Measurement of Carrier Dynamics in Photovoltaic CZTSe by Time-Resolved Terahertz Spectroscopy

Siming Li[1], Michael A. Lloyd[2], Andrew A. Golembeski[3], Brian E. McCandless[2], Jason B. Baxter[1]

[1] Drexel University, Department of Chemical and Biological Engineering, Philadelphia, PA, 19104, USA

[2] University of Delaware, Institute of Energy Conversion, Newark, DE, 19716, USA

[3] University of Rochester, Department of Chemical Engineering, Rochester, NY, 14611, USA

***Abstract* — We demonstrate the use of time-resolved terahertz spectroscopy coupled with numerical modeling of the transport equations to elucidate photoexcited carrier dynamics in a photovoltaic absorber. By measuring a high-quality $Cu_2ZnSnSe_4$ single crystal that exhibited device efficiency of 8.6%, we show that critical parameters including mobility, surface recombination velocity, and Shockley-Read-Hall lifetime can be obtained. Mobility values of 80 cm^2/Vs were validated with Hall effect measurements. Surface recombination velocity could be reduced by at least two orders of magnitude, to 10^4 cm/s, with appropriate chemical and mechanical polishing. Carrier lifetimes exceeding 10 ns indicate promise for devices with high photovoltage. Terahertz spectroscopy provides complementary insight to conventional time-resolved photoluminescence and is particularly valuable for materials that are not strongly emissive.**

I. Introduction

The design of efficient solar cells requires understanding how photoexcited carrier lifetimes, mobilities, and recombination mechanisms depend on structure and processing of photovoltaic (PV) absorber materials. Carrier dynamics in PV absorbers have conventionally been characterized by time-resolved photoluminescence (TRPL), which has indicated that V_{oc} increases logarithmically with carrier lifetime in CdTe and CIGS over wide ranges of processing conditions [1, 2]. Modeling of the TRPL response has provided insight into recombination mechanisms [3, 4]. However, not all materials are suitable for TRPL. Alternative non-contact probes can enable measurement of carrier dynamics for a broader range of materials.

Terahertz time-domain spectroscopy (THz-TDS) is a powerful technique to probe conductivity in conventional semiconductors because carriers typically have scattering rates on the order of 10^{12}-10^{14} s^{-1}. Time-resolved terahertz spectroscopy (TRTS) probes the transient far-IR response after photoexcitation with an optical pump pulse, with sub-picosecond time resolution [5]. Terahertz spectroscopy offers several advantages compared to TRPL. TRTS provides an alternative approach to measuring lifetime by tracking the transient photoconductivity, as well as enabling the calculation of carrier densities and mobilities. Additionally, THz-TDS enables determination of permittivity, free carrier density, and mobility via a non-contact measurement of the film without photoexcitation [5]. Measurements without photoexcitation primarily probe majority carriers, while measurements with photoexcitation under high injection conditions measure total conductivity including both electrons and holes.

Here we report on the application of TRTS to measure carrier dynamics and understand recombination mechanisms in single crystal $Cu_2ZnSnSe_4$ (CZTSe). While terahertz spectroscopy has been used for many years in other fields of science [5], it has rarely been applied to PV absorber materials [6, 7]. We have used a combination of numerical modeling of the transport equations with TRTS under different photoexcitation conditions to elucidate dominant recombination mechanisms and rate constants. We found that surface recombination controls the dynamics on the sub-nanosecond time scale, but surface recombination could be reduced by a factor of 10^2 by polishing and chemical treatment of the as-cleaved crystal.

II. CZTSe Crystal Growth and Properties

Single crystals of CZTSe material were synthesized using methods described by Bishop et al. [8]. Elemental precursors of 5-6N purity were sealed in quartz ampules at a base pressure of 5×10^{-6} torr. CZTSe growth and grain ripening were promoted at 750°C over a 20-day period. Ampoules were allowed to naturally cool to room temperature over approximately 36 hours. For this work, one particular single crystal was extracted from the resulting multicrystalline boule and mechanically planarized. One side was then further polished with a fine alumina slurry to reduce mechanical damage resulting from the abrasive grinding step. The crystal was treated with a 10-minute solution etch with 0.125% bromine in methanol to clean the surface before characterization.

The sample used for this study was 4x3x1 mm in size and was confirmed to be a single crystal by Laue diffraction. Energy-dispersive X-ray fluorescence spectroscopy (XRF) calibrated with inductively coupled plasma mass spectroscopy (ICP) showed Cu/(Zn+Sn) = 0.87 and Zn/Sn = 1.22. These values fall within the Cu-poor, Zn-rich regime that has been

shown to promote optimal efficiency in CZT(S,Se) devices [9]. Crystals exhibited strong p-type conduction with DC mobility of 89 cm^2/Vs and hole concentration of 8.7×10^{16} cm^{-3}, as determined by Hall effect measurement. The band gap of a sister crystal was determined by spectrally resolved photoluminescence and external quantum efficiency measurements to be 0.95-0.98 eV. A solar cell fabricated from the sister crystal exhibited an efficiency of 8.6% with V_{oc} = 389 mV, J_{sc} = 35.2 mA/cm^2, and FF = 62.6%, demonstrating the high quality of the CZTSe.

III. Ultrafast Carrier Dynamics

TRTS was carried out in transmission geometry using 50-fs pulses from a regeneratively amplified Ti:Sapphire laser. THz pulses were generated and detected by optical rectification and free-space electro-optic sampling with ZnTe crystals [5]. The optical pump wavelength was tuned with an optical parametric amplifier, and the pump – probe delay time was controlled using an optical delay line. The crystal was cooled to 77 K in an optical cryostat to freeze out holes, avoiding deleterious absorption of the terahertz probe by non-photoexcited carriers.

Fig. 1a shows the dynamics of the differential transmitted terahertz probe, normalized to the maximum response, for two pump wavelengths incident on the unpolished surface of the crystal. We have previously shown that the mobility is independent of pump – probe delay time [10], so can conclude that the dynamics are proportional to the photoexcited carrier density integrated through the sample thickness. The response shows an instantaneous rise as carriers are photoexcited, then a decay as they recombine or are trapped in non-conductive states. Dynamics are faster with higher energy photons because they are absorbed more strongly, and generated carriers are prone to surface recombination. With 400 nm excitation, 80% of the carriers recombine within 100 ps. Conversely, lower energy photons have longer penetration depths and carriers are less likely to recombine at the surface. With 900 nm excitation, 40% of carriers remain after 1.4 ns, consistent with our previous report for CZTSSe thin films [10].

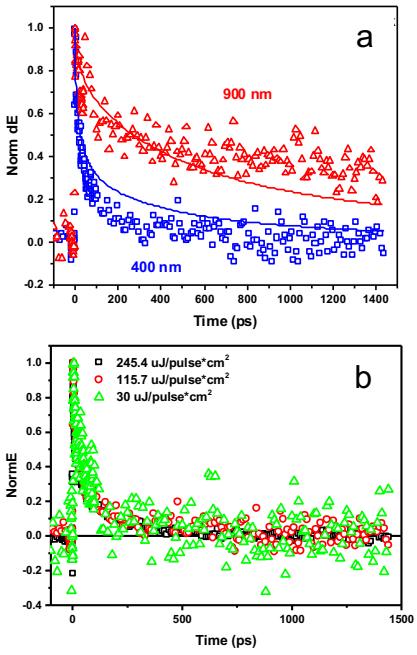

Fig. 1. TRTS dynamics of unpolished crystal under (a) variable pump wavelength and (b) variable pump fluence.

Figure 1b shows normalized dynamics at three pump fluences spanning a range of 10x. Dynamics are independent of fluence, which indicates that Auger and radiative recombination are not significant. Recombination can be attributed to trap-mediated events in the bulk (Shockley-Read-Hall, SRH) and at the surface.

In our previous paper, we fit the dynamics with an empirical bi-exponential model, where the fast and slow time constants were roughly assigned to surface and bulk recombination [10]. Here we show that dynamics can instead be modeled by the time-dependent transport equations to extract physical parameters that provide key insight into solar cell design.

The measured signal, $\Delta E_{THz}(t)$, is proportional to $\int \Delta n(x,t)dx$, where Δn is the photoexcited carrier density, x is the distance into the crystal, and t is the pump-probe delay time. The transport equations can also be solved to find $\Delta n(x,t)$, which is controlled by mobility (μ), SRH lifetime (τ_{SRH}), surface recombination velocity (S), and absorption coefficient at the pump wavelength (α). We neglect the photo-Dember effect and assume that electrons and holes move in a way that preserves charge neutrality. This enables solution of the continuity equation for a single carrier using an ambipolar mobility, rather than simultaneously solving the continuity equations for both carriers along with Poisson's equation. To find $\Delta n(x,t)$, we numerically solved the continuity equation

$$\frac{\partial \Delta n}{\partial t} = D\frac{\partial^2 \Delta n}{\partial x^2} - \frac{\Delta n}{\tau_{SRH}} \qquad (1)$$

with an initial carrier density profile determined by Beers' Law with absorption coefficient α, subject to a surface recombination boundary condition at the front surface and $\Delta n=0$ at the rear surface. D, τ_{SRH}, and S were allowed to vary to achieve the best fit for the thickness-integrated photoexcited carrier density. α at 400 and 900 nm was fixed at 2.1 and 0.5 $x10^5$ cm^{-1}, respectively, from spectroscopic ellipsometry of a CZTSe single crystal of similar composition in Ref. [11]. Kinetic traces can be fit individually or in groups with shared parameters to reduce uncertainty.

Both data sets in Fig. 1a were fit with a globally shared set of parameters, except for the absorption coefficients. The model fits are shown as lines. The best fit parameters are $S > 10^6$ cm/s, D=0.53 cm^2/s (giving ambipolar mobility of 80 cm^2/Vs at 77 K that is consistent with the Hall effect measurement), and τ_{SRH}>10 ns. Clearly, surface recombination is the dominant loss mechanism under these conditions. τ_{SRH} indicates long lifetimes desirable for high-efficiency devices,

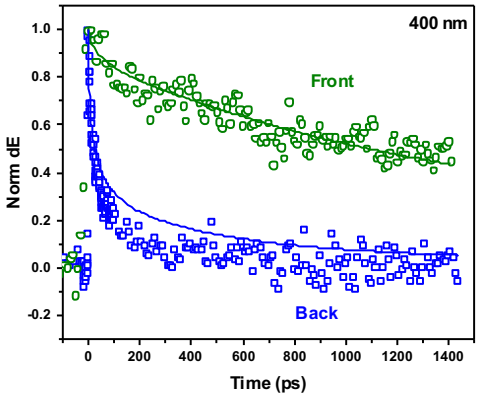

Fig. 2. TRTS dynamics with 400 nm photons incident on the front (polished) and back (unpolished) sides of the crystal, illustrating the difference resulting from surface recombination.

but exhibited large uncertainty due to the fast surface recombination and the length of the optical delay line in the TRTS, which limited pump-probe delay times to 1.4 ns.

For comparison, the photoconductivity can be determined from the magnitude of the terahertz response, and the mobility can be calculated subject to assumptions regarding the generation profile. Photoexcitation with 14 μJ/cm^2 fluence at 400 nm results in an average density of electron-hole pairs of 6x10^{18} cm^{-3} over the skin depth and total terahertz mobility, $\mu_n+\mu_p$, of 280 cm^2/Vs. Further details of the analysis can be found in Ref. [6]. Assuming similar electron and hole mobilities, the terahertz mobility is consistent with mobility derived from the transport model to within a factor of 2.

Surface recombination velocity of the unpolished surface of the CZTSe crystal is unacceptably high for device applications. However, *S* could be considerably reduced by polishing the surface before the Br/methanol etch. Fig. 2 shows the photoexcited carrier dynamics with and without polishing, using photoexcitation at 400 nm to exaggerate the effect of surface recombination. Lines show the model fits, where the bulk parameters are the same as in Fig. 1a but the fitted value of $S_{polished}$ was 1x10^4 cm/s. Polishing reduced the surface recombination velocity by at least two orders of magnitude.

Photoexcitation of the polished crystal with 900 nm photons minimized the effects of surface recombination and resulted in nearly flat dynamics over the 1.4 ns range measured, confirming the previous estimate of τ_{SRH}>10 ns. Such lifetimes are comparable to the best reported in literature [9].

The transient profile of the carrier density was reconstructed from the fitted parameters of the model and is shown in Fig. 3a and 3b for the unpolished and polished surface, respectively. Our assumptions dictate that the carrier density profile will be the same for electrons and holes. Simulations of the unpolished crystal face show that the predominant transport is diffusion toward the surface due to the fast recombination. In contrast, when surface recombination is passivated by the polishing process, diffusion is primarily into

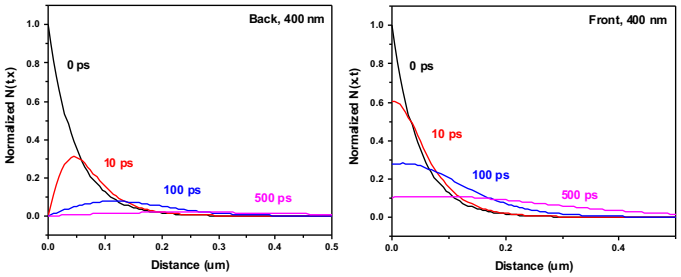

Fig. 3. Evolution of the photoexcited electron density, Δn(x,t), after an initial 400 nm photoexcitation pulse, with surface recombination velocities depending on polishing treatment.

the crystal because of the initial concentration gradient that arises from the Beers' law absorption profile.

IV. Conclusions

The combination of TRTS and numerical simulations of the transport equations can provide unique insight into photoexcited carrier dynamics and limiting recombination mechanisms relevant to thin film solar cells. Here, the single-crystal CZTSe eliminates complications arising from grain boundaries and high densities of point defects and secondary phases associated with thin film growth. Under these conditions, we found SRH lifetimes exceeding 10 ns at 77 K, with surface recombination as the dominant loss mechanism, and ambipolar mobilities of 80 cm^2/Vs. The mobility is similar to that found by conventional Hall effect, which is an encouraging validation of this method. These parameters would result in diffusion lengths of ~700 nm, which is similar to the thickness necessary for light absorption, and the long lifetimes indicate promise for high photovoltages.

Acknowledgements

The authors acknowledge support from the National Science Foundation through collaborative awards DMR-1507988 and DMR-1508042.

References

[1] W. K. Metzger, D. Albin, D. Levi, P. Sheldon, X. Li, B. M. Keyes, *et al.*, "Time-resolved photoluminescence studies of CdTe solar cells," *Journal of Applied Physics,* vol. 94, pp. 3549-3555, 2003.

[2] I. L. Repins, W. K. Metzger, C. L. Perkins, J. V. Li, and M. A. Contreras, "Correlation Between Measured Minority-Carrier Lifetime and Cu(In, Ga)Se$_2$ Device Performance," *IEEE Transactions on Electron Devices,* vol. 57, p. 2957, 2010.

[3] A. Kanevce, D. H. Levi, and D. Kuciauskas, "The role of drift, diffusion, and recombination in time-resolved photoluminescence of CdTe solar cells determined through numerical simulation," *Progress in Photovoltaics: Research and Applications,* 2013.

[4] M. Maiberg, T. Hölscher, S. Zahedi-Azad, and R. Scheer, "Theoretical study of time-resolved luminescence in semiconductors. III. Trap states in the band gap," *Journal of Applied Physics,* vol. 118, p. 105701, 2015.

[5] J. B. Baxter and G. W. Guglietta, "Terahertz Spectroscopy," *Analytical Chemistry,* vol. 83, pp. 4342-4368, 2011.

[6] H. Hempel, A. Redinger, I. Repins, C. Moisan, G. Larramona, G. Dennler*, et al.*, "Intragrain charge transport in kesterite thin films-Limits arising from carrier localization," *Journal of Applied Physics,* vol. 120, 2016.

[7] L. Q. Phuong, M. Okano, G. Yamashita, M. Nagai, M. Ashida, A. Nagaoka*, et al.*, "Photocarrier dynamics in undoped and Na-doped Cu_2ZnSnS_4 single crystals revealed by ultrafast time-resolved terahertz spectroscopy," *Applied Physics Express,* vol. 8, p. 062303, 2015.

[8] D. M. Bishop, B. E. McCandless, R. Haight, D. B. Mitzi, and R. W. Birkmire, "Fabrication and Electronic Properties of CZTSe Single Crystals," *IEEE Journal of Photovoltaics,* vol. 5, pp. 390-394, 2015.

[9] S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, T. K. Todorov, and D. B. Mitzi, "Low band gap liquid-processed CZTSe solar cell with 10.1% efficiency," *Energy & Environmental Science,* vol. 5, p. 7060, 2012.

[10] G. W. Guglietta, K. R. Choudhury, J. V. Caspar, and J. B. Baxter, "Employing time-resolved terahertz spectroscopy to analyze carrier dynamics in thin-film Cu2ZnSn(S,Se)4 absorber layers," *Applied Physics Letters,* vol. 104, p. 253901, 2014.

[11] M. León, S. Levcenko, R. Serna, I. V. Bodnar, A. Nateprov, M. Guc*, et al.*, "Spectroscopic ellipsometry study of $Cu_2ZnSnSe_4$ bulk crystals," *Applied Physics Letters,* vol. 105, p. 061909, 2014.