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# 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, $\tau_B$, 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 $\tau_B$ in polycrystalline thin films. By comparing time-resolved photoluminescence data measured with 1PE and 2PE, we extract $\tau_B$ and surface recombination velocity $S$, and resolve charge separation at the pn junction. For coevaporated kesterite ($Cu_2ZnSnSe_4$) absorbers, we find $S=(0.8–2.1)\times 10^4$ cm s$^{-1}$ and $\tau_B=7.0\pm 0.5$ ns. For corresponding photovoltaic devices, charge separation occurs in $\leq 2$ ns.



## 1. Introduction

Interest in kesterite ($Cu_2ZnSnS_xSe_{4-x}$ 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, $\tau_B$, is thought to be an important contributor to $V_{OC}$ loss [3]. Although there are several approaches for the analysis of $\tau_B$ [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 1, 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.

We employ a new approach to analyze minority-carrier dynamics and recombination in polycrystalline $Cu_2ZnSnSe_4$ (CZTSe) thin films and PV devices. By varying excitation photon energy so that electron–hole pairs are created either $<0.15$ μm 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 $\tau_B$. 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 1). 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-μm Mo back contact. Then, 1.5 μm of slightly Cu-poor and Zn-rich CZTSe was co-evaporated while the substrate was maintained at 510 °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%,

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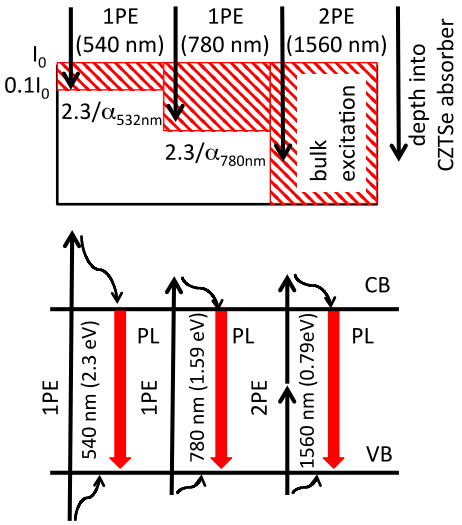


**Scheme 1.** Illustration of one-photon and two-photon excitation (1PE and 2PE, respectively) in thin film materials. Shaded area represents depth at which excitation light is attenuated to 10% of its initial intensity.

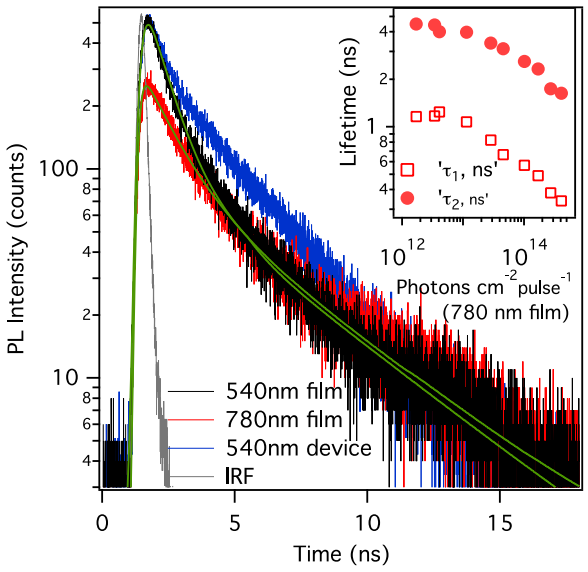


**Fig. 1.** 1PE TRPL decays measured using excitation at 540 nm (black, data for polycrystalline film; blue, data for corresponding PV device) and 780 nm (red, data for polycrystalline film). Excitation intensity was $2.3\times10^{12}$ photons $cm^{-2}$ $pulse^{-1}$ (540 nm) and $1.7\times10^{12}$ photons $cm^{-2}$ $pulse^{-1}$ (780 nm). Instrumental response function is shown in gray; results of two-exponential fitting of the data in green. Inset shows lifetime $\tau_1$ and $\tau_2$ intensity dependence determined with 780 nm excitation for polycrystalline film. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

open-circuit voltage = 373 mV, fill factor = 66.5%, and short-circuit current = 33.4 mA/$cm^2$.

### 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 $\geq$ 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 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 $\alpha_{540\ nm}=1.7\times10^5\ cm^{-1}$ and $\alpha_{780\ nm}=4.1\times10^4\ cm^{-1}$ [20].) Because polycrystalline film is $\approx$ 1.5 μm 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 $1.7\times10^{17}\ cm^{-3}$ (540 nm) and $2.7\times10^{16}\ cm^{-3}$ (780 nm). Because net acceptor concentration in co-evaporated CZTSe is $p\approx2\times10^{16}\ cm^{-3}$ [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:

$$I_{PL}=A_1exp(-t/\tau_1)+A_2exp(-t/\tau_2) \quad (1)$$

where $I_{PL}$ is PL intensity, $t$ is time, and $A_1/A_2$ are amplitudes of $\tau_1/\tau_2$ decay components. Lifetimes of the longer decay component were $\tau_2$ = 4.4 ns irrespective if 540 nm and 780 nm excitation was used. Lifetimes of the faster decay components were different: $\tau_{1\_540\ nm}$ = 0.78 ns and $\tau_{1\_780\ nm}$ = 1.17 ns. The relative amplitude of the faster decay component is larger when 540-nm excitation was used: $A_{1\_540\ nm}$ = 88% and $A_{1\_780\ nm}$ = 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 $\tau_1/\tau_2$ are approximately constant when excitation intensity is varied from $(1.7–4.0)\times10^{12}$ photons $cm^{-2}$ $pulse^{-1}$. This characteristic suggests that when 780 nm excitation was employed, $\tau_1$ 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 $\alpha_{540\ nm}$), $\tau_{1\_540\ nm}$ 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