Combined Electrical and Optical Characterisation of Recombination Mechanisms and Minority Carrier Lifetime in Solar Cells

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Abstract
This work presents the development of a measurement system which combines optical and electrical characterisation of carrier lifetime and recombination mechanisms of thin film solar cells. It combines spectrally-resolved photoluminescence (PL), time-resolved photoluminescence (TRPL), and transient photocurrent (TPCD), which are measured using a single excitation laser source at the same spot of the solar cell.
Initial PL, TRPL and TPCD measurements have been conducted on CdS/CdTe and MZO/CdTe samples. The resulting PL spectra show emission peaks corresponding to the material bandgap. Under the same excitation conditions and same measurement spot, initial TRPL and TPCD measurements were successfully conducted, yielding effective carrier lifetime values (τ_1=1.39ns, τ_2=3.91ns) and (τ=40.5ns), respectively for the CdS/CdTe sample and (τ_1=0.98ns, τ_2=3.3ns) and (τ=36.8ns), respectively for the MZO/CdTe sample. These values are affected by different recombination processes in solar cells. Therefore, as well as characterising solar cell material quality, the electronic properties of the finished PV device can also be characterised.

1. Introduction
Carrier lifetime is one factor that defines material quality of solar cells and affects the overall efficiency of a photovoltaic (PV) device. Accurate determination of carrier lifetime is important for developing high efficiency PV devices. Time-resolved photoluminescence (TRPL), transient photovoltage decay (TPVD) and transient photocurrent decay (TPCD) are three such characterisation techniques.
The carrier lifetime is analysed using the transient decay of the optical signal from TRPL and the electrical signal from TPVD/TPCD measurements. TPCD is measured when the PV device is near short-circuit (I_{SC}) conditions while TPVD is measured near open-circuit (V_{OC}) conditions [1]. Transient decay is affected by different physical processes in solar cells to various degrees. TRPL is mainly influenced by the radiative recombination and diffusion of minority carriers in the quasi-neutral regions [2], whereas transient electrical characterisation is affected by all the recombination processes (including Shockley-Read-Hall (SRH) non-radiative and Auger) and other factors, such as device junction/measurement system capacitance, series and shunt resistances [3][4]. Furthermore, it is difficult to determine or quantify the source of SRH recombination using only TRPL [5].
For these reasons, it is advantageous to combine TRPL and TPCD/TPVD using a single excitation laser source to separate the contributions of radiative and non-radiative SRH recombination, identifying material defects and sources of SRH recombination. Crucially, this is done within the same measurement system, avoiding the repositioning errors inherent in sequential characterisation in different measurement systems and thus probing the same point in the solar cell. Furthermore, this approach can be used to establish a link between material quality and PV device efficiency.
A measurement system combining PL and TRPL and TPCD/TPVD is currently being developed at CREST and is near completion. The details of this system and the initial results are presented and discussed in this work.

2. Combined Measurement System
Figure 1 shows the overall measurement system schematic. The excitation source is a pulsed picosecond laser with a wavelength of 640nm. The laser is reflected onto a 650nm dichroic mirror. The dichroic mirror re-directs the laser light into a 10× objective lens which focusses the laser onto the sample.
The resulting luminescence from laser excitation of the sample is collected and collimated by the same objective lens. It is transmitted through the 650nm dichroic mirror, blocking most of the laser light. A 650nm high pass filter is used to block any remaining laser light. The luminescence is focussed by a lens into the input slit (600µm) of a monochromator. The monochromator is used for wavelength scanning during PL measurements and for selecting the TRPL measurement wavelength.
A rotating prism mirror is used at the output of the monochromator to direct the luminescence to three photodetectors: An amplified InGaAs photodiode with an extended wavelength range

(500nm-1700nm) and two photomultiplier tubes (PMT) (230-920nm range) and (950-1700nm range). Both PMTs use an adjustable iris for signal attenuation. The PMTs are connected to a time correlated single photon counting (TCSPC) PCIe electronic board to measure TRPL while the photodiode is connected to a National Instruments data acquisition card to measure spectrally resolved PL.

For electrical measurements, the sample is contacted by probes which are connected to an 11GHz digital sampling oscilloscope with a 50Ω input impedance via a matching SMA coaxial cable. The synchronisation signal of the laser driver is connected to the trigger channel of the oscilloscope for triggering of TPCD measurements.

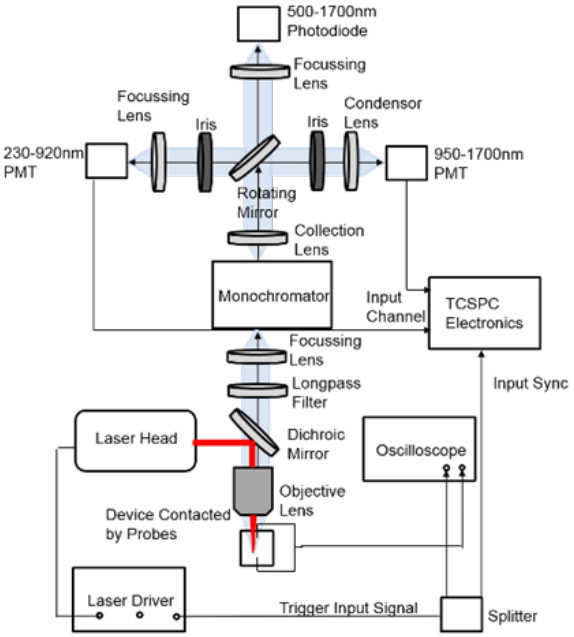

Figure 1 Measurement system schematic

3. Combined Measurements

Initial combined PL, TRPL and TPCD measurements were conducted on a Cadmium Sulfide/Cadmium Telluride (CdS/CdTe) sample and a Magnesium Zinc oxide/ Cadmium Telluride (MZO/CdTe) sample which were both fabricated at CREST.

3.1 PL Measurements

PL is a contactless technique which can be used to characterise the bandgap, defects and recombination mechanisms of semiconductor materials. The laser excitation was pulsed at 2.5MHz for the CdTe samples. The wavelength range of the scan was from 700nm (1.77eV) to 1000nm (1.24eV) and a measurement time of 0.1s at each point. An average of 3 measurements was recorded for each sample.

Figure 2 shows normalised PL spectra of the samples. It was observed from qualitative analysis that the PL spectra of the samples have one or two broad emission peaks which correspond to the material bandgap, which is the main source of radiative band-to-band recombination. The CdS/CdTe sample has two main emission peaks at ~1.47eV and ~1.50eV. The peak at 1.50eV is attributed to the CdTe layer while the peak at 1.47eV is attributed to the CdS_xTe_{1-x} layer. The formation of this CdS_xTe_{1-x} layer results from the diffusion of S into the CdTe layer, which is caused by the annealing $CdCl_2$ treatment as detailed in [6][7].

The MZO/CdTe sample uses a transparent n-type window layer of MZO instead of CdS. This is to reduce the light absorbed in the window layer to allow for greater light absorption in the CdTe p-type layer [8]. This is reflected in the PL spectrum of MZO/CdTe, where there is a main emission peak at 1.51eV which is due to excitation and radiative recombination in the CdTe layer.

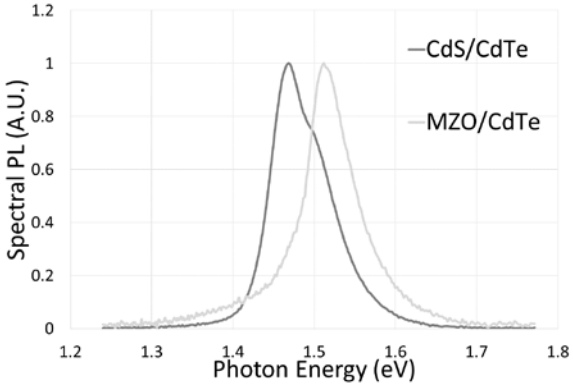

Figure 2 Normalised PL spectra of a CdS/CdTe and MZO/CdTe sample

3.2 TRPL Measurements

Once the PL spectrum of a sample has been measured, the wavelength where the PL emission signal is the highest can be selected for TRPL. TRPL measurements in this work were conducted using the TCSPC method. TCSPC works by the detection of single photons from the sample emission and measuring their time of arrival with respect to a reference signal. A repetitive excitation source is required to accumulate a large number of photon events. The minority carrier lifetime is extracted for further analysis from the histogram of photon arrival time [9]. The decay curves are typically fitted with the multi-exponential model:

$$I = y + \sum_i A_i \, exp^{(-t/\tau_i)}$$

Where y is the offset, A is the amplitude, t is the time and τ is the extracted carrier lifetime

Figure 3 shows the TRPL curves of the two CdTe samples. The monochromator wavelength was set at 846nm (1.47eV) for the CdS/CdTe sample and 821nm (1.51eV) for the

MZO/CdTe sample to measure TRPL at the PL maximum where the rate of radiative recombination is highest. A laser frequency of 2.5MHz was used for excitation and as the reference signal for the TCSPC card. The measurement integration time was 30s and a background measurement was subtracted from the decay curves. The number of exponential decays used for fitting depends on the decay profile. For these particular samples, a double exponential decay function was found to be a suitable fit for the curves. This double fitting has also has also been used to fit TRPL decays of CdTe cells in previous work [10]. τ_1 is the charge separation in the PN junction τ_2 is the recombination in the bulk material [10]. The extracted values were (τ_1=1.39ns, τ_2=3.91ns) for the CdS/CdTe sample and (τ_1=0.98ns, τ_2=3.3ns for the MZO/CdTe sample which is in the expected ns regime for CdTe [10][11]. It should be noted that the instrument response function (IRF) of the system has not been deconvoluted during the fitting, which will result in a slight overestimation of the carrier lifetime.

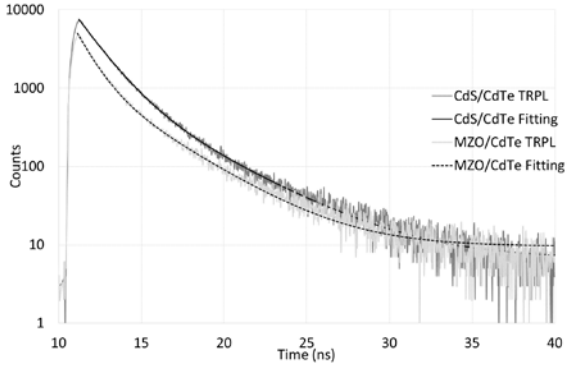

Figure 3 Room temperature TRPL decay curves of a CdS/CdTe and MZO/CdTe sample measured at 846nm and 821nm, respectively with 30s integration time fitted with a double exponential decay function

3.3 TPCD Measurements

The next step was to combine the above optical characterisation with transient electrical characterisation from the previous work [12]. During TPCD measurements, the PV device is connected directly to the oscilloscope. Each laser pulse creates excess carriers and thus generates a photovoltage. The subsequent decay is measured as a function of time and the effective minority carrier lifetime can be extracted. TPCD and TRPL were measured simultaneously at the same excitation spot with the same laser.

The TPCD curves in Figure 4 show an initial rapid rise of voltage followed by a slower exponential decay process. During measurements, it was observed that the TPCD peak voltage depended on laser focus point (distance from sample to objective lens). As the area of the excitation laser point decreased moving towards the working distance of the objective lens, the peak voltage decreased. Increasing the intensity of the laser had little effect in the signal. This is likely due to the decreased excitation area resulting in free carriers having to travel further to the probes than if the excitation area was larger. Fewer charge carriers will be extracted and transported to the external circuit, resulting in a lower measured voltage.

A single exponential decay was used to fit the two decay curves and carrier lifetimes of 40.5ns for CdS/CdTe and 36.8ns for MZO/CdTe were extracted. As was expected, the carrier lifetime measured electronically by TPCD is longer than optically by TRPL. This is because TPCD is not only affected by the recombination processes, but also by the charge collection and extraction efficiency of the device as well. Furthermore, there was also no external light biasing, so junction capacitance and trap energy level capture effects will dominate the TPCD extracted carrier lifetime.

TPCD therefore provides information on the overall finished PV device efficiency. The TRPL carrier lifetime values are measured optically and are proportional to the radiative recombination rate [5]. TRPL cannot quantify or identify the source of SRH recombination, which is detrimental to the overall PV device efficiency. Using both of these extracted carrier lifetime values, the SRH recombination can potentially be quantified and material defects can be identified, improving the finished PV device efficiency.

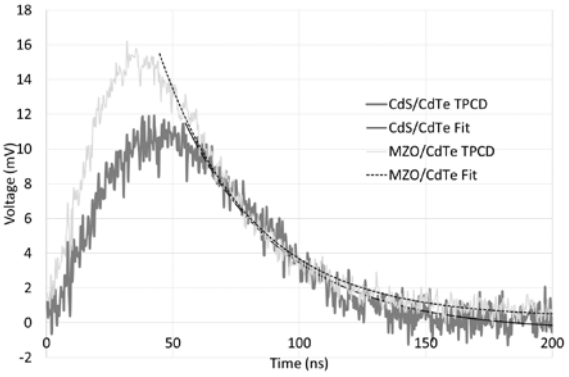

Figure 4 Corresponding room temperature TPCD curves of a CdS/CdTe and MZO/CdTe sample measured under 640nm wavelength and 2.5MHz frequency excitation without external biasing light

4. Summary and Future Work

This work has presented a newly developed measurement system combining PL, TRPL and TPCD. Initial measurements were conducted on CdS/CdTe and MZO/CdTe samples at the

same spot to allow for comparable results. PL yielded the material band gap. TRPL yielded the carrier lifetimes affected mainly by radiative recombination. TPCD yielded the carrier lifetime affected by all the recombination processes, charge extraction/transport times and device/system capacitances. The next step is to conduct further analysis to distinguish and quantify the SRH recombination lifetime to identify material defects. Future work will involve introducing bias lighting to the sample to reduce junction capacitance, improving the signal-to-noise of the TPCD, measuring and deconvoluting the IRF to increase the accuracy of the extracted carrier lifetime values of TRPL. Finally, only the (230-920nm) PMT was operational at the time of writing, once the other PMT is operational, TRPL measurements can be conducted on samples with band gaps in the NIR region.

Acknowledgements

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