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Direct evidence of causality between chemical purity and band-edge potential fluctuations in nanoparticle ink-based $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ solar cells

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Abstract

Kesterite solar cells based on chalcogenide $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) are a viable approach to thin film photovoltaics, utilising Earth-abundant, non-toxic elements. CZTSSe films produced from nanoparticle inks offer a cost-effective solution-based method of fabrication. However, improving efficiency in these devices has proved challenging, in part due to the presence of detrimental complex defects within the bulk of the CZTSSe absorber. In this study, the behaviour of nanoparticle-based CZTSSe absorbers and solar cells

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made from relatively low and high quality grade chemicals is investigated with a view to improving cost-effectiveness of the ink-based fabrication process. Photoluminescence (PL) spectroscopy revealed the presence of similar shallow acceptor plus shallow donor states in both low and high purity precursor absorbers. We demonstrate a relationship between the average depth of energy band-edge potential fluctuations and absorber quality where the higher grade chemical precursor-based absorber outperforms the lower purity version. In addition, the low purity precursor absorber had a higher total defect density resulting in a 10 meV increase in the average electrostatic potential fluctuations. Deep level transient spectroscopy (DLTS) in solar devices indicated the presence of detrimental deep defect states in both types of absorber. Notwithstanding the high purity precursor absorber with lower defect density, the power conversion efficiencies of both types of CZTSSe solar cells were similar ($\sim 5\%$), implying an issue other than defects in the absorber bulk inhibits device performance as evidenced by quantum efficiency analysis and current-voltage measurements.

Keywords: $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe), Thin film solar cells, Photoluminescence (PL), Deep Level Transient Spectroscopy (DLTS), Defects

1. Introduction

In recent years, the impetus to fabricate low-cost thin-film photovoltaics from naturally abundant, non-toxic elements has focused research interest on copper-based quaternary chalcogenide kesterites, such as $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) and $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})$ (CZTSSe) (Kumar et al., 2015; Liu et al., 2016). These materials offer a more sustainable alternative to the current commercially-available thin-film solar cell absorbers CdTe and $\text{CuIn}_y\text{Ga}_{1-y}\text{Se}_2$ (CIGS). They are direct bandgap semiconductors with high absorption coefficients in the visible range ($\alpha > 10^4 \text{ cm}^{-1}$) and CZTSSe has the additional benefit of a tunable bandgap dependent on the S/Se ratio (1.0 eV, $x=1$ to 1.5 eV, $x=0$) (He et al., 2012; Siebentritt and Schorr, 2012). Despite a single junction CZTSSe solar cell having a theoretical Shockley-Queisser maximum efficiency limit of 32.2%, polycrystalline CZTSSe devices using a solution approach with reactive hydrazine as the solvent, have only attained a power conversion efficiency (PCE) of 12.6% (Wang et al., 2013). A less hazardous strategem based on CZTS nanoparticle inks annealed in the presence of Se has achieved device efficiency approaching 10% (Hages et al., 2016). Polycrystalline thin-film solar cells are inherently susceptible to the formation of mid-gap defects, which act as electron traps within the bulk of the absorber, and defects at the buffer-absorber interface which inhibit charge transport. Due to the complexity of the pentanary kesterite crystal structure, a variety of intrinsic lattice defects can form which influence the optical and electronic properties of the CZTSSe absorber (Chen et al., 2013). Density functional theory and first principle calculations have been employed to identify a number of intrinsic defects in bulk CZTSSe,

26 which range from charged point defects such as elemental vacancies, anti-
 27 sites and interstitials to neutral defect complexes. Some defects, like shallow
 28 acceptors V_{Cu}^- and Cu_{Zn}^- , are beneficial and are responsible for the p -type
 29 conductivity of the absorber. Conversely, deleterious defects such as deep
 30 donor antisites Sn_{Cu}^{3+} and Sn_{Zn}^{2+} , form mid-gap traps which act as effective
 31 electron-hole recombination centres.

32 Band-tails may also be present within the kesterite bulk which have
 33 been suggested as contributing to Shockley-Read-Hall (SRH) recombination
 34 (Mendis et al., 2013). Two rudimentary processes are understood to cause
 35 band-tailing: i) an elevated concentration of highly-compensated charged de-
 36 fects which result in an electrostatic potential fluctuation of the valence and
 37 conduction bands (VB and CB, respectively) and ii) changes in compositional
 38 and/or crystalline homogeneity of the absorber, which cause the VB and CB
 39 edges to waver, inducing bandgap fluctuations (Gokmen et al., 2013).

40 In this article we present complementary photoluminescence (PL) and
 41 deep level transient spectroscopy (DLTS) studies of nanoparticle-based CZTSSe
 42 thin films and devices fabricated from low and high purity precursor chem-
 43 icals (subsequently referred to as film LP and HP, respectively). The evo-
 44 lution of PL spectra over a range of cryogenic temperatures can be used to
 45 elucidate details of shallow defects within both types of CZTSSe absorber,
 46 whereas DLTS is used to probe deeper, mid-gap states. Employing both
 47 techniques in conjunction provides comprehensive quantitative information
 48 on root-mean-square potential fluctuation depths of band edges (γ), defect
 49 activation energies (E_A), defect concentrations (N_t) and defect capture cross-
 50 sections (σ_t) of both types of absorber, which is correlated to the structural

51 quality of the material.

52 **2. Experimental details**

53 Low and high quality grade metallic sources and solvent oleylamine were
54 used for CZTS nanoparticle synthesis to investigate their influence on the
55 absorbers' behaviour and subsequent solar cells' performance. Low and high
56 purity nanoparticle inks were prepared by varying the metallic sources and
57 solvent as listed in Supp. Table S1. CZTS nanoparticles were fabricated
58 using a hot-injection method where a sulphur-OLA solution was injected
59 into a hot metallic precursors-OLA solution (Qu et al., 2014). The resulting
60 nanoparticle inks were deposited on molybdenum substrates via spin coating
61 to form the CZTS precursor thin film with a thickness around $1\text{ }\mu\text{m}$ (Qu
62 et al., 2016a). In order to produce efficient absorbing layers, CZTS precursor
63 thin films were then selenised to introduce grain growth, resulting in CZTSSe
64 absorbers with film thickness $\sim 1\text{ }\mu\text{m}$. This process has been described in
65 greater detail in our previous work (Qu et al., 2016b). The crystal structure
66 of both types of film is kesterite in nature determined from X-ray diffraction
67 (XRD). The solar cells were subsequently integrated with a configuration of
68 Mo/CZTSSe/CdS/*i*-ZnO/ITO/Ni-Al. The CdS buffer layer ($\sim 55\text{ nm}$) was
69 deposited using a chemical bath process. *i*-ZnO ($\sim 35\text{ nm}$) and ITO (indium
70 tin oxide, $\sim 200\text{ nm}$) layers were then deposited by magnetron sputtering to
71 act as the transparent oxide layers. Front contact grids which are composed
72 of Ni ($\sim 50\text{ nm}$) and Al ($\sim 1\text{ }\mu\text{m}$) layers were deposited through a shadow
73 mask by electron beam evaporation. Finally, nine $\sim 0.16\text{ cm}^2$ cells were de-
74 fined by mechanical scribing on each substrate (Campbell et al., 2018). PL

75 spectra were measured using a Horiba Jobin Yvon fully automated spectrom-
 76 eter fitted with an InGaAs PMT detector cooled to -30°C to reduce noise.
 77 A 532 nm continuous wave diode-pumped solid state (CW-DPSS) laser was
 78 used as an excitation source. All PL measurements were performed on se-
 79 lenised absorber layers deposited on Mo coated glass. PL measurements at
 80 varying temperatures were performed by placing the sample in a Janis SHI-
 81 4-2 closed cycle refrigeration cryostat using compressed He gas coupled with
 82 a Lakeshore Model 335 temperature controller. Time-resolved photolumines-
 83 cence (TRPL) experiments were performed at 6 K using 800 nm 1.5 ps laser
 84 pulses generated by a tunable mode-locked Ti:Sa laser with a repetition rate
 85 of 80 MHz. The laser beam is focused onto the sample on a $1/e^2$ diameter
 86 spot of $\sim 100\ \mu\text{m}$ and an average power of 20 mW. The PL signal is dispersed
 87 by a f -6.5 spectrometer and detected by a synchro-scan Hamamatsu streak
 88 camera with an overall time resolution of 15 ps. Deep level transient spec-
 89 troscopy (DLTS) analysis was performed using a PhysTech FT1230 HERA
 90 DLTS system. Emission capacitance transients were recorded using reverse
 91 and pulse biases of 5 V and 0 V respectively with a pulse duration of 10 ms.
 92 Three transient period widths were recorded 19.2 ms, 192 ms and 480 ms
 93 with time constants for the transients being determined via Fourier trans-
 94 form analysis (DLFTS) (Weiss and Kassing, 1988). Quality of the diodes
 95 was assessed prior to DLTS measurements using capacitance-voltage (C - V)
 96 and current density-voltage (J - V) analysis with C - V measurements being
 97 used to calculate shallow acceptor concentration N_A . A temperature range
 98 of 80-300 K was used however samples showed significant variation in reverse
 99 capacitance values above 220 K hence only data < 220 K was analyzed. Solar

100 cell J - V parameters were measured using an Abet Technologies solar simu-
 101 lator at 1-sun (100 mW/cm^2) illumination equivalent to air mass 1.5 global
 102 spectrum with the light power density calibrated using a Si reference cell.
 103 External quantum efficiency measurements were performed using a Bentham
 104 spectral response system (calibrated using a Si-InGaAs reference cell) under
 105 unbiased conditions. C-V parameters were evaluated using an Agilent E4980a
 106 LCR meter and a Shimadzu UV-2600 UV-Vis spectrophotometer was used to
 107 obtain transmission/reflection data for CZTSSe films on soda-lime glass
 108 (SLG).

109 **3. Results and discussion**

110 CZTSSe is considered a highly-doped and highly-compensated semicon-
 111 ductor due to a high defect density such that the average distance s between
 112 defects is less than the defect Bohr radius (Shklovskij and Efros, 1984). The
 113 defects tend to be charged and a random distribution of these unscreened
 114 charged defects results in electrostatic potential fluctuations inducing band
 115 tails (Bauknecht et al., 2001). The presence of both donor and acceptor
 116 defects within the material bulk infers that the material is also highly-
 117 compensated. Electrostatic potential fluctuations manifest as parallel shifts
 118 in valence and conduction band (VB and CB) edges with constant bandgap
 119 energy E_g (Campbell et al., 2018). The consequential band tails with energy
 120 lower than E_g have an exponentially decaying density of states which pro-
 121 duce a broad asymmetric PL spectrum at room temperature (Levanyuk and
 122 Osipov, 1981). Similarly, bandgap fluctuations in the CZTSSe material may
 123 be induced by Cu-Zn disorder in the kesterite lattice structure (Schorr, 2011;

124 Choubrac et al., 2013), leading to the formation of non-stoichiometric defect
 125 complexes such as $[V_{Cu}^- + Zn_{Cu}^+]$ and $[Zn_{Sn}^{2-} + 2Zn_{Cu}^+]$ (Chen et al., 2013).
 126 Slow-cooling at a rate of 10 °C/hr after the high-temperature annealing stage
 127 of CZTSSe absorber fabrication has been shown to promote clusters of or-
 128 dered and disordered areas suggesting the random distribution of charged
 129 antisite defect Cu_{Zn}^- is reduced (Paris et al., 2014; Schwarz et al., 2013).
 130 Consequently, a reduction in local variations of Cu-Zn disorder produces
 131 clusters of lower and higher E_g phases which induces potential fluctuations
 132 in the VB and CB of the material.

133 A model describing the defect-related nature of absorption tails caused
 134 by electrostatic potential fluctuations has been proposed by Siebentritt et al.
 135 (Siebentritt et al., 2006). The low energy tail of PL band $I(E)$ is fitted to a
 136 Gaussian function,

$$I(E) \sim \exp\left(-\frac{(E - E_0)^2}{2\gamma^2}\right) \quad (1)$$

137 where E_0 is the average emission energy with respect to fluctuating potentials.
 138 The magnitude of γ is directly related to the total charged radiative and non-
 139 radiative defect density N_t (Dirnstorfer et al., 1998). Evaluating γ from PL
 140 emission spectra therefore allows the absorber total defect density N_t to be
 141 deduced.

142 Another generally accepted model to describe the behaviour of sub bandgap
 143 defects in CZTSSe is the quasi-donor/acceptor-pair (QDAP) model (Yu,
 144 1977; Schumacher et al., 2006) which is fundamentally linked to the elec-
 145 trostatic potential model. In this case, the distribution of radiative donor
 146 and acceptor states contributing to the potential fluctuation are governed by

the Coulombic interaction between the charged defect states. The spectral position of the PL band energy maximum E_{PL} is described by (Schumacher et al., 2006),

$$E_{PL} = E_g - (E_D + E_A) + \frac{e^2}{4\pi\epsilon_0\epsilon_r s} \quad (2)$$

where E_D and E_A are the donor and acceptor energy levels within the CB and VB edges, respectively, ϵ_0 is permittivity of vacuum, ϵ_r is relative permittivity (or dielectric constant) and s is the separation distance between donor and acceptor. The QDAP process is subject to caveats: (i) the spatial separation between charged donor and acceptor defects is large enough that the Coulombic interaction between them is negligible and, (ii) all QDAP states are fully occupied when the QDAP PL peak no longer blue-shifts with increasing excitation intensity, indicating maximum Coulombic attraction between defects (Gunawan et al., 2012). At the point of maximum Coulombic attraction (fully occupied QDAP defects), the blue-shift magnitude of QDAP PL peak ΔE is equivalent to the Coulomb potential energy at that point,

$$\Delta E = \frac{e^2}{4\pi\epsilon_0\epsilon_r s} \quad (3)$$

Thus, the average separation distance s between acceptor/donor can be derived from Eq.(3) and QDAP defect density N_D estimated by assuming a uniform distribution of defects within a spherical volume of radius r ,

$$r = s = \left(\frac{4\pi N_D}{3} \right)^{-\frac{1}{3}} \quad (4)$$

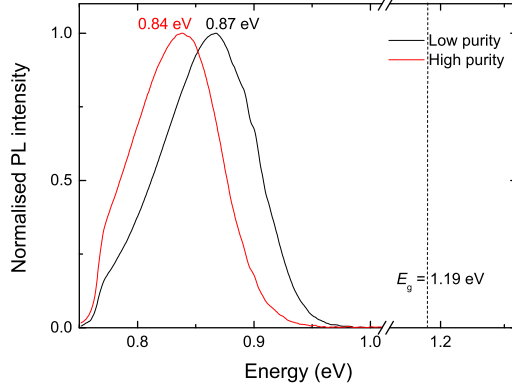


Figure 1: PL of sample LP and HP at 6 K with laser power below PL peak saturation intensity to avoid band-related recombination. The dashed line indicates room temperature bandgap energy E_g of both types of sample.

165 The normalised 6 K PL spectra of LP and HP films at excitation intensity
 166 just below E_{PL} peak saturation are illustrated in Fig. 1. The broad asym-
 167 metric shape of the PL bands for both absorbers show a gradual rise in PL
 168 intensity on the low energy side and sharper decline on the high energy side
 169 of the PL peak, indicating significant band-tailing in the materials. The PL
 170 peak maxima are located at 0.86 and 0.84 eV for LP and HP films respec-
 171 tively. The energy peaks are considerably red-shifted from the corresponding
 172 room temperature bandgap energy of 1.19 eV, determined from EQE data
 173 (discussed later in this section) for both types of absorber. Such a large
 174 red-shift could be explained by the presence of deep donor defect Sn_{Zn} with
 175 an energy level ~ 420 meV below conduction band minima (CBM) or deep
 176 acceptor states V_{Sn} or Cu_{Sn} with energy levels ~ 400 and 420 meV above
 177 valence band maxima (VBM), respectively (Chen et al., 2013). The full

width at half maximum (FWHM) of the PL spectra exhibit a slight decrease
from 96 meV for film LP to 92 meV for film HP, with maximum intensity of
the PL band of film HP half the intensity of film LP. The low temperature
excitation-dependent intensity of the PL spectra for both absorbers is shown
in Fig. 2a. The PL band intensity saturates at lower laser power for film HP
and a high energy shoulder at ~ 0.92 eV emerges upon increasing excitation
beyond the threshold intensity (see Supp. Fig. S1). Above the threshold,
the lower energy peak red-shifts as the high energy shoulder increases in in-
tensity. Gershon *et al.* observe similar behaviour in CZTS films and state
the high energy shoulder is due to a recombination process associated with
extended band states and only appears after all localised (QDAP) states are
fully saturated (Gershon *et al.*, 2013). This is further evidence QDAP ra-
diative recombination is dominant in the CZTSSe films studied here. The
appearance of a high energy shoulder was not observed in the PL bands for
film LP, indicating all QDAP states are not occupied. An empirical asym-
metric double sigmoidal function was used to fit the PL spectra in order
to evaluate the peak maxima at each excitation intensity (Krustok *et al.*,
1999; Yakushev *et al.*, 2017). Both films exhibit a substantial blue-shift of
PL peak maxima with increasing laser power until reaching saturation point
of PL emission. Fig. 2b shows the evolution of PL band peaks E_{PL} for
the CZTSSe samples over a laser intensity range up to the threshold value.
Changes in excitation intensity produce a shift in $E_{PL}(\beta)$ at a rate of β
equals 14 and 15 meV/decade and an energy blue-shift magnitude ΔE of 30
and 37 meV for HP and LP films, respectively. Oscillations in the PL bands
around 0.9 eV are associated with water vapour absorption of light.

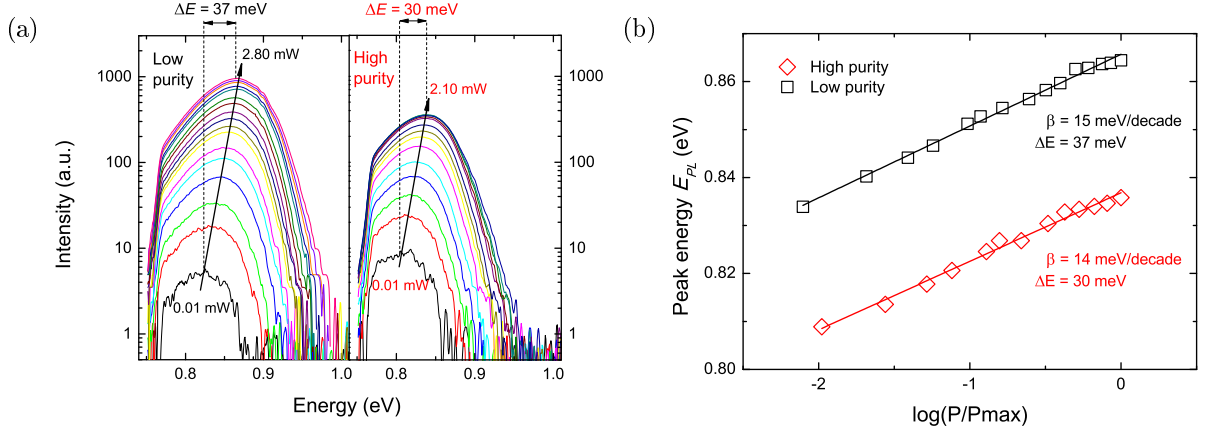


Figure 2: (a) Excitation-dependent PL spectra of sample LP and HP with laser power P up to saturation point of PL emissions together with respective ΔE blue-shift values in E_{PL} and (b) evolution of PL band maxima with increasing P of LP and HP films with associated shift rates β at 6 K.

203 Evidence of a significant red-shift in E_{PL} compared to E_g together with
 204 large ΔE plus β values for both LP and HP films indicate QDAP defects
 205 are predominantly responsible for potential fluctuations in the valence band
 206 maxima and conduction band minima (VBM and CBM) of the CZTSSe ab-
 207 sorbers. As both films were slow-cooled at a rate of $\sim 7^\circ\text{C}/\text{min}$ after anneal-
 208 ing, it is expected that any bandgap variations contributing to the potential
 209 fluctuations should be reduced as the rapid cooling process promotes a more
 210 disordered kesterite structure. It is evident that electrostatic potential fluc-
 211 tuations exist in both films with average amplitude γ values of 48.6 and 58.7
 212 meV for films HP and LP respectively which are similar to those previously
 213 reported (Gokmen et al., 2013). The QDAP defect density N_D in film LP
 214 ($2.1 \times 10^{18} \text{ cm}^{-3}$) is double that of film HP ($1.1 \times 10^{18} \text{ cm}^{-3}$) and correlates
 215 to a reduction in average defect separation s from 6.0 to 4.8 nm in films HP

216 and LP respectively. Here, electrons and holes are spatially separated and
 217 localised in potential wells within the energy band edges and any radiative
 218 recombination requires tunneling of charge carriers from one potential well
 219 to another. Increasing the separation distance of the defect centres reduces
 220 the probability of radiative emission. The concentration of net (free) charge
 221 carriers reduces as the charged QDAP defect density increases. Reducing
 222 the density of free carriers lowers the screening effect on the charged defects
 223 which, in turn, increases perturbation in the depth of the fluctuating poten-
 224 tial γ . The QDAP density is a measure of the shallow donor and acceptor
 225 defect concentration responsible for radiative recombination within the ma-
 226 terial and may not represent the total defect density N_t as the presence of
 227 deep and/or non-radiative defects is not accounted for. Therefore the total
 228 defect density can be estimated from γ values derived from PL spectra of
 229 both films (Dirnstorfer et al., 1998). The optical parameters of LP and HP
 230 films are outlined in Table 1.

231 Temperature dependence of the PL bands was measured at an excita-
 232 tion power slightly lower than the threshold value (at which the high energy
 233 shoulder emerges) in order to prevent contributions to PL emissions from
 234 band-related transitions. PL spectra of both films over a range of cryogenic
 235 temperatures are presented in Fig. 3a. It is apparent that PL emissions are
 236 quenched at a lower temperature in film HP and both films exhibit a red-shift
 237 in E_{PL} with increasing temperature. The magnitude of the red-shift in E_{PL}
 238 (κ) for both types of absorber are shown in Fig. 3b. Initially E_{PL} red-shifts
 239 with rising temperature at a similar rate of 0.05 and 0.09 meV/K for films
 240 LP and HP respectively. PL emission from film HP is then quenched at a

241 temperature of ~ 100 K, whereas κ increases rapidly above ~ 80 K at a rate
 242 of 0.84 meV/K in film LP before emissions are finally quenched at ~ 140 K.
 243 Thermal quenching can be surmised to originate from the thermal depopu-
 244 lation of defect states and/or the activation of non-radiative recombination
 245 centres. Similar behaviour was observed by Grossberg et al. in an optical
 246 study of defect clusters in CZTS polycrystals (Grossberg et al., 2014). They
 247 state the observed evolution of E_{PL} with increasing temperature in CZTS
 248 polycrystals followed the temperature dependence of the bandgap energy of
 249 the material (Sarswat and Free, 2012). Another study by Yakushev et al.
 250 revealed comparable temperature trends in PL spectra of CZTSe thin films
 251 with varying Cu content (Yakushev et al., 2017).

Table 1: List of optical parameters of low and high purity CZTSSe samples.

	Low purity	High purity	Defect (Chen et al., 2013)
γ (meV)	58.7	48.6	
ΔE (meV)	36.8	29.6	
Defect spacing s (nm)	4.8	6.0	
QDAP density N_D (cm^{-3})	2.1×10^{18}	1.1×10^{18}	
Defect density N_t (cm^{-3})	2.3×10^{19}	1.4×10^{19}	
E_a (meV)	(1) 38.3 ± 3.8	(1) 40.1 ± 6.4	V_{Cu}
	(2) 3.2 ± 0.5	(2) 5.9 ± 0.5	Sn_{Cu}

252 The Varshni equation was used to fit the asymptotic low temperature

behaviour of E_{PL} in both LP and HP films (Varshni, 1967),

$$E_g(T) = E_g(0) - \left(\frac{AT^2}{T+B} \right) \quad (5)$$

where $E_g(0)$ is the bandgap of the semiconductor at 0 K and A, B are fitting parameters specific to the absorber material. Using the fitting parameters extracted from application of the Varshni model, $E_g(0)$ values of 1.24 eV for both films were extrapolated from the room temperature E_g estimate of 1.19 eV. E_{PL} in both films appear to follow the E_g trend at lower temperatures until ~ 80 K where it deviates markedly in film LP. If electrostatic potential fluctuations of the VBM and CBM are present in the absorbers due to clusters of charged QDAP defects, shallow and deep potential energy wells which follow the fluctuating band edges are formed. Due to a lack of thermal energy at low temperature, carriers are trapped in shallow wells resulting in incomplete occupation of deeper/least energetic wells. As temperature increases the carriers are energised and liberated to fill the deepest wells with a consequent red-shift in E_{PL} . PL emission is quenched in both films due to increasing activation of non-radiative mid-gap recombination centres with rising temperature. The large red-shift in E_{PL} of film LP at temperatures > 80 K suggests a different defect is involved in radiative transitions.

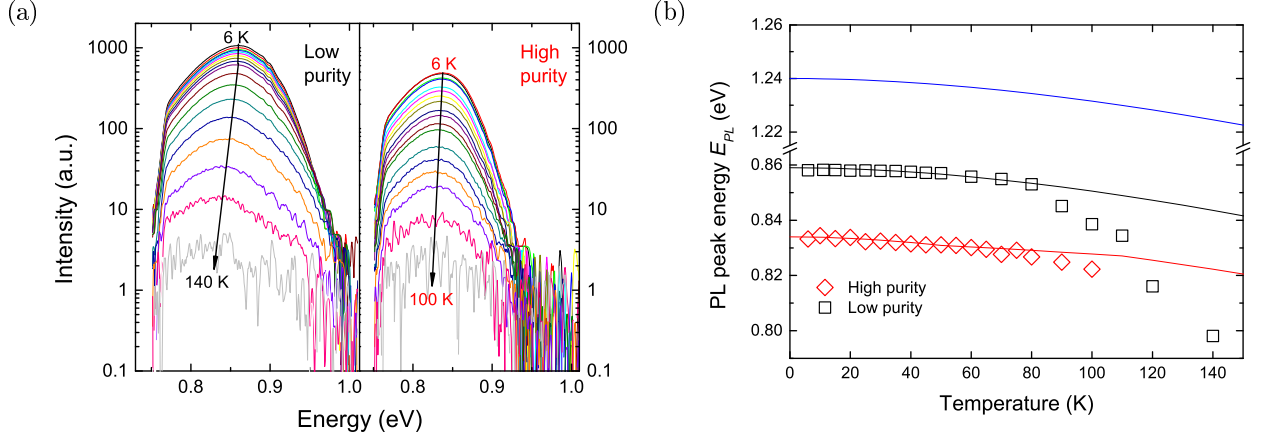


Figure 3: (a) Temperature-dependent PL of sample LP and HP with laser power below PL peak saturation intensity to avoid band-related recombination and (b) evolution of PL band maxima E_{PL} of LP and HP films with increasing temperature. Eq. (5) was used to extrapolate room temperature E_g values to 0 K (blue curve) and temperature-dependent E_{PL} data fitted with same equation (red/black curves).

As temperature increases (up to ~ 80 K) carriers are ionised and redistributed into other radiative and non-radiative defect states which quench PL emission ($T > 140$ K). Activation energies of the defects involved in radiative recombination can be determined by analysis of the temperature-dependent PL spectra intensity using a two activation energy model proposed by (Luckert et al., 2011),

$$I(T) = \frac{I_0}{1 + C_1 \exp\left(-\frac{E_{a1}}{kT}\right) + C_2 \exp\left(-\frac{E_{a2}}{kT}\right)} \quad (6)$$

where I_0 is the integrated intensity extrapolated to 0 K, k is the Boltzmann constant, C_1 and C_2 are the process rate parameters and E_{a1} and E_{a2} are the thermal activation energies for the involved defect states. Application of the model to the Arrhenius plots for both films (Fig. 4a) estimated activation

280 energies of $E_{a1} = 40.1 \pm 6.4$ meV, $E_{a2} = 5.9 \pm 0.5$ meV and $E_{a1} = 38.3 \pm$
 281 3.8 meV, $E_{a2} = 3.2 \pm 0.5$ meV for film HP and LP, respectively. The low
 282 activation energies indicate the presence of shallow donor (3-6 meV) and
 283 shallow acceptor (38-48 meV) states in both films. A kesterite defect study
 284 by Chen et al. would suggest Sn_{Cu} and V_{Cu} are the corresponding donor
 285 and acceptor states. They state the Sn 5p electron has a high orbital energy
 286 which can be easily ionised, hence the Sn_{Cu} (0/+) defect is located just
 287 below the conduction band minimum, which is in agreement with the very
 288 shallow donor level observed in both types of absorber (Chen et al., 2013).
 289 Also the ionised V_{Cu}^- defect is the predominant acceptor responsible for p -
 290 type conductivity in these CZTSSe absorbers producing a reasonably high
 291 concentration of holes (in the region of 10^{15} - 10^{16} cm $^{-3}$). The presence of an
 292 additional Sn-related acceptor defect (V_{Sn} , Zn_{Sn} or Cu_{Sn}) could explain the
 293 anomalous red-shift in E_{PL} observed in film LP (see Fig. 3b).

294 The minority carrier dynamics of LP and HP CZTSSe thin films were
 295 studied using time-resolved photoluminescence (TRPL) decays, see Fig. 4b.
 296 Similar to PL, electron-hole($e-h$) pairs are generated, in this case, by a short
 297 pulse of incident photons and the time-dependence of the emitted light from
 298 recombination of $e-h$ pairs is monitored. The minority carrier lifetime τ is
 299 determined from the decay time of charge carrier recombination. In order
 300 to evaluate τ , the TRPL decay curves were fitted with a double exponential
 301 function (Ohnesorge et al., 1998):

$$I_{PL}(t) = A_1 e^{-\left(\frac{t}{\tau_1}\right)} + A_2 e^{-\left(\frac{t}{\tau_2}\right)} \quad (7)$$

302 where $I_{PL}(t)$ is the luminescence intensity at time t after the excitation pulse,
 303 A_1 and A_2 are the PL intensities corresponding to the injection regimes

and τ_1 and τ_2 are the fast and slow decay times. The initial fast decay τ_1 can be ascribed to high carrier injection immediately after the excitation pulse and the long tail τ_2 attributed to the minority carrier lifetime of the material (Gunawan et al., 2010; Repins et al., 2012).

Lifetimes of 0.20 and 0.44 ns were observed for films LP and HP, respectively. The lower τ value for film LP would suggest more non-radiative bulk/surface recombination centres are present in the absorber, which is in agreement with the total defect density N_t determined from excitation-dependent PL measurements. Raadik et al. propose the shorter carrier lifetime could be related to a higher degree of Cu/Zn disorder in the bulk of the CZTSSe absorber (Raadik et al., 2017). Therefore different recombination processes may be active in LP and HP films. The unexpectedly low carrier lifetime at 6 K observed in this study could be due to high recombination rates at the unpassivated absorber surface.

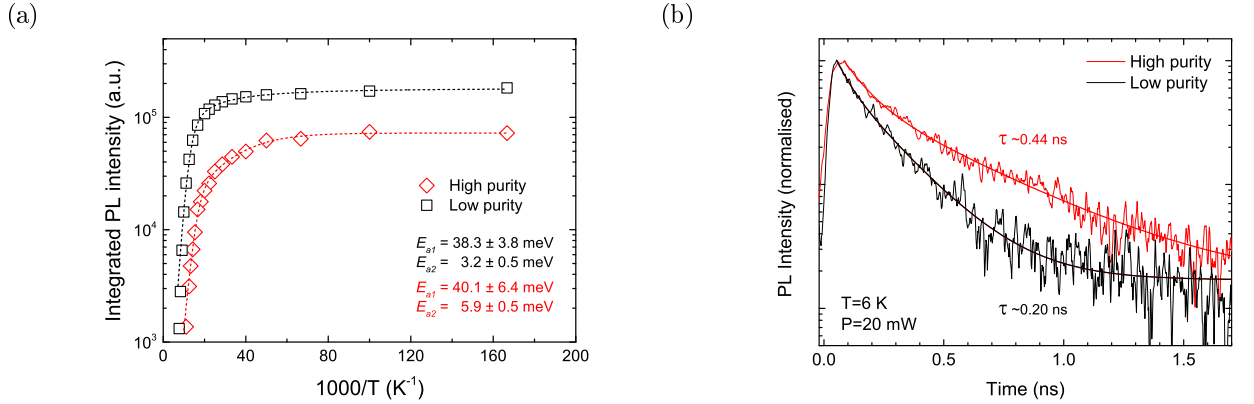


Figure 4: (a) Arrhenius plots of integrated PL intensities and (b) TRPL decays at 6 K for films LP and HP. The solid lines are results of fitting with bi-exponential function.

In order to probe deep defect levels in the CZTSSe devices beyond the

scope of PL spectroscopy, deep level transient spectroscopy (DLTS) is employed to quantify trap activation energies E_T , trap densities N_T and their capture cross-sections σ_T . Supp. Fig. S2 show DLTS spectra for samples LP and HP respectively. In this measurement setup positive ΔC peaks are indicative of hole trap levels with energy values measured with respect to the valence band. Peak positions are analysed over three different transient period widths (19.2 ms, 192 ms, 480 ms) and for a range of correlator functions (Weiss and Kassing, 1988), used to generate Arrhenius plots shown in Fig. 5a. Values for E_T and σ_T are extracted from fitting to the Arrhenius plot whilst the trap density is determined from the magnitude of the capacitance change relative to the reverse bias capacitance (see Table 2).

Table 2: List of electronic parameters of low and high purity CZTSSe samples.

		Trap level	Capture cross-	Trap density	Possible
		E_T (meV)	section σ_T (cm ²)	N_T (cm ⁻³)	defect
Low purity	(1)	86 ± 7	$(1.08 \pm 0.95) \times 10^{-20}$	$(1.70 \pm 0.22) \times 10^{14}$	Cu_{Zn}
	(2)	167 ± 10	$(2.20 \pm 1.99) \times 10^{-20}$	$(3.17 \pm 0.32) \times 10^{13}$	Cu_{Sn} , Zn_{Sn} , V_{Sn}
High purity	(1)	87 ± 6	$(3.61 \pm 1.59) \times 10^{-21}$	$(6.38 \pm 0.05) \times 10^{14}$	Cu_{Zn}

For sample HP a single peak is clearly visible at an energy of $E_T = 87 \pm 6$ meV. The peak is very broad indicating the observed peak may in fact be a distribution of deep levels closely spaced in energy. Attempts were made to separate these levels via a Laplace analysis method (Dobaczewski et al., 2004) however such analysis did not give a definitive answer and was too dependent on the analysis conditions used i.e. number of overlapping transients

337 permissible. This sample also showed some evidence of a negative peak, in-
 338 dicative of an electron trap, at ~ 170 K. On closer inspection, this was found
 339 to predominantly occur for short period widths and is in fact measurement
 340 artifact related to the recovery time of the capacitance signal. Sample LP
 341 showed the same deep level present at $E_T = 86 \pm 9$ meV, although the lower
 342 purity sample displayed a slightly lower concentration of this trap level. A
 343 second trap state not observable in the HP sample was also observed at an
 344 energy of $E_T = 168 \pm 12$ meV but an order of magnitude lower density, 3.17
 345 $\times 10^{13} \text{ cm}^{-3}$, than for the shallower level. The natural assumption would
 346 be that this secondary trap level has arisen as a result of some contaminant
 347 within the process solution. It is assumed that the same trap level at 86-87
 348 meV above the VBM in both types of absorber is antisite Cu_{Zn} (Chen et al.,
 349 2013). Although the concentration of this defect is higher in device HP than
 350 LP, their potentially deleterious effect is mitigated by a lower carrier capture
 351 cross-section ($\sigma_{HP} \sim 4 \times 10^{-21} \text{ cm}^2$ compared to $\sigma_{LP} \sim 1 \times 10^{-20} \text{ cm}^2$). Ab
 352 initio calculations show that the additional defect level in film LP could be
 353 Sn-related (V_{Sn} , Cu_{Sn} or Zn_{Sn}) with the likelihood of the defect being Zn_{Sn} ,
 354 considering the LP absorber is Cu-poor and Zn-rich (see Supp. Table S2).
 355 The concentration of any Sn-related defects in film HP should be reduced as
 356 the film is compositionally closer to the preferred Cu/(Zn+Sn) ratio of 0.8,
 357 see Table 3) (Collord et al., 2015; Fairbrother et al., 2015). CZTSSe films
 358 which have low Cu/(Zn+Sn) and high Zn/Sn ratios are predisposed due to
 359 the presence of high populations of $[Zn_{Sn} + 2Zn_{Cu}]$ charge compensated clus-
 360 ters which are one of the defect complexes responsible for non-stoichiometry
 361 in this type of absorber material.

Table 3: Cu/(Zn+Sn) and Zn/Sn ratios of LP and HP thin films and solar cell parameters of subsequently fabricated best devices (with average values in brackets).

	Low purity	High purity
Cu/(Zn+Sn)	0.84	0.82
Zn/Sn	1.07	1.08
V_{OC} (V)	0.31 (0.31)	0.32 (0.32)
J_{SC} (mA/cm ²)	27.2 (26.0)	25.6 (23.7)
FF (%)	59.9 (57.9)	61.9 (56.7)
Efficiency η (%)	5.1 (4.7)	5.1 (4.2)
Carrier lifetime τ (ns)	0.20	0.44
Carrier diffusion L_d (nm) length	203	369

Further studies of the electronic properties of LP and HP solar cells were performed using current density-voltage (J - V), capacitance-voltage (C - V) and external quantum efficiency (EQE) analysis. Fig. 5b shows the J - V plots of the best performing LP and HP devices under 1-sun illumination with the inset showing the average device open circuit voltage V_{OC} and short circuit current density J_{SC} . It is noted that the average V_{OC} of HP cells was slightly higher than that of the LP cells, see inset of Fig. 5b. Conversely, LP devices have a higher J_{SC} value (26.1 mA/cm²) in comparison to that seen in HP devices (23.7 mA/cm²). Similar observations were made by Yakushev et al. for Cu₂ZnSnSe₄ (CZTSe) devices with varying Cu/(Zn+Sn) and Zn/Sn ratios

372 and were attributed to the degree of Cu-Zn order/disorder in the crystal
 373 lattice (Yakushev et al., 2017). EQE plots for LP and HP devices are shown in
 374 Fig. 5c, where it can be seen that device LP has enhanced carrier extraction
 375 in the wavelength range 600-1000 nm. This anomalous behaviour could be
 376 explained by a lower concentration of free charge carriers and will be explored
 377 in more detail later in this section. The minority carrier diffusion length
 378 L_d for both types of absorber was calculated from EQE measurements in
 379 conjunction with optical absorption coefficient α measurements (determined
 380 from transmittance/reflectance data, see Supp. Fig. S3) using a method by
 381 Courel et al. (Courel et al., 2016). It was shown that EQE^{-1} is a linear
 382 function of α^{-1} such that:-

$$EQE(\lambda)^{-1} = \frac{1}{(1 - R(\lambda))} \left(1 + \frac{\alpha(\lambda)^{-1}}{L_d} \right) \quad (8)$$

383 where $R(\lambda)$ is the reflectance of the cell with an intercept on the α^{-1} equal
 384 to L_d , see Fig. 5d. Diffusion length values of 203 and 369 nm were de-
 385 termined for LP and HP devices respectively. The reported L_d values are
 386 significantly lower than the value of 750 nm observed in the CZTSSe solar
 387 cell with record efficiency of 12.6% (Wang et al., 2013). The longer diffusion
 388 lengths of carriers in film HP strongly correlates with higher carrier lifetimes
 389 measured in CZTSSe bulk. C - V measurements were performed to estimate
 390 the depletion region width w and doping density N_A in the CZTSSe absorber
 391 layers of devices LP and HP. The inset in Fig. 5d shows the plot of $1/C^2$
 392 versus reverse bias voltage where $\langle w \rangle = A\epsilon_0\epsilon_r/C$ is determined from the
 393 measured capacitance value at zero bias and N_A is derived from the slope
 394 $d(1/C^2)/dV$. Very short space charge regions widths of 63 and 61 nm were
 395 observed for devices LP and HP respectively, with corresponding apparent

396 doping densities of 2.5×10^{16} and $3.3 \times 10^{16} \text{ cm}^{-3}$, in agreement with those
 397 observed by Qu et al. (Qu et al., 2018). A high doping density is usually
 398 associated with a short depletion width in CZTSSe solar cells as $w \propto N_A$
 399 (Ganchev et al., 2011; Haight et al., 2014).

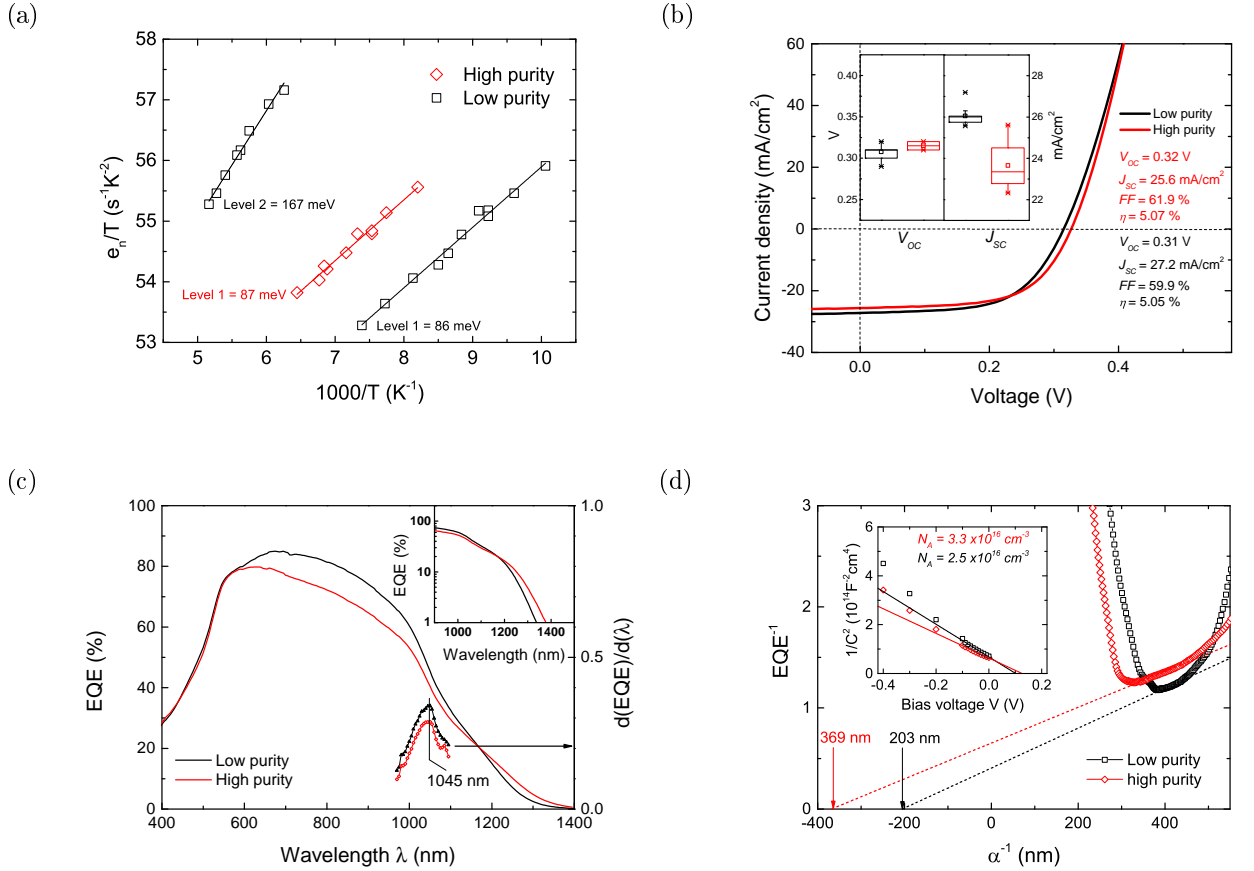


Figure 5: (a) Extracted Arrhenius plots from DLTS spectra, (b) J-V curves of best performing devices with inset showing box plots of average device V_{OC} and J_{SC} parameters, (c) EQE plots with inset showing extended absorption due to tail states in sample HP and (d) calculation of depletion region width w_0 and apparent doping density N_A for samples LP and HP.

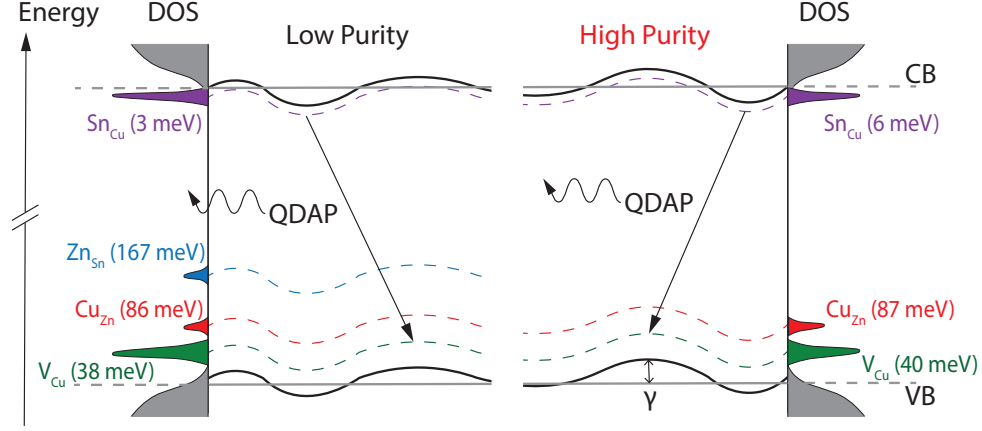


Figure 6: Schematic of electrostatic potential fluctuations in the band edges of LP and HP absorbers with associated defects and densities of state (DOS). The predominant radiative recombination process in both samples involves QDAP defects Sn_{Cu} and V_{Cu} .

400 Following the selenisation of the CZTS nanoparticle films, EDS compo-
 401 sitional analysis of the LP and HP CZTSSe absorbers revealed a greater Cu
 402 and Sn loss was observed in LP films, whereas HP films suffered a larger Zn
 403 loss. Subsequent Cu/Zn+Sn and Zn/Sn ratios of 0.84, 0.82 and 1.07, 1.08 for
 404 respective LP and HP absorbers demonstrate HP films are closer to the pre-
 405 ferred CZTSSe composition of Cu/Zn+Sn = 0.8 and Zn/Sn = 1.2 (Collord
 406 et al., 2015; Fairbrother et al., 2015). With regard to the elemental losses,
 407 it would be reasonable to assume that there could be higher concentrations
 408 of Cu- and Sn-related defects in LP films. Recent studies have shown the
 409 degree of Cu-Zn order/disorder has a significant impact on the bandgap and
 410 crystallinity of CZTSSe absorbers and may be the main cause of bandgap
 411 and electrostatic potential fluctuations within the material, as shown in Fig.
 412 6 (Rey et al., 2014; Scragg et al., 2015; Rey et al., 2018; Schorr, 2011).

413 Considering the small decrease in Cu/Zn+Sn and small increase in Zn/Sn
 414 ratios in LP films compared to HP films, higher concentrations of A-type de-
 415 fects ($[V_{Cu}+Zn_{Cu}]$ neutral complexes) may be present in HP films together
 416 with higher concentrations of B-type defects ($[Zn_{Sn}+2Zn_{Cu}]$ neutral com-
 417 plexes) in LP films (Lafond et al., 2012; Gurieva et al., 2015). Although the
 418 presence of Zn_{Cu} donor defect was not directly observed in either film, their
 419 presence can be inferred as high populations of benign $[V_{Cu}+Zn_{Cu}]$ clusters
 420 are expected in non-stoichiometric CZTSSe absorbers (Chen et al., 2013).

421 Perhaps the most interesting observation in this study is the presence of
 422 an additional acceptor defect in the LP device located ~ 167 meV above the
 423 VBM, speculatively attributed to antisite Zn_{Sn} . Chen et al. have shown the
 424 Zn_{Sn} defect has negligible impact on p -type conductivity but could contribute
 425 to luminescence and act as recombination centres (Chen et al., 2013). The
 426 presence of radiative Zn_{Sn} defects could explain the increased QDAP den-
 427 sity and PL intensity seen in film LP compared to film HP. The significant
 428 red-shift of the PL peak in film LP at temperatures greater than 80 K could
 429 be attributed to radiative recombination involving the Zn_{Sn} acceptor. The
 430 lower QDAP concentration in film HP could also account for quenching of
 431 the PL signal at a lower temperature (~ 100 K) in this film compared to film
 432 LP (~ 140 K). It is also possible the anomalous temperature-dependent PL be-
 433 haviour in film LP could involve Cu_{Zn} - Sn_{Cu} QDAP due to the thermal escape
 434 of holes from the shallower V_{Cu} acceptor state to the slightly deeper Cu_{Zn}
 435 state, see Fig. 6. According to Chen et al. a number of self-compensated
 436 defect clusters can be formed in quaternary kesterites. They show the overall
 437 formation energy of these defect clusters is significantly decreased relative to

438 the sum of the individual defects. As the clusters are charge-neutral and
 439 bound by strong Coulomb attraction, their presence should not be detected
 440 directly by PL analysis. However, some defect clusters can produce a sig-
 441 nificant shift in the valence and conduction band edges, effectively reducing
 442 the bandgap of the absorber. Large populations of clusters $[2V_{Cu}+Sn_{Zn}]$
 443 or $[2Cu_{Zn}+Sn_{Zn}]$ could exist in both types of absorber given the observed
 444 large red-shift of E_{PL} in comparison to the bandgap of the absorbers at 6
 445 K (~ 300 meV) which cannot be solely attributed to QDAP defects. The
 446 presence of neutral defect clusters would reduce the concentration of shallow
 447 acceptor defects which contribute to the overall p-type conductivity of the
 448 absorber material. From capacitance-voltage measurements, film LP has a
 449 slightly lower apparent doping density N_A in comparison to that of film HP
 450 indicating the degree of compensation is greater in this film. The measured
 451 concentration of V_{Cu} antisite defects (which are mainly responsible for the
 452 p-type conductivity of Cu-poor/Zn-rich CZTSSe films) is around 10^{19} cm^{-3}
 453 in both types of absorber whereas both films show $N_A \sim 10^{16} \text{ cm}^{-3}$ confirming
 454 the material is highly compensated.

455 All optical and electronic parameters indicate films prepared from high
 456 purity precursor chemicals are of a higher quality than those fabricated from
 457 lower grade materials. However, this improvement in film quality does not
 458 translate to an increase in completed device efficiency as both types of device
 459 have similar best η values of ~ 5.1 %. A previous study of CZTSSe solar
 460 cells fabricated using the same nanoparticle inks-based method has revealed
 461 the devices typically have a contact barrier height of ~ 40 meV between the
 462 CZTSSe absorber and Mo back contact (Campbell et al., 2018). This low

463 barrier height would suggest the back contact of both types of device is not
 464 a factor constraining cell performance and, therefore, attention should be
 465 focused on improving buffer/absorber junction and other components in the
 466 device architecture.

467 One important parameter which could be utilised to indicate the quality of
 468 CZTSSe absorbers is the mean depth of potential fluctuations γ . Considering
 469 a high concentration of Zn_{Sn} defects present in absorber LP (which could
 470 contribute to an elevated QDAP density), we see a direct correlation of such
 471 QDAP density with γ , suggesting γ is a useful indicator of the presence of
 472 specific defects which generate band tails in the material. Yakushev et al.
 473 observe a similar reduction in γ values when the studied CZTSe films became
 474 Cu-poorer and Zn-rich, attributing this change to improved ordering of
 475 Cu-Zn atoms within the crystal lattice of the thin film (Yakushev et al.,
 476 2017). A similar reduction in γ values are noted in this study. Bourdais et
 477 al. investigated the effect of Cu-Zn disorder on the V_{OC} deficit in kesterite
 478 solar cells also noted that ordering of the CZTSSe absorbers by slow cooling
 479 improved the V_{OC} deficit in their devices by 40 meV. Therefore, a reduction
 480 in γ value could indicate a reduction in Cu-Zn disorder with an associated
 481 increase in V_{OC} (Bourdais et al., 2016). Fig. 6 highlights the main results of
 482 the combined optical and electronic studies, principally:

- 483 (i) Fluctuations in the band edges of both types of absorber, predomi-
 484 nantly caused by variations in electrostatic potential, with an average depth
 485 of γ equal to 59 and 49 meV in films LP and HP respectively
- 486 (ii) Same shallow donor (Sn_{Cu}) and shallow acceptor (V_{Cu} , Cu_{Zn}) defects
 487 present in the bulk of both types of CZTSSe absorber

- 488 (iii) Additional deep Sn-related acceptor defect (probably Zn_{Sn}) located
 489 167 meV above the VBM present in sample LP
- 490 (iv) Radiative recombination primarily involving QDAP donor Sn_{Cu} and
 491 acceptor V_{Cu} defects located 3-6 meV below CBM and 38-40 meV above
 492 VBM
- 493 (v) V_{Cu} chiefly responsible for p -type conductivity in both types of thin
 494 film.

495 4. Conclusion

496 In depth optical spectroscopy and electronic studies of CZTSSe absorber
 497 layers fabricated from low and high purity precursor chemicals are presented.
 498 The high purity chemical recipe produced Cu-poorer and Zn-richer CZTS
 499 nanoparticles. Following selenisation of the stacked spin-coated CZTS films,
 500 a Zn loss was observed in the HP absorber while a Sn loss was seen in the LP
 501 absorber. Comprehensive temperature and excitation dependent analysis of
 502 PL spectra together with DLTS enabled identification of shallow and deep
 503 defects and QDAP recombination as the predominant recombination mecha-
 504 nism in both types of thin film. The loss of Sn could account for the presence
 505 of additional Sn-related defects identified in the LP film. Notwithstanding
 506 the improvement in quality of film HP, detailed analysis of the electronic
 507 properties of LP and HP solar cells revealed similar performance in both
 508 types of device. This implies an underlying issue other than defects in the
 509 absorber bulk inhibits device performance which warrants further investiga-
 510 tion.

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694 **Appendix A. Supplementary material**

Table S1: Chemical composition and concentration details of low/high purity CZTS nanoparticle recipe.

	Low purity recipe		High purity recipe	
<i>Copper(II)</i> <i>acetylacetonate</i> <i>(Cu(acac)₂)</i>	97%	<i>Sigma Aldrich</i>	99.99%	<i>Sigma Aldrich</i>
<i>Zinc</i> <i>acetylacetonate</i> <i>(Zn(acac)₂)</i>	<i>not provided</i> <i>by supplier</i>	<i>Alfa Asear</i>	99.995%	<i>Sigma Aldrich</i>
<i>Tin(IV)</i> <i>bis(acetylacetonate)</i> <i>dichloride (Sn(acac)₂Cl₂)</i>	95%	<i>Alfa Asear</i>	98%	<i>Sigma Aldrich</i>
<i>Elemental sulphur (S)</i>	99.98%	<i>Sigma Aldrich</i>	99.98%	<i>Sigma Aldrich</i>
<i>Oleylamine (OLA)</i>	<i>technical grade</i> 70%	<i>Sigma Aldrich</i>	98%	<i>Sigma Aldrich</i>

Table S2: The composition of precursor and selenised films on bare SLG

		Cu	Zn	Sn	S	Se	$\frac{Cu}{Zn + Sn}$	Zn/Sn	$\frac{Se}{Se + S}$
	Solvent	(at%)	(at%)	(at%)	(at%)	(at%)			
HP	Precursor	23.93	16.88	14.24	45.95		0.74	1.19	
	Selenised	20.61	13.13	12.12	5.57	48.53	0.82	1.08	0.90
LP	Precursor	23.17	14.3	14.16	48.04		0.80	1.03	
	Selenised	19.09	11.80	11.02	5.02	53.06	0.84	1.07	0.91

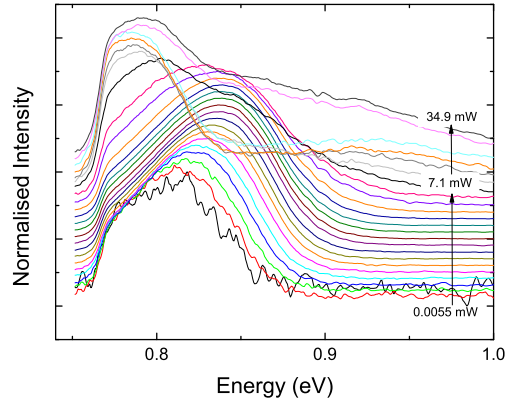


Figure S1: Emergence of high energy 'shoulder' in PL spectra of film HP indicating saturation of QDAP defects and an increasing contribution to PL intensity from band-related radiative recombination.

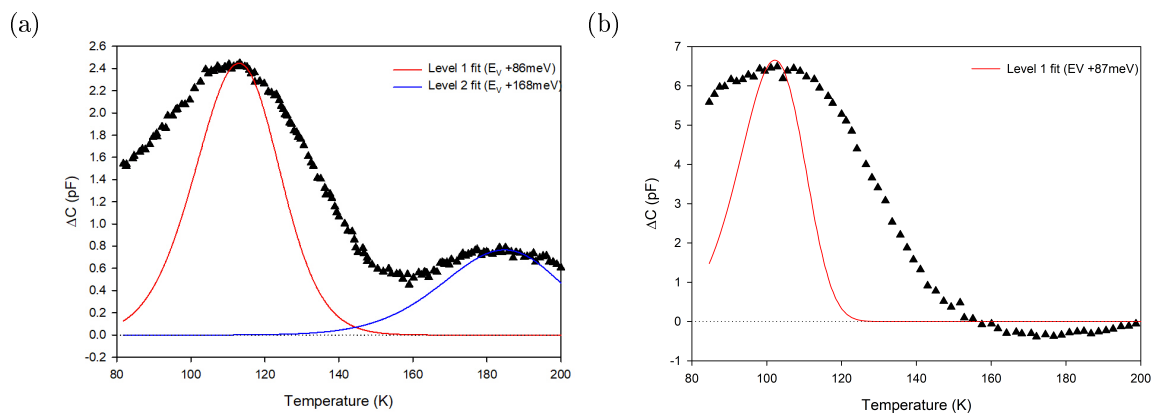


Figure S2: DLTS spectra recorded for (a) sample LP and (b) sample HP.

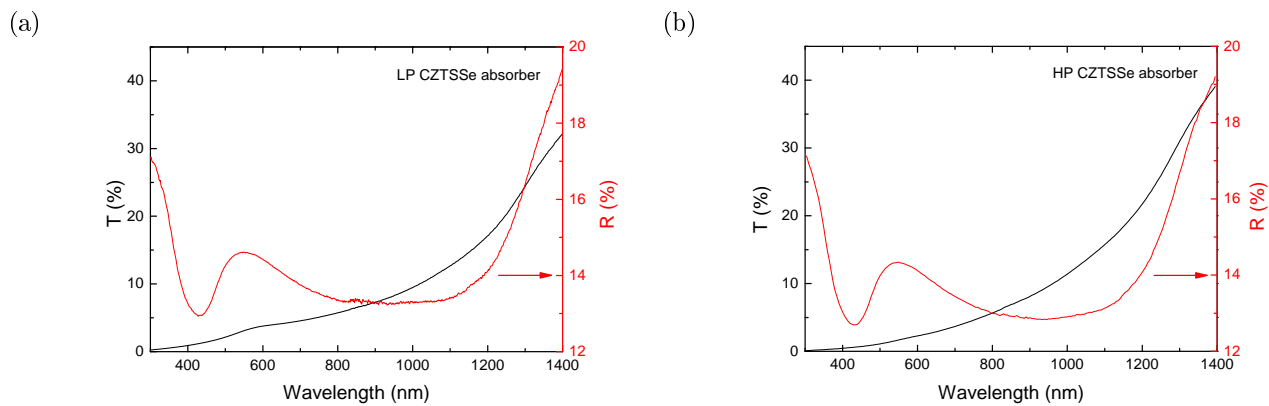


Figure S3: Transmission and absorption data of CZTSSe absorbers deposited on bare soda lime glass of (a) film LP and (b) film HP.