Extracting Mobility-Lifetime Product in Solar Cell Absorbers Using Quantum Efficiency Analysis

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Extracting Mobility-Lifetime Product in Solar Cell Absorbers Using Quantum Efficiency Analysis

Jeremy R. Poindexter¹, Riley E. Brandt¹, Niall M. Mangan¹, Tonio Buonassisi¹

¹Massachusetts Institute of Technology, Cambridge, MA 02139, USA

ABSTRACT

The long-wavelength quantum efficiency (QE) response of photovoltaic absorbers is determined by the length scales for minority carrier collection. However, extracting quantitative measurements of minority carrier mobility-lifetime product ($\mu\tau$) is complicated by uncertainty in other factors such as the depletion width, electric field, and the absorption coefficient. We apply previously developed methods to obtain estimates for $\mu\tau$ in a tin(II) sulfide (SnS) solar cell. We compare three analytic models for the minority carrier collection probability as a function of absorber depth to determine which model most accurately captures the behavior in our devices. For models in which multiple parameters are unconstrained, a random numerical search is used to optimize the fit to experimental QE for SnS. To identify sources of error, we perform a sensitivity analysis by fitting with SCAPS-1D. Our analysis shows that changes in absorption most strongly affect estimates for $\mu\tau$, highlighting the need to obtain accurate, device-specific absorption data. Further modeling and experimental constraints are required to obtain self-consistent values for $\mu\tau$ that correspond to actual device performance.

INTRODUCTION

Quantum efficiency (QE) analysis has proven a useful tool for evaluating minority carrier collection in many photovoltaic (PV) absorbers, as QE directly relates to the minority carrier mobility-lifetime product, $\mu\tau$. In particular, an increase in $\mu\tau$ for a given material typically results in an increase in the long-wavelength region of the QE spectrum (i.e., close to the band gap of the material). For materials that exhibit diffusion-dominated collection of minority carriers (e.g., silicon), increases in long-wavelength QE are directly related to increases in $\mu\tau$ through a linear relationship [1–3]:

$$\frac{1}{QE} \approx 1 + \frac{1}{L_{eff}} \times \frac{1}{\alpha}$$

(1)

where $L_{eff}$ is an effective diffusion length and $\alpha$ is the absorption coefficient. The approximation in equation (1) holds for $\alpha t >> 1$ and $t/L_{eff} >> 1$ (where $t$ is absorber thickness). For diffusion-dominated collection, $L_{eff} \approx L_{diff}$, the minority carrier diffusion length. $L_{diff}$ is related to $\mu\tau$ based on the Einstein relation:

$$L_{diff} = \sqrt{\frac{k_B T}{q \mu\tau}}$$

(2)
where $k_B$ is Boltzmann’s constant, $T$ is absolute temperature, and $q$ is elementary charge.

Many “thin film” PV absorbers exhibit a mix of drift-assisted and diffusion-assisted minority carrier collection, complicating the extraction of $\mu \tau$ and invalidating the relationship described in equation (1). These materials absorb strongly in the visible and have depletion widths comparable to absorber thickness. Other factors can affect the long-wavelength QE response in devices based on these materials, including changes in depletion width and electric field, uncertainty in the absorption coefficient, and recombination at interfaces and surfaces.

We investigate several models to extract $\mu \tau$ from QE measurements on solar cells in which the absorber is tin(II) sulfide (SnS). Though promising due to the abundance of its constituent elements and its suitable band gap of 1.1–1.3 eV [4, 5], SnS has been limited to efficiencies below five percent when integrated into devices [6, 7]. These low efficiencies are likely due to low values of $\mu \tau$ [8].

To extract $\mu \tau$ in SnS, we apply a general form for the QE that incorporates separate generation and collection terms to obtain estimates of $\mu \tau$ for different models for minority carrier collection. Following Scheer [9], the QE can generally be described as:

$$QE(\lambda, V) = \int_0^t \frac{G(\lambda, x)P_C(x, V)}{\Phi(\lambda)} \, dx$$  \hspace{1cm} \text{(3)}$$

where $\Phi(\lambda)$ is the photon flux of the incident light and $x$ is depth within the absorber. In this work, we use the Beer-Lambert law for the generation function, $G = (1 - R)I_0e^{-\alpha x}$, where $R$ is the reflectance and $I_0$ is the incident photon flux (here equal to $\Phi$). The form of the collection function, $P_C$, depends on the carrier collection mechanism, i.e., drift or diffusion, as well as recombination rates throughout the device, due to its relation to the excess carrier density [10, 11]. We compare three different analytic models for the collection function: a single exponential model (diffusion-dominated), the Gärtner model, and a double exponential model (drift-diffusion).

**RESULTS**

Figure 1a shows external quantum efficiency (EQE) and internal quantum efficiency (IQE) data for a SnS solar cell. SnS was deposited via thermal evaporation onto a Mo-covered Si/SiO$_2$ substrate. Zn(O,S), ZnO, and ITO were subsequently deposited to form electrical contacts. Further details regarding the experimental fabrication procedures are described elsewhere [6].

First, we apply the diffusion-dominated collection model expressed in equation (1). Though we expect drift collection to significantly contribute to minority carrier collection in SnS, the diffusion-dominated collection model provides a useful point of comparison, as this model has been validated for other materials, namely silicon, and used on SnS previously [12]. Figure 1b shows absorption data for SnS from which a plot of IQE$^{-1}$ vs. $\alpha^{-1}$ was produced for the wavelength range 650–750 nm (Figure 1c). A value for $L_{\text{diff}}$ of 204 nm was extracted from the slope of this plot using equation (1) (assuming $T$ to be 300 K), which agrees well with the use of this method to extract $L_{\text{diff}}$ for SnS performed by Reddy et al. [12] We then use equation (3) to calculate the expected QE for this diffusion length using $P_C = e^{-x/L_{\text{diff}}}$ for $0 \leq x \leq t$. The result is plotted in Figure 2 (thin solid black line) along with the experimental data.
Figure 1. (a) IQE (solid line) and EQE (dotted line) data for a SnS solar cell. The shaded area represents the region of the QE curve over which fitting was performed. The QE response decreases in the short-wavelength region primarily due to parasitic absorption in the ITO and Zn(O,S) over-layers. (b) Absorption coefficient data for SnS calculated from optical reflectance and transmittance measurements. (c) Extracted $L_{\text{diff}}$ from the inverse of the slope of a plot of IQE$^{-1}$ vs. $\alpha^{-1}$ for a wavelength range of 650–750 nm.

Next, we use the Gärtner model [13] to extract $L_{\text{diff}}$. The collection profile for this model is a piecewise function with $P_c = 1$ for $0 \leq x \leq W$, where $W$ is the width of the depletion region, and with $P_c = e^{-(x-W)/L_{\text{diff}}}$ for $W < x \leq t$. This model assumes 100% collection in the depletion region. We calculate the QE using this model for a set of values for $L_{\text{diff}}$ and $W$ and compare against the experimental data. We use a random search algorithm to find the best fit for $L_{\text{diff}}$ and $W$ using 1 nm and 1 μm as the lower and upper bound for both parameters. The range of values for $L_{\text{diff}}$ and $W$ whose fits resulted in a root mean square error below 0.025 is listed in Table I, and the best fit is plotted in Figure 2 (dotted blue line).

Table I. Parameters used to generate QE fits. The range of values corresponds to fits whose root mean squared error was below 0.025. For the Gärtner model, $L_{\text{diff}}$ and $W$ (as well as $L_{\text{drift}}$ for the drift-diffusion model) were allowed to vary. For the SCAPS-1D fit, all parameters besides $L_{\text{diff}}$ were held constant.

<table>
<thead>
<tr>
<th>model/fit</th>
<th>$L_{\text{diff}}$ (nm) [range]</th>
<th>$\mu \tau$ (cm$^2$/V)</th>
<th>W (nm) [range]</th>
<th>$L_{\text{drift}}$ (nm) [range]</th>
<th>root mean squared error</th>
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<td>single exponential ($L_{\text{diff}}$)</td>
<td>204 [204]</td>
<td>1.61E-08</td>
<td>—</td>
<td>—</td>
<td>0.0599</td>
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<td>Gärtner model</td>
<td>2 [2–134]</td>
<td>1.55E-12</td>
<td>129 [40–146]</td>
<td>—</td>
<td>0.0171 [&lt; 0.025]</td>
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<tr>
<td>drift-diffusion; fixed $L_{\text{diff}} = 200$ nm</td>
<td>5 [5]</td>
<td>9.67E-12</td>
<td>298</td>
<td>200</td>
<td>0.0547</td>
</tr>
<tr>
<td>numerical fit (SCAPS-1D)</td>
<td>50 [50]</td>
<td>9.67E-12</td>
<td>447</td>
<td>196</td>
<td>0.0468</td>
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Calculated and fitted QE curves over a wavelength range of 600–1000 nm using three analytic models and one numerical model using SCAPS-1D. The black circles represent the experimental data. Fits were obtained by numerically finding the value of $L_{\text{diff}}$ (and when applicable, $W$ and $L_{\text{drift}}$) which minimized error relative to the experimental data.

To allow for recombination in the depletion region, a model incorporating a drift length, $L_{\text{drift}}$, similar to that presented by Galluzzi [14] and previously performed on cuprous oxide solar cells [15] was implemented. The QE was calculated using a piecewise collection function with $P_c = e^{-x/L_{\text{drift}}}$ for $0 \leq x \leq W$ and $P_c = e^{-W/L_{\text{drift}}} e^{-(x-W)/L_{\text{drift}}}$ for $W < x \leq t$. The best fit is plotted in Figure 2 (dotted orange line). A second QE curve was calculated using this model fixing $L_{\text{drift}}$ at 200 nm (thick solid red line). $L_{\text{drift}}$ was allowed to vary between 1 nm and 10 μm.

Finally, a numerical model in SCAPS-1D [16] was used to fit the experimental data. The electric field, depletion region, and carrier dynamics were calculated throughout the device. Therefore, drift collection, diffusion collection, and the depletion width were self-consistent, a feature not yet implemented in the analytic models. The absorption data from Figure 1b was used to calculate QE, and the curves were fit numerically. The best fit is plotted in Figure 2 (green plus symbols). $L_{\text{drift}}$ was calculated by approximating the electric field as $E \approx qN_A W/\varepsilon$ using SnS hole concentration, $N_A = 10^{16}$ cm$^{-3}$, SnS dielectric constant, $\varepsilon = 40$, and $W = 447$ nm.

DISCUSSION

The single exponential fit follows the general shape of the experimental data but does closely match its slope. The Gärnter model fit agrees well with the experimental data, but the extracted value for $\mu \tau$ is much smaller than expected. For this model to hold, depletion region recombination must be negligible, implying that $L_{\text{drift}} \gg W$, as explained by Galluzzi [14]. For $\mu \tau = 1.6 \times 10^{12}$ cm$^2$/V (for $L_{\text{drift}} = 2$ nm), and to satisfy $\mu \tau \gg W^2/V_{\text{bi}}$, the built-in voltage $V_{\text{bi}}$ would have to exceed 100 V. This suggests that the assumption of uniform depletion-region collection is invalid for our cells. Fits using the drift-diffusion model produced similar results—again the resulting best-fit value for $\mu \tau$ is small, contradicting the large fitted value for $L_{\text{drift}}$. Numerically fitting with SCAPS-1D yielded a higher value for $\mu \tau$; however, the best fit results in higher error. Estimated values for $\mu$ (30 cm$^2$/V·s) and $\tau$ (100 ps) as determined from Hall effect measurements.
and previous SCAPS-1D modeling, respectively [8], suggest a value of $\mu r$ near $3.0 \times 10^{-9}$ cm$^2$/V, which lies within the fitted range for both the Gartner and drift-diffusion models. Thus these fits, while not fully constrained, demonstrate consistency with previously performed studies.

To analyze possible errors and uncertainties in extracted $L_{\text{diff}}$ values, a sensitivity analysis was performed using SCAPS-1D. Individual parameters were varied, and QE was recalculated leaving only $L_{\text{diff}}$ unconstrained. The results, shown in Figure 3, suggest the absorption coefficient is the most important factor for extracting accurate values of $L_{\text{diff}}$ and thus $\mu r$. The absorption data was calculated from optical reflectance and transmittance measurements on a separate SnS film on glass neglecting any multiple internal reflections. To improve the precision and accuracy of fits, more accurate absorption data should be obtained by measuring absorption on device-relevant substrates using methods that are more robust than those which assume specific paths for various wavelengths of light.

![Figure 3](image)

Figure 3. Sensitivity plot of extracted $L_{\text{diff}}$ to other device parameters. Each parameter was varied in a SCAPS-1D simulation, and $L_{\text{diff}}$ was fit to experimental QE data using the SCAPS-1D built-in fitting routine.

Figure 3 also shows a significant sensitivity of $L_{\text{diff}}$ to the Zn(O,S)/SnS band offset and SnS hole concentration. The band offset affects interface recombination (particularly when increasingly “cliff-like”) and depletion width. Interestingly, $L_{\text{diff}}$ seems relatively insensitive to changes in interface recombination velocity. Eron [17] and Paire [18] have described an interface collection efficiency factor that may be an important fourth parameter to include along with $L_{\text{diff}}$, $W$, and $L_{\text{drift}}$ for cases when QE is seen to be sensitive to interface recombination.

While not employed in this study, voltage and light bias have been used to constrain parameter fitting in QE. Implementing such constraints requires further knowledge of the dependencies of $L_{\text{diff}}$, $W$, and $L_{\text{drift}}$, and interface recombination rates with voltage and light bias. Voltage bias is commonly used to adjust depletion width when measuring QE [19–21], yielding information about how much collection occurs due to drift vs. diffusion. Less frequently used but also powerful, light bias can be used to alter carrier concentrations, affecting recombination dynamics, e.g., at interfaces. Further constraints of $W$ and $L_{\text{drift}}$ using these methods—when combined with accurate absorption data—would increase the accuracy of extracted $\mu r$.

CONCLUSIONS

In summary, we compare three analytic models for minority carrier collection and a numerical simulation to extract $\mu r$ in SnS solar cells. Models where $L_{\text{diff}}$, $W$, and $L_{\text{drift}}$ were fit resulted in QE fits that were not self-consistent, suggesting future models should impose
relationships between these parameters during fitting. In general, extracted $\mu r$ values seem quite sensitive to errors in the absorption coefficient, highlighting the importance of obtaining accurate absorption data for materials. Voltage and light bias may assist in further decoupling collected currents due to drift and diffusion.

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REFERENCES