Time-Resolved Recombination Analysis in Kesterite Polycrystalline Thin Films and Photovoltaic Devices with One-Photon and Two-Photon Excitation

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Abstract

Minority carrier lifetime, τ_B , is one of the key metrics for polycrystalline solar cell absorbers. Based on different spatial carrier-generation profiles obtained using one-photon and two-photon excitation (1PE and 2PE, respectively), we developed a new approach to determine τ_B in polycrystalline thin films. By comparing time-resolved photoluminescence data measured with 1PE and 2PE, we extract τ_B and surface recombination velocity S , and resolve charge separation at the pn junction. For coevaporated kesterite ($\text{Cu}_2\text{ZnSnSe}_4$) absorbers, we find $S = (0.8\text{--}2.1) \times 10^4 \text{ cm s}^{-1}$ and $\tau_B = 7.0 \pm 0.5 \text{ ns}$. For corresponding photovoltaic devices, charge separation occurs in $\leq 2 \text{ ns}$.

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1. Introduction

Interest in kesterite ($\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ and related alloys) photovoltaics is primarily driven by the lower cost and Earth abundance of the constituent elements [1,2]. However, kesterite photovoltaic (PV) solar cells typically have lower open-circuit voltage (V_{OC}) than expected based on the material bandgap, E_g . Short minority-carrier lifetime, τ_B , is thought to be an important contributor to V_{OC} loss [3]. Although there are several approaches for the analysis of τ_B [4], only time-resolved photoluminescence (TRPL) has been applied as a direct measure of recombination in kesterite thin films and PV devices [5-17]. As illustrated in Scheme I, laser pulses in a traditional one-photon excitation (“1PE”) TRPL measurement are absorbed close to the surface, and therefore, the PL signal is mostly emitted from the surface region of the polycrystalline film. Thus, with 1PE, it might not be possible to distinguish bulk and surface recombination.

Scheme I. Illustration of one-photon and two-photon excitation (1PE and 2PE, respectively) in thin film materials. Shaded area represents depth at which excitation light is attenuated to 10% of its initial intensity.

We employ a new approach to analyze minority-carrier dynamics and recombination in polycrystalline $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin films and PV devices. By varying excitation photon energy so that electron-hole pairs are created either $<0.15\text{ }\mu\text{m}$ from the interface (540-nm excitation) or uniformly in the polycrystalline film (two-photon excitation, 2PE) [18,19], we independently analyze recombination at the surface and in the bulk to determine surface recombination velocity, S , and τ_B . With 2PE, the excitation photon energy is smaller than the bandgap, and simultaneous absorption of two photons is necessary to create an electron-hole pair (Scheme I). Lower two-photon absorption probability (in comparison with one-photon absorption) ensures more uniform initial carrier distribution in the thin polycrystalline film. By using 2PE TRPL, we are also able to directly observe charge separation in CdS/CZTSe polycrystalline PV devices.

2. Materials and Methods

2.1. Samples

A brief summary of the growth of CZTSe films and PV devices used in this study is recounted below, while more a more detailed description can be found in the literature.[6,7] First, soda-lime glass substrates were coated with a $1\text{-}\mu\text{m}$ Mo back contact. Then, $1.5\text{ }\mu\text{m}$ of slightly Cu-poor and Zn-rich CZTSe was co-evaporated while the substrate was maintained at $510\text{ }^\circ\text{C}$. Upon removal from the growth chamber, the sample was cut into several pieces. Those pieces that received no additional processing are termed “absorbers” or “polycrystalline films” in the remainder of the study. The device structure was completed on other pieces,

utilizing the typical buffer and window layers the commonly used for both CZTSe and CIGS photovoltaics. These layers, in order of deposition, consist of 500 Å bath-deposited CdS, 1000 Å resistive ZnO, 1000 Å conductive ZnO:Al, and metal grids to aid in current collection.

The absorber studied in this paper produced devices with the following current-voltage parameters, without antireflective coating: total-area AM1.5 power conversion efficiency = 8.3%, open-circuit voltage = 373 mV, fill factor = 66.5%, and short-circuit current = 33.4 mA/cm².

2.2. Measurements

Excitation was provided by the optical parametric amplifier pumped by a Yb:KGW laser with 1.1-MHz repetition rate and pulse length of 0.3 ps (Orpheus/Pharos, Light Conversion). Excitation wavelength was 540 nm (similar to some earlier TRPL measurements on kesterites) [5,8,11-17], 780 nm [10], and 1560 nm. Excitation at 1560 nm (0.79 eV) is below the bandgap of the material used in this study ($E_g \approx 1$ eV) [6] and absorption of two photons is necessary to create an electron-hole pair. Because 1560-nm photon energy is half that of 780-nm photons, excited states created with 2PE at 1560 nm are expected to correspond to excited states obtained with 1PE at 780 nm. A multimode-optical-fiber-based 1PE and 2PE TRPL spectrometer for time-correlated single-photon counting was described [18]. Excitation spot diameter of 0.2 mm in 1PE and 0.02 mm in 2PE was estimated by using calibrated pinholes and assuming a Gaussian-shaped excitation beam. Spectrally integrated photoluminescence was measured with 1150-nm long-pass filters and a Hamamatsu R5509-42 photomultiplier. When PL signal intensity was

low, the background scattering was subtracted from the data. Instrumental response function (IRF) had a full width at half maximum (FWHM) of 0.35 ns. Deconvolution of IRF was applied to resolve lifetimes ≥ 0.1 ns. The same setup was used to measure total PL intensity, which was determined by integrating TRPL transients over time.

3. Results and Discussion

3.1. One-photon excitation (1PE) TRPL decays for CZTSe polycrystalline film and PV device

Fig. 1. 1PE TRPL decays measured using excitation at 540 nm (black, data for polycrystalline film; blue, data for corresponding PV device) and 780 nm (red, data for polycrystalline film). Excitation intensity was 2.3×10^{12} photons cm⁻² pulse⁻¹ (540 nm) and 1.7×10^{12} photons cm⁻² pulse⁻¹ (780 nm). Instrumental response function is shown in grey; results of two-exponential fitting of the data in green.

Inset shows lifetime τ_1 and τ_2 intensity dependence determined with 780 nm excitation for polycrystalline film.

Fig. 1 shows TRPL decays measured on a polycrystalline film with excitation at 540 nm (black) and 780 nm (red) using low laser power. According to Beer's law, light is attenuated to 10% of its intensity at the depth of $2.303/\alpha$, which is only 0.14 μm when 540-nm excitation is used and about four times larger, 0.56 μm , when 780-nm excitation is used. (Absorption coefficients are $\alpha_{540\text{nm}} = 1.7 \times 10^5 \text{ cm}^{-1}$ and $\alpha_{780\text{nm}} = 4.1 \times 10^4 \text{ cm}^{-1}$ [20].) Because polycrystalline film is $\approx 1.5 \mu\text{m}$ thick and surface recombination velocity, S , is not known, it is not clear if 1PE TRPL decays measured on thin films represent surface recombination, bulk recombination, or some combination of these two processes. Carrier separation due to surface band bending [21] might also contribute to observed TRPL decays when excitation is limited to the surface region. The initial carrier concentration (estimated assuming $2.303/\alpha$ absorption depth) for decays in Fig. 1 was $1.7 \times 10^{17} \text{ cm}^{-3}$ (540 nm) and $2.7 \times 10^{16} \text{ cm}^{-3}$ (780nm). Because net acceptor concentration in co-evaporated CZTSe is $p \approx 2 \times 10^{16} \text{ cm}^{-3}$ [10], high injection effects could also affect initial decay components for 540 nm excitation [5].

The two-exponential model (with deconvolution of IRF) was applied in data analysis:

$$I_{PL} = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2) \quad (1)$$

where I_{PL} is PL intensity, t is time, and A_1/A_2 are amplitudes of τ_1/τ_2 decay components. Lifetimes of the longer decay component were $\tau_2 = 4.4$ ns irrespective of 540 nm and 780 nm excitation was used. Lifetimes of the faster decay components were different: $\tau_{1_540nm} = 0.78$ ns and $\tau_{1_780nm} = 1.17$ ns. The relative amplitude of the faster decay component is larger when 540-nm excitation was used: $A_{1_540nm} = 88\%$ and $A_{1_780nm} = 70\%$ of the total decay amplitude, which supports attribution of the first decay component to recombination at the surface or to high-injection effects. Inset in Fig. 1 shows that with 780 nm excitation lifetimes τ_1/τ_2 are approximately constant when excitation intensity is varied from $(1.7 - 4.0) \times 10^{12}$ photons cm^{-2} pulse $^{-1}$. This characteristic suggests that when 780 nm excitation was employed, τ_1 in Fig. 1 was largely due to surface recombination. (High injection yields bimolecular decays where lifetime strongly depends on excitation intensity [5].) Because with 540 nm excitation injection was higher (due to larger α_{540nm}), τ_{1_540nm} might be affected by bimolecular recombination.

Further, Fig. 1 shows that 1PE TRPL measurement does not completely resolve charge-separation dynamics in polycrystalline PV devices. Decay measured with 540-nm excitation for a device (blue) is similar to that for the polycrystalline film (black). Based on these data, it is not clear what effect surface structures (CdS/CZTSe interface in a PV device vs. bare CZTSe absorber in polycrystalline film) and electronic band structures have on recombination and charge separation. To better differentiate 1PE data for polycrystalline films and PV devices we analyzed time-integrated PL intensity in Fig. 2.

Fig. 2. Integrated 1PE PL intensity dependence for polycrystalline film (red symbols) and PV device (blue symbols). Black solid lines indicate change of slope from 0.90 ± 0.03 at low injection to 1.77 ± 0.02 at high injection for polycrystalline film sample.

PL intensity, I_{PL} , for a p-type semiconductor is proportional to

$$I_{PL} \propto B \times (p + \Delta p) \times \Delta n, \quad (2)$$

where B is the radiative recombination coefficient, and $\Delta n = \Delta p$ are concentrations of photogenerated electrons and holes, respectively. For low injection, $p \gg \Delta p$ and $I_{PL} \propto \Delta n \propto I_{laser}$, where I_{laser} is excitation intensity. For high injection, $\Delta p \gg p$ and $I_{PL} \propto \Delta n^2 \propto I_{laser}^2$. These two limiting cases could be distinguished from the slope of the I_{PL} vs. I_{laser} graph in Fig. 2. When $I_{laser} = (2.3-53) \times 10^{12}$ photons cm⁻² pulse⁻¹, the

slope is 0.90 ± 0.03 . Slope increases to 1.77 ± 0.02 at high injection, which could indicate transition from low- to high-injection in measurements on polycrystalline film. Intensity-dependent PL characteristics for a PV device are different (Fig. 2, blue symbols), because charge-separation of electron/hole pairs also changes PL intensity and lifetimes. This is further analyzed in Section 3.3.

Next, we estimate surface recombination velocity, S , from the analysis of the first decay component τ_1 measured for a polycrystalline film. When laser excitation is absorbed close to the surface, S could be estimated from the initial slope (i.e., $1/\tau_1$) of the time-resolved data [22,35]:

$$\frac{1}{\tau_1} = \frac{1}{\tau_B} + \alpha S . \quad (3)$$

Eq. (3) was derived to analyze photoconductive decays for silicon [22] and applied to TRPL data for CdTe single crystals, [18] polycrystalline films, [18] and epilayers [35]. When $\alpha S \gg \tau_B^{-1}$, as is the case for direct-bandgap absorbers with large S , Eq. (3) does not allow estimating τ_B [18,35]. (Both terms could be determined for silicon [22].) Below, we show that τ_B could be measured when electron-hole pairs are created in the bulk of the absorber by employing 2PE.

When τ_1 determined with 540-nm and 780-nm excitation (Fig. 1) are used in Eq. (3) assuming $\tau_B \gg \tau_1$ (see Section 3.2), S could be estimated as $S = (0.8\text{--}2.1) \times 10^4 \text{ cm s}^{-1}$. Estimated S is smaller than that for polycrystalline or single-crystal CdTe ($S = (0.5\text{--}1.5) \times 10^5 \text{ cm s}^{-1}$ [18]), but higher than that for polycrystalline CuIn₁.

$x\text{Ga}_x\text{Se}_2$ with $x = 0.3$ (CIGS), where $S < 10^3 \text{ cm s}^{-1}$ [23]. In PV devices, S could be different due to changes in chemical and electronic structure. In particular, band alignment at the buffer (commonly, CdS) and absorber interface critically changes the interface recombination impact on the device [1]. Therefore, surface recombination velocity $S = (0.8\text{--}2.1) \times 10^4 \text{ cm s}^{-1}$ estimated in measurement on polycrystalline film is not necessarily the same as interface recombination velocity in a CdS/CZTSe PV device.

3.2. Two-photon excitation (2PE) TRPL decays for polycrystalline film

When ultrafast laser pulses of high intensity, but with photon energy smaller than E_g , are applied to semiconductors, electron-hole pairs could be created in a two-photon absorption process (Scheme I). The advantage of this approach is that carriers are photogenerated at the focus of the laser beam—which, for thick samples, could be separated from the surface [24,18,19]. In the case of $\approx 1.5\text{-}\mu\text{m}$ -thick absorbers, excitation volume spans all polycrystalline film (Scheme I). Because metal (Mo) layer is present as a substrate for polycrystalline film [6,7], 1560-nm photons that were not absorbed in the first pass could be reflected from the metal and generate additional electron-hole pairs. The reflection coefficient for Mo film at 1560 nm is ≈ 0.74 [20]. This value suggests that generation largely happens during the first pass of the 1560-nm laser beam through the absorber.

Fig. 3. Integrated PL intensity dependence measured with two-photon excitation (2PE) for CZTSe polycrystalline film.

To verify that one-photon absorption to/from defect bands or discrete states does not significantly contribute to PL signal when 1560 nm excitation was used, Fig. 3 shows 2PE PL intensity dependence. The slope of this line is 1.61 ± 0.06 , whereas the corresponding exponent for 1PE at low injection was 0.90 ± 0.03 (Fig. 2). Thus, PL intensity dependence in Fig. 3 agrees with a nonlinear two-photon generation process [18,24,25]. (As estimated below, this data was measured under low-injection.) Quantum efficiency spectra for CZTSe PV devices also show that absorption through defect states cannot be large [6,10,17].

Fig. 4. 2PE TRPL decay measured with excitation intensity 1.0×10^{16} photons cm^{-2} pulse $^{-1}$ (4.5-mW average laser power). Inset shows 2PE TRPL lifetime dependence on excitation intensity.

The excitation beam diameter in this 2PE measurement is ≈ 0.02 mm.

Relatively large excitation spot allows for lower injection and simplifies data analysis because carrier diffusion effects are significantly reduced [35]. Fig. 4 shows 2PE TRPL decay measured with low excitation intensity of 1.0×10^{16} photons cm^{-2} pulse $^{-1}$. This decay could be described as single-exponential with $\tau_B = 7.0 \pm 0.5$ ns. Within the uncertainty of the measurement, the lifetime was the same when the polycrystalline film was translated laterally and when the average laser power was decreased to 5.7×10^{15} photons cm^{-2} pulse $^{-1}$ or increased to 1.7×10^{16} photons cm^{-2} pulse $^{-1}$. Two-photon absorption coefficient, β , is not known for kesterites. Many

semiconductors have $\beta \approx 20 \text{ cm GW}^{-1}$ [26]. (This value is somewhat uncertain, because β also depends on the laser pulse length, and few β measurements employed pulses $< 1 \text{ ps}$.) If we assume $\beta = 20 \text{ cm GW}^{-1}$, $\beta I = 88 \text{ cm}^{-1}$ (where $I = 4.4 \text{ GWcm}^{-2}$ is excitation peak intensity, which corresponds to $1.0 \times 10^{16} \text{ photons cm}^{-2} \text{ pulse}^{-1}$ and 0.3-ps pulse length). Based on the estimated βI value, much less than 1% of 1560-nm photons are absorbed in polycrystalline CZTSe, and the injection level is $< 10^{15} \text{ cm}^{-3}$, which is an order of magnitude lower than the net acceptor concentration in coevaporated CZTSe ($p \approx 2 \times 10^{16} \text{ cm}^{-3}$ [10]).

Because 2PE TRPL decay in Fig. 4 was measured at low injection, it can be described as single-exponential, lifetime is independent of injection (in $(5.7\text{--}17) \times 10^{15} \text{ photons cm}^{-2} \text{ pulse}^{-1}$ range), and most of the PL signal is collected from the bulk of the absorber, the lifetime determined in this measurement could be regarded as the minority-carrier lifetime (i.e., $\tau_B = 7.0 \pm 0.5 \text{ ns}$).

As 1560-nm excitation power is increased, decays cease to be single-exponential and the lifetime of the dominant decay component decreases, as illustrated in the inset of Fig. 4. This effect might be related to high injection, albeit accurate injection-level analysis is not possible until kesterite two-photon absorption coefficients are measured and optical path length for 2PE excitation is determined.

Polycrystalline kesterites are disordered semiconductors and their PL emission spectra have been analyzed with models for donor-acceptor pairs (DAP) [27] and electrostatic potential fluctuations [28,13]. Such recombination happens by tunneling, the rate of which is very sensitive to the distance between defects;

therefore, lifetime changes with the injection level. Further, in the case of DAP recombination, PL decays are not exponential and the apparent lifetime decreases when the concentration of defects is increasing [29]. Spectroscopic and injection-level recombination analysis, similar to that recently reported for CIGS [30], is not yet possible because, in addition to tunneling recombination, kesterites have strong Shockley-Read-Hall (SRH) recombination due to unknown midgap states [28]. Thus, comparison of TRPL lifetimes for kesterites reported by different groups needs to be done with caution, because recombination mechanisms (SRH, tunneling, surface/interface) could vary for different absorber and device preparations, and could depend on measurement conditions.

Lifetime $\tau_B = 7$ ns is relatively short (e.g., corresponding value for CIGS could be as high as 200 ns [23,30]) and could be limited by recombination in the bulk or recombination at grain boundaries. Theory provides guidance about the identity of potential recombination centers in the bulk [31] and at grain boundaries [32]. Spectroscopic analysis of kesterite films and crystals with well-controlled composition is needed to test predictions about the origin of recombination centers. We note that for CZTSe films studied here, surface recombination does not appear to contribute to 2PE TRPL lifetimes, and the inherent complication of 1PE analysis could be avoided.

3.3 Two-photon excitation (2PE) TRPL decays for CdS/CZTSe PV device

Fig. 5. 2PE TRPL decays for CdS/CZTSe PV device measured with excitation intensity $1.0\text{--}8.4 \times 10^{16}$ photons cm^{-2} pulse $^{-1}$.

Fig. 5 shows intensity-dependent 2PE TRPL decays measured for a polycrystalline CdS/CZTSe PV device. The absorber for this device corresponds to polycrystalline film studied in Figs. 1 - 4. In section 3.2, we showed that 2PE measurement in this excitation range corresponds to low-injection (estimated as $<10^{15} \text{ cm}^{-3}$). The dynamics in Fig. 5 are much faster than corresponding data for polycrystalline film (Fig. 4), which is attributed to charge separation in a PV device. Therefore, 2PE measurement allows unambiguous identification of minority carrier lifetime (2PE measurement on a polycrystalline kesterite film) and observation of

charge separation dynamics (2PE measurement on a PV device). With 1PE, measurements on kesterite films and devices often yielded similar data [5-17], and therefore physical interpretation of TRPL decays in terms of material and device parameters are somewhat ambiguous.

Fig. 6. Lifetimes τ_1 and τ_2 obtained by fitting data in Fig. 5 to a two-exponential decay model.

2PE TRPL decays for a PV device in Fig. 5 are not single-exponential. Detailed computational analyses of TRPL data for thin film PV devices have been used in order to separate recombination and transport characteristics [33,34]. Two-exponential decay model has been used in computational studies; therefore we also apply this model to the data in Fig. 5. Intensity-dependent lifetimes of the decay components τ_1 and τ_2 are summarized in Fig. 6.

Numerical simulations or TRPL data have shown that the decay component τ_1 , when measured at lowest injection, usually indicates charge separation (drift) [33,34]. Because $\tau_B = 7$ ns (Fig. 4) and $\tau_1 < 0.5$ ns (Fig. 6), data suggest that charge separation is faster than recombination. Complex τ_1 intensity dependence suggest that charge separation dynamics are affected by the electric field due to photogenerated carriers, and numerical simulations that accurately reflect excitation conditions in 2PE measurement are necessary in order to determine drift and diffusion components of the decay.[33,34] To establish generation parameters for simulations, two-photon absorption coefficient β needs to be determined for polycrystalline kesterite absorbers.

The component τ_2 also has complex excitation-intensity dependence (Fig. 6). Simulations indicated that S and τ_B change τ_2 , and, in most cases, $\tau_2 < \tau_B$ [33,34]. In agreement with earlier computational studies, lifetime τ_2 measured for devices (Fig. 6, $\tau_2 = 1\text{--}2$ ns) is about four times shorter than τ_B measured for films (Fig. 4, $\tau_B = 7$ ns).

Thus, 2PE measurements on polycrystalline films appear to provide better assessment for τ_B . For TRPL data measured on PV devices, without detailed computational analysis, it is not possible to separate effects due to charge separation and recombination, regardless if 1PE or 2PE excitation conditions are used. 1PE TRPL measurements on polycrystalline films are dominated by surface recombination, whereas surface recombination effects on 2PE data are reduced due to the bulk generation profile provided by this measurement.

4. Summary

We have shown that combination of 1PE and 2PE TRPL analysis applied to polycrystalline thin films and PV devices allows determination of surface recombination velocity, bulk lifetime, and charge-separation dynamics at the pn junction. For state-of-the-art vacuum-deposited CZTSe absorbers, we find $S = 0.8\text{--}2.1 \times 10^4 \text{ cm s}^{-1}$ and $\tau_B = 7 \text{ ns}$.

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