Overcoming the limitations of transient photovoltage measurements for studying recombination in Organic solar cells

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Transient photovoltage (TPV) measurements are frequently used to study the recombination lifetime of thin-film solar cells through using the decay of a small optically-induced voltage perturbation to probe the charge dynamics of devices at open circuit. However, the validity of this method to probe organic semiconductors has recently come in doubt due to large discrepancies in reported carrier lifetime values for the same system, and the reporting of unrealistic reaction values. In this work, we first explore the validity of TPV to extract reliable charge carrier lifetimes in thin-film solar cells through the use of time-dependent drift diffusion simulations. Here we show that irrespective of the recombination mechanism considered, the output recombination rate calculated from simulated TPV decays ($\boldsymbol{K_{TPV}}$) is only a valid measure of the input recombination rate ($\boldsymbol{K_{rec}}$) in the cases where the recombination is slow, or the mobility of the device is significantly high for Organic photovoltaic device (OPV) (figure 1). The effect of other parameters on the commonly assumed correlation between the recombination rate and the TPV lifetime have been explored, and we found the correlation to be only valid in very limited cases.

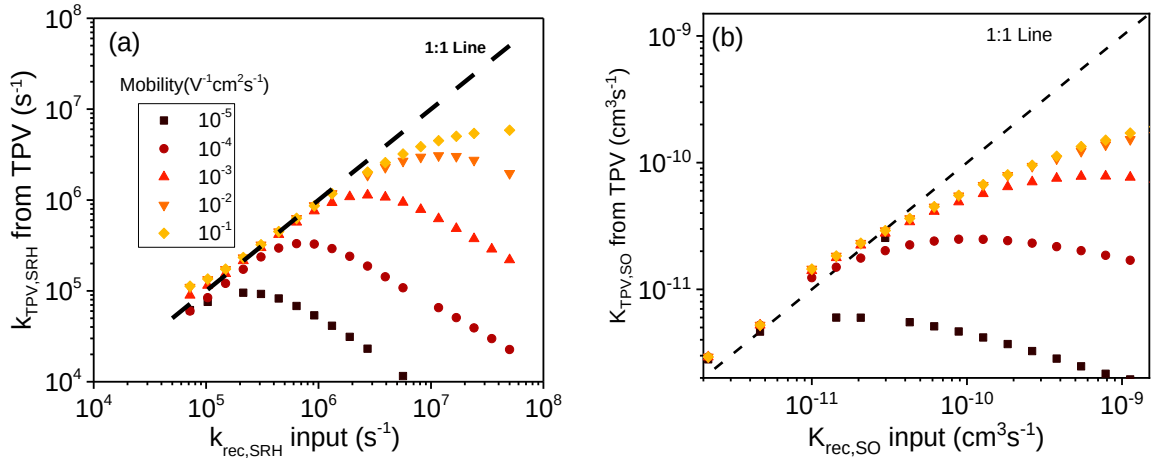

Figure 1. Simulated TPV decay rate constant against input recombination rate coefficient for different mobility values and a uniform generation rate ($\boldsymbol{G = 2.5 \times 10^{21} cm^{-3} s^{-1}}$) in a device dominated by a) first order and b) second order bulk recombination mechanisms. $\boldsymbol{k_{rec,srh}}$ and $\boldsymbol{K_{rec,SO}}$ are the input recombination rate constant for first order and second order recombination, respectively. $\boldsymbol{k_{TPV,srh}}$ and $\boldsymbol{K_{TPV,SO}}$ are the estimated recombination rate constant from the simulated TPV decay using the TPV lifetime for first order and second order recombination, respectively.

Following these results, we have analysed the charge carrier evolution inside of the absorber during the TPV decay for two different case, a slow recombination case where $\boldsymbol{K_{TPV} \approx K_{rec}}$ and fast recombination case where

$K_{TPV} \ll K_{rec}$(figure 2).For The studied slow and fast recombination cases the evolution of the charges carriers during the TPV experiment is significantly different. For the slow recombination case, the charges increase and decrease quite homogeneously across the absorber, showing a good agreement between the average charge carriers decay and the photovoltage decay. The fast recombination case on the other hand shows a significantly inhomogeneous charge carrier density evolution across the absorber, with charge carriers in the middle of the absorber that decay with a lifetime $\tau_{Ch,1}$ which is an order of magnitude lower than the lifetime $\tau_{Ch,2}$ of the charges close to the interfaces. In the latter case the photovoltages decay reflects the evolution of the charges close to the interfaces.

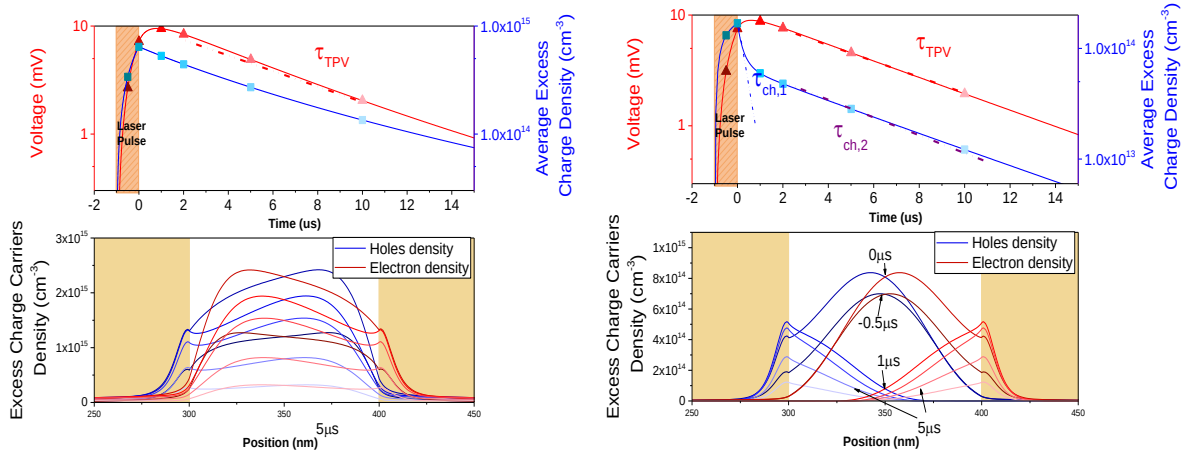

Figure 2 a,c) Photovoltage decay (red curve, red and pink markers) and averaged excess charge decay in the device (blue curve, blue markers) for the slow recombination case (a) and the fast recombination case (c). b,d) Evolution of electron and hole density in the intrinsic layer during the TPV experiment for the slow recombination case (b) and the fast recombination case (d). The colour map in plot b and d is taken at the time corresponding to the markers with the same colour shade. The TPV lifetime is represented in this plot as τ_{TPV}, the fast charge decay lifetime is $\tau_{Ch,1}$,and the slow charge decay lifetime $\tau_{Ch,2}$

From the charge carrier's decay in the fast recombination case, we have established that τ_{TPV} is related to the charges carriers close to the interfaces between the transport layers and the absorber. To understand what controls the TPV lifetime for the cases where it is not close to its expected value, our analysis focusses on this interfacial region. We first note that at open circuit condition, the field at the interface is not negligible, and is even stronger in the fast recombination case compared to the slow recombination one. By solving the equation in an extreme case, where the recombination is neglected at those interfaces, and only the displacement current affect the excess charge carriers at those interface, we established an equation for the TPV lifetime $\tau_{tpv} = \frac{\epsilon\epsilon_0}{\sqrt{\frac{G}{K_{rec,SO}}}\mu}$ that describes significantly well the TPV decay for most of the cases where it is not a valid measure of the recombination input alone.

Finally, we developed an experimental technique to probe the excess charge carrier introduced by the laser during the TPV experiment to both assess the validity of the TPV for the measured device, as well as extracting a more representative recombination rate constant. We applied this new technique to measure the recombination dynamic in various (fullerene and non-fullerene) organic solar cell systems. We show that using this technique we more accurately determine the recombination lifetime as well as the dominant recombination mechanism at different light intensities.