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Examination of electronic structure differences between CIGSSe and CZTSSe by photoluminescence study
Kong Fai Tai, Talia Gershon, Oki Gunawan, and Cheng Hon Alfred Huan

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I. INTRODUCTION

Earth-abundant Cu2ZnSn(S,Se)4 (CZTSSe) solar cells have attracted much interest over the past decade with steady improvement in efficiency reaching 12.6%.1 However, the efficiency is limited by a severe open-circuit voltage deficit \( V_{OC,def} \equiv E_g e - V_{OC} \), where \( e \) is the electron’s charge. Compared to the world-record efficiency of 21.7% Cu(In,Ga)Se2 (CIGSe) solar cell with an open-circuit voltage (\( V_{OC} \)) of 748 mV and a \( V_{OC,def} \) of 382 mV,2 the 12.6% CZTSSe solar cell with the same band gap (\( E_g \)) of 1.13 eV has a larger \( V_{OC,def} \) of 617 mV.1 A severe \( V_{OC,def} \) could be caused by electrostatic potential fluctuations of the valence and conduction bands,3 which are induced by a random distribution of unscreened charged defects. These charged defects may be donors, acceptors, or both in the case of highly compensated semiconductors. The spatially varying charge density leads to a local perturbation of the band structure which results in the formation of band tails.1 The exponentially decaying band tail states with energy smaller than \( E_g \) results in a broad asymmetric photoluminescence (PL) spectrum at room temperature.5,6 In materials suffering from this problem, the average depth of the electrostatic potential fluctuation (\( \gamma \)) of the bands can be estimated by 6,7

\[
\gamma(R) = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r} \left( \frac{N_t R^3}{R^2} \right)^{1/2},
\]

where \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the relative permittivity (or dielectric constant), \( N_t \) is the total defect density with mean square fluctuation on the order of \( (N_t R^3)^{1/2} \) within a volume \( R^3 \), \( N_t \) includes all radiative and non-radiative charged defects with energy states inside of \( E_g \). We note that the depth of the fluctuating potential is proportional to \( N_t \), which plays a crucial role in the intrinsic bulk properties of a semiconductor.

We note that the two prevalent models for understanding the sub-bandgap defect structures of CIGSSe and CZTSSe, i.e., the electrostatic potential fluctuation and the QDAP (quasi donor/acceptor pair) models are inherently inter-related. The potential fluctuation model estimates the average depth \( \gamma \) of the fluctuating conduction and valence bands of the semiconductor, whereas the QDAP model describes the distribution of radiative donors and acceptor states (part of \( N_t \)) that contribute to this potential fluctuation. The QDAP model can be used to estimate the average separation between donor and acceptor and its density based on the Coulombic interaction between the charged donor and acceptor, as reflected in the recombination photon energy of8,9

\[
E = E_g - E_D - E_A + \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r s},
\]

where \( E_D \) and \( E_A \) are the donor and acceptor energy level separated from the conduction band minimum and valence band maximum, respectively, and \( s \) is the separation distance.
between donor and acceptor. Due to the interaction and clustering of charged defects, the “quasi” term is used to distinguish QDAP from the conventional donor-acceptor-pair (DAP) recombination with no interaction between defects, though Eq. (2) is also used to describe the photon energy of DAP recombination.

In this work, we measured power-dependent and temperature-dependent photoluminescence (PL), as well as carrier lifetime of hydrazine solution-processed Cu(In,Ga) (S,Se)2 (CIGSSe), CZTSSe with low (CZTSSe1) and high (CZTSSe2) S/(S + Se) ratio. We introduce a new method for qualitatively assessing $\gamma$ by examining the carrier lifetime as a function of photon energy ($d\tau/dE$). Additionally, the upper bound of $N_t$ can be estimated from the power-dependent PL spectra, which can be used to calculate $\gamma$. Both methods show that $\gamma$(CIGSSe) < $\gamma$(CZTSSe1) < $\gamma$(CZTSSe2). Furthermore, a so-called “activation energy” ($E_a$) is calculated from the Arrhenius plot of the PL intensity vs. temperature, where $E_a$ is defined as the energy required to de-trap carriers from the localized states they occupy at 7 K and redistribute them into other states; we note that this value depends on both the energetic depth of the state with respect to $E_G$ as well as energetic availability of other states, including the band edge as well as other localized (potentially non-radiative) states. Thermal redistribution of carriers from radiative to non-radiative defect states would result in the observation of a higher value of $E_a$.10

We show that $E_a$(CIGSSe) < $E_a$(CZTSSe1) < $E_a$(CZTSSe2). By examining the temperature-dependence of the defect peak, we show that the shallow $E_a$ in CIGSSe allows for the thermalization of carriers into the band tail at higher temperatures, whereas this does not occur for CZTSSe and the thermalized carriers are effectively quenched by non-radiative channels. The values of $\gamma$ and $E_a$ have a direct impact on the $V_{OC}$ of the solar cells.

II. EXPERIMENTAL

All of the samples were fabricated using hydrazine solution preparation and spin-coating performed in a nitrogen-filled glove box. Caution: hydrazine is highly toxic and reactive and must be handled using appropriate protective equipment to prevent physical contact with either vapor or liquid. CIGSSe solutions were prepared by dissolving separately In2Se3 with Se addition and Cu2S with S addition, followed by mixing. A single layer 120 nm thick was first coated from a 0.3 M CIGSSe solution with Cu0.92In0.8Ga0.2(S,Se)2 composition, resulting in a film thickness of ~2 $\mu$m. The film was annealed on a ceramic hot plate with a temperature of 540°C.

The values of $E_a$(CIGSSe) have a direct impact on the $V_{OC}$ of the solar cells. The solar cell efficiencies were measured using a Newport solar simulator with simulated AM1.5G spectrum, equipped with light stabilization system to ensure stable 1 sun (100 mW/cm²) illumination. The PL spectra were measured using a Hamamatsu time-correlated single photon counting (TCSPC) system equipped with an InGaAs PMT detector cooled to ~80°C. The solid state laser excitation has a wavelength of 532 nm, repetition rate of 15 kHz and a pulse duration of 1 ns. Power-dependent PL measurements were performed by passing the laser beam through a calibrated motorized neutral density filter prior to the sample. The laser has a Gaussian TEM00 profile such that the laser intensity passing through the pinhole with radius r can be described by: $I(r) = I_0 \exp((-\ln 2 \times r^2/b^2))$, where $I_0$ is the original laser intensity, and b is the beam radius at full-width-half-maximum (FWHM) intensity. By measuring the laser power with ($I(r)$) and without ($I_0$) the pinhole (diameter of 127 $\mu$m), the beam radius was found to be 171 $\mu$m. Therefore, the laser intensity (laser power/$b^2$) and laser fluence (laser intensity/15 kHz) can be calculated accordingly. Minority carrier lifetime and PL measurements at varying temperatures were carried out by placing the sample in a Janis SuperTran-VP continuous liquid He flow cryostat and using a Cryocon temperature controller integrated into the system. All PL measurements were carried out on completed CIGSSe and CZTSSe devices. No difference was found in PL measurements between device and bare film.

III. RESULTS AND DISCUSSION

A. Films’ characteristics and device performance

Two CZTSSe films with low (CZTSSe1) and high (CZTSSe2) S/(S + Se) ratio were fabricated to represent pure-selenide CZTSe and pure-sulphide CZTS, respectively. The chemical compositions were found out by ICP, with Cu/(Zn + Sn) = 0.9 for both films, Zn/Sn = 1.0 (1.1) and S/(S + Se) = 0.1 (0.9) for CZTSSe1 (CZTSSe2). The $E_a$ of each film was extrapolated from the inflection point (maximum slope) of the quantum efficiency near the band edge. The band gap and device performance parameters are summarized in Table I. All devices have reasonably good efficiency and device parameters compared to the champion devices from each class and band gap.

B. Excitation-dependent PL

Fig. 1 shows the PL spectra recorded as a function of incident laser fluence at 7 K for all three samples. At low
laser fluence, the main PL peaks for all the samples (~1.08, ~0.95, ~1.20 eV for CIGSSe, CZTSSe1 and CZTSSe2, respectively) are significantly below $E_g$, implying that the dominant recombination involves sub-bandgap states. In addition, the power law relationship $I \sim P^m$ can be used as a metric to assess whether the recombination is a band-to-band transition ($m > 1$) or involves defect levels ($m < 1$). As seen in Fig. 1, the PL peak height saturates at high laser fluence due to the finite number of defect states available. This indicates $m < 1$, which the main PL peaks can similarly be assigned to QDAP emission according to Ref. 8 However, as the laser fluence increases above a certain threshold above which all charged defects ($N_t$) within $E_g$ become occupied, a distinct “shoulder” emission appears at higher photon energy. The shoulder emission involves band- to band-tail related recombination as reflected by the short recombination lifetime (< 10 ns) as carriers become more delocalized. This will be discussed in more detail in Sec. III C. Therefore, we can roughly estimate $N_t$ by calculating the electron-hole pairs generated in the sample by the threshold laser fluence at which the shoulder emission appears.

The threshold laser fluence occurs at 29.3, 192.1, 397.0 $\mu$J cm$^{-2}$ for CIGSSe, CZTSSe1, and CZTSSe2, respectively. Assuming the incident light is fully absorbed by all the three films within the first 100 nm (absorption coefficient of $10^5$ cm$^{-1}$ at 532 nm), the corresponding electron-hole pairs generated ($N_{e-h}$), and thus the upper bound of $N_t$ ($2 \times N_{e-h}$) are calculated to be 0.16, 1.0, and 2.2 $\times 10^{19}$ cm$^{-3}$ for CIGSSe, CZTSSe1 and CZTSSe2, respectively. By substituting the tunnelling length $R = \hbar/\sqrt{m_t \gamma}$ into Eq. (1), $\gamma$ can be estimated using the following equation:

$$
\gamma = \frac{e^2}{4\pi e_0 \epsilon_r} \frac{N_{e-h}^2 \hbar^2}{m_t m_0},
$$

where $m_t$ is the reduced effective mass given by $m_t = (m_e m_h)/(m_e + m_h)$, $m_e$ is the electron effective mass, $m_h$ is the hole effective mass, $m_0$ is the electron mass, and $\hbar$ is the reduced Planck’s constant. From previous reports, the calculated and experimental values of the dielectric constants and effective masses for CIGSSe and CZTSSe were used. Therefore, the upper bound of $\gamma$ can be extracted using the estimated (upper bound of) $N_t$, as summarized in Table II. We do not believe that the main sub-$E_g$ PL peak can be attributed to band gap fluctuations.

<table>
<thead>
<tr>
<th>Device</th>
<th>$E_g$ (eV)</th>
<th>Eff (%)</th>
<th>FF (%)</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$(E_g - V_{OC})$ (mV)</th>
<th>$n_t$ ($\times 10^{19}$)</th>
<th>$R_{S,L}$ (Ω cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIGSSe</td>
<td>1.16</td>
<td>15.2</td>
<td>75.0</td>
<td>623.0</td>
<td>32.6</td>
<td>547.0</td>
<td>1.55 (1.58)</td>
<td>0.75</td>
</tr>
<tr>
<td>CZTSSe1</td>
<td>1.08</td>
<td>10.3</td>
<td>63.0</td>
<td>491.8</td>
<td>33.2</td>
<td>588.2</td>
<td>1.94 (1.61)</td>
<td>1.17</td>
</tr>
<tr>
<td>CZTSSe2</td>
<td>1.49</td>
<td>6.0</td>
<td>59.0</td>
<td>557.0</td>
<td>21.3</td>
<td>933.0</td>
<td>2.84 (2.51)</td>
<td>2.57</td>
</tr>
</tbody>
</table>

**TABLE I.** Band gap ($E_g$) and device parameters of studied samples. $n_t$ ($\times 10^{19}$) is the ideality factor under light (dark) and $R_{S,L}$ is the series resistance under light.

**TABLE II.** A summary of parameters extracted from CIGSSe, CZTSSe1, and CZTSSe2.

<table>
<thead>
<tr>
<th></th>
<th>CIGSSe</th>
<th>CZTSSe1</th>
<th>CZTSSe2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$ (eV)</td>
<td>1.16</td>
<td>1.09</td>
<td>1.49</td>
</tr>
<tr>
<td>$n_t$ ($\times 10^{19}$)</td>
<td>0.09</td>
<td>0.07</td>
<td>0.18</td>
</tr>
<tr>
<td>$n_t$ ($\times 10^{19}$)</td>
<td>0.25</td>
<td>0.09 – 0.33</td>
<td>0.22 – 0.71</td>
</tr>
<tr>
<td>$\epsilon_r$ (Refs. 17 and 21)</td>
<td>12.0</td>
<td>8.1</td>
<td>6.7</td>
</tr>
<tr>
<td>Threshold laser</td>
<td>29.3</td>
<td>192.1</td>
<td>397.0</td>
</tr>
<tr>
<td>$N_{e-h}$ (cm$^{-3}$)</td>
<td>$7.9 \times 10^{18}$</td>
<td>$5.1 \times 10^{19}$</td>
<td>$1.1 \times 10^{20}$</td>
</tr>
<tr>
<td>Upper bound of $N_t$ (cm$^{-3}$)</td>
<td>$1.6 \times 10^{19}$</td>
<td>$1.0 \times 10^{20}$</td>
<td>$2.2 \times 10^{20}$</td>
</tr>
<tr>
<td>Upper bound of $\gamma$ (meV)</td>
<td>36.1</td>
<td>107–115</td>
<td>141–144</td>
</tr>
</tbody>
</table>

$^{a} \epsilon_r$ for CZTSSe1 is obtained from bandgap interpolation from Refs. 17 and 19.
in these three materials as the recombination lifetimes of the main PL peak probed at low temperature are much higher (more than three orders of magnitude) than the lifetimes probed at room temperature, indicating that spatial tunneling (i.e., through highly localized states) is required for electron-hole recombination. The large density of charged defects is thus expected to contribute to spatial potential fluctuations of the bands.3

Photo-excited carriers can be trapped at the charged donor ($D^-$) and acceptor ($A^-$) sites to produce neutral donor ($D^0$) and acceptor ($A^0$) centers. In returning to equilibrium, electrons at $D^0$ will recombine radiatively with holes at $A^0$. This process is known as DAP transition which can be described by the reaction9

$$D^0 + A^0 \rightarrow \hbar\omega + D^+ + A^-.$$  (4)

The emitted photon energy ($\hbar\omega$) is increased by the amount of $e^2/4\pi\varepsilon_0\varepsilon_r s$ as stated in the last term of Eq. (2) because the energy of the final state in reaction (4) is lowered by the Coulombic attraction.9 Previous reports have also estimated the QDAP density using Eq. (2) by making two assumptions. The first assumption is that the Coulombic attraction between $D^-$ and $A^-$ is negligible at low laser fluence, i.e., the charged defects are spaced too far apart to interact. The second assumption is that all QDAP states are occupied when the blue-shift of the QDAP peak saturates, i.e., maximum Coulombic attraction. Therefore, equating the last term in Eq. (2) to the magnitude of the blue-shift allows us to estimate the average separation distance $s$ between donor and acceptor,8 and the QDAP density can be estimated by assuming $r = (4\pi N_d/3)^{-1/3}$.8

The peak positions of the PL spectra in Fig. 1 were fitted using asymmetric double sigmoidal function. Thus, the saturated blue-shift magnitude of the QDAP peak positions can be derived and used to estimate the QDAP density. QDAP density was found to have a similar trend with $N_t$ such that QDAP density: CIGSSe $<$ CZTSSe1 $<$ CZTSSe2. This further verifies that the severe potential fluctuations in CZTSSe with $\gamma$(CIGSSe) $<$ $\gamma$(CZTSSe1) $<$ $\gamma$(CZTSSe2), are caused by the increasing defect concentration. Note that reduced dielectric constant $\varepsilon_r$ in CZTSSe also increases the $\gamma$ due to reduced defect screening. The high $N_t$ and deeper $\gamma$ in CZTSSe2 are further reflected in the shorter shoulder emission at maximum laser fluence. This is due to a higher defect density within $E_g$ such that more photo-excited carriers are needed to fully occupy the defect states leaving fewer remaining photo-excited carriers to occupy the higher energy band-tail or band states. Table III summarizes the QDAP density for all the three samples. The significant difference in magnitude between QDAP density and $N_{e-h}$ could be due to (i) assumption of fully absorbed laser excitation by the materials (for conservative estimation of upper bound $\gamma$) and (ii) high non-radiative recombination rate such that generated electron-hole pair do not necessarily result in radiative emitted photon. However, QDAP density is within the estimated $N_{e-h}$, indicating a reasonable defect densities calculated.

### C. Lifetime vs. photon energies

The recombination lifetimes at different photon energies were probed at 7 K to gauge the degree of carrier localization in the different materials. All of the lifetime measurements were recorded using as low as possible laser fluence to avoid a high carrier injection which lowers the measured lifetime (rate of success in Poisson probability of $< 15\%$). Each decay curve is fitted using a quadratic recombination model22

$$I(t) = \frac{I_0 \exp(-t/\tau)}{1 + (C/A)n_0[1 - \exp(-t/\tau)]},$$  (5)

where $I(t)$ is the PL intensity at time $t$, $I_0$ is the PL intensity at time zero, $A$ and $C$ are the coefficients for linear and quadratic recombination processes, and $\tau$ is the recombination lifetime. The fitted recombination lifetimes ($\tau$) at various photon energies were plotted on a logarithmic scale (right axis) in Fig. 1. For all of the three samples, there are two slopes observed in lifetime vs. photon energy data (d$I$/d$E$). The first slope corresponds to photon energies below the QDAP peak energy; within this regime, $\tau$ values are almost constant. This indicates that the QDAP recombination is primarily limited by the tunneling probability between spatially separated donor and acceptor, and the long $\tau$ beyond 1 $\mu$s signifies a low probability of tunneling. We note that the tunneling probability does not depend solely on QDAP separation distance, but other factors as well such as the carriers’ energy and effective masses, the barrier height ($\gamma$) and the barrier width ($R$).23 Therefore, we do not observe a lower $\tau$ for the QDAP recombination in CZTSSe2 although the QDAP separation distance is shorter. The second slope observed in the d$I$/d$E$ relationship occurs at photon energies larger than the QDAP peak energy. In this regime, $\tau$ decreases rapidly with increasing energy, ranging from 10 ns to 1 $\mu$s. The fast-changing $\tau$ with energy could be due to an energetic overlap between the band tail states and the

### Table III. QDAP density extracted from the saturated blue-shift magnitude of the QDAP peak. P1 is the peak position at the lowest possible laser excitation and P2 is the position with saturated blue-shift QDAP peak. $s$ is the estimated average defect spacing.

<table>
<thead>
<tr>
<th>Device ($t_c$)</th>
<th>P1 (eV)</th>
<th>P2 (eV)</th>
<th>$s$ (nm)</th>
<th>QDAP density (cm$^{-3}$)</th>
<th>Laser fluence for P2 (µJ cm$^{-2}$)</th>
<th>$N_{e-h}$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIGSSe (12.0)$^{20}$</td>
<td>1.080</td>
<td>1.088</td>
<td>15.5</td>
<td>$6.4 \times 10^{16}$</td>
<td>14.5</td>
<td>$2.7 \times 10^{18}$</td>
</tr>
<tr>
<td>CZTSSe1 (8.1)$^{19}$</td>
<td>0.940</td>
<td>0.960</td>
<td>8.8</td>
<td>$3.5 \times 10^{17}$</td>
<td>93.3</td>
<td>$2.5 \times 10^{19}$</td>
</tr>
<tr>
<td>CZTSSe2 (6.7)$^{19}$</td>
<td>1.175</td>
<td>1.224</td>
<td>4.4</td>
<td>$2.9 \times 10^{18}$</td>
<td>192.5</td>
<td>$5.2 \times 10^{19}$</td>
</tr>
</tbody>
</table>
localized defect states and/or recombination between tail states; in either case, the carriers become increasingly delocalized at increasingly higher energy states of the defect band or the band tail, resulting in faster recombination.

At photon energies in the shoulder emission region, the recombination lifetimes decrease down to <10 ns for all the three samples. Recombination with such short lifetime involves band- or band-tail related transitions (i.e., band-impurity (BI), band-tail (BT), band-band (BB), tail-impurity (TI), and tail-tail (TT)), where the shorter lifetimes represent transition from more delocalized states. We propose a model wherein each PL spectrum contains contributions from multiple recombination mechanisms, each of which results in emission at different energies. With increasing photon energy, the recombination mechanisms include: QDAP (impurity-to-impurity, II) → TI → TT → BI → BT → BB, i.e., increasing degrees of carrier delocalization. Furthermore, we hypothesize that the sharp decrease of τ with energy (the second slope) occurs when band- and band-tail related recombination are involved, i.e., TI, TT, BI, BT, and BB. However, the band- or band-tail related recombination mechanisms are intermixed in the PL spectrum and the lifetime shows a mono-exponential decay with respect to photon energy, and thus the recombination mechanisms are indistinguishable.

Recombination lifetimes of ~0.5 ns have been previously reported for band-to-band (BB) recombination in GaAs, where the rapid recombination involves highly delocalized carriers.24 BB recombination was observed in CIGSSe and CZTSSe1 as evidenced by the extension of the shoulder emission beyond the room-temperature E_g of these materials. However, BB transition was not observed in CZTSSe2 for the same conditions of carrier injection due to the severe band tail, or large γ, and/or higher concentration of non-radiative states. Although the recombination of CZTSSe2 involves more localized states such that BB transition was not observed, a longer τ (> 0.5 ns) was not observed at high photon energy, which could be due to the higher non-radiative recombination (explained in Sec. III D) which lead to an overall lower recombination lifetime from the relation: 1/τ = 1/τ_{radiative} + 1/τ_{non-radiative}.25 The BB transition should be observed in CZTSSe2 if excited with higher laser fluence, as noted by the slight extension of the shoulder emission at (slightly increased) maximum laser fluence (Fig. 1(c)).

From the slope of dτ/dE in the higher-energy range, one could gauge the degree of the fluctuating potential qualitatively. With larger γ, the density of the band-tail states extend further into the band gap, i.e., band-tail spans a larger energy range inside E_g. Since recombination involving the band tails are likely to occur when τ varies between 10 ns and 1 μs, a larger energy span of the band tail will result in a shallower slope of dτ/dE. In other words, a steep slope in the plot of τ vs. photon energies would be observed in a sample with shallow γ. Therefore, measuring τ at different photon energies is a direct indication of the degree of the potential fluctuation. Indeed, the slope of τ vs. photon energies in Fig. 1 is inversely proportional to γ, with dτ/dE: CIGSSe > CZTSSe1 > CZTSSe2.

D. Temperature-dependent PL

Temperature-dependent PL was measured using a laser fluence just below what is required for the shoulder emission to occur (i.e., the “threshold” laser fluence described earlier) for each sample. This laser fluence was adjusted such that the PL emission likely stems from pure QDAP recombination. This allows us to examine changes to the PL spectral shapes associated with defect recombination and extract a value for E_a. There are multiple parameters that influence E_a, including the donor or acceptor energy levels (i.e., the depth of the defect states from the band edge), as well as the availability of non-radiative states into which the carriers may be redistributed. Both deeper defect levels and the availability of non-radiative states will increase the E_a value that is extracted from an Arrhenius plot.10

Fig. 2 shows the PL spectra of CIGSSe, CZTSSe1, and CZTSSe2 recorded as a function of temperature. The laser fluence in each sample is stated in the figure. One obvious
The difference in the CIGSSe spectra is the significant blue-shift in peak position with temperature, while a similar peak shift was not observed in either CZTSSe1 or CZTSSe2. Fig. 3 shows the integrated PL intensity normalized to the maximum intensity in each case. The normalized PL intensity saturates at temperature region 1 (T < 80 K). As temperature increases in region 2 (80–180 K), carriers were ionized and re-distributed into other energy states, including the non-radiative defect states which quench the PL. Due to a lower laser fluence used in CZTSSe1 (to avoid the occurrence of band-related “shoulder” emission), the PL intensity was lower and the PL was fully quenched beyond a temperature of 140 K. Therefore, an Arrhenius rate relation was fitted on temperature region 2 for a fair comparison between the three materials. In addition, a previous report has inferred that the $E_a$ extracted from 95–170 K is likely related to bulk defects; thus the data gathered between 80 and 180 K (Region 2) is sufficient for the extraction of $E_a$ for the bulk defects (including the effect of non-radiative states). From the Arrhenius plot in Fig. 3, the extracted $E_a$ values from region 2 are found to be 20.1 ± 7.6 meV, 47.9 ± 6.8 meV, and 67.1 ± 26.9 meV for CIGSSe, CZTSSe1, and CZTSSe2, respectively. The trends in the extracted values of $E_a$ for each sample are consistent with the measurements discussed earlier. Furthermore, the shallow $E_a$ in CIGSSe explains the fact that CIGSSe does not show a distinct kink as in CZTSSe in the power-dependent PL measurement (Fig. 1) because the QDAP recombination and the band-related recombination are not as well separated in energy.

The shallow $E_a$ in CIGSSe is comparable to the thermal energy at room temperature ($k_BT \sim 25$ meV, where $k_B$ is the Boltzmann constant). At low temperature, recombination in CIGSSe is dominated by the transition of carriers localized in QDAP states. As temperature increases, carriers in the QDAP states thermalize into the band states, from which recombination is dominated by band-related transition (either BT or BB transition) with photon energy near $E_g$ at room temperature. This explains the significant blue-shift of the PL peak position with increasing temperature in CIGSSe (Fig. 2(a)) as the recombination mechanism changes. The PL intensity decreases with increasing temperature due to the activation of non-radiative centers or lattice vibration (phonons) that quench the photo-excited carriers.

In CZTSSe1, $E_a$ is almost double compared to CIGSSe, and $E_a$ is much larger than the thermal energy at room temperature. Compared to CIGSSe, a higher laser fluence was used to excite CZTSSe1 and CZTSSe2, but a lower PL intensity was observed at high temperature. In addition, the decay rate of PL intensity with temperature in CZTSSe1 and CZTSSe2 is faster than CIGSSe. Both of these observations clearly indicate the presence of higher density of non-radiative recombination centers in CZTSSe1 and CZTSSe2. The presence of efficient non-radiative recombination centers would increase the extracted value of $E_a$, as mentioned earlier. However, we also find that the states in CZTSSe1 and CZTSSe2 are deeper inside of $E_g$ compared to CIGSSe. The depth of the defect states causes carriers to remain localized in these states even as the temperature rises, as evidenced by the lack of a blue-shifting peak with increasing temperature (Fig. 2). Thus, the higher $E_a$ values observed in CZTSSe1 and CZTSSe2 contain a contribution from both deeper radiative states as well as a higher density of non-radiative states. Comparing the $E_a$ values for CZTSSe1 and CZTSSe2, the higher $E_a$ value in CZTSSe2 could have at least two possible explanations: (1) CZTSSe2 contains a higher density of bulk non-radiative recombination centers; non-radiative centers are usually mid-gap states, and it is possible that the sample with higher S-content (CZTSSe2) has a higher density of such centers due to the higher volatility of sulphur during annealing resulting in the formation of mid-gap S-vacancies.26,27 This is also consistent with the transient photocapacitance spectroscopy study that observe defect band at 0.8 eV from the valence band that becomes closer to the center of the gap and thus more harmful.28 (2) CZTSSe2 contains deeper intrinsic defect levels; for example, the dominant acceptor defect (i.e., the CuZn antisite) and other defects ($V_{Sn}$, $Cu_{Sn}$, $Zn_{Cu}$, $Sn_{Cu}$,$Sn_{Zn}$, $Cu_{i}$, $Zn_{i}$, $V_{S}$) are calculated to be deeper in the sulphide-CZTS compared to the selenide-CZTSe.27 Note that these factors also contribute to the unfavorable increase in the ideality factor in higher bandgap CZTSSe like CZTSSe2 as shown in Table I.

**IV. SUMMARY**

Band tails induced by unscreened charged defects are described by the depth of the fluctuating potential ($\gamma$). The total defect density ($N_d$) and QDAP density were estimated and found to be CIGSSe $<$ CZTSSe1 $<$ CZTSSe2 where CZTSSe2 has higher $S/(S + Se)$ ratio than CZTSSe1. A direct measurement of the lifetime at different photon energies ($d\tau/dE$) reflects the degree of carrier localization and therefore it qualitatively gauges the magnitude of $\gamma$. With increasing defect density, larger $\gamma$ results in a deeper penetrating tail states inside the band gap, which effectively reduce the achievable $V_{OC}$, i.e., increases the $V_{OC,def}$. Lastly, the stronger PL intensity loss with increasing temperature and higher activation energies ($E_a$) in both CZTSSe samples indicates the presence of significant non-radiative recombination centers and also deeper defect states. Therefore, further improvement in CZTSSe solar cells should focus on
reducing defect density and non-radiative recombination channels.

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