Photoluminescence Excitation Spectroscopy Characterization of Cadmium Telluride Solar Cells

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***Abstract* — The use of steady-state photoluminescence spectroscopy as a contactless characterization tool, suitable for in-line optical characterization, has been previously demonstrated for high efficiency solar cells such as GaAs. In this paper, we demonstrate the use of PLE characterization on a thin film CdS/CdTe np heterojunction solar cell, and compare the results to measured EQE and I-V data. In contrast to previous work on high-quality GaAs, the PLE and EQE spectra do not match closely here. We still find, however, that reliable material parameters can be extracted from the PLE measurements. We also provide a physical explanation of the limits defining the cases when the PLE and EQE spectra may be expected to match.**

I. Introduction

Photoluminescence Excitation Spectroscopy (PLE) measures the photoluminescent response of a semiconductor material as a function of illumination wavelength. Previous publications have demonstrated that PLE measurements of solar cells are analogous to the external quantum efficiency (EQE) in some cases, and can be used in conjunction with time resolved photoluminescence (TRPL) plus and a self-consistent modeling framework to provide additional information on bulk and surface recombination [1]. Furthermore, as a contactless, steady-state measurement, PLE is potentially suitable for in-line optical characterization of solar cell devices [2].

In this work, we have taken PLE measurements of a CdS/CdTe np heterojunction solar cell fabricated at CSU, following an approach described in previous work [3]. The device structure is shown in Fig. 1. When an np junction is present in a device, the presence of an electric field causes carriers generated in the depletion region to drift across the junction. This leads to enhanced radiative recombination at the junction in open circuit, as holes generated in the CdS and electrons generated in the CdTe are swept into the junction [4]. If the recombination from carriers generated in the CdTe absorber layer is dominant, the PLE of the open-circuited cell can be analogous to the EQE of the short-circuited cell and even have a similar spectral dependence [5], even though the carrier collection mechanism is different. The EQE measures the total ratio of generated carriers that are collected at the device contacts (J_{sc}/q) to the incident photon flux ϕ_{inc} [6].

$$EQE = \frac{J_{sc}}{q\phi_{inc}} \tag{1}$$

The PLE, on the other hand, measures the total number of carriers that radiatively recombine compared to the incident photon flux [6]:

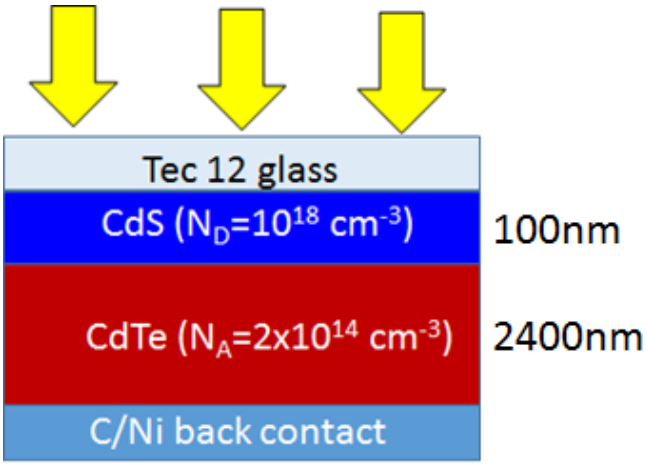

Fig. 1: Device structure of measured CdTe solar cell. The front and back surface recombination velocities (SRVs) are assumed to be 10^7 cm/s.

$$PLE = \frac{\phi_{emit}}{\phi_{inc}} \tag{2}$$

PLE is an open circuit measurement, while EQE is measured at short circuit, but in an ideal solar cell with perfect photocurrent collection and zero non-radiative recombination, the measured PLE and EQE will be similar, as long as the following condition is met [7]:

$$\phi_{emit}(V) \propto \frac{J_{sc}}{q} \tag{3}$$

On the other hand, if there is significant photocurrent loss at open circuit, this condition will fail and the shape of the plotted PLE and EQE vs. wavelength will be significantly different. As we will show, however, it is still possible to extract many of the same parameters from the PLE as are traditionally extracted from EQE by using numerical simulation, including absorption and recombination parameters.

II. Experimental Method

PLE measurements were taken using the LED illumination based system described in [8]. This system uses an array of 13 LEDs with different peak wavelengths to excite the sample. A monochromator consisting of a diffraction grating and a slit, used to select the wavelength of the incident light. Additional resolution can be achieved by adjusting the angle of the grating. The incident photon flux is kept constant across all wavelengths, yielding data proportional to the PLE signal.

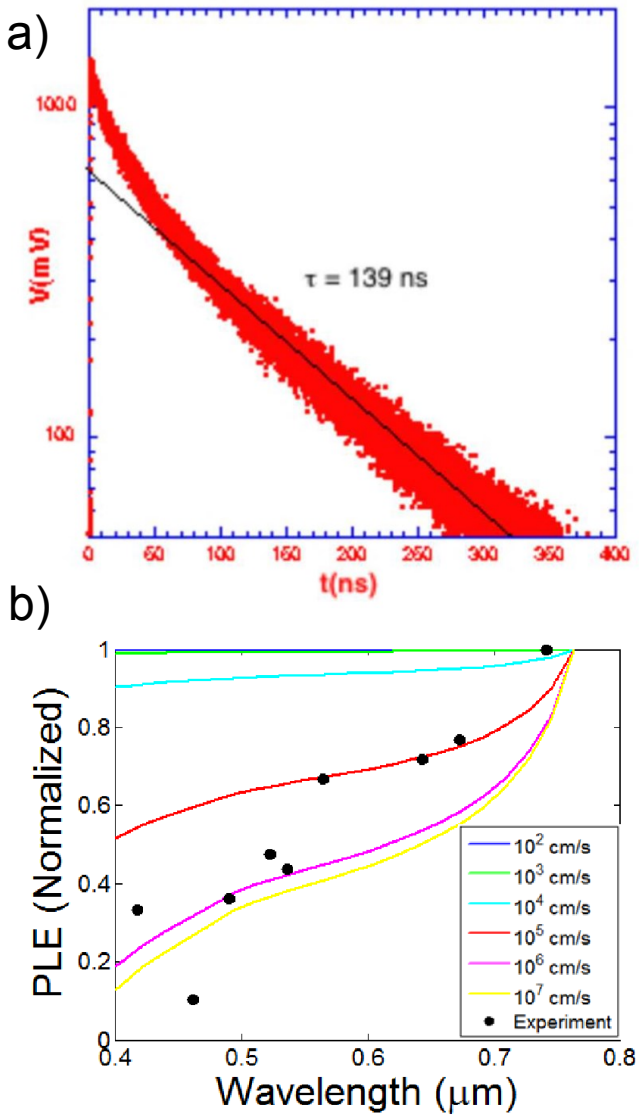

Fig. 2: Experimentally measured data for a CdTe wafer. a) The measured TRPL using two-photon counting with a 1064 nm laser, showing a bulk lifetime of 139ns. b) PLE measurements showing an estimated SRV larger than 10^5 cm/s.

A beam splitter is used to separate the monochromatic light source into two beams. One beam is directed toward the sample and the other is measured by a photodetector to record the total incident photon flux. The resulting PLE emission from the sample is directed toward a high-gain photodetector through a second monochromator set to the wavelength corresponding to the band edge of the sample, preventing any reflection of the incident LED light from reaching the photodetector. The LEDs are modulated with a 400 Hz ac voltage, and the photodetector is connected to a lock-in amplifier to measure the PLE signal from the sample while disregarding ambient light from other sources.

The optical reflection spectrum of the CdTe sample was also measured as a function of angle and polarization using a JA Woolam variable angle spectroscopic ellipsometer [9]. This data was then combined with the incident photon flux to determine the photon flux absorbed by the sample as a function of wavelength.

III. Experimental Results

Initial measurements were taken on an unpassivated CdTe wafer. TRPL measurements were used to measure the bulk lifetime of 139 ns [Fig. 2(a)], and PLE measurements were taken using the method described in the previous section [Fig. 2(b)]. These measurements were then used as a baseline for comparison with the results from the completed devices.

Due to low carrier concentration and high non-radiative recombination, the PLE signal measured from the CdTe wafer had very low intensity, with a lock-in amplifier current on the order of 10 μA, at the lower end of what the system can measure. This leads to significant noise in the measured PLE at short wavelength, making it difficult to extract the SRV. Using numerical simulation, however, a fit to the experimental data provided in Fig. 2(b) shows that the SRV is above 10^5 cm/s.

For the CdS/CdTe heterojunction, the PLE spectrum looks quite different than the spectrum measured for the wafer. A sharp peak is observed an excitation wavelength of 470 nm as shown in Fig. 3. This peak can be partially explained based on the effects of enhanced recombination at the junction compared to the bulk, as discussed previously. Because the signal at these wavelengths is nearly 2 orders of magnitude stronger than that measured for the wafer at short wavelengths, we conclude that radiative recombination at the junction must be enhancing the PLE at these wavelengths.

We note, however, that there is a very sharp cutoff at 550 nm, which corresponds to the absorption edge of CdS. We therefore hypothesize that a large portion of the signal comes from carriers that are generated in the CdS layer and diffuse to the junction to recombine in the CdTe layer rather than carriers generated in the CdTe itself. In the next section, we will investigate this hypothesis through numerical simulation.

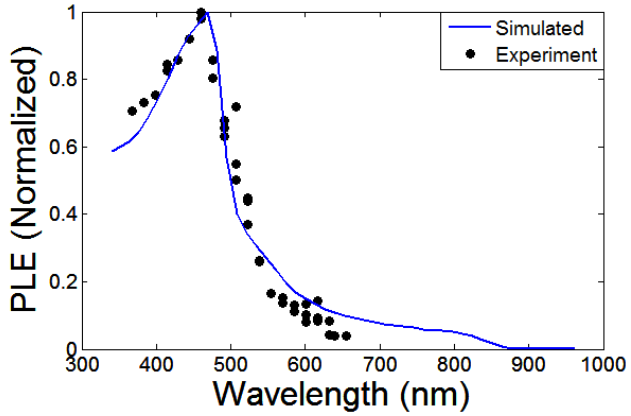

Fig. 3: Experimentally measured PLE (circles) compared to the PLE simulated using the Sentaurus device simulator (solid line).

IV. Numerical Simulation

The PLE response was simulated for the CdS/CdTe junction using standard material parameters for crystalline CdTe and CdS [10]. The simulation fit the measured data by varying the surface and bulk recombination parameters to find the best match to the experimental data. Because the bulk and surface recombination affect different parts of the PLE spectrum, adjusting these parameters independently in the simulation yields a good fit.

When the recombination at the front surface is increased, the slope of the PLE below 500 nm increases due to absorption and non-radiative recombination in the CdS layer [Fig. 4(a)]. Increasing the non-radiative bulk lifetime in the CdTe layer proportionately lowers the amount of radiative emission in the CdTe [Fig. 4(b)]. At even longer wavelengths, the simulated PLE signal cuts off completely above 870 nm, corresponding to the band edge of CdTe [10]. We find best fit parameters of front SRV = 10^6 cm/s and $\tau < 1$ ns by comparing the simulation to the measured data. This lifetime matches well with values reported by the CSU group for CdS/CdTe devices fabricated using similar processes [11], which reports lifetimes below 0.9 ns. Although we assumed an Ohmic contact in the back, our simulation results are fairly insensitive to barrier heights below 0.5 eV.

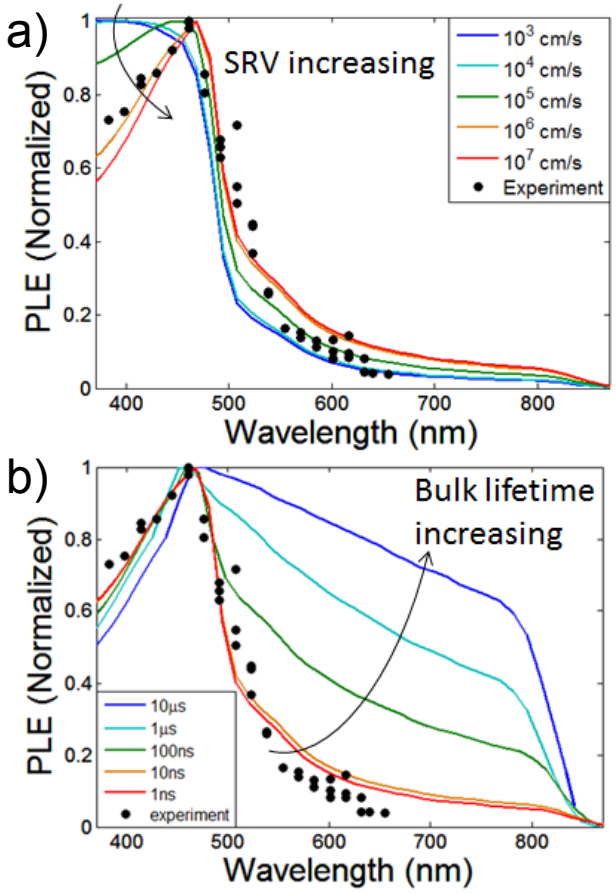

Fig. 4 Measured PLE compared to a) Simulated PLE with different surface recombination velocities and, b) different bulk lifetimes in CdTe absorber layer.

In the previous section, we hypothesized that the sharp peak we observe in the experimental data is the result of enhanced radiative recombination at the junction of CdS and CdTe. The simulated radiative recombination at several different illumination wavelengths supports this hypothesis. For a device with low bulk lifetime (~1 ns) and hole concentration ($2x10^{14}$ cm^{-3}) such as this one, the majority of the radiative recombination occurs near the junction. Carriers generated deeper in the absorber layer by longer wavelengths are therefore more likely to recombine non-radiatively, reducing the PLE signal. The greatest amplitude occurs at 460 nm, corresponding to the peak PLE signal. The PLE signal cuts off at 550 nm near the band edge of CdS, indicating that the majority of the radiatively recombining carriers may originate in the CdS layer.

To test this hypothesis, we simulated the solar cell structure with absorption alternatively disabled in the CdS layer and the CdTe layer, and we compared the results to the experimentally measured PLE in the solar cell and CdTe wafer (Fig. 5). By disabling absorption in the CdTe layer, the simulation will only generate electron-hole pairs in the CdS region, which then must diffuse to the CdTe region to recombine. It is important to note that any carriers that recombine in the CdS layer will not contribute to the PLE signal, as only photons with a wavelength corresponding to the band edge of CdTe are picked up by the photodetector.

As we can see from the blue line in Fig. 5, the CdS generation is primarily responsible for the large peak in the simulated data and matches the peak in the experimental data. In contrast, the CdTe generated PLE (Fig. 5, red line) is much weaker and only contributes to the overall PLE signal at long wavelengths above the CdS band edge. From the plot, we can see that the measured amplitude of the PLE signal from the solar cell is comparable to that of the wafer at long wavelengths.

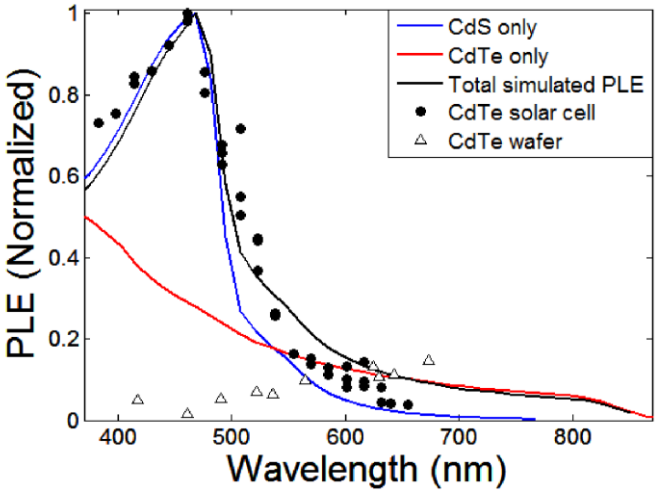

Fig. 5 Decomposition of simulated PLE with absorption in CdS only (blue line) and CdTe only (red line). The CdTe only simulation matches closely with the measured long wavelength data for the CdTe solar cell (circles) and is on the same order as the data measured for the CdTe wafer (triangles).

V. Discussion and Future Work

A. Comparison to EQE

In this section, we compare the measured PLE signal to the measured and simulated EQE. Our simulation uses a reported mobility for crystalline CdTe of 880 $cm^2/V{\cdot}s$ for the electrons and 90 $cm^2/V{\cdot}s$ for the holes, so the diffusion length is quite long. Even with the low srh lifetime measured from the PLE we still calculate a diffusion length of 1.5 μm, which is longer than the absorption length of most photons with wavelengths up to the band edge of CdTe (Fig. 6a). Because of this, the collected photocurrent measured by the EQE is still quite high even up to an 800 nm wavelength, despite the relatively short bulk lifetime (Fig. 6b). Using the same parameters we used to fit the measured PLE, we are able to get a reasonably good fit to the measured EQE. The small differences at short wavelengths may be due to a difference in the CdS absorption edge. Even though the shape of the PLE spectrum is quite different from the EQE for solar cells with a large amount of non-radiative recombination, the results of the two measurements are still self-consistent. These results demonstrate that reliable material parameters can be extracted from PLE measurements even when PLE and EQE spectra are quite different.

B. Future Work

In this paper, we have demonstrated a particular case where the measured PLE of a solar cell is not similar to the EQE. We attribute the difference in the PLE and EQE to the low radiative efficiency and carrier concentration in the CdTe bulk. As shown in Fig. 4, for higher bulk SRH lifetimes, the shape of the PLE spectrum flattens, approaching the measured EQE. We have not, however, determined a general quantitative limit for these parameters under which the conclusions of [4] become invalid.

We intend to further investigate the conditions when Eq. 3 can be considered a valid approximation using further simulations and experiments with higher bulk lifetimes and acceptor doping levels. We will attempt to determine a quantitative limit that describes when a cell's photocurrent collection can be considered to be "good enough" so that the PLE can be taken as a good approximation of the EQE. Knowing the precise limits of this approximation will be invaluable for researchers who wish to utilize PLE measurements as a contactless substitution for EQE for in-line optical characterization, as suggested in [4].

We have further demonstrated that useful performance parameters can be determined from numerical analysis of the PLE spectra for cells, even when they do not meet the criteria of having high photocurrent collection efficiency. The usefulness of PLE measurements could therefore be further enhanced if an analytic expression were derived for characterizing bulk lifetime and surface recombination from plots like those shown in Fig. 4. Augmenting the PLE instrument capability to take absolute PL measurements would also help make this data more useful [8].

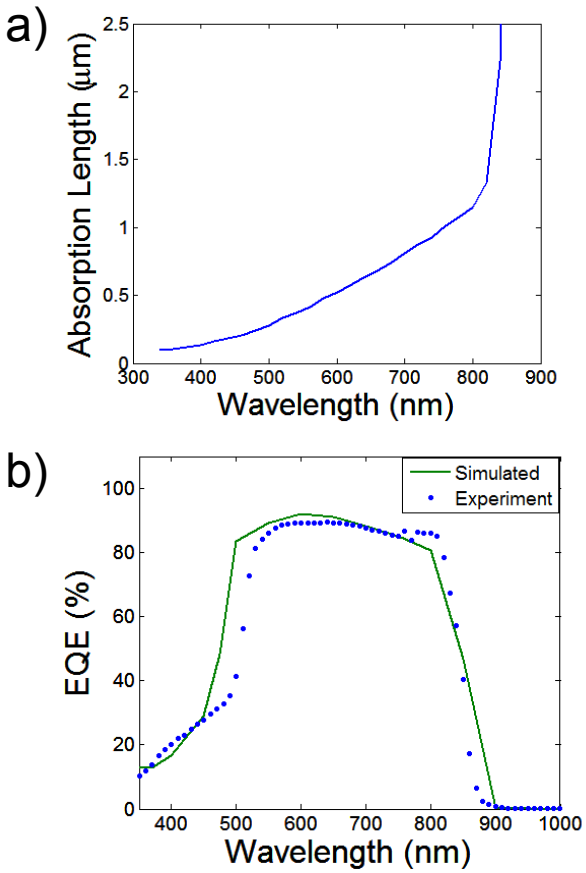

Fig. 6 a) Absorption length for CdTe and b) experimentally measured EQE (circles) compared to simulated EQE (line).

VI. Conclusions

CdTe absorbers typically show very low radiative efficiency, generating relatively low PLE signals. We have nevertheless successfully measured a PLE signal from a CdS/CdTe np heterojunction solar cell. Using numerical simulation combined with PLE, we measured a recombination lifetime below 1 ns and an SRV between 10^5 and 10^6 cm/s, which are consistent with previously published results for a crystalline CdTe wafer [12].

For the CdTe solar cell, we observed an unusually-shaped PLE spectrum much different than our EQE measurements, characterized by a sharp peak at 470 nm. We were, however, able to explain the unusual behavior precisely with detailed numerical simulations. Our model shows that the observed peak is due to photon absorption in the CdS layer, followed by carrier diffusion and recombination at the junction. These results suggest that PLE may be a useful, contactless, in-line characterization tool for solar cells.

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