Examination of electronic structure differences between CIGSSe and CZTSSe by photoluminescence study

Tai, Kong Fai; Gershon, Talia; Gunawan, Oki; Huan, Cheng Hon Alfred

2015

Tai, K. F., Gershon, T., Gunawan, O., & Huan, C. H. A. (2015). Examination of electronic structure differences between CIGSSe and CZTSSe by photoluminescence study. *Journal of Applied Physics*, 117(23), 235701-.

<https://hdl.handle.net/10356/104250>

<https://doi.org/10.1063/1.4922493>

© 2015 American Institute of Physics (AIP). This paper was published in *Journal of Applied Physics* and is made available as an electronic reprint (preprint) with permission of American Institute of Physics (AIP). The published version is available at: [<http://dx.doi.org/10.1063/1.4922493>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 21:29:53 SGT

Examination of electronic structure differences between CIGSSe and CZTSSe by photoluminescence study

Kong Fai Tai, Talia Gershon, Oki Gunawan, and Cheng Hon Alfred Huan

Citation: [Journal of Applied Physics](#) **117**, 235701 (2015); doi: 10.1063/1.4922493

View online: <http://dx.doi.org/10.1063/1.4922493>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/117/23?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Interference effects in photoluminescence spectra of Cu₂ZnSnS₄ and Cu\(In,Ga\)Se₂ thin films](#)

J. Appl. Phys. **118**, 035307 (2015); 10.1063/1.4926857

[Reducing interface recombination for Cu\(In,Ga\)Se₂ by atomic layer deposited buffer layers](#)

Appl. Phys. Lett. **107**, 033906 (2015); 10.1063/1.4927096

[Fiber-fed time-resolved photoluminescence for reduced process feedback time on thin-film photovoltaics](#)

Rev. Sci. Instrum. **86**, 013907 (2015); 10.1063/1.4905535

[Influence of different sulfur to selenium ratios on the structural and electronic properties of Cu\(In,Ga\)\(S,Se\)₂ thin films and solar cells formed by the stacked elemental layer process](#)

J. Appl. Phys. **116**, 174503 (2014); 10.1063/1.4900991

[The role of structural properties on deep defect states in Cu₂ZnSnS₄ studied by photoluminescence spectroscopy](#)

Appl. Phys. Lett. **101**, 102102 (2012); 10.1063/1.4750249

AIP | APL Photonics

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief

Examination of electronic structure differences between CIGS_{Se} and CZTSSe by photoluminescence study

Kong Fai Tai,¹ Talia Gershon,^{2,a)} Oki Gunawan,^{2,a)} and Cheng Hon Alfred Huan¹

¹*Division of Physics and Applied Physics, School of Physical & Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371*

²*IBM T.J. Watson Research Center, PO Box 218, Yorktown Heights, New York 10598, USA*

(Received 5 April 2015; accepted 2 June 2015; published online 16 June 2015)

In this paper, we elaborate on the interpretation and use of photoluminescence (PL) measurements as they relate to the “donor/acceptor” and “electrostatic potential fluctuations” models for compensated semiconductors. Low-temperature (7 K) PL measurements were performed on high-efficiency Cu(In,Ga)(S,Se)₂ and two Cu₂ZnSn(S,Se)₄ solar cells with high- and low-S/(S + Se) ratio, all fabricated by a hydrazine solution-processing method. From excitation-dependent PL, the total defect density (which include radiative and non-radiative defects) within the band gap (E_g) was estimated for each material and the consequent depth of the electrostatic potential fluctuation (γ) was calculated. The quasi-donor-acceptor pair (QDAP) density was estimated from the blue-shift magnitude of the QDAP PL peak position in power-dependent PL spectra. As a further verification, we show that the slope of the lifetime as a function of photon energies ($d\tau/dE$) is consistent with our estimate for the magnitude of γ . Lastly, the energetic depth of the QDAP defects is examined by studying the spectral evolution of the PL as a function of temperature. The shallow defect levels in CIGS_{Se} resulted in a significant blue-shift of the PL peak with temperature, whereas no obvious shift was observed for either CZTSSe sample, indicating an increase in the depth of the defects. Further improvement on Cu₂ZnSn(S,Se)₄ solar cell should focus on reducing the sub- E_g defect density and avoiding the formation of deep defects. © 2015 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4922493>]

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 ($V_{OC,def} = E_g/e - V_{OC}$), 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.⁴ 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 (γ) of the bands can be estimated by^{6,7}

$$\gamma(R) = \frac{e^2}{4\pi\epsilon_r\epsilon_0} \frac{(N_t R^3)^{1/2}}{R}, \quad (1)$$

where ϵ_0 is the permittivity of vacuum, ϵ_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 CIGS_{Se} 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 γ 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 of^{8,9}

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

where E_D and E_A are the donor and acceptor energy level separated from the conduction band minimum and valence band maximum, respectively, and s is the separation distance

^{a)}Author to whom correspondence should be addressed. Electronic mail: ogunawa@us.ibm.com

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 γ 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 γ . Both methods show that $\gamma(\text{CIGSSe}) < \gamma(\text{CZTSSe1}) < \gamma(\text{CZTSSe2})$. 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 $E_a(\text{CIGSSe}) < E_a(\text{CZTSSe1}) < E_a(\text{CZTSSe2})$. 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 γ 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 slightly higher Ga content Cu_{0.92}In_{0.72}Ga_{0.28}(S,Se)₂ onto a Mo-coated soda lime glass substrate, followed by three layers spin-coated from a 1.1 M CIGSSe solution with Cu_{0.92}In_{0.8}Ga_{0.2}(S,Se)₂ composition, resulting in a film thickness of $\sim 2 \mu\text{m}$. The film was annealed on a ceramic hot plate with a temperature of 540 °C as described previously.^{11,12} Devices were completed with chemical-bath-deposited CdS (60 nm), sputtered ZnO (80 nm), and indium-doped tin oxide (ITO, 130 nm).

CZTSSe films were prepared using a hydrazine-based pure solution approach, as described in Ref. 13 with chemical composition in the solution targeting a Cu-poor and Zn-rich stoichiometry of Cu/(Zn + Sn) = 0.8 and Zn/Sn = 1.1. To control the S/Se ratio, pure S and high Se-content solutions were prepared

individually and mixed accordingly to desired S/Se ratio. The mixed solution was then spin-coated onto the Mo-coated soda lime glass substrate and annealed at a temperature in excess of 500 °C.^{1,13} The chemical composition of the two final CZTSSe thin films were later determined by inductive coupled plasma (ICP) mass spectrometer. For complete devices, CZTSSe films deposition were followed by standard chemical-bath deposition of 25 nm CdS and sputtering of 10 nm ZnO and 50 nm ITO.^{1,14} Finally, $\sim 2 \mu\text{m}$ thick Ni/Al top metal contact and $\sim 0.1 \mu\text{m}$ MgF₂ antireflection coating were deposited by electron-beam evaporation on all the CIGSSe and CZTSSe devices.

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 μm), the beam radius was found to be 171 μm . Therefore, the laser intensity (laser power/ πb^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_g 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.^{1,2,15}

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

TABLE I. Band gap (E_g) and device parameters of studied samples. n_L (n_D) is the ideality factor under light (dark) and $R_{S,L}$ is the series resistance under light.

Device	E_g (eV)	Eff (%)	FF (%)	V_{OC} (mV)	J_{SC} (mA cm ⁻²)	$(E_g/e - V_{OC})$ (mV)	n_L (n_D)	$R_{S,L}$ (Ω cm ²)
CIGSSe	1.16	15.2	75.0	623.0	32.6	547.0	1.55 (1.58)	0.75
CZTSSe1	1.08	10.3	63.0	491.8	33.2	588.2	1.94 (1.61)	1.17
CZTSSe2	1.49	6.0	50.9	557.0	21.3	933.0	2.84 (2.51)	2.57

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 ($m < 1$).¹⁶ 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- or 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 $\mu\text{J cm}^{-2}$ 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),^{17,18} 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 $2.2 \times 10^{20} \text{ cm}^{-3}$ for CIGSSe, CZTSSe1 and CZTSSe2, respectively. By substituting the tunnelling length $R = \hbar / \sqrt{m_r \gamma}$ into Eq. (1),⁷ γ can be estimated using the following equation:⁷

$$\gamma^5 = \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r} \right)^4 \frac{N_t^2 \hbar^2}{m_r m_0}, \quad (3)$$

where m_r is the reduced effective mass given by $m_r = (m_e m_h) / (m_e + m_h)$, 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.^{17,19,20} Therefore, the *upper bound* of γ 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

FIG. 1. Power-dependent PL (left axis) recorded at 7 K for (a) CIGSSe, (b) CZTSSe1, and (c) CZTSSe2. The vertical dashed line corresponds to the band gap (E_g) of each sample and the legend indicates the laser pulse fluence corresponding to each spectrum (the legend for CZTSSe2 is the same as CZTSSe1). The fitted recombination lifetimes at different photon energies are marked by the black square symbols (right axis).

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

	CIGSSe	CZTSSe1	CZTSSe2
E_g (eV)	1.16	1.09	1.49
m_e^* (m_0) (Refs. 17 and 21)	0.09	0.07	0.18
m_h^* (m_0) (Refs. 17 and 21)	0.25	0.09 – 0.33	0.22 – 0.71
ϵ_r (Refs. 17, 19, and 20)	12.0	8.1 ^a	6.7
Threshold laser fluence ($\mu\text{J cm}^{-2}$)	29.3	192.1	397.0
N_{e-h} (cm^{-3})	7.9×10^{18}	5.1×10^{19}	1.1×10^{20}
Upper bound of N_t (cm^{-3})	1.6×10^{19}	1.0×10^{20}	2.2×10^{20}
Upper bound of γ (meV)	36.1	107–115	141–144

^a ϵ_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

The emitted photon energy ($\hbar\omega$) is increased by the amount of $e^2/4\pi\epsilon_0\epsilon_r s$ 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 $\gamma(\text{CIGSSe}) < \gamma(\text{CZTSSe1}) < \gamma(\text{CZTSSe2})$, are caused by the increasing defect concentration. Note that reduced dielectric constant ϵ_r in CZTSSe also increases the γ due to reduced defect screening. The high N_t and deeper γ 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 γ) 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

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

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 τ is the recombination lifetime.

The fitted recombination lifetimes (τ) 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 ($d\tau/dE$). The first slope corresponds to photon energies below the QDAP peak energy; within this regime, τ 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 τ beyond 1 μ 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 (γ) and the barrier width (R).²³ Therefore, we do not observe a lower τ for the QDAP recombination in CZTSSe2 although the QDAP separation distance is shorter. The second slope observed in the $d\tau/dE$ relationship occurs at photon energies larger than the QDAP peak energy. In this regime, τ decreases rapidly with increasing energy, ranging from 10 ns to 1 μ s. The fast-changing τ 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.

Device (ϵ_r)	Peak position		s (nm)	QDAP density (cm^{-3})	Laser fluence for P2 ($\mu\text{J cm}^{-2}$)	N_{e-h} (cm^{-3})
	P1 (eV)	P2 (eV)				
CIGSSe (12.0) ²⁰	1.080	1.088	15.5	6.4×10^{16}	14.5	2.7×10^{18}
CZTSSe1 (8.1) ¹⁹	0.940	0.960	8.8	3.5×10^{17}	93.3	2.5×10^{19}
CZTSSe2 (6.7) ¹⁹	1.175	1.224	4.4	2.9×10^{18}	192.5	5.2×10^{19}

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) $\rightarrow$ TI $\rightarrow$ TT $\rightarrow$ BI $\rightarrow$ BT $\rightarrow$ 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: $1/\tau = 1/\tau_{\text{radiative}} + 1/\tau_{\text{non-radiative}}$.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 $d\tau/dE$ 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 μ s, a larger energy span of the band tail will result in a shallower slope of $d\tau/dE$. 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 $d\tau/dE$: 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

FIG. 2. Temperature-dependent PL with laser fluence below threshold laser fluence to avoid band-related recombination (“shoulder emission”).

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,¹⁰ 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 ($k_B T \sim 25$ 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 Cu_{Zn} antisite) and other defects (V_{Sn} , Cu_{Sn} , Zn_{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 (γ). The total defect density (N_t) and QDAP density were estimated and found to be $\text{CIGSSe} < \text{CZTSSe1} < \text{CZTSSe2}$ 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 γ . With increasing defect density, larger γ results in a deeper penetrating tail states inside the band gap, which effectively reduce the achievable V_{OC} , i.e., increases the $V_{\text{OC,def}}$. 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

FIG. 3. Arrhenius plot from temperature-dependent PL. E_a are extracted from region 2 and the dashed line shows the Arrhenius fit.

reducing defect density and non-radiative recombination channels.

ACKNOWLEDGMENTS

K. F. Tai would like to thank Dr Guichuan Xing for the fruitful discussion and acknowledge the scholarship program from Clean Energy Program Office, National Research Foundation (NRF) of Singapore and the financial support from Energy Research Institute at NTU (ERI@N). For the CZTS_{Se} study, the information, data, or work presented herein was funded in part by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Program, under Award No. DE-EE0006334; it was also part of a joint development project between Tokyo Ohka Kogyo Co., Ltd., Solar Frontier K. K. and IBM Corporation.

- ¹W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, and D. B. Mitzi, *Adv. Energy Mater.* **4**, 1301465 (2014).
- ²P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, and M. Powalla, *Phys. Status Solidi (RRL)* **9**, 28 (2015).
- ³T. Gokmen, O. Gunawan, T. K. Todorov, and D. B. Mitzi, *Appl. Phys. Lett.* **103**, 103506 (2013).
- ⁴A. Bauknecht, S. Siebentritt, J. Albert, and M. C. Lux-Steiner, *J. Appl. Phys.* **89**, 4391 (2001).
- ⁵A. P. Levanyuk and V. V. Osipov, *Sov. Phys. Usp.* **24**, 187 (1981).
- ⁶A. L. Efros and B. I. Shklovskii, *Electronic Properties of Doped Semiconductors*, 1st ed. (Springer-Verlag, Berlin/Heidelberg, 1984), p. 297.
- ⁷I. Dirnstorfer, M. Wagner, D. M. Hofmann, M. D. Lampert, F. Karg, and B. K. Meyer, *Phys. Status Solidi A* **168**, 163 (1998).
- ⁸T. Gershon, B. Shin, N. Bojarczuk, T. Gokmen, S. Lu, and S. Guha, *J. Appl. Phys.* **114**, 154905 (2013).
- ⁹M. Cardona and P. Y. Yu, *Fundamentals of Semiconductors* (Springer, 2005), p. 356.
- ¹⁰T. Gershon, B. Shin, N. Bojarczuk, M. Hopstaken, D. B. Mitzi, and S. Guha, *Adv. Energy Mater.* **5**, 1400849 (2015).
- ¹¹D. B. Mitzi, M. Yuan, W. Liu, A. J. Kellock, S. J. Chey, V. Deline, and A. G. Schrott, *Adv. Mater.* **20**, 3657 (2008).
- ¹²T. K. Todorov, O. Gunawan, T. Gokmen, and D. B. Mitzi, *Prog. Photovolt: Res. Appl.* **21**, 82 (2013).
- ¹³T. K. Todorov, H. Sugimoto, O. Gunawan, T. Gokmen, and D. B. Mitzi, *IEEE J. Photovolt.* **4**, 483 (2014).
- ¹⁴M. T. Winkler, W. Wang, O. Gunawan, H. J. Hovel, T. K. Todorov, and D. B. Mitzi, *En. Environ. Sci.* **7**, 1029 (2014).
- ¹⁵B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, and S. Guha, *Prog. Photovolt: Res. Appl.* **21**, 72 (2013).
- ¹⁶T. Schmidt, K. Lischka, and W. Zulehner, *Phys. Rev. B* **45**, 8989 (1992).
- ¹⁷C. Persson, *J. Appl. Phys.* **107**, 053710 (2010).
- ¹⁸S. Minoura, K. Kodera, T. Maekawa, K. Miyazaki, S. Niki, and H. Fujiwara, *J. Appl. Phys.* **113**, 063505 (2013).
- ¹⁹O. Gunawan, T. Gokmen, C. W. Warren, J. D. Cohen, T. K. Todorov, D. A. R. Barkhouse, S. Bag, J. Tang, B. Shin, and D. B. Mitzi, *Appl. Phys. Lett.* **100**, 253905 (2012).
- ²⁰J. Lee, J. D. Cohen, and W. N. Shafarman, *Thin Solid Films* **480**, 336 (2005).
- ²¹C. Persson, *Appl. Phys. Lett.* **93**, 072106 (2008).
- ²²B. Ohnesorge, R. Weigand, G. Bacher, A. Forchel, W. Riedl, and F. H. Karg, *Appl. Phys. Lett.* **73**, 1224 (1998).
- ²³A. L. Efros and B. I. Shklovskii, *Electronic Properties of Doped Semiconductors*, 1st ed. (Springer-Verlag, Berlin/Heidelberg, 1984), p. 290.
- ²⁴J. I. Pankove, *Optical Processes in Semiconductors* (Dover Publications, New York, 1975).
- ²⁵R. J. Nelson and R. G. Sobers, *J. Appl. Phys.* **49**, 6103 (1978).
- ²⁶S. Chen, J.-H. Yang, X. G. Gong, A. Walsh, and S.-H. Wei, *Phys. Rev. B* **81**, 245204 (2010).
- ²⁷S. Chen, A. Walsh, X.-G. Gong, and S.-H. Wei, *Adv. Mater.* **25**, 1522 (2013).
- ²⁸D. W. Miller, C. W. Warren, O. Gunawan, T. Gokmen, D. B. Mitzi, and J. D. Cohen, *Appl. Phys. Lett.* **101**, 142106 (2012).