance. At
25 10^{14} protons.cm⁻², the additional fast interfacial recombination significantly reduced the carrier
26 lifetime. However, the slower time constant obtained from the double exponential fitting is in the
27 same range as the lifetimes calculated for the lower fluences, suggesting that the bulk
28 recombination lifetime is not significantly reduced at this high fluence. This is consistent with the
29 main source of the performance loss at 10^{14} protons.cm⁻² being degradation of the Spiro-OMeTAD
30 interface, while trap states formed in the perovskite layer do not affect the performance
31 significantly.



1
 2 **Figure 4:** (a) TPV decays for each sample at 0.1 sun equivalent light intensity. Single exponential fitting is suitable
 3 for devices up to 10^{13} protons. cm^{-2} . The additional process observed at short times ($<1 \mu\text{s}$) for the 10^{14} protons. cm^{-2}
 4 device results in double exponential fitting being required at that fluence. (b) Charge carrier lifetime versus charge
 5 density as a function of proton fluence. Open triangle represents the slower time constant obtained from the double
 6 exponential fitting at 10^{14} p. cm^{-2} (device V_{oc} was unstable below this intensity therefore charge density calculation
 7 was not possible).

8 CONCLUSIONS

9 In summary, the radiation hardness of perovskite solar cells (standard planar architecture)
 10 fabricated on AZO/quartz substrates to 150 keV protons has been investigated. Record power
 11 conversion efficiency up to 15% has been obtained using low cost, non-toxic, room temperature
 12 deposited AZO transparent conductive oxide, which is almost a 3% absolute increase in PCE as
 13 compared to previous works. Although a high fraction of the 150 keV protons are stopped in the
 14 AZO layer, the optical properties of AZO/quartz substrates remain unchanged, even after
 15 irradiation up to 10^{15} protons. cm^{-2} . Perovskite solar cells fabricated on these substrates using a
 16 triple cation perovskite active layer and Spiro-OMeTAD HTL show high tolerance to protons
 17 radiations up to a fluence of 10^{13} protons. cm^{-2} . In comparison, Si and GaAs solar cells are known
 18 to be destroyed or highly deteriorated at this level of radiations. Significant deterioration of the
 19 cells is observed at 10^{14} and 10^{15} protons. cm^{-2} , which is ascribed to degradation of the Spiro-
 20 OMeTAD HTL during proton irradiation, as shown by degenerated Spiro-OMeTAD Raman
 21 spectra, additional interfacial recombination process and hindering of charges extraction
 22 properties. Although the structural and optical properties of perovskite remain intact up to high

1 fluence levels, TPV measurements indicate an increase in minority carrier density and lifetime
2 from 10^{12} protons.cm⁻², which is explained by formation of radiation-induced shallow trap states
3 in the perovskite bulk. It is thought that these trap states release charge carriers efficiently and do
4 not affect the performance of the cells for low fluence levels. Therefore, it is demonstrated here
5 that AZO TCO can be promising for perovskite solar cells to be used in space, with both decent
6 PCE and good stability against proton irradiation. Furthermore, this study provides deeper
7 scientific understanding on the interfacial degradation due to proton irradiation, which can be
8 useful for the development of future high PCE perovskite solar cells with ultra-high stability
9 against proton irradiation.

10 **METHODS AND EXPERIMENTAL SECTION**

11 **Cell preparation and testing**

12 Quartz glass substrates (UV grade fused silica glass, JGS2, Kintec, Hong Kong) were cleaned by ultrasonication in
13 Hellmanex (2%, deionized water) for 5 minutes, then further sonicated with deionized water for 15 minutes, Acetone
14 for 10 min and then 2-propanol for 5 before being dried via a N₂ gun. AZO (~700 nm) served as a transparent bottom
15 contact was radio-frequency (RF) sputtered using a Moorfield Nanolab 60 sputtering system with power density of
16 2.46 W.cm⁻². The sheet resistance of deposited AZO is 23-25 Ω/□. Before the ETL was deposited, the substrates were
17 treated in oxygen plasma for 5 min. A planar layer of SnO₂ at a thickness of ~25 nm was subsequently deposited via
18 spin coating at a spin speed of 3000 rpm and an acceleration 3000 rpm for 30 s. The SnO₂ precursor solution was
19 fabricated from commercial tin oxide nanoparticles (15% colloidal dispersion in H₂O, Alfa Aesar) diluted in deionized
20 water (1:6.5, volume ratio). This was followed by sintering the substrates at 150°C for 30 min in a fume hood. The
21 triple cation perovskite films were deposited in a N₂ atmosphere using single-step deposition method from the
22 precursor solution containing FAI (172 mg) (Dyesol), PbI₂ (507 mg) (TCI), MABr (22 mg) (Dyesol) and PbBr₂ (73
23 mg) (TCI) in anhydrous N,N-Dimethylformamide (99.8%, Sigma-Aldrich)/dimethylsulphoxide (99.7%, Sigma-
24 Aldrich) (8:2 (v:v)). Thereafter, 53 μL of CsI (99.999% trace metal, Sigma-Aldrich), (390 mg, 1 ml DMSO) was
25 added to the precursor solution. The precursor solution was spin-coated onto the planar SnO₂ films in a two-step
26 program at 1000 and 6000 rpm. for 10 and 20 s, respectively. During the second step, 300 μl of chlorobenzene (99.9%)
27 was dropped on the spinning substrate 5 s prior to the end of the program. This was followed by annealing the films
28 at 100°C for 1 hour. To complete the fabrication of devices, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-
29 spirobifluorene (Spiro-OMeTAD, 90 mg in chlorobenzene) as a hole-transporting material (HTM) was deposited by
30 spin coating 100 μL of the prepared solution at 4000 rpm for 20 s. The Spiro-OMeTAD (Sigma-Aldrich) was doped
31 with Bis(trifluoromethane)sulfonimide lithium salt (99.95%, Sigma-Aldrich) dissolved in acetonitrile (520 mg/ml),
32 Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) Tris(bis(trifluoromethylsulfonyl)imide) (FK 209, from
33 Dyenamo) and 4-tert-Butylpyridine (96%, Sigma-Aldrich) with concentrations of 34 μL, 10 μL and 19 μL
34 respectively. Finally, device fabrication was completed by thermally evaporating gold wire (99.9% 1mm, Kurt
35 J.Lesker) to form a ~70 nm gold layer as a back contact.

36 **Protons bombardment**

38 The proton beam irradiation was carried out at the Surrey Ion Beam Centre in UK. The reference samples have
39 travelled together with the irradiated samples. All the samples were packed in N₂ atmosphere in the dark during
40 traveling. The reference samples (not irradiated) were exposed to air when the other samples were also exposed to
41 air just before the proton irradiation and during the travel back to Swansea. Sample loading was carried out in a class
42 100 clean room. The perovskite cells were mounted directly onto 4 in. support plates which were inserted into a
43 carousel wheel in the sample chamber. Silver paste was applied to allow charges to be conducted to the back of the

1 samples and in the holder plate to avoid charges accumulation. Samples were loaded in a $7^\circ/0^\circ$ tilt/twist orientation
2 to the incident beam and implanted under vacuum ($2.3 \pm 0.2 \times 10^{-6}$ mbar). The samples were placed to receive direct
3 impact of the protons, with the back contact (gold electrode) facing the proton source. Indeed, the quartz substrate is
4 thick enough to shield the cells from the proton irradiation, so that it would be impossible to measure the effect of
5 protons irradiation on the perovskite layer if the quartz was facing the proton source. A Danfysik 1090 low energy
6 high current implanter was used to implant 150 keV protons into the samples (from the Silver side). The fluence rate
7 was controlled to $3 \times 10^{10}/\text{cm}^2 \cdot \text{s}$ for fluence 10^{12} protons. cm^{-2} and $3 \times 10^{11}/\text{cm}^2 \cdot \text{s}$ for fluences 10^{13} to 10^{15}
8 protons. cm^{-2} .
9

10 **Devices and thin films characterization**

11 UV-Vis Characterization

12
13 UV-VIS Transmittance experiments were undertaken on full device structure using a UV/VIS/NIR spectrometer
14 (Lambda 750, PerkinElmer) with an integrating sphere in range 180 to 1000 nm with 1 nm steps. For diffuse
15 reflectance measurements, samples with structure quartz/perovskite/gold were placed on the output port of an
16 integrating sphere with the quartz substrate facing the light beam.
17

18 X-Ray diffraction

19
20 X-ray diffraction measurements were carried out using a Bruker D8 Discover instrument with a $\text{CuK}\alpha$ beam
21 (wavelength is 0.15418 nm) at 40 kV and 40 mA, scan parameters of 1.3 s/step at 0.02° of 2θ step size. All
22 measurements were carried out on samples with structure quartz/perovskite/gold, so that the perovskite crystalline
23 structure was measured through the gold layer.
24

25 Raman and PL Characterization

26
27 The Raman and PL measurements were performed with a Renishaw inVia Raman system (Renishaw plc., Wotton-
28 Under-Edge, UK) in backscattering configuration. A 532 nm laser and 50x objective were used (NA: 0.50, spot size
29 $\approx 1 \mu\text{m}$). For the Raman measurements, a laser power of 150 μW and acquisition time of 10 s were used to measure
30 25 different points, which were averaged in a single spectrum. For the PL measurements, a laser power of 300 nW
31 and an acquisition time of 2 s were used to measure 121 different points, which were also averaged. Raman spectra
32 of Spiro OMeTAD were measured on the gold side (outside gold electrodes), whereas PL spectra of perovskite film
33 were taken from the glass side.
34

35 EQE Measurements

36
37 External quantum efficiency (EQE) measurements were made using a monochromatic light source in AC mode with
38 chopping frequency of 70 Hz (QEX10 PV Measurements). The system was calibrated using a NIST-certified
39 calibration cell (PV Measurements) and data points were taken by sweeping the wavelength from 300 to 900 nm and
40 recording a value every 10 nm.
41

42 J-V Characterization

43
44 The current-voltage (J-V) characteristics of the perovskite devices were recorded with a digital source meter
45 (Keithley model 2400, USA) and 450 W xenon lamp (Sol3A Class AAA Solar Simulator, Oriel, USA). The light
46 source was equipped with an Air Mass filter (Newport) to correct the output of the xenon lamp to better match the
47 AM1.5G solar spectrum. Both forward and reverse bias scans were taken from 1.2 to -0.1 V with a sweep interval of
48 0.015 V, resulting in 81 data points respectively. The current limit was set to 100 mA. The Air Mass 0 J-V
49 characteristics follow the same experiment set-up and measurement parameters as AM1.5G. However, the AM1.5G
50 filter was replaced with an AM0 filter. Alongside this replacement, the lamp was calibrated by integrating the
51 measured EQE J_{sc} and matching the pixel J_{sc} under the AM0 spectrum with this value.
52

53 Transient Photovoltage measurements

54

1 TPV measurements were performed using a commercially available transient measurement system
2 (Automatic Research GmbH). This system uses a 635 nm red laser diode driven by a waveform generator
3 (Keysight 33500B) to give a 500 ns pulse length. Background illumination was provided by a white LED
4 with its intensity calibrated to generate the same device photocurrent as measured using the solar
5 simulator - this intensity is referred to as '1 Sun equivalent'. An intensity range was then calibrated using
6 a silicon photodiode. Transient responses were captured by a digital storage oscilloscope (Keysight
7 DSOX2024A), the number of sample averages being adjusted to optimise signal noise and measurement
8 time. The device under test was held at open-circuit by a custom-built voltage follower (1.5 TΩ input
9 impedance). TPC measurements were performed using a current amplifier (Femto DHPA-100).

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15 Author Contributions

16 The manuscript was written through contributions of all authors. All authors have given approval to the final version of the
17 manuscript.

18 CONFLICTS OF INTEREST

19 There are no conflicts to declare.

20 ACKNOWLEDGEMENTS

21 The authors would like to thank Airbus Endeavr Wales for their financial support. The authors would also like acknowledge to
22 the Ser Cymru funding from the Welsh Assembly Government (Ser Solar), the EPSRC fund (Grant No. EP/M025020/1), and the
23 Welsh European Funding Office (SPARC II). The authors would also like to thank the EPSRC through the SPECIFIC Innovation
24 and Knowledge centre Phase 2 (EP/N020863/1). The IMPACT operation has been part-funded by the European Regional
25 Development Fund through the Welsh Government and Swansea University.

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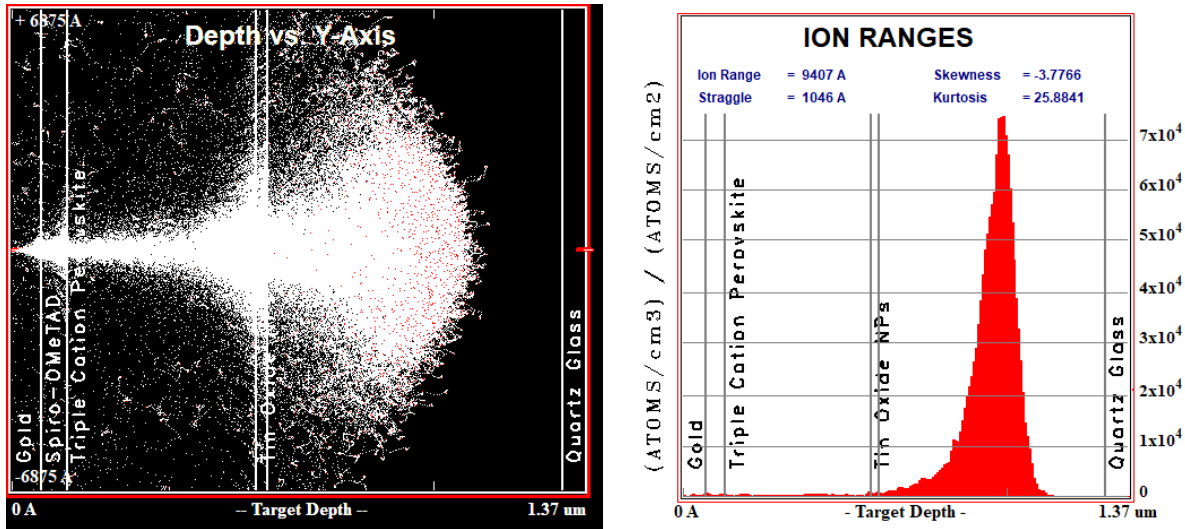
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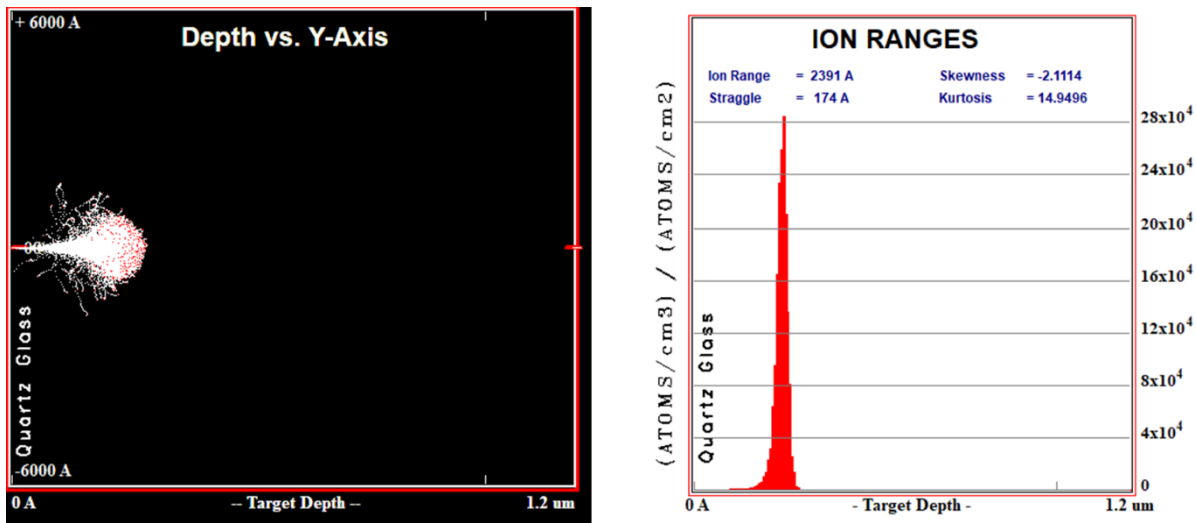
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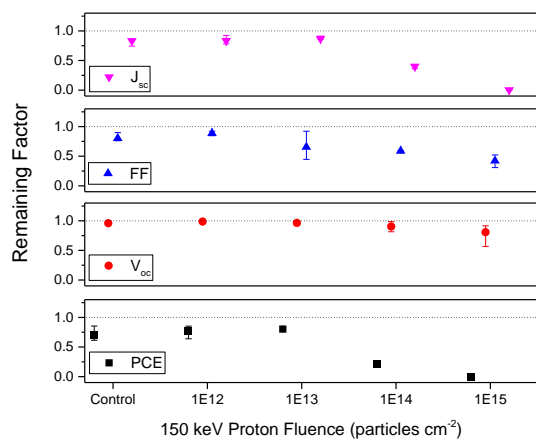
1 SUPPORTING INFORMATION



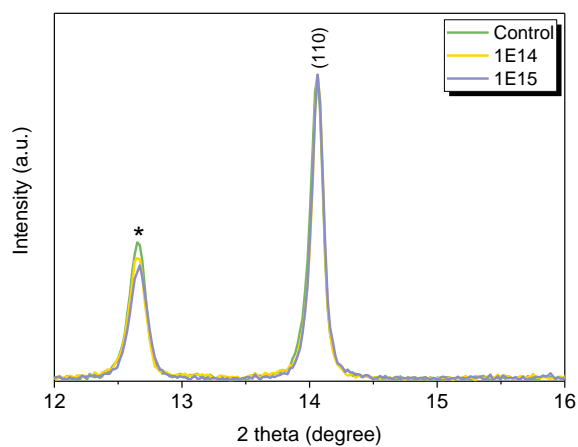
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3 **Figure S1.** SRIMS Simulation of the perovskite cells undergoing particle bombardment at 150 keV from the gold
4 side. Schematic diagram with particle stopping points (left) and Ion Ranges histogram (right), shows that the AZO
5 acts as a barrier and stops nearly all protons with this energy.



6
7 **Figure S2.** SRIMS Simulation of a quartz substrate undergoing particle bombardment at 150 keV. Schematic
8 diagram with particle stopping points (left) and Ion Ranges histogram (right), show that all protons with this energy
9 are stopped in the first 230 nm of the 1 mm quartz substrate.

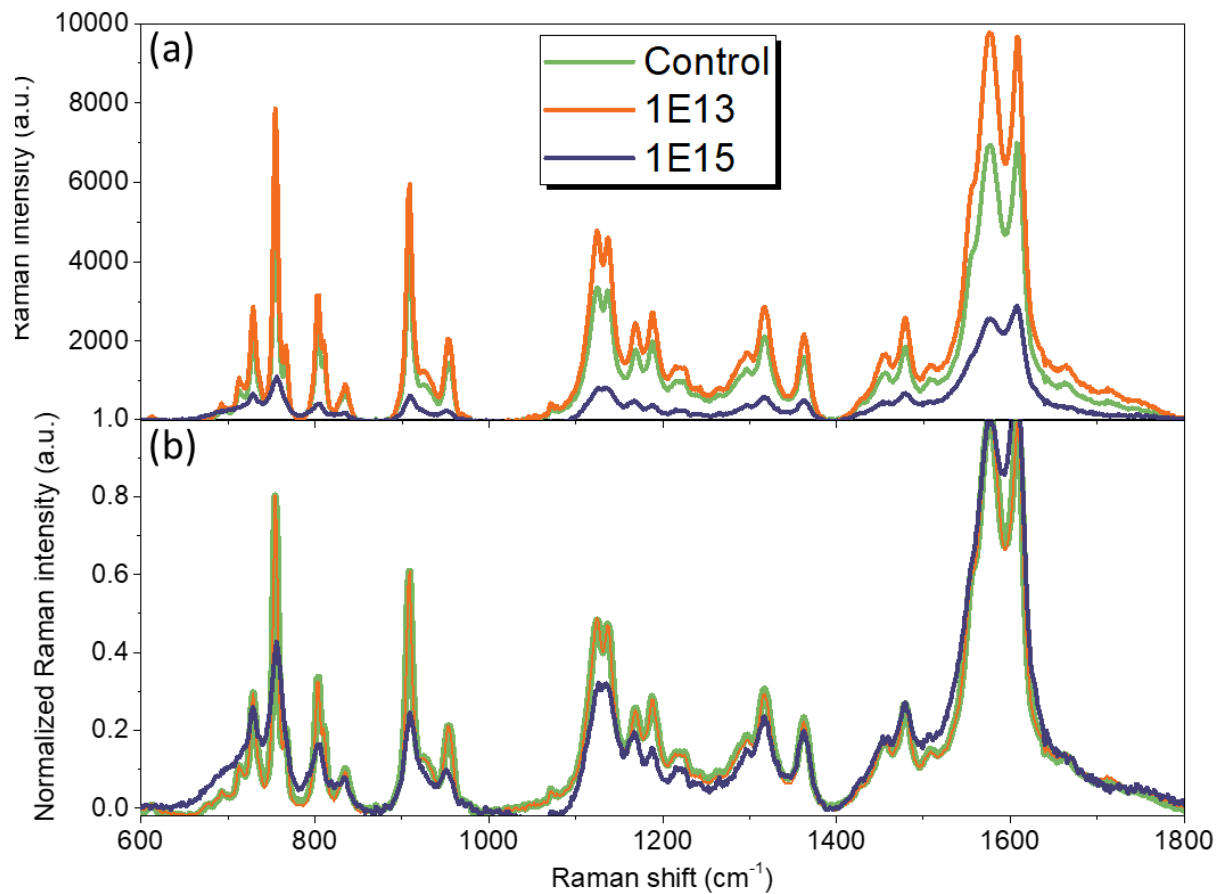


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 2 **Figure S3.** Changes of photovoltaic characteristics (J_{sc} , FF, V_{oc} , and PCE) of perovskite solar cells under AM0
 3 illumination as a function of protons fluence. Averaged values measured for a total of 6 different cells for each
 4 fluence



5
 6 **Figure S4.** Normalized XRD spectra of perovskite thin films on quartz for control sample and samples irradiated
 7 with 10^{14} and 10^{15} protons.cm⁻²

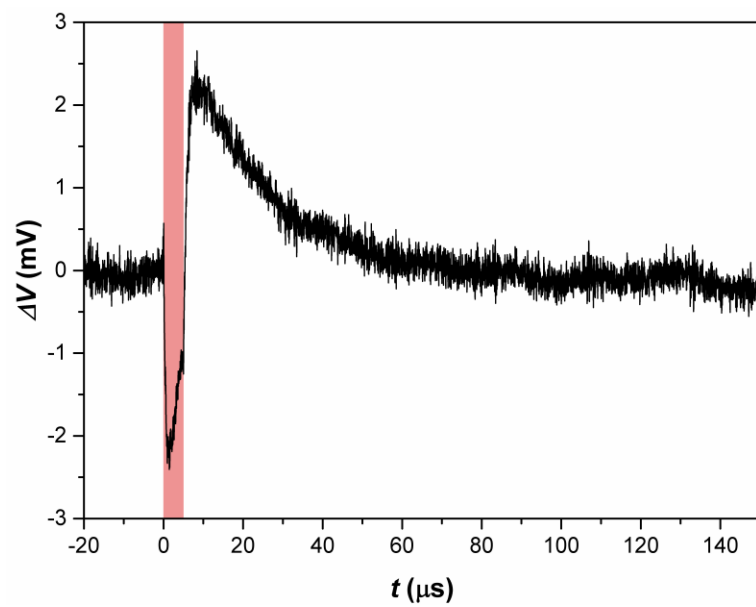
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1

2 **Figure S5.** (a) Raman spectra of Spiro OMeTAD for the control sample and sample irradiated with 10^{13} and 10^{15}
3 protons. cm^{-2} . (b) Same spectra after normalization (divided by intensity at 1575 cm^{-1}).

4



1
2 **Figure S6.** TPV response for device bombarded with 10^{15} protons.cm⁻² measured at 1 Sun equivalent intensity. Laser
3 pulse (red shaded region) induces a rapid negative deflection (decrease in V_{oc}) in the TPV response indicative of fast
4 interfacial recombination.

5