

1 **Measurement of band offsets and shunt resistance in CdTe solar cells through temperature**  
2 **and intensity dependence of open circuit voltage and photoluminescence**

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14 Band offsets at the back contact and front window layer in CdTe-based solar cells affect  
15 photovoltaic performance and challenge standard characterization methods. By analyzing the  
16 temperature and excitation dependence of both open circuit voltage and absolute  
17 photoluminescence intensity, we show that the effects band offsets can be separated from the  
18 effects of recombination and shunting. Solar cells were grown with MgZnO window layers and  
19 compared to cells with CdS window layers containing varying amounts of oxygen. It was  
20 demonstrated that band alignment rather than reduced recombination velocity is the reason for  
21 the success of MgZnO as a front interface contact. An assortment of thin back contact interlayers  
22 were also deposited, and a PbTe interlayer showed some promise as an Ohmic contact to the  
23 CdTe, though it appears to induce a photoconductive shunt. Finally, we show that the shunting  
24 resistance given by a standard current-voltage curve technique generally does not represent a  
25 physically meaningful quantity unless it is well below one kiloOhm square cm.

26 Keywords: Photovoltaic device characterization; Loss analysis; Model fitting; Contact barrier;  
27 Recombination; Injection dependence

28 **1. Introduction**

29 The achievement of an ohmic back contact has been elusive in CdTe-based solar cells. The  
30 ubiquitous back-contact barrier, of height  $\Phi_b$ , is a challenge for standard characterization  
31 methods and for further improving photovoltaic performance. The back-contact barrier decreases  
32 the fill factor and open circuit voltage ( $V_{OC}$ ) in complicated ways, (Pan et al., 2006) and distorts  
33 capacitance-voltage (C-V) measurements of the doping concentration. (Li et al., 2012) When  
34 measuring trapping center properties by capacitance-frequency (admittance spectroscopy, or AS)  
35 technique, trap signatures can be altered by the presence of  $\Phi_b$  (Marin et al., 2013) and apparent  
36 signatures can be wholly produced. (Li et al., 2010) It has been questioned whether  $\Phi_b$  may

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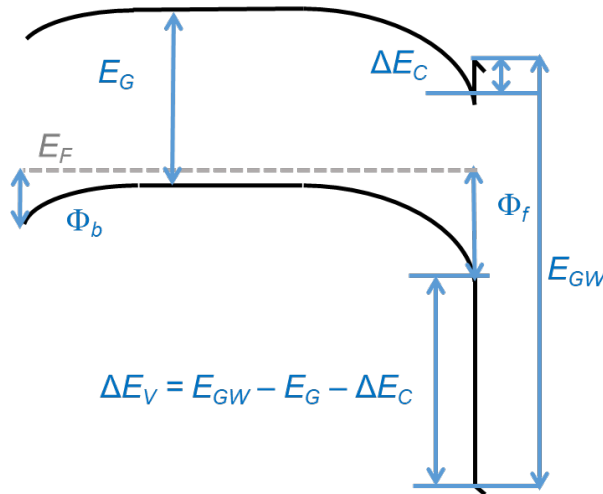
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37 render admittance spectroscopy unusable for its original purpose of characterizing deep centers.  
38 (Lauwaert et al., 2013)

39 A reduced  $\Phi_b$  is generally desirable for the back contact. While metals with deep work functions  
40 are more likely to be successful for contact to  $p$ -type materials, other factors at the back interface  
41 have considerable influence as well. For example, it has been found that a Te-rich back surface  
42 tends to result in improved performance. It is possible that a thin layer with a favorable  
43 conduction band offset from CdTe may be formed from Cu-Te compounds, (Jaegermann et al.,  
44 2009; Wang et al., 2017) and that such a layer would have an electron blocking effect.  
45 Alternatively, the Te may itself form an intermediate band offset between the absorber and back  
46 contact. (Song et al., 2018) Another possible mechanism is that the Te may block Cu from  
47 diffusing into the CdTe absorber and reaching the front buffer layer, (Xia et al., 2014) where  
48 excessive Cu becomes deleterious. (Korevaar et al., 2011)

49 Other factors at the back contact include the use of interlayers in an attempt to lessen the shunt  
50 conductance ( $G_{SH}$ ) between the front and back electrodes. (Major et al., 2017; Tessema and  
51 Giolando, 2012) Even without a true pinhole contact, any sufficiently thin region within the  
52 absorber can exhibit space-charge-limited current (SCLC), where the conductance is  
53 approximately proportional to voltage  $V$  with a proportionality constant  $K$ , or  $G_{SH} \approx K V$ .  
54 (Dongaonkar et al., 2010)

55 In addition to shunt conduction, various band offsets that may affect solar cell performance are  
56 shown in Fig. 1. In this diagram, a 4- $\mu\text{m}$  thick  $p$ -CdTe absorber layer is depicted with a band gap  
57 of  $E_G = 1.5$  eV and a 90-nm thick buffer of CdS having a band gap of  $E_{GW} = 2.5$  eV. The front  
58 absorber-buffer junction conduction band offset ( $\Delta E_C$ ), and the (hole-blocking) front valence  
59 band offset can be expressed in terms of  $\Delta E_C$  and the band gaps as shown. The barrier height of  
60 the main junction is  $\Phi_f$ .



61  
62 Fig. 1. Band offsets that may affect solar cell performance. A 4  $\mu\text{m}$  thick  $p$ -type absorber layer is depicted  
63 with a band gap of  $E_G = 1.5$  eV and a 90 nm thick buffer having a band gap of  $E_{GW} = 2.5$  eV.

64 In this study, a number of interlayers are deposited at the back contact-absorber interface in an  
65 attempt to improve the back-contact properties of the solar cells. To correlate device properties  
66 such as band offsets and shunt with experimentally obtainable characteristics, we employ a  
67 measurement and analysis technique coupling the temperature and excitation dependence of  $V_{OC}$   
68 and photoluminescence intensity (PL-I) with numerical simulation studies.

69 A potentially overwhelming number of methods exist for correlating device properties to  
70 experimental current-voltage (JV) results. (Chan et al., 1986; Jordehi, 2016; Khan et al., 2011)  
71 These techniques are somewhat limited in their ability to provide physical insight, since, *e.g.*, the  
72 proportion of interfacial versus bulk recombination has no clear relationship with the  
73 contribution of each diode in a two-diode lumped-parameter circuit model. Additionally, the  
74 existence of a back-contact band offset is not generally considered in these models.

75 In recent years, temperature-dependent  $V_{OC}$  has been used to probe recombination characteristics  
76 (Li et al., 2014) while avoiding the complexities of series resistance. (Hegedus and Shafarman,  
77 2004; Turek, 2014) In that method, the  $V_{OC}$  versus temperature relationship near room  
78 temperature is extrapolated to absolute zero. The extrapolated voltage value ( $qE_a$ ) can be  
79 correlated with the location of recombination within the device. More recently, it has been found  
80 that the value of  $qE_a$  can change with excitation, and this may be affected by front junction band  
81 offsets. (Brandt et al., 2017)

82 This study has the goal of extracting a set of solar cell parameters from multiple measurement  
83 types. In addition to the  $V_{OC}$  and PL-I, we adopt the value of  $\Phi_b$  from the rollover method on the  
84 current-voltage-temperature (JVT) curves. (Koishiyev et al., 2008) Only a few studies have  
85 aimed to combine multiple measurement types. (Mangan et al., 2015; Richter et al., 2015;  
86 Schoneberg et al., 2018; Sun et al., 2016) The effort presented here differs from these others in  
87 several important ways. First, series resistance complications are avoided, since although the  
88 rollover portion of the JV curve is in the forward current region, the rollover method should be  
89 robust against the effects of varying series resistance. (Demtsu et al., 2006) Second, rather than  
90 revising a model for each measurement technique to account for each new experimental feature  
91 qualitatively, the most suitable parameters are determined *quantitatively* by arriving at the least  
92 square error fit to the temperature- and excitation-dependent  $V_{OC}$  data, and simultaneously to the  
93 PL-I data. To define a single rms difference between data and model for both open circuit  
94 voltage and PL-I, the PL-I data must be converted to units of eV. Therefore, the *absolute* PL  
95 intensity was measured, and the quasi-Fermi level splitting between the electron and hole  
96 populations ( $\Delta E_F$ ) within the absorber was extracted from a calculation based on the Generalized  
97 Planck's Law. (Swartz et al., 2019)

98 Various back interlayers and front window layers are explored. The analysis shows that some  
99 interlayers were successful at reducing shunt conductance, but an interlayer was not found which  
100 reduced the barrier height without an accompanying increase in shunt resistance. The analysis  
101 also provided a way of obtaining the front window conduction band offset.

## 102 **2. Experimental Details**

103 Superstrate structures were fabricated beginning with three sequences of front buffer layers. The  
104 first sequence began with 2.3 mm thick AF45 borosilicate glass coated with bilayers of fluorine-  
105 doped tin oxide SnO<sub>2</sub>:F (FTO) with 500nm thickness and undoped SnO<sub>2</sub> (TO) with 100 nm  
106 thickness, grown at the National Renewable Energy Laboratory (NREL) in a low pressure  
107 chemical vapor deposition system at 550°C. Tetramethyltin (TMT) was the tin precursor and  
108 bromotrifluoromethane was the F dopant source in an oxygen-rich ambient. Then, CdS:O with a  
109 thickness of 80 nm was deposited by magnetron sputtering, in a 6% O<sub>2</sub> in Ar ambient at 5 mTorr  
110 deposition pressure without heating. This window will be labeled CdS:O<sup>6</sup>. CdTe was deposited  
111 by close space sublimation (CSS) at 600 °C, at 16 Torr in a 6.25% O<sub>2</sub> in He ambient. A CdCl<sub>2</sub>  
112 activation anneal was performed at 400 °C in dry air, followed by rinsing in methanol and drying  
113 with N<sub>2</sub> gas to remove extra CdCl<sub>2</sub> from the surface.

114 A blade-coated layer of CdTe nanoparticles (NP) in a pyridine solution was then added to reduce  
115 surface roughness, eliminate pinholes, and allow for the deposition of interlayers. (Details to be  
116 published later by S. Rab, *et. al.*) A second CdCl<sub>2</sub> activation anneal was carried out for the added  
117 NP material by dipping the samples into a solution of CdCl<sub>2</sub> in methanol with ~15 mg/mL  
118 concentration, heated at 60 °C for 15 s, rinsed with isopropanol, dried with a stream of N<sub>2</sub>, placed  
119 on a 350 °C Al block for 20 s, then placed onto an Al block at room temperature for rapid  
120 cooling. Back contact Cu doping was done by submerging in a dilute 0.1mM solution of CuCl<sub>2</sub>  
121 and DI water for 2 min followed by rinsing in DI water and drying with N<sub>2</sub>, followed by a 225  
122 °C, 30 min anneal, then 150 °C for 1 hour. Various interlayers were grown on devices with NP.  
123 Spin-coated Spiro-MeOTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-  
124 spirobifluorene) and EH44 (2,7-Di(N,N-dimethoxyphenylamino)-N-(2-ethylhexyl)carbazole) are  
125 organic hole transport materials used in perovskite solar cells. (Leijtens et al., 2016) Evaporated  
126 selenium and sputter coated indium tin oxide (ITO) are known to have deep work functions,  
127 particularly ITO with Cl and Au, which is often used to accomplish the formation of Ohmic  
128 contacts to *p*-type materials. (Guo et al., 2010; Helander et al., 2011b) SnTe interlayers and PbTe  
129 interlayers were grown by molecular beam epitaxy to a thickness of 250 nm and doped with Tl to  
130 a high *p*-type concentration of 10<sup>19</sup> cm<sup>-3</sup> to mitigate the back contact barrier. (Lee et al., 2012)  
131 Finally, a 100 nm thick Au layer was deposited by thermal evaporation, forming 0.25 cm<sup>2</sup> area  
132 devices.

133 A second window sequence, grown at the University of Toledo, began with 3.2 mm thick TEC-  
134 15M commercial substrates, which consist of soda lime glass coated with SiO<sub>2</sub> to prevent sodium  
135 migration, then FTO with 500nm thickness and undoped TO with 100nm thickness. CdS:O was  
136 deposited by sputtering to a thickness of 80 nm with 1% O<sub>2</sub> in Ar ambient at 10 mTorr  
137 deposition pressure at 270 °C. This CdS:O<sup>1</sup> window layer was followed by CdTe grown by CSS  
138 at 660 °C, 50 Torr He ambient. A CdCl<sub>2</sub> activation anneal was performed at 400 °C in dry air,  
139 followed by rinsing in methanol and drying with N<sub>2</sub> gas to remove extra CdCl<sub>2</sub> from the surface.  
140 Cu doping was achieved by the evaporation of ~ 3 nm of Cu and 40 nm of Au, forming 0.09 cm<sup>2</sup>  
141 area devices, followed by a 30 min anneal at 200 °C.

142 A third window sequence was grown at the University of Toledo on 3.2 mm thick TEC-15M  
143 substrates. MgZnO (MZO) was deposited by sputtering without heating at 6 mTorr pressure.

144 CdTe on this layer was grown by CSS at 560 °C. A CdCl<sub>2</sub> activation anneal was performed at  
145 400 °C in dry air, with the exception of a final MgZnO device where it took place at 420 °C in an  
146 O-free ambient (He gas). The CdCl<sub>2</sub> activation step was followed by rinsing in methanol and  
147 drying with N<sub>2</sub> gas to remove extra CdCl<sub>2</sub> from the surface. Back contact Cu doping was done by  
148 submerging in a dilute solution of CuCl<sub>2</sub> and DI water for 2 min followed by rinsing in DI water  
149 and drying with N<sub>2</sub>, followed by a 225 °C, 30 min anneal. Finally, a 40 nm thick Au layer was  
150 deposited by thermal evaporation, forming 0.09 cm<sup>2</sup> area devices.

151 To measure power conversion efficiency (PCE) at room temperature, a class A solar simulator  
152 lamp was used. To measure temperature- and excitation-dependent open-circuit voltage,  
153 illumination was provided by a spectrally uniform laser-driven light source filtered from 400 to  
154 850 nm, focused with achromatic lenses, controlled by neutral density filters, and measured with  
155 a power meter. Knowing the spectra for the power meter response, the source, and the filters  
156 allows us to convert measured power meter current to photons cm<sup>-2</sup> s<sup>-1</sup>. Since AM1.5  
157 illumination gives a flux of 1.7×10<sup>17</sup> photons cm<sup>-2</sup> s<sup>-1</sup>, with energy greater than the 1.5 eV band  
158 gap of CdTe, that flux was considered 1 sun equivalent. The current-voltage-temperature-  
159 intensity (JVTI) measurements were performed with this illumination inside of a helium closed-  
160 cycle cryogenic system at Texas State University using a Keysight B2912A source measure unit.

161 AC measurements were made with a Keysight E4990A impedance analyzer. For C-V, DC bias  
162 was varied from -1.0 to 0.7 V. For AS, the frequency sweep was additionally varied from 1 kHz  
163 to 1 MHz and the AC modulation amplitude was 35 mV<sub>rms</sub>.

164 To measure the temperature- and excitation-dependent PL-I, devices were illuminated with a 660  
165 nm diode laser focused by a 6.5× objective lens into a microscopy cryostat. The spot diameter  
166 was found to be 120 μm using the knife edge method on a cleaved wafer. (Passlack et al., 1998)  
167 The laser power, controlled by neutral density filters, was measured with a NIST-traceable  
168 power meter to obtain the intensity.

169 The superstrate solar cell devices were illuminated through the glass, which had a thickness of  $d$   
170 = 2.3 or 3.2 mm. Therefore, after the cleaved wafer was removed, the focus point was lowered to  
171 the floor of the stage where the active device would rest, then also raised by  $(1/1 - 1/n_g)d$  to  
172 account for the altered focus point of the laser light, where  $n_g = 1.5$  is the index of refraction of  
173 the glass.

174 The resulting PL was collected through the same objective and passed through filters to remove  
175 the laser light. The PL intensity was recorded by a photomultiplier (PMT) attached to a lock-in  
176 amplifier with the laser chopped at 400 Hz. The laser intensity could be changed by a series of  
177 calibrated neutral density filters. To relate the number of photons to a raw detector signal, we  
178 measured the signal from an excitation laser spot on a Spectralon reflectance standard. (Swartz et  
179 al., 2019)

180 Studies were conducted and analyzed varying the temperature from 200 to 350 K, since the  
181 properties below 200 K can be dominated by more detailed effects such as carrier freeze-out,  
182 band gap temperature dependence, and inhomogeneous barrier heights. (Fiat et al., 2012)  $V_{oc}$   
183 was analyzed up to 350 K to ensure resolution of its temperature dependence near room

184 temperature. (Li et al., 2014) The excitation range for PL-I was chosen to be high enough for all  
185 samples to have a strong signal-to-noise ratio and yet low enough for laser spot heating effects to  
186 be minor. (Sohal et al., 2018)

### 187 3. Analysis

188 The measurement of JVTI allowed the determination of  $\Phi_b$  through the rollover effect.  
189 (Koishiyev et al., 2008) The measurements of temperature and intensity dependent  $V_{OC}$  and PL-I  
190 allowed the extraction of a number of physical parameters: the conduction band offset  $\Delta E_C$ , the  
191 SCLC shunt constant  $K = G_{SH}/V$ , and the effective capture coefficient for recombination  
192 centers, both within the absorber  $c_a = N_{ta}\sigma_a v_{th}$  and at the absorber-buffer interface  $c_s =$   
193  $N_{ts}\sigma_s v_{th}$ , where  $N_{ta}$  is the density of recombination centers,  $N_{ts}$  is the sheet density of  
194 recombination centers at the interface,  $\sigma$  is the respective capture cross section, and  $v_{th}$  is the  
195 carrier thermal velocity.  $c_a$  is also the reciprocal of the minimum lifetime for a carrier type  
196 which could be caused by the absorber's recombination center, and  $c_s$  is also the maximum  
197 recombination velocity which could be caused by the interface recombination center.

198 The mobilities, effective masses, and permittivity  $\epsilon$  were taken from the commonly used  
199 baseline. (Gloeckler et al., 2003) The absorber doping density was  $p = 1 \times 10^{14} \text{ cm}^{-3}$  from C-V  
200 measurements. Within the heavily doped  $\text{SnO}_2:\text{F}$  front contact, the  $E_F$  is 3.8 eV above its valence  
201 band. (Helander et al., 2011a) Given a 2.7 eV valence band offset between CdTe and  $\text{SnO}_2$ ,  
202 (Klein, 2015) the front contact barrier height ( $\Phi_f$ ) was therefore taken as 1.1 eV.

203 Since injection-dependent measurements are being considered, we cannot assume low injection  
204 or a constant minority carrier lifetime, particularly with such low doping. We will however make  
205 the common simplifying assumptions that dominant recombination states must be within the  
206 mid-gap energy range and that the capture cross sections for electrons and holes are equal. (Böer,  
207 2013 ; Grover et al., 2013) In this case the recombination rate at a given location, where the  
208 electron concentration is  $n$  and the hole concentration is  $p$ , becomes  $R = c_{a,s} np/(n + p)$ . Each  
209 parameter set yielded the quantities  $V_{OC}$  and  $\Delta E_F$  through a numerical model solving the  
210 continuity and Poisson's equations. (Seidman and Choo, 1972) The parameter set was adjusted  
211 to find the minimum square difference fit to the temperature- and excitation-dependent  $V_{OC}$  and  
212 PL-I data simultaneously, using a differential evolution algorithm. (Storn and Price, 1997)

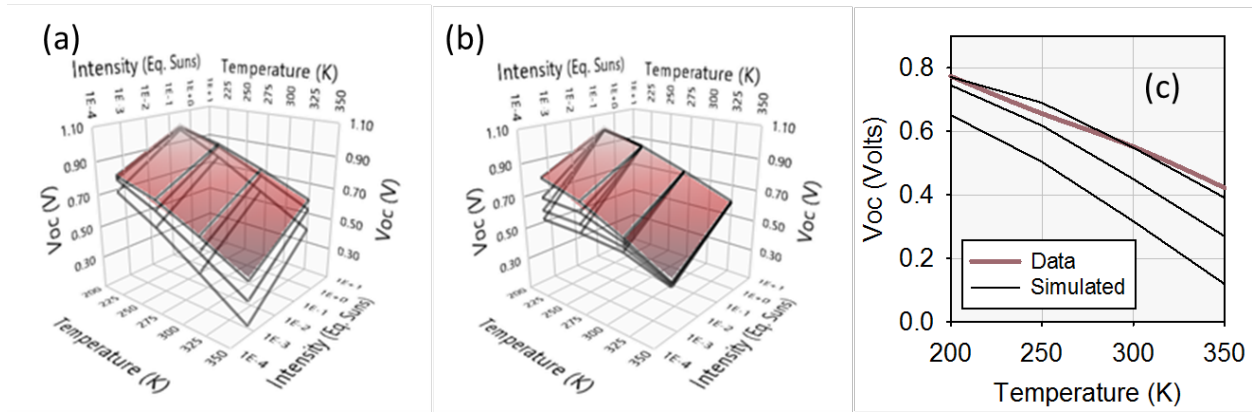
### 213 4. Results

214 Examples of the effect each experimental variable has on  $V_{OC}$  are shown in Fig. 2. The data are  
215 from what will be called the Control sample, listed first in Table I. The  $V_{OC}$  is typically greatest  
216 at low temperatures and high intensities where it is limited by the difference in the built-in  
217 voltages of the front and back junctions. (Halverson et al., 2013; Ott et al., 2015) In Fig. 2 (a),  
218 the simulated effect of increasing non-radiative recombination in the absorber material ( $c_a$ ) is  
219 shown, illustrating the uncertainty in the  $c_a$  parameter as fit to the measured voltages. The  
220 increasing slope of open circuit voltage with temperature ( $dV_{OC}/dT$ ) is consistent with an  
221 increasing activation energy  $qE_a$ . The activation energy method of evaluating recombination  
222 associates a higher  $qE_a$  with more dominant bulk recombination, and so there is a qualitative

223 agreement with the method presented here. (Grover et al., 2013; Li et al., 2014) In Fig. 2 (b) an  
 224 increased shunt causes the low intensity  $V_{OC}$  to drop, though shunting is less important at high  
 225 intensity. (Proctor and Nguyen, 2015) Fig. 2 (c) replots the lowest intensity points in Fig. 2 (a) in  
 226 2D for clarity.

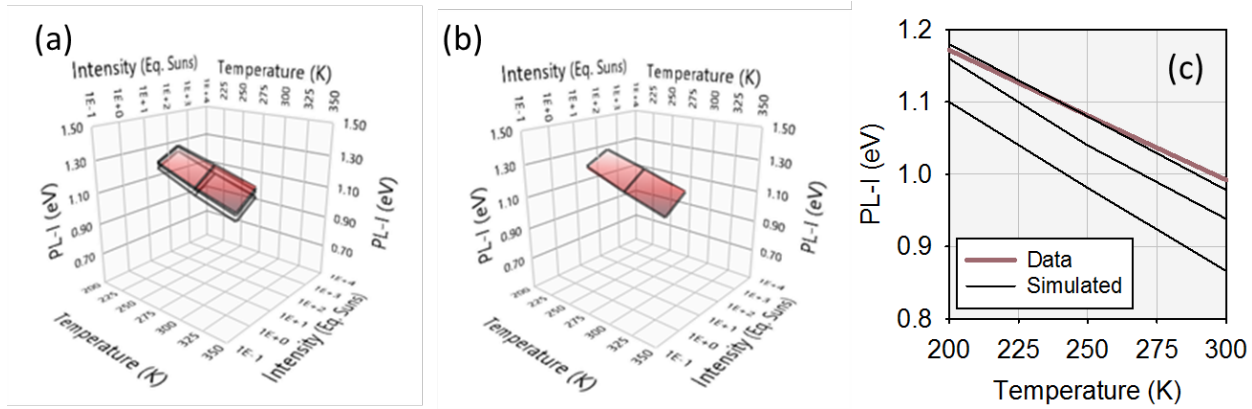
227 In Fig. 3 (a), also from the Control sample, non-radiative recombination is shown to cause a drop  
 228 in the PL intensity as well. Meanwhile, the PL-I corresponding to shunting in Fig. 3 (b) is  
 229 unaffected, since it is taken experimentally at a high intensity where shunting is less important.

230



231

232 Fig. 2.  $V_{OC}$  versus temperature and excitation intensity for the Control sample.  $V_{OC}$  data is shown as a  
 233 surface, and the grids are simulated  $V_{OC}$  values, with parameters varying as: (a)  $c_a$  is increased from 1.3  
 234 to 13 to  $130 \times 10^7 \text{ s}^{-1}$ , and as (b) the shunting constant  $K$  is increased from 4 to 6 to 8 to  $10 \times 10^5 (\Omega \text{ V}$   
 235  $\text{cm}^2)^{-1}$ . Each parameter increase (for both  $c_a$  and  $K$ ) corresponds to a grid with a lower  $V_{OC}$ . (c) Shows  
 236 for clarity a cross section view of the lowest intensity points in (a).



237

238 Fig. 3. PL-I converted to  $\Delta E_F$  versus temperature and excitation intensity for the Control sample.  
 239 Experimental PL-I data is drawn as a surface, and the grids are simulated PL-I values, with parameters  
 240 varying as: (a)  $c_a$  is increased from 1.3 to 13 to  $130 \times 10^7 \text{ s}^{-1}$ , and as (b) the shunting constant  $K$  is  
 241 increased from 4 to 6 to 8 to  $10 \times 10^5 (\Omega \text{ V cm}^2)^{-1}$ . Each parameter increase (for both  $c_a$  and  $K$ )  
 242 corresponds to a grid with a lower PL-I. (c) Shows a cross section view of the lowest intensity points in  
 243 (a).

244 In addition to recombination within the absorber, interfacial recombination may be significant,  
245 and it is known to be compounded by a negative or cliff-like  $\Delta E_C$ . This is because such an offset  
246 can position a high  $n$ -type concentration in the buffer layer in close proximity to a high  $p$ -type  
247 concentration at the front edge of the absorber. (Song et al., 2016) Additionally,  $\Delta E_C$  can directly  
248 affect the electrical properties, even without considering interfacial recombination. (Sozzi et al.,  
249 2014)

250 For the Control sample, introducing a negative or cliff-like  $\Delta E_C$  had a weak effect on  $V_{OC}$ . This  
251 is because the interfacial recombination coefficient  $c_s$  turned out to be fairly small. For  
252 illustration purposes, the result of a -0.1 eV cliff-like step in  $\Delta E_C$  is shown in Fig. 4 (a) with an  
253 inflated  $c_s$  (essentially an infinite surface recombination velocity at the CdTe-window interface)  
254 to make the effects of cliff-like offset more visible. In this case, the slope of  $V_{OC}$  with  
255 temperature remains gentle with increasing interfacial recombination, in contrast to the case of  
256 increasing bulk recombination seen in Fig. 2 (a). This is again consistent with the method of  
257 evaluating recombination mechanisms by slopes, which associates a high intercept of the room  
258 temperature  $V_{OC}$  slope, in the zero-temperature limit, with dominant bulk recombination.  
259 (Grover et al., 2013; Li et al., 2014)

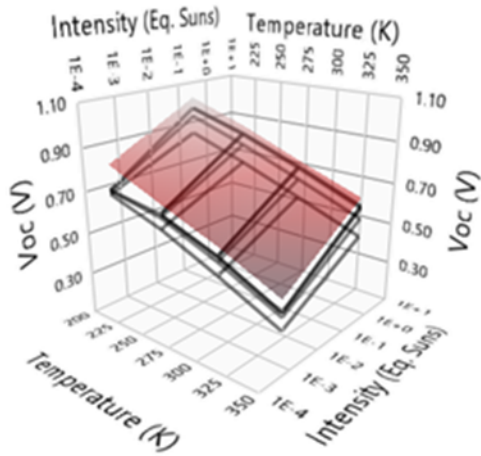
260 A positive or spike-like  $\Delta E_C$  results in an anomalous temperature peak of the  $V_{OC}$ , as in Fig. 4  
261 (b). This spike-related maximum in the  $V_{OC}$  (Schubbert et al., 2015) is more pronounced at high  
262 illumination, appearing between 250 and 300 K. The maximum can interfere with the standard  
263 method of probing recombination by finding  $qE_a$  from room temperature  $V_{OC}$ . Here, it is being  
264 used to evaluate absorber-buffer band offsets by fitting  $\Delta E_C$  to the  $V_{OC}$  data.

265 Note that some of these quantities have overlapping effects on  $V_{OC}$ ; for example the increased  
266 interfacial recombination shown in Fig. 4 (a) is most effective at suppressing the low  
267 temperature, low intensity  $V_{OC}$ . This is similar to the primary effect of shunt resistance shown in  
268 Fig. 2 (b). Therefore these two parameters can become difficult to resolve, particularly when  
269 other effects are present.

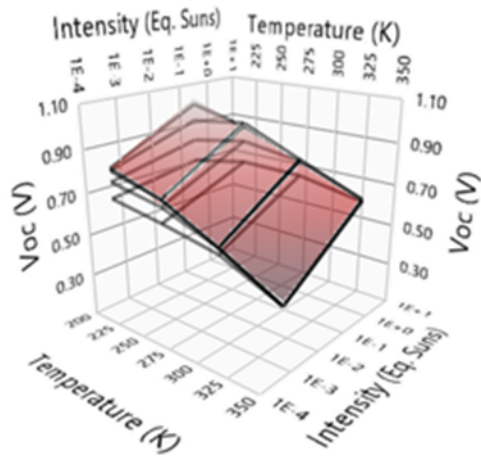
270 To remove ambiguity, the analysis of PL-I-T is helpful. Comparing Fig. 5 (a) to Fig. 3 (b), we  
271 see that the interfacial recombination has a deleterious effect on PL intensity while shunting has  
272 no effect. Thus, requiring agreement of the model outputs to both  $V_{OC}$  and PL-I data  
273 distinguishes these cases. In general,  $V_{OC}$  is controlled by both the rate of recombination and by  
274 band offsets, but the intensity of PL tends to be sensitive to recombination, not band offsets.  
275 (López Salas et al., 2017)

276

(a)



(b)

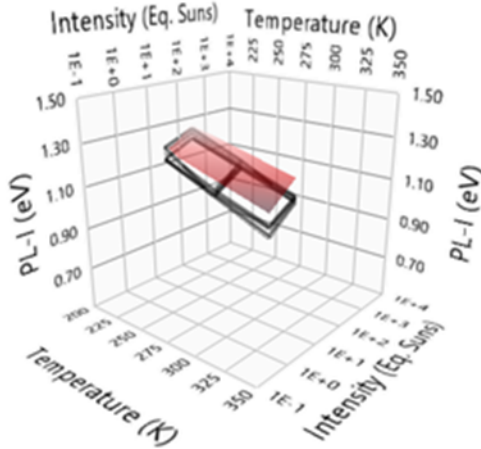


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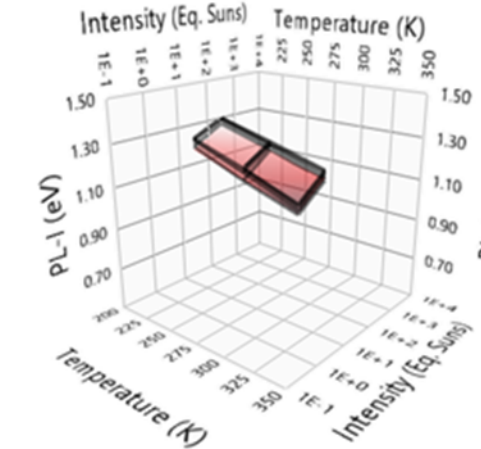
278 Fig. 4.  $V_{OC}$  versus temperature and excitation intensity for the Control sample.  $V_{OC}$  data is drawn as a  
279 surface, and the grids are simulated  $V_{OC}$  values, with parameters varying as: (a)  $\Delta E_C$  is changed from 0 to -0.1 to -0.2 to -0.3 eV, making it more cliff-like. Also,  $c_s$  was inflated by a factor of 10,000x in these  
280 simulations, which is essentially setting an infinite recombination velocity at the interface. (b)  $\Delta E_C$  is  
281 changed from 0 to +0.1 to +0.2 to +0.3 eV, making it more spike-like. Each parameter step (for both  $c_s$   
282 and  $\Delta E_C$ ) corresponds to a grid with a lower  $V_{OC}$  .  
283

284

(a)



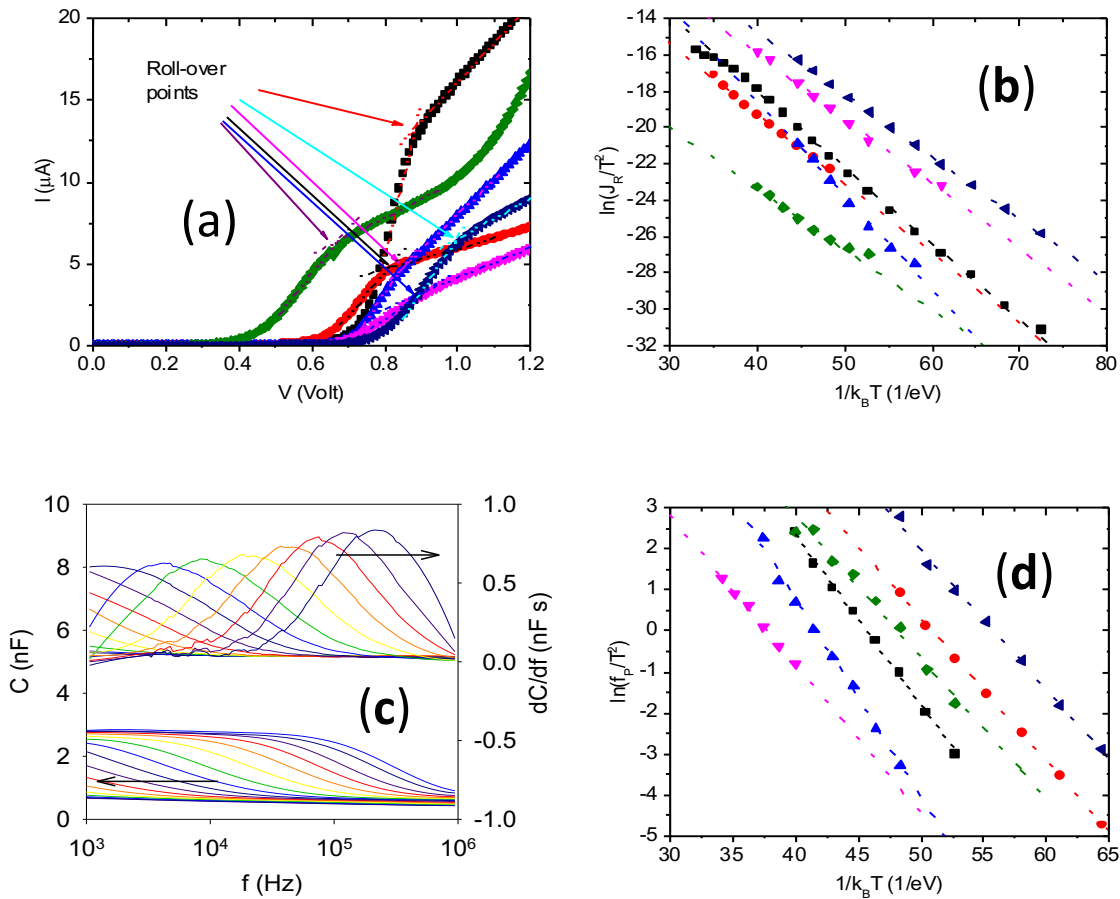
(b)



285

286 Fig. 5. PL-I versus temperature and excitation intensity. Experimental PL-I data is drawn as a surface, and  
287 the grids are simulated PL-I values, with parameters varying as: (a)  $\Delta E_C$  is changed from 0 to -0.1 to -0.2  
288 to -0.3 eV, making it more cliff-like. Also,  $c_s$  was inflated by a factor of 10,000x in these  
289 simulations, which is essentially setting an infinite recombination velocity at the interface. (b)  $\Delta E_C$  is  
290 changed from 0 to +0.1 to +0.2 to +0.3 eV, making it more spike-like. Each parameter step (for both  $c_s$  and  $\Delta E_C$ )  
291 corresponds to a grid with a lower PL-I.

292



293

294

295 Fig. 6. Comparison of JV-based and capacitance-based methods for measuring back contact offset.  
 296 Results from the CdS:O<sup>6</sup> samples in Table 1 are shown for illustration. (a) The current of the roll-over  
 297 point of a JV curve, here shown at 190K, was found as a function of temperature and placed on (b) an  
 298 Arrhenius plot whose slope provides the barrier height energy. (c) The frequency of the inflection point of  
 299 an admittance curve was found as a function of temperature and placed on (d) an Arrhenius plot whose  
 300 slope provides the AS value of barrier height energy.

301 Results used to extract  $\Phi_b$  are shown in Fig. 6. In all cases, the  $\Phi_b$  from the JVT rollover effect  
 302 was 1.1-1.3 times the value from AS, as expected from previous reports. (Li et al., 2010)

303 The resulting fitted parameters can be seen in Table I, along with  $\Phi_b$  and the PCE under AM1.5  
 304 solar illumination. The first device on the list is considered the Control sample. A dozen devices  
 305 were made with the blade-coated CdTe nanoparticle (NP) layer and a dozen without. NP was  
 306 found to assist in reproducibility, with the best non-NP devices equivalent to the Control device.

307 We found that lowering the deposition oxygen ratio of CdS:O from 6% to 1% resulted in a more  
 308 cliff-like  $\Delta E_C$  ( $< 0$ ), as might be expected from a decrease in band gap. (Kephart et al., 2015)  
 309 Although, other studies involving a more drastic lowering of oxygen content have suggested that  
 310 it could instead increase the band gap by decreasing S-Te diffusion. (Meysing et al., 2016) The

311 complete substitution of the CdS:O (and undoped SnO<sub>2</sub>) buffer with a MgZnO buffer causes a  
 312 strongly spike-like offset ( $\Delta E_C > 0$ ). This is clear from Fig. 7, which develops the same  
 313 temperature peak seen in Fig. 4 (b).

314 The bulk recombination coefficient  $c_a$  varied from  $1\text{-}5 \times 10^7 \text{ s}^{-1}$ , with the exception of the final  
 315 MgZnO device where the CdCl<sub>2</sub> activation step took place in an O-free ambient (He gas). The  
 316 PCE increased from 14 to 15%, and this was attributed to a reduced  $c_a = 5 \times 10^6 \text{ s}^{-1}$ .

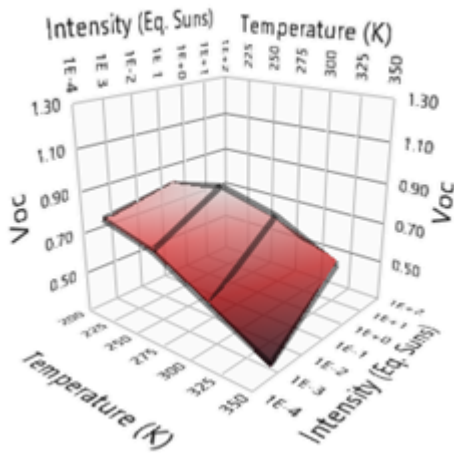
317 The interfacial recombination coefficient  $c_s$  varied from  $10^4$  to  $10^6 \text{ cm s}^{-1}$ . Measurements were  
 318 sensitive to the value of  $c_s$  primarily for the two CdS:O<sup>1</sup> samples ( $3 \times 10^5 \text{ cm s}^{-1}$ ) as these had a  
 319 cliff-like  $\Delta E_C$ , making the interface a dominant source of recombination. Thus, this analysis  
 320 allows the detection of the band alignment as the reason for MZO's success as a front interface  
 321 contact. In comparison to CdS:O the surface recombination velocity is unimproved or even  
 322 inferior.

323

Device structure starting with glass/SnO <sub>2</sub> :F/	PCE	$\Delta E_C$	$c_a$	$c_s$	$\Phi_b$	$K$	dJ/dV
	%	eV	$10^7$ $\text{s}^{-1}$	$10^5$ $\text{cm s}^{-1}$	eV	$10^{-5}$ $(\Omega \text{ V cm}^2)^{-1}$	$10^{-5}$ $(\Omega \text{ cm}^2)^{-1}$
SnO <sub>2</sub> /CdS:O <sup>6</sup> /CdTe/NP/Au	16	0.01	1.3	0.3	0.38	4.3	29
SnO <sub>2</sub> /CdS:O <sup>6</sup> /CdTe/NP/ITO/Au	14.7	-0.01	1.3	0.5	0.45	1.0	38
SnO <sub>2</sub> /CdS:O <sup>6</sup> /CdTe/NP/Se/Au	15.6	0.04	3.4	0.3	0.36	6.0	86
SnO <sub>2</sub> /CdS:O <sup>6</sup> /CdTe/NP/SnTe/Au	13.5	0.05	1.5	0.1	0.59	0.8	21
SnO <sub>2</sub> /CdS:O <sup>6</sup> /CdTe/NP/Spiro/Au	10.9	0.07	5.7	1.0	0.4	5.3	130
SnO <sub>2</sub> /CdS:O <sup>6</sup> /CdTe/NP/EH44/Au	15	0.01	2.0	0.2	0.38	5.5	100
SnO <sub>2</sub> /CdS:O <sup>1</sup> /CdTe/Au	13	-0.16	4.7	2.9	0.45	4.1	74
SnO <sub>2</sub> /CdS:O <sup>1</sup> /CdTe/HI etch/Au	15	-0.18	2.4	3.8	0.35	4.1	46
MgZnO/CdTe/Au	14	0.20	2.5	11	0.38	0.1	100
MgZnO/CdTe/O-free activ./Au	15	0.22	0.5	8.0	0.38	0.1	110

324

325 Table I. Fitting results, with power conversion efficiency, rollover-based barrier height, and slope of the  
 326 JV curve at the short circuit point.



327

328 Fig. 7.  $V_{oc}$  data (surface) and simulated (mesh) for the MgZnO/CdTe/oxygen-free activated/Au device,  
 329 illustrating the existence of a spike-like absorber-buffer conduction band offset.

330 None of the back-contact interlayers was found to make a major reduction of  $\Phi_b$ , though a  
 331 hydroiodic (HI) acid etch had reduced the barrier by 0.1 eV below an untreated back surface.  
 332 What variation in  $\Phi_b$  the interlayers caused did not correlate to changes in PCE. In the case of a  
 333 Se interlayer, for example, the barrier was slightly decreased while the efficiency fell. One  
 334 interpretation relies on problems in specifying the measured  $\Phi_b$  due to inhomogeneous back  
 335 contact barrier. That is, certain regions of each back contact might have a lower or higher  $\Phi_b$  due  
 336 to local variations in composition. The effective barrier of  $\Phi_b^*$  would then be dominated by the  
 337 lower barrier regions, leading to a temperature-dependent value of  $\Phi_b^* \approx \Phi_b - s^2/(2 k_B T)$  where  $s$   
 338 is the standard deviation of the barrier height. (Tung, 1991; Werner and Gütler, 1991) The same  
 339 interpretation was previously suggested when it was found that the amount of  $p$ -type doping  
 340 from Cu incorporation was unable to explain the beneficial effect of Cu on the back  
 341 surface. (Klein, 2015; Perrenoud et al., 2013)

342 However, the rollover measurements were made in the range 180 K to 280 K. Thus, for the  
 343 measured rollover  $\Phi_b$  to differ appreciably from the room temperature  $\Phi_b$ , the standard  
 344 deviation  $s$  would need to be very large, yet there is no evidence of a strong quadratic  
 345 dependence of rollover on reciprocal temperature, nor do previous estimates show a drastic  
 346 change in  $\Phi_b$  at such a temperature range in CdTe devices. (Fiat et al., 2012)

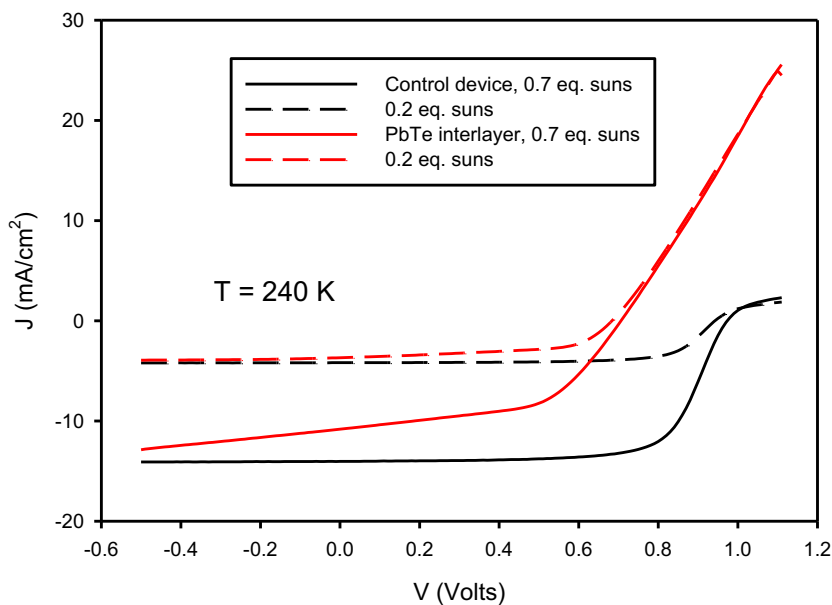
347 Another cause of PCE variation would be shunting at the front junction. One standard method of  
 348 estimating shunt conductance is from the derivative  $dJ/dV$  at the short circuit (zero voltage)  
 349 point. (Bosio et al., 2018; Ruschel et al., 2016) However, the apparent shunt found from a JV  
 350 curve is distorted by voltage-dependent collection current and also by the band offsets in  
 351 heterojunction solar cells. Even when ignoring the effects of  $\Phi_b$ , this derivative can have an  
 352 extremely strong dependence on the value of the front band offset  $\Delta E_C$ . (Li et al., 2018; Sun et  
 353 al., 2016) The  $V_{oc}$ -T-I and PL-I-T technique allows an estimation of physical shunting  
 354 conductance, rather than the lumped parameter of  $dJ/dV$ . Since a device's normal operating

355 range is  $\sim 0.9$  Volts, the SCLC shunt conductance constant  $K$  in  $(\Omega \text{ V cm}^2)^{-1}$  may be compared  
 356 directly to the slope in  $(\Omega \text{ cm}^2)^{-1}$  shown Table I, and the shunting is found to be an order of  
 357 magnitude weaker than the slope method would suggest. Most strikingly, the MZO windows  
 358 yield the worst apparent shunt ( $dJ/dV$ ) yet the best shunt from the fitted VOC-T-I & PL-I-T  
 359 data.

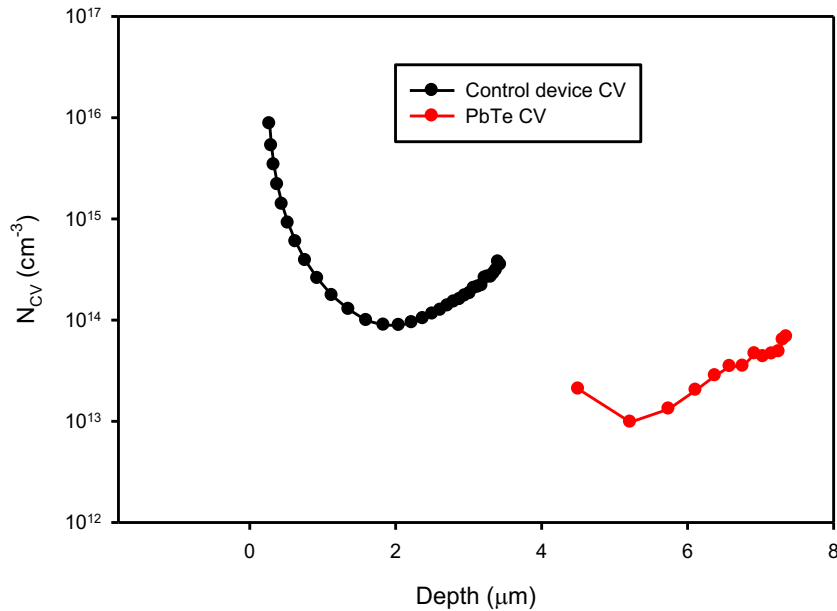
360 That the slope method gives an inaccurate value is clear from the low intensity  $V_{OC}$ , where the  
 361 device is simply not being provided with enough photocurrent to account for an Ohmic shunt of  
 362 conductance  $dJ/dV$ . This suggests that the many reported estimations of shunting by the  
 363 standard slope method largely do not represent a physically meaningful shunting path in  
 364 heterojunction solar cells. Shunt resistances estimated by the slope method must not be taken as  
 365 representing a physical shunting connection unless they are far below  $1 \text{ k}\Omega \text{ cm}^2$ .

366 One result which does not appear in the Table is that of the PbTe:Tl interlayered device. This  
 367 device was unusual because there is no rollover, and hence no evidence of  $\Phi_b$  in the JV curve  
 368 shown in Fig. 8. We include the Control device, for direct comparison, which shows the rollover  
 369 near 1 V. Moreover, the PbTe:Tl device's C-V results, shown in Fig. 9 as a Mott plot,  $N_{CV}$   
 370  $= (2/q\epsilon) / [d(C^2)/dV]$ , do not show the U-shape expected for structures with a back contact  
 371 barrier, (Li et al., 2012) as seen on the Control sample's C-V result which is representative of all  
 372 of the other devices.

373 It is possible that the lack of a U-shaped C-V result could be related to a Cu diffusion effect seen  
 374 in previously reported C-V results that were similar in appearance and depth. (Boucher et al.,  
 375 2014; Rimmaudo et al., 2017) But, in the present case, the Cu was already deposited and diffused  
 376 before the PbTe interlayer, and even the sample with a SnTe interlayer did not exhibit these  
 377 effects despite undergoing a close to identical process. The time-resolved photoluminescence  
 378 (TRPL) lifetime was the highest for the PbTe device as well. (Details to be published later by S.  
 379 Rab, *et. al.*) All of these suggest that PbTe:Tl is forming an excellent Ohmic contact.



381 Fig. 8. Comparison of typical JV curves the with those from the PbTe:Tl back contact interlayer device.  
382



383  
384 Fig. 9. Room temperature comparison of typical C-V effective doping concentration curves with those of  
385 the PbTe:Tl back contact interlayer device.

386 However, this device has the lowest efficiency of all (9%) with a  $V_{OC}$  that does not rise above  
387 700 mV. We believe that there is an additional presence of a strong photoconducting shunt,  
388 caused by the PbTe interlayer. The effect can be seen on the more strongly illuminated JV curves  
389 in Fig. 8. While the slope method is not normally quantitative, the overall linear form of the JV  
390 curve suggests a very high shunt of  $200 \Omega cm^2$ , but only when illuminated. It appears that the  
391 interface between PbTe and CdTe is undergoes complicated changes in band bending with light,  
392 which is not unexpected from previous studies of strong band-bending and persistent  
393 photoconductivity when these materials are grown together in single crystal form. (Swartz et al.,  
394 2016; Zhang et al., 2014)

## 395 5. Conclusions

396 In summary, the back-contact barrier and the front buffer conduction band offset present special  
397 challenges for heterojunction solar cells such as those based on CdTe. Not only do they impact  
398 cell performance, but methods for their characterization are still unsettled. Further, they  
399 compound the difficulty of characterizing more conventional obstacles such as recombination  
400 centers and shunting.  $V_{OC}$ -T-I allows a certain amount of insight, associating clear, measurable  
401 features with the desired offsets and shunts. When complemented with PL-I-T, signatures of  
402 band offsets which are otherwise difficult to distinguish from recombination effects become  
403 more resolvable. With numerical simulation, the recombination characteristics, offsets, and  
404 shunts can be obtained quantitatively.

405 ITO and SnTe:Tl interlayers were successful at reducing shunt, but the barrier height did not  
406 show the hoped-for reduction. The other interlayers attempted did not significantly reduce the  
407 shunt or barrier, though HI etching reduced the back-barrier height by 0.1 eV in CdS:O<sup>-</sup> samples  
408 suggesting that a direct reduction in  $\Phi_b$ , rather than a Cu diffusion reduction mechanism, is  
409 responsible for the improved performance of a Te-rich surface. Heavily Tl doped PbTe appeared  
410 to reduce or eliminate the barrier height, yet it was marred by strongly photoconducting shunt.  
411 This suggests a possibility that *p*-PbTe, in combination with another interlayer, may eliminate  
412 the shunt effect while lowering the barrier.

413 The doping of CdS with oxygen to widen the band gap appears to have effect of raising its  
414 conduction band with respect to CdTe, yielding a less cliff-like offset. The increasingly popular  
415 MgZnO (MZO) front buffer has a large spike-like offset which effectively reduces interfacial  
416 recombination without reducing recombination velocity, and tuning the Mg/Zn ratio to obtain a  
417 reduction in gap of 0.1 eV may prove beneficial.

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