Microsecond Carrier Lifetimes in Polycrystalline CdSeTe Heterostructures and in CdSeTe Thin Film Solar Cells

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***Abstract*—We report significant advances in understanding and reducing nonradiative Shockley-Read-Hall recombination in polycrystalline $CdSe_xTe_{1-x}$, leading to microsecond charge carrier lifetimes. In undoped Al_2O_3-passivated heterostructures we find external radiative efficiency 0.2%, quasi-Fermi level splitting 950 mV, mobility 100 $cm^2/(Vs)$, and diffusion length 14 μm. In solar cells measured lifetimes can exceed 1 μs. We interpret this data to indicate MgZnO/CdSeTe interface recombination velocity <100 cm/s. Based on our results, it appears CdTe PV technology has potentially overcome longstanding "recombination lifetime" limitation and in the near future will transition to improving other aspects of device design.**

Keywords—recombination, photoluminescence, CdTe, thin film, solar cells, charge carrier lifetime

I. Introduction

Silicon PV leads in the market, but direct bandgap thin film materials, especially CdTe, have potentially lower cost structure with comparable efficiency, superior temperature and spectral coefficients, and lower degradation. Efficiency improvements for all PV technologies are needed. For CdTe, roadmaps indicate paths to 25% cell efficiency if recombination losses are reduced. The largest current limitation is V_{OC} (open circuit voltage) which in record-efficiency polycrystalline CdTe solar cells is 880 mV, or 76% of the Shockley-Queisser (SQ) limit for the 1.42 eV bandgap. In single crystal solar cells higher V_{OC} was demonstrated (1017 mV in p-type and 1096 mV in n-type; 1.50 eV CdTe bandgap). Making comparable improvements in polycrystalline devices is a considerable research opportunity.

One of the challenges is identifying dominant V_{OC} loss locations, which can include interfaces or absorber bulk. In addition to recombination loses, V_{OC} can be reduced due to electronic disorder / potential fluctuations / band tails that effectively reduce bandgap and thus voltage entitlement.

Interface recombination can lead to considerable losses in CdTe solar cells. To reduce interface recombination, large-grain polycrystalline double heterostructures (DHs) passivated with Al_2O_3 were developed. While the passivation mechanism is not fully understood, interface recombination velocity S < 100 cm/s, and due to reduced interface recombination in DHs we can analyze semiconductor bulk properties. For $CdSe_xTe_{1-x}$ DHs with x = 0.2, quasi-Fermi level splitting qFLS = 950 mV, carrier lifetime 750 ns, external radiative efficiency 0.2%, mobility 100 $cm^2/(Vs)$, and diffusion length 14 μm. [1] Thus, with passivating and carrier-selective device contacts, more efficient solar cells should be possible. In this paper we describe some additional x = 0.2 heterostructure characteristics and compare electro-optical properties for model (Al_2O_3/CdSeTe) and device (MgZnO (MZO)/CdSeTe) interfaces.

For devices, we investigated MZO/CdSeTe/CdTe/Te architecture, which recently achieved 20% power conversion

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efficiency. [2] Unlike DHs, devices are doped. We show that lifetimes in As-doped devices can reach 1 μs, therefore dopants do not introduce significant recombination centers.

II. Experimental

A. Device and heterostructure fabrication

More than 50 $CdSe_xTe_{1-x}$ DHs were fabricated and characterized. [1] Device fabrication will be described at this conference by co-authors. [2]

B. Characterization

One- and two-photon excitation (1PE/640nm and 2PE/1120 nm) TRPL, photoluminescence (PL), cathodoluminescence (CL), and light induced transient grating (LITG) spectroscopy were used to study CdSeTe electronic properties.

III. Results and Discussion

A. Charge carrier lifetimes in Al_2O_3 heterostructures

We reported 430 ns, [3] 700 ns, [4] and 750 ns [1] lifetimes (as measured by TRPL) in $Al_2O_3/CdSe_{0.2}Te_{0.8}/Al_2O_3$ DHs. Such lifetimes exceed earlier results, and we consider if carrier trapping/detrapping can be responsible for increased lifetimes. We address this issue from injection-dependent (Fig. 1) and temperature-dependent (Fig. 2) TRPL measurements.

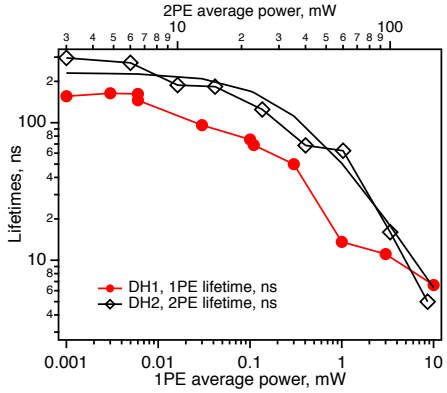

Fig. 1. Injection-dependent 1PE and 2 PE TRPL lifetimes for two DHs.

Injection-dependent lifetimes τ_{TRPL} in Fig. 1 are well described by a model that takes into account SRH (lifetime τ_{SRH}) and radiative (lifetime τ_{rad}) recombination rates:

$$\frac{1}{\tau_{TRPL}} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{rad}} = \frac{1}{\tau_{SRH}} + B(doping + injection) \quad [1]$$

Where B = 1×10^{10} cm^3/s is a radiative recombination coefficient. At <10 μW (1PE) and <10 mW (2PE) measured lifetimes become injection-independent and are accurate low-injection SRH lifetimes. This excitation corresponds to $<10^{15}$ cm^{-3}, which is expected hole density for undoped CdSeTe. Data is dominated by radiative recombination at higher injection. When injection is varied 10,000 times, data in Fig. 1 does not indicate "trap saturation".

TRPL(temperature) measurements allow evaluating radiative, SRH, and detrapping (lifetime τ_{trap}) rates because these processes have different temperature dependence. Representative data is shown in Fig. 2, where at 50 – 200 K recombination rate is essentially independent of temperature, and measured lifetimes decrease by 4x when temperature increases from 200 K to 350 K.

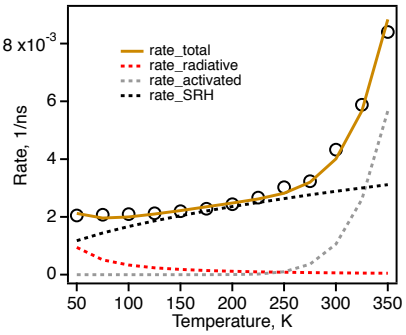

Fig.2. Temperature-dependent recombination rates measured with low-injection 2PE TRPL. Dashed lines show SRH, radiative, and detrapping rates, solid line shows overall fit to Eq. [2].

Data in Fig. 2 were fit as a sum of three temperature-dependent processes: [5]

$$\frac{1}{\tau_{TRPL}} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{trap}} = \frac{C_{SRH}}{T^{0.5}} + C_{rad}T^{1.5} + \frac{C_{trap}}{T^{0.5}}\exp\left(\frac{E_a}{kT}\right) \quad [2]$$

Where C_i are constants and T is temperature. Fit (solid line) indicates that at <330 K data is dominated by SRH recombination (black), and at >330 K by exponentially activated rate with activation energy E_a = 0.29 ± 0.05 eV. Hole traps at similar energy were identified in undoped single crystal CdTe DHs. [6] This feature is important and such defects might be present in devices, but defects 0.29 eV above the valence band maximum are not minority carrier traps.

In summary, detailed TRPL analysis here and earlier [1, 4] for DHs with x = 0.2 is consistent with a "simple" recombination model described by Eqs. [1] and [2].

B. Comparison of TRPL lifetimes for MZO and Al_2O_3 DHs

Alumina is insulating, so DHs described in Section A are model structures that can't be used in electrical devices such as solar cells. Some state-of-the art solar cells [2] use MZO front buffer layers, and it is interesting to compare recombination properties at MZO/CdSeTe and Al_2O_3/CdSeTe interfaces. Figure 3 shows initial results of such analysis.

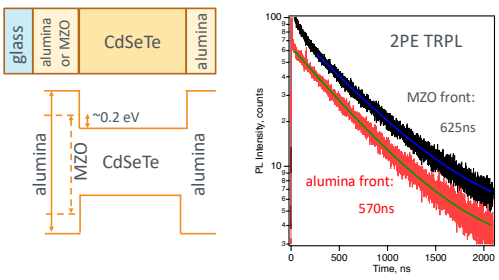

Fig.3. Left: Illustration of Al_2O_3/Al_2O_3 and MZO/Al_2O_3 DHs. Right: Low injection 2PE TRPL decays for MZO and Al_2O_3 heterostructures.

We fabricated DHs illustrated in Fig. 3, where the front interface of the $CdSe_{0.2}Te_{0.8}$ absorber is passivated by Al_2O_3 or MZO while keeping other fabrication steps the same. [1] The back-contact is passivated with Al_2O_3 in both structures. 2PE TRPL lifetimes measured under similar excitation conditions are comparable, 570ns for Al_2O_3 front interface and 625 ns for MZO front interface.

Assuming that bulk and grain boundary (GB) properties in Al_2O_3 and MZO DHs are the same, which is supported by PL and CL data, interface recombination velocity S_{int} is similar for MZO/CdSeTe and Al_2O_3/CdSeTe interfaces, and estimated value $S_{int} \leq 200$ cm/s. Additional measurements and analysis are needed for MZO/CdSeTe interfaces, and structures such as shown in Fig. 3 provide test samples for such investigations.

C. TRPL lifetimes in devices

Figure 4 shows device structure and TRPL data for As-doped CdSeTe/CdTe/CdSeTe device. As-doping is used to increase net acceptor density in the absorber. While near interface CdSeTe layer is undoped, As can diffuse to the front of the device during the $CdCl_2$ treatment. [2] Absorber for the case shown in Fig. 4 is relatively thick, which reduces the impact of the back-contact recombination.

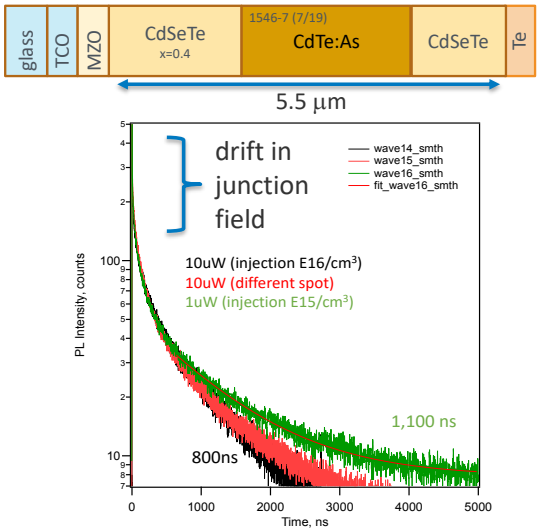

Fig.4. As-doped solar cell structure and low injection TRPL measured through glass/front junction

TRPL data for devices is complicated because of carrier drift and diffusion in the space charge field of the junction. Numerical analysis is required to estimate interface recombination velocities, bulk lifetimes, and other parameters. [7] We are developing such simulations for current device architectures. [8] When the impact of the back-contact recombination is reduced, the lifetime for the "tail of TRPL decay" can be similar to the minority carrier lifetime. For the case shown in Fig. 4, such lifetimes are 800 – 1100 ns. Similar results were reproduced for a number of solar cell structures. Modeling is in progress to determine bulk lifetime, band offset, doping, and other parameter sensitivity. [8]

IV. Summary

TRPL measurements on state-of-the-art polycrystalline CdSeTe DHs and CdSeTe/CdTe devices show that carrier lifetimes can reach and exceed 1 µs, which indicates excellent bulk and front interface electronic properties. Quasi-Fermi level separation is approaching 1V [1, 9], but device V_{OC} does not increase proportionally with lifetimes, as was observed in absorbers without Se. [10,11]

It appears that CdTe PV technology has potentially overcome longstanding "recombination lifetime" limitation, and in the near future will transition to improving other aspects of solar cell device design. The fundamental mechanisms that lead to recombination lifetime increase from ≈2 ns [11] to 1 µs (here and Refs. [1, 2]) still need to be understood in terms of device and material defect models, and this knowledge needs to be applied when making more efficient solar cells.

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