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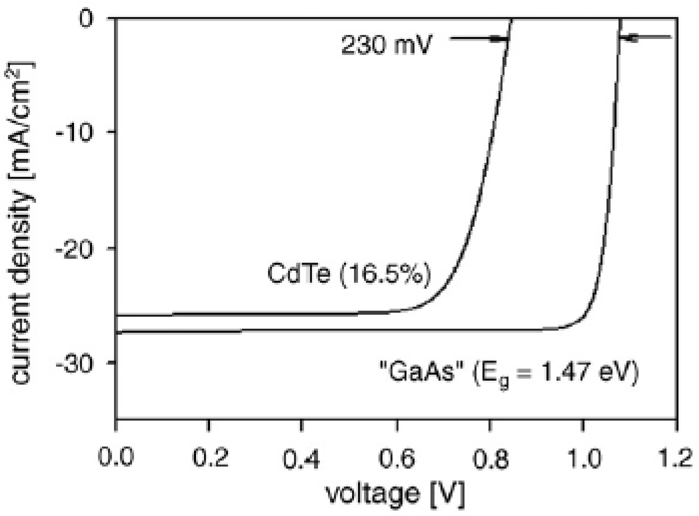
Outline

- The need for time-resolved photoluminescence (TRPL) measurements and their interpretation
- What impacts TRPL decays on px CdTe devices-
    - Dependence on experimental conditions
    - Dependence on material parameters
- How to separate drift, diffusion and recombination in a TRPL measurement
- Spatial distribution of generated carriers in CdTe absorbers

Increase V_{oc} in CdTe solar cells

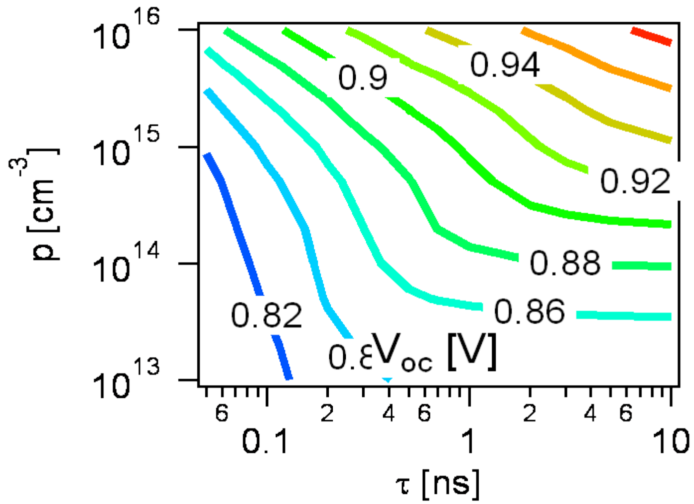
- V_{oc} is the most limiting parameter in thin cell performance
- V_{oc} can be increased by higher doping or lifetime
- Accurate measurement necessary (TRPL)

Comparison of a CdTe cell and high efficiency GaAs cell



Sites et al. Thin Solid Films (2007)

Simulated V_{oc} as a function of doping and minority-carrier lifetime in CdTe solar cells

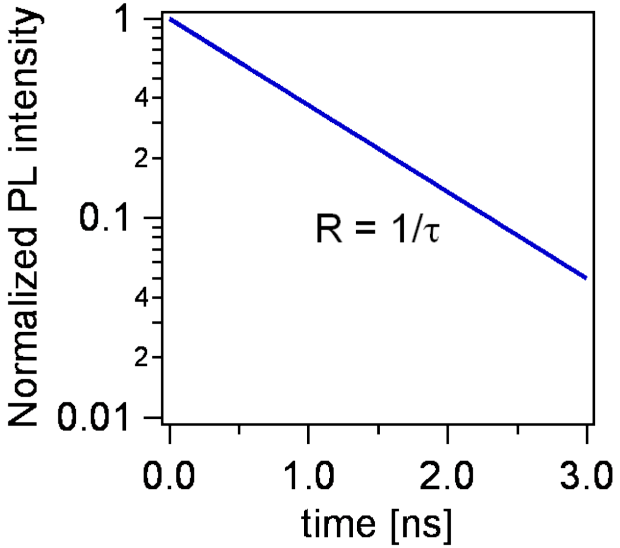


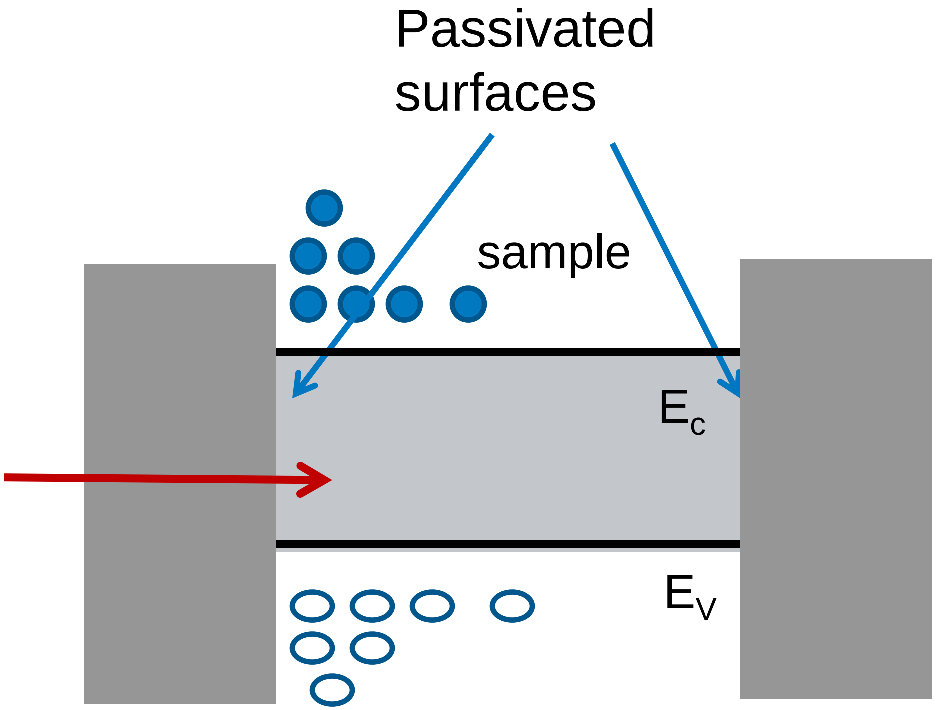
Kanevce et al. Journal of Photovoltaics (2011)

TRPL measurement

- TRPL is nondestructive and relatively quick measurement
- Ideally TRPL is measured on a double heterostructure
  - Decay is single exponential
  - Minority-carrier lifetime can be deduced from the slope

$$I = I_0 \exp(-t/\tau)$$

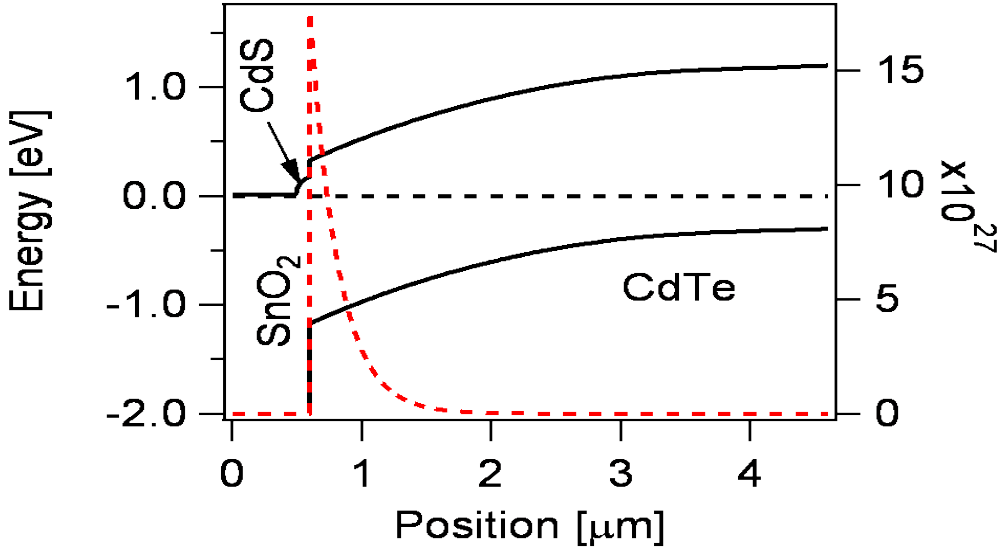


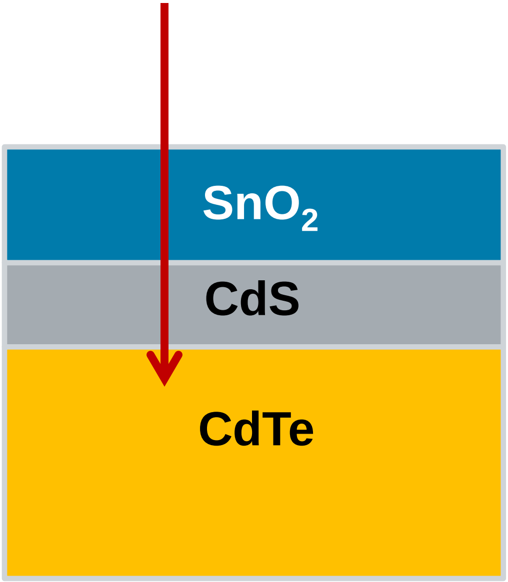


TRPL measurement on a CdTe device

- CdTe is usually grown as a superstrate structure
- Photo-carriers are generated in the space-charge region
- Carrier kinetics and their decays are affected by drift, diffusion, bulk and interface recombination

Band diagram and generation rate
λ = 635 nm

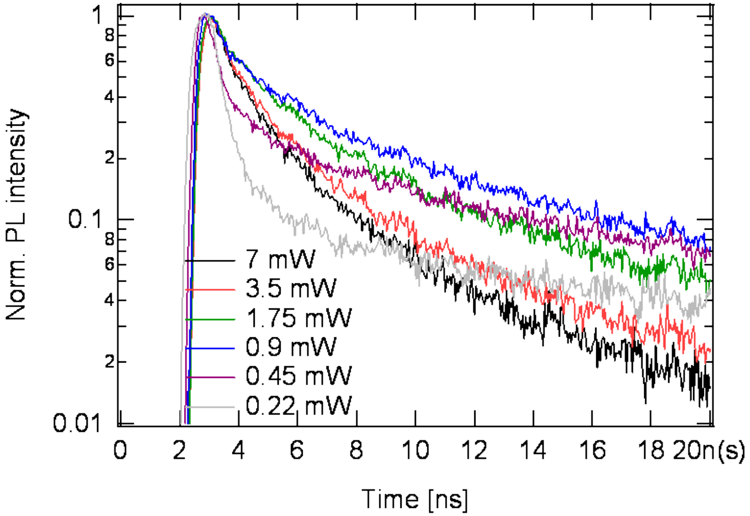




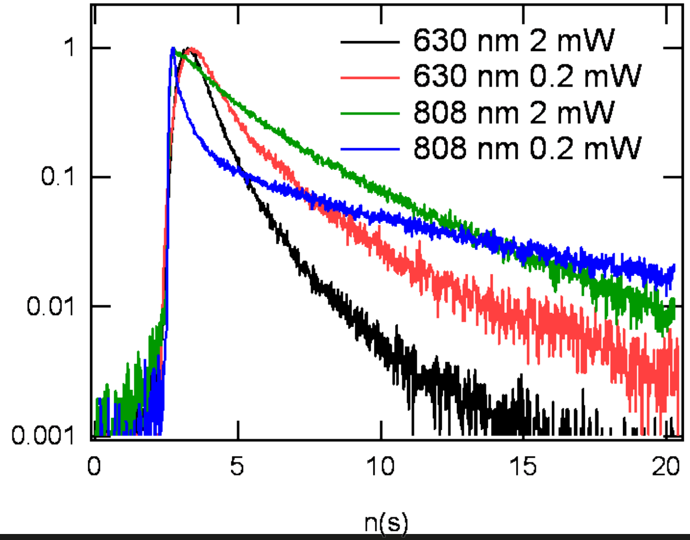
How to interpret TRPL on a CdTe device

- Decay is double exponential and dependent on experimental conditions
- Which part of the decay determines the minority carrier lifetime?
- What do the different parts of the decay mean?
- By more measurements, can we learn more than lifetime?

Measured TRPL decays; Single device, but laser power varied. TRPL measured by D. Kuciauskas

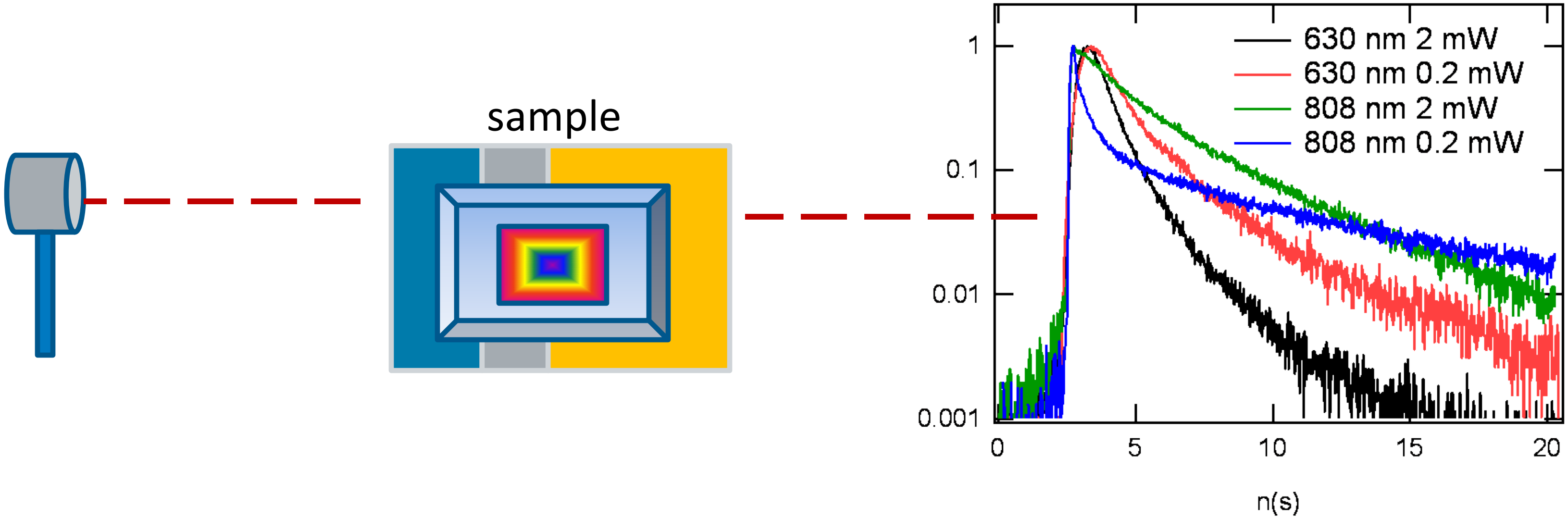


Measured TRPL decays; Single device, but experimental conditions varied. Samples grown by J. Duenow, TRPL measured by D. Kuciauskas



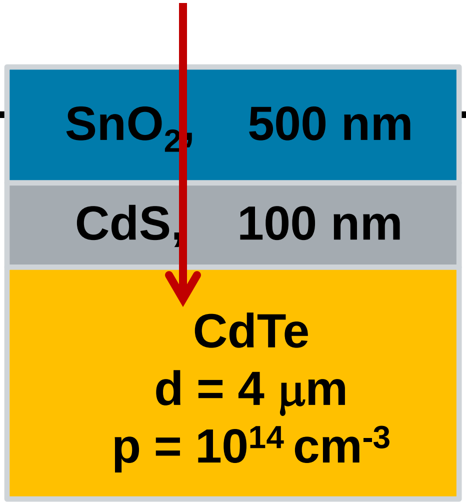
Modeling TRPL on a CdTe device

- In an experiment, one sees the decay
- A model can serve as a window inside the measurement
- It can show what happens in a device during a measurement.
- Can calculate the carrier distribution, electric fields and currents



The model

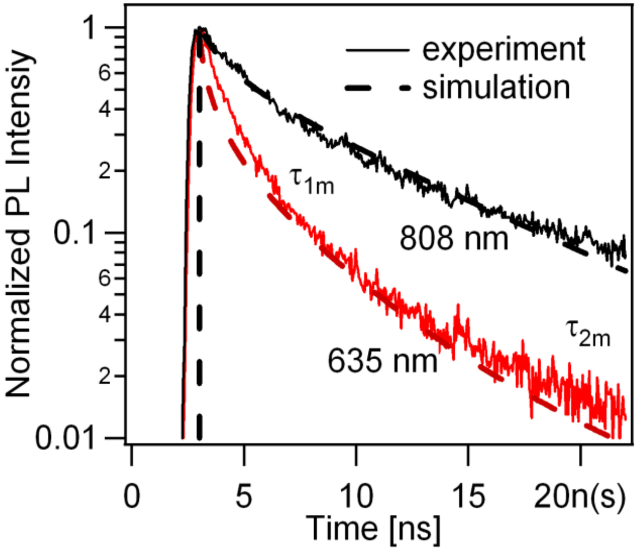
- Modeling software: Sentaurus Device by Synopsys
- Assumptions in the model:
- 3 layers:(SnO_2, CdS and CdTe)
- Each layer has:
  - Uniform carrier density and uniform defect density
- 1D model
  - Lateral nonuniformities and grain boundaries not taken into account
- Good match of experimental results



SnO_2, 500 nm

CdS, 100 nm

CdTe
d = 4 μm
p = 10^{14} cm^{-3}

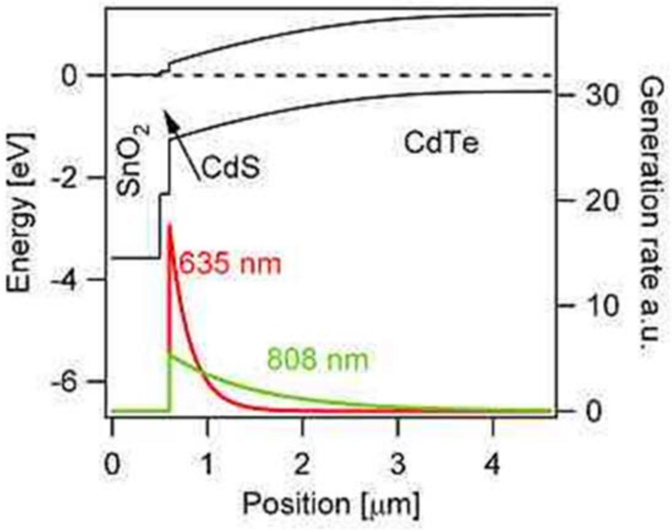


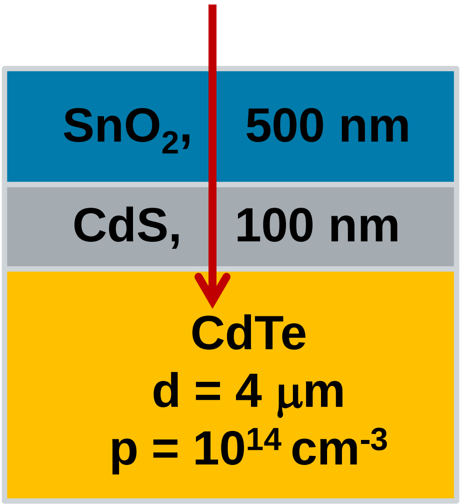
Kanevce et al. IEEE PVSC (2012)

The model

- Transient simulation
- Carriers excited with a short monochromatic light pulse
    - (635 nm or 808 nm)
- For 635 nm, 3×10^{15} cm^{-3} photo-carriers are generated at CdS/CdTe interface
- Assumed: photoluminescence signal is proportional to the total radiative recombination rate in absorber

$$R(x,t) = B(p(x,t)n(x,t) - p_0(x,t)n_0(x,t))$$





SnO_2, 500 nm

CdS, 100 nm

CdTe
d = 4 µm
p = 10^{14} cm^{-3}

Outline

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- What impacts TRPL decays on px CdTe devices-
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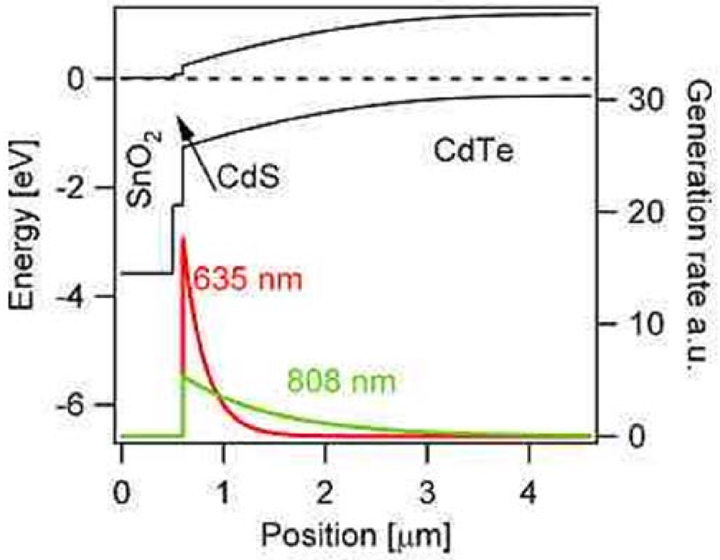
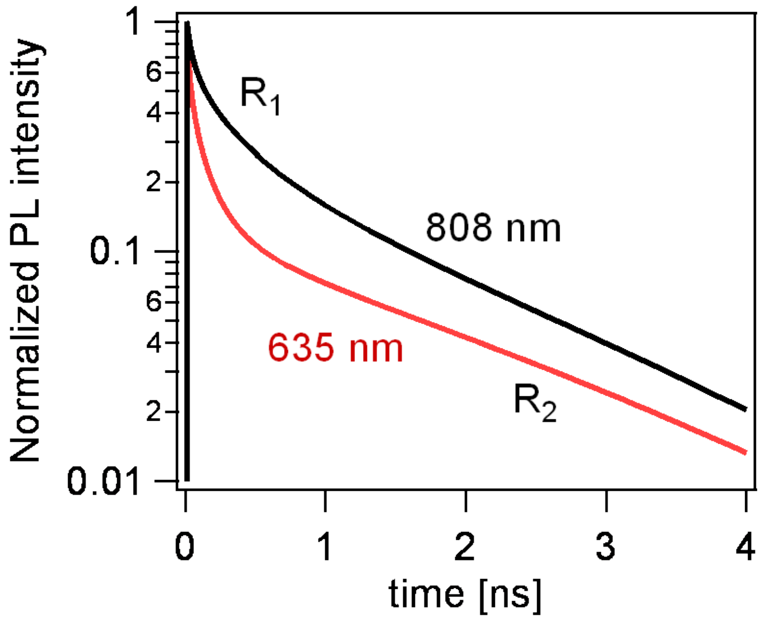
- How to separate drift, diffusion and recombination in a TRPL measurement
- Spatial distribution of generated carriers in CdTe absorbers
- Summary

Two wavelength illumination

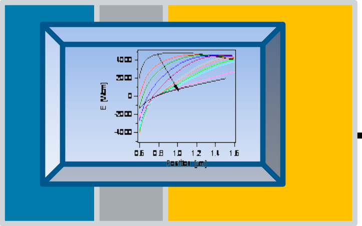
- Different wavelengths have different penetration depth
- Low wavelength is more sensitive to interface and drift
- Lower wavelength has more pronounced double exponential behavior



Simulated TRPL decays at different wavelengths

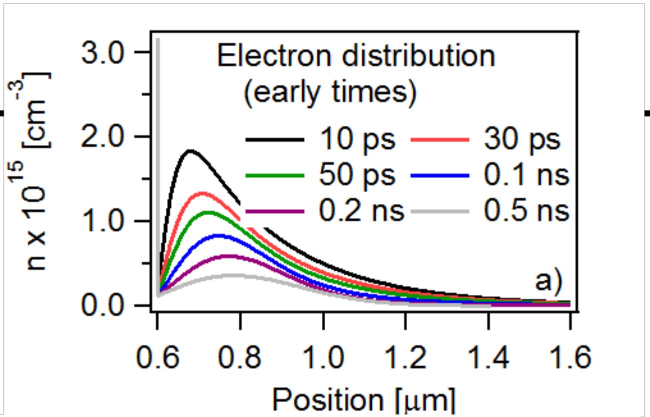


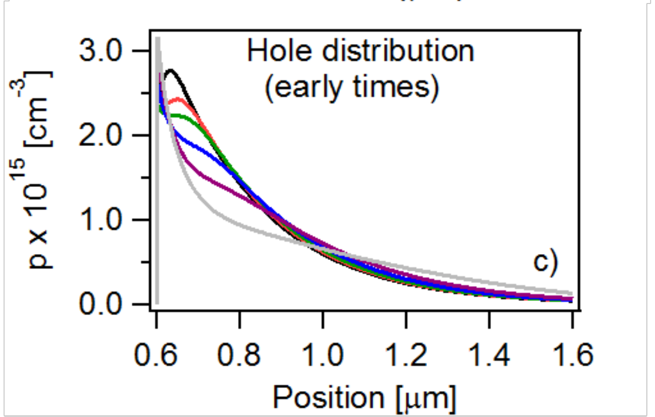
Kanevce et al. Prog. Photovolt: Res. Appl. doi:10.1.1002/pip.2369 (2013)

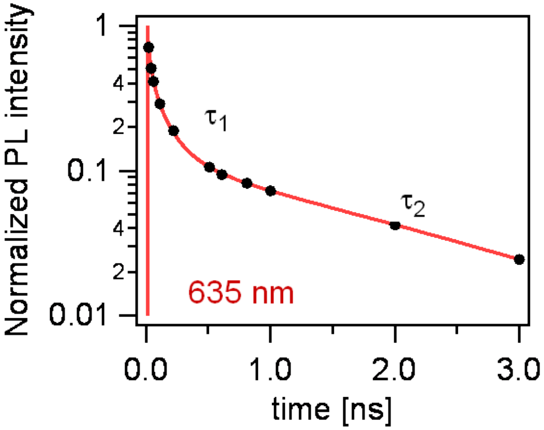


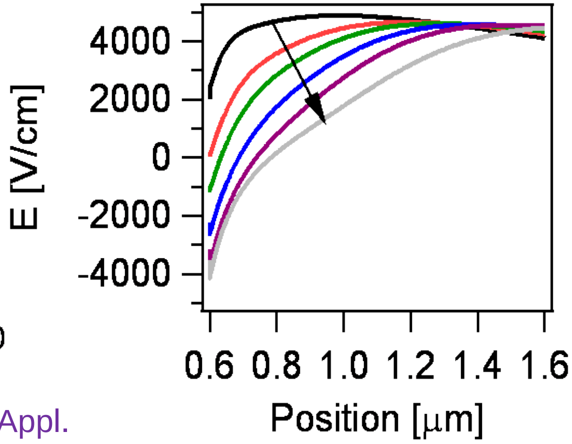
Carrier motion during the decay (early times)

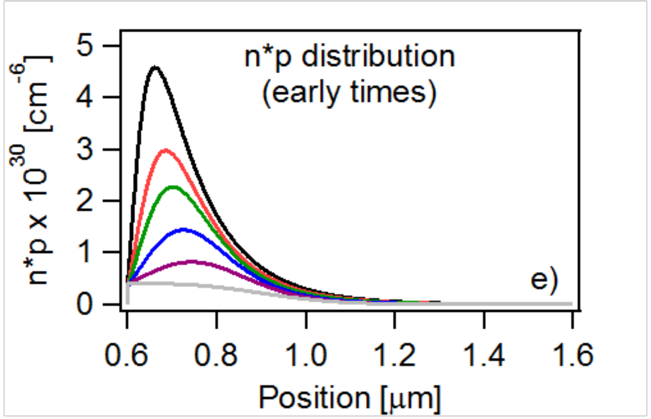
- During the early times (τ_1) maximum electron distribution moves away from the interface
- The carrier dynamics alters the electric field



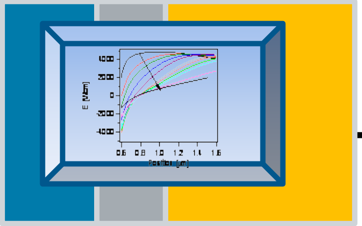






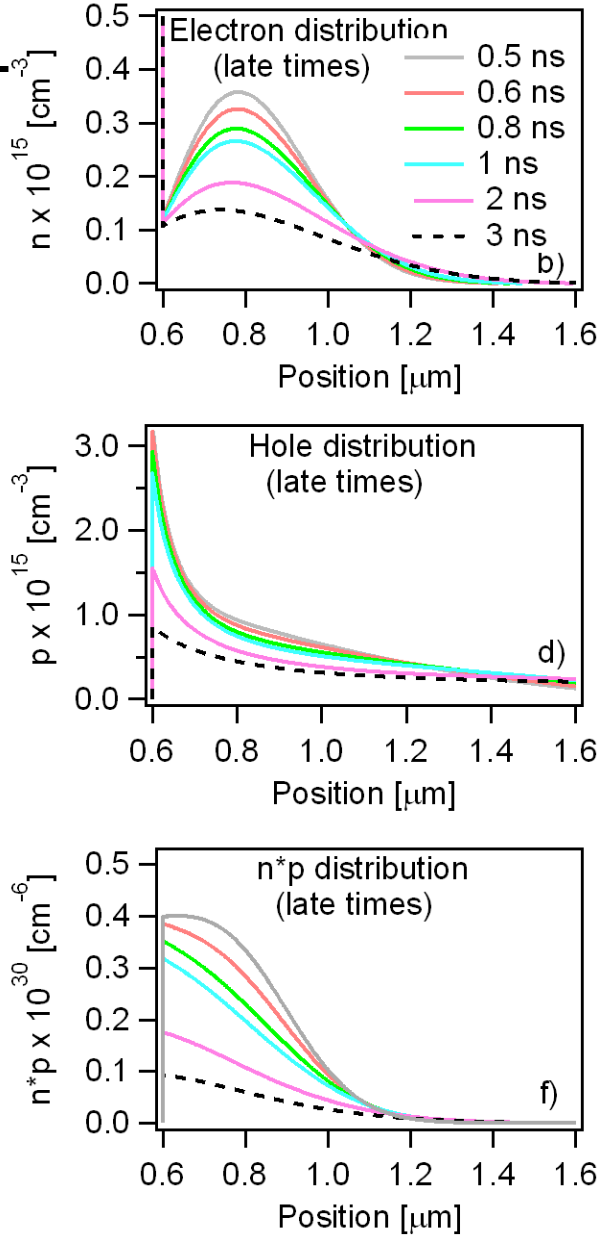


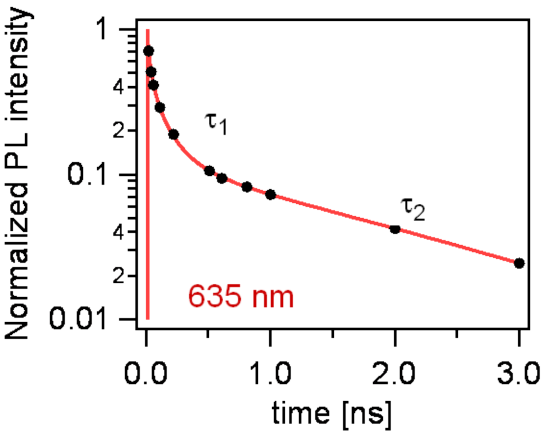
Kanevce et al. Prog. Photovolt: Res. Appl. doi:10.1.1002/pip.2369 (2013)

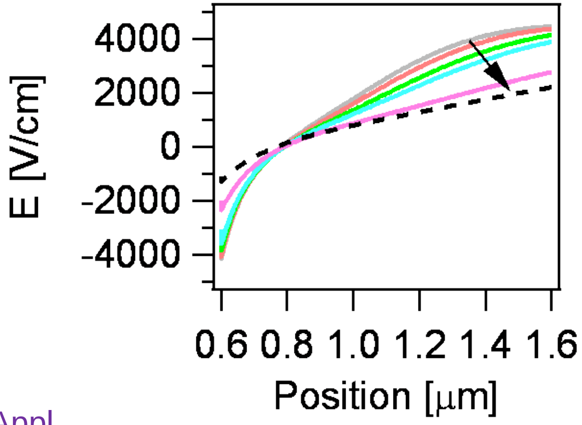


Carrier motion during the decay (later times)

- During the later times (τ_2) maximum electron and hole distribution move much less







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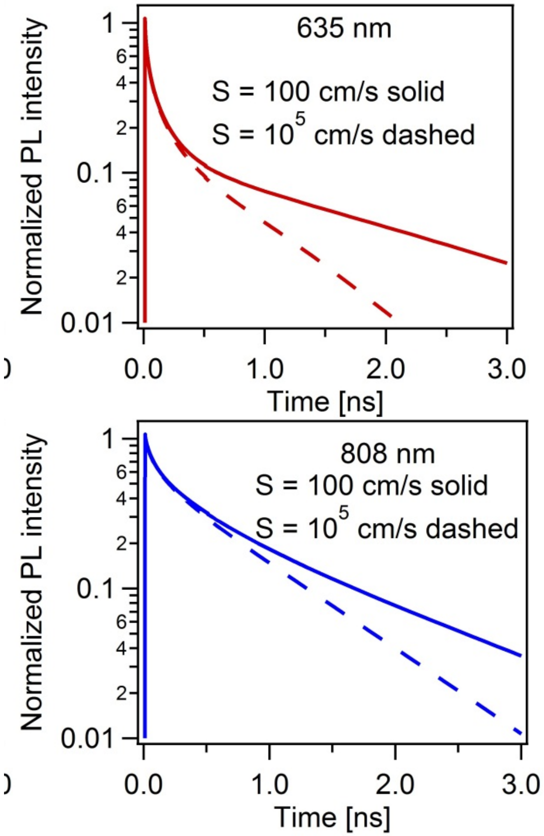
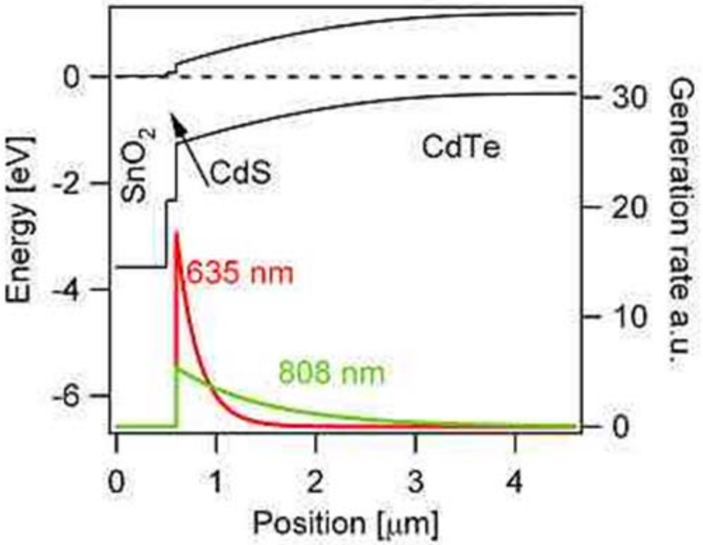
Interface and bulk recombination

- Interface recombination affects τ_2
- Higher impact on 635 nm
- Bulk impacts τ_2 as well
- Higher impact on 808 nm

Simulated TRPL decays at different S



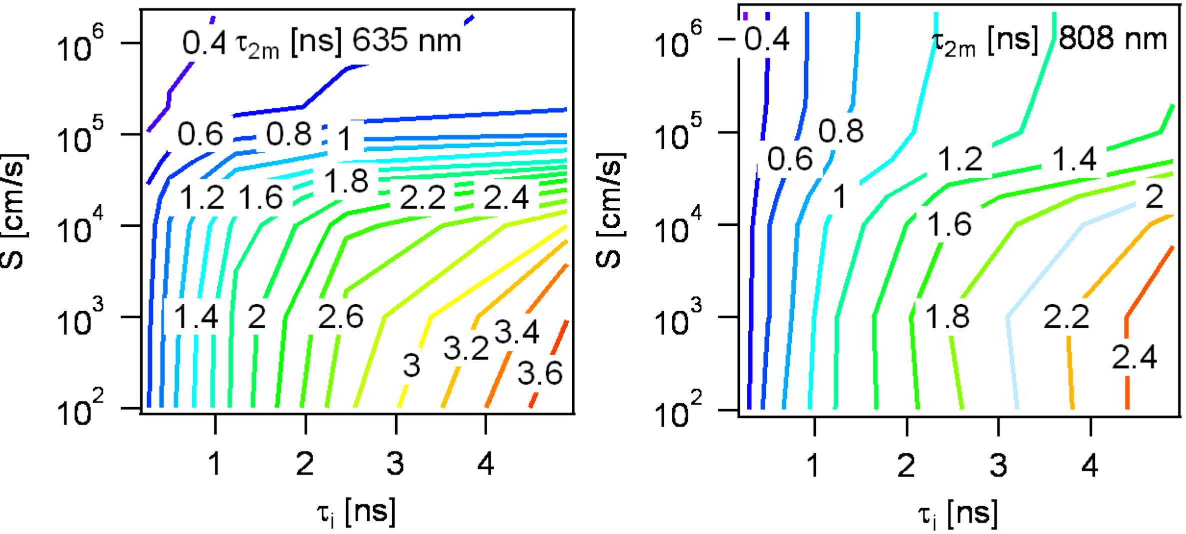


Kanevce et al. IEEE PVSC (2012)

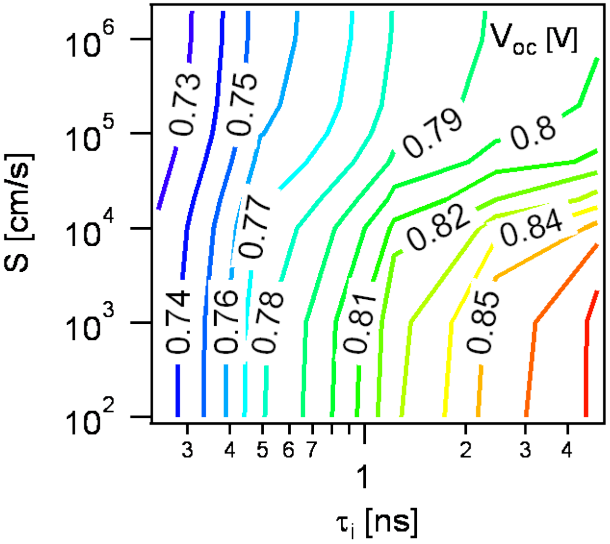
Interface, bulk recombination and V_{oc}

- Comparing decays at two wavelengths can direct towards the dominant recombination mechanism
- The decay slope indicator of V_{oc}

Slope of the second part of the decay (τ_2) as a function of bulk lifetime and interface recombination



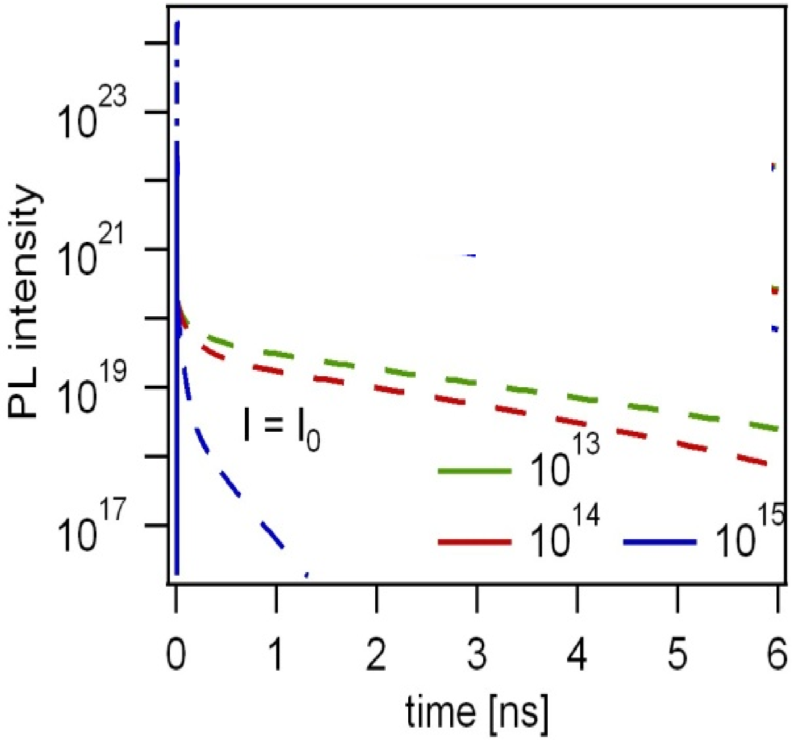
V_{oc} as a function of bulk lifetime and interface recombination



Impact of doping and injection on TRPL

- I_0 creates $3x10^{15}$ cm^{-3} at the CdS/CdTe interface
- For $I = I_0$, and $p = 10^{15}$ cm^{-3} the drift dominates the decay
- For $I = 100\ I_0$ – no impact of doping on the decay

Simulated TRPL decays for a CdTe device for different doping densities and different injection levels



Summary (part 1)

- Carrier decays after a short-light pulse illumination have been simulated to enhance the interpretation of TRPL measurements
- TRPL decays in thin-film solar cells are influenced by the carrier dynamics, including drift, diffusion, interface and bulk recombination
- For 635 nm illumination, the decays are affected more by the interface properties and drift compared to the 808 nm decays
- By comparing the decays at different wavelengths, it may be possible to estimate whether the dominant recombination is located at the interface or in the bulk

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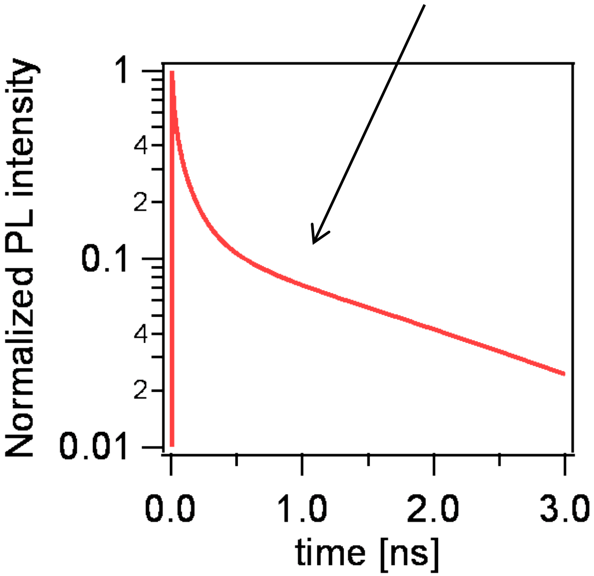
Dissecting different mechanisms

- PL intensity at each point in time ~(n*p)

- The slope of the decay (rate of change (R_{oc})) is:

$$R_{oc} = -\frac{1}{B}\frac{\partial(R)}{\partial t} = -\frac{\partial(np)}{\partial t} = -p\frac{\partial n}{\partial t} - n\frac{\partial p}{\partial t}$$

Slope ~ Rate of change (Roc)



- From the continuity equations:

$$\frac{\partial n}{\partial t} = G - R + \frac{1}{q}\frac{\partial Jn}{\partial x} = G - R + \mu_n \frac{\partial}{\partial x}(nE) + D_n\frac{\partial^2 n}{\partial x^2}$$

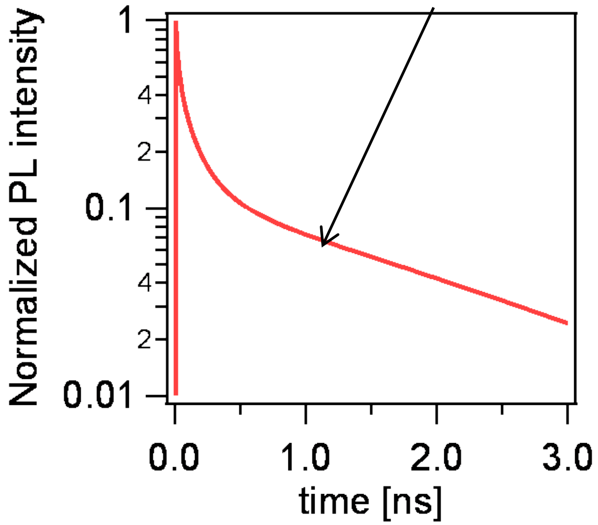
* p

$$\frac{\partial p}{\partial t} = G - R - \frac{1}{q}\frac{\partial Jp}{\partial x} = G - R - \mu_p \frac{\partial}{\partial x}(pE) + D_p\frac{\partial^2 p}{\partial x^2}$$

* n

Dissecting different mechanisms

- The derivative of n*p product **(**rate of change R_{oc}) is determined by 6 different carrier dynamics components

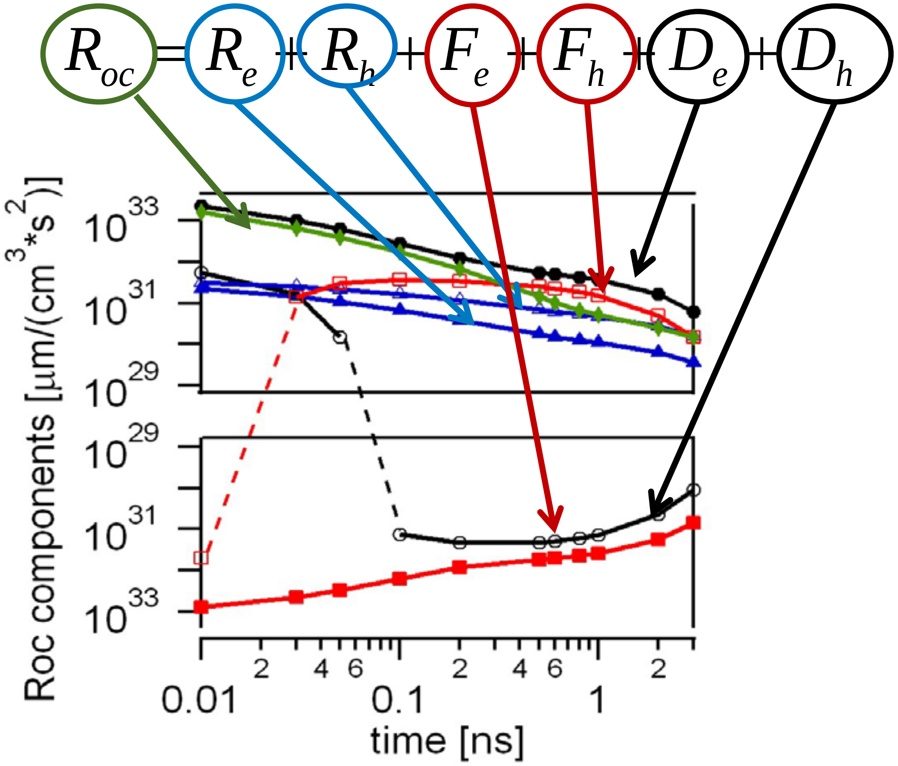


Slope ~ Rate of change (Roc)

$$Roc = -\frac{\partial(np)}{\partial t} = \underbrace{nR}_{\text{Electron recombination }(R_e)} + \underbrace{pR}_{\text{Hole recombination }(R_h)} - \underbrace{p\mu_n \frac{\partial}{\partial x}(nE)}_{\text{Electron drift }(F_e)} + \underbrace{n\mu_p \frac{\partial}{\partial x}(pE)}_{\text{Hole drift }(F_h)} - \underbrace{pD_n \frac{\partial^2 n}{\partial x^2}}_{\text{Electron diffusion }(D_e)} - \underbrace{nD_p \frac{\partial^2 p}{\partial x^2}}_{\text{Hole diffusion }(D_h)}$$

6- factor analysis

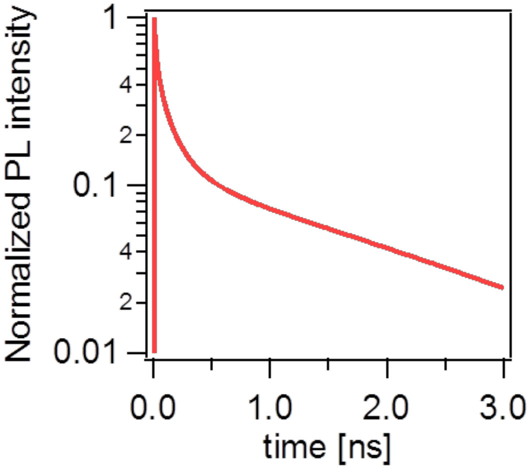
$$Roc = -\frac{\partial(np)}{\partial t} = nR + pR - p\mu_n \frac{\partial}{\partial x}(nE) + n\mu_p \frac{\partial}{\partial x}(pE) - pD_n \frac{\partial^2 n}{\partial x^2} - nD_p \frac{\partial^2 p}{\partial x^2}$$



$$R_{oc} = R_e + R_h + F_e + F_h + D_e + D_h$$

Kanevce et al. Prog. Photovolt: Res. Appl. (2013)

- At early times, recombination is much lower than R_{oc}
- Electron drift and diffusion have largest magnitudes, but opposite directions



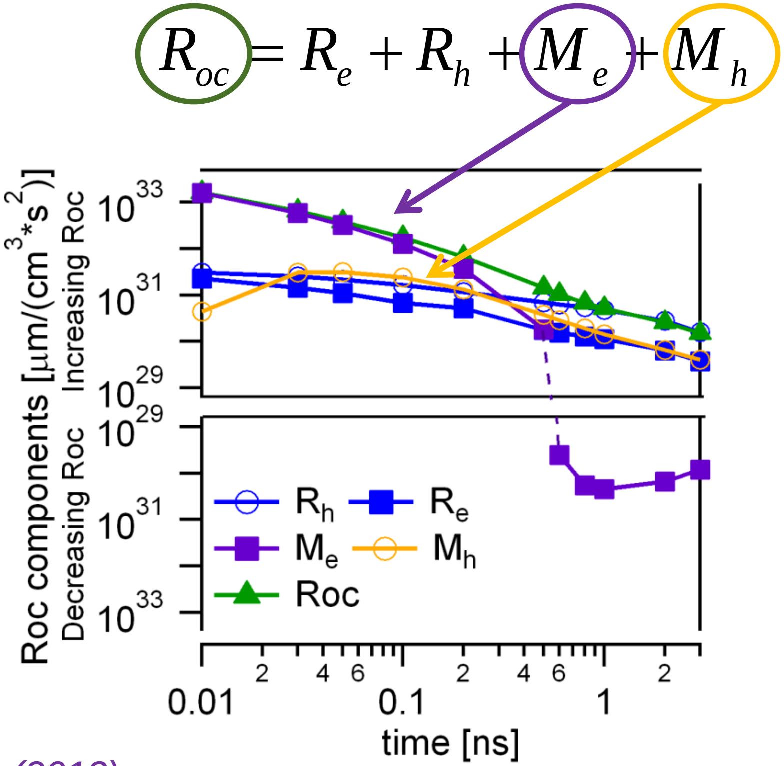
4-factor analysis

- Electron motion dominates the TRPL slope at early times
- At later times, the electron motion decreases the R_{oc}

$$R_{oc} = R_e + R_h + F_e + F_h + D_e + D_h$$

$$M_e = F_e + D_e$$

$$M_h = F_h + D_h$$



$$R_{oc} = R_e + R_h + M_e + M_h$$

Kanevce et al. Prog. Photovolt: Res. Appl. (2013)

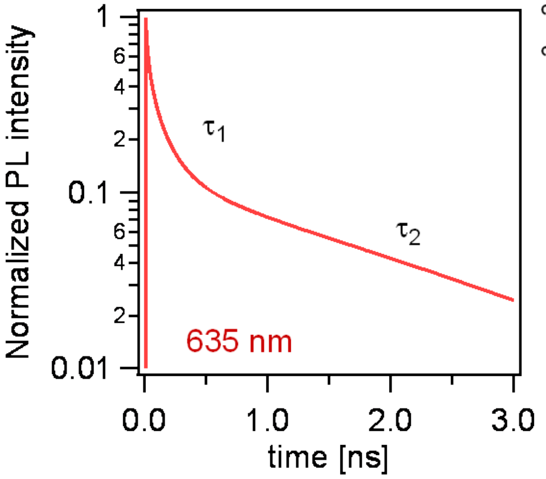
2-factor analysis

Recombination or carrier motion

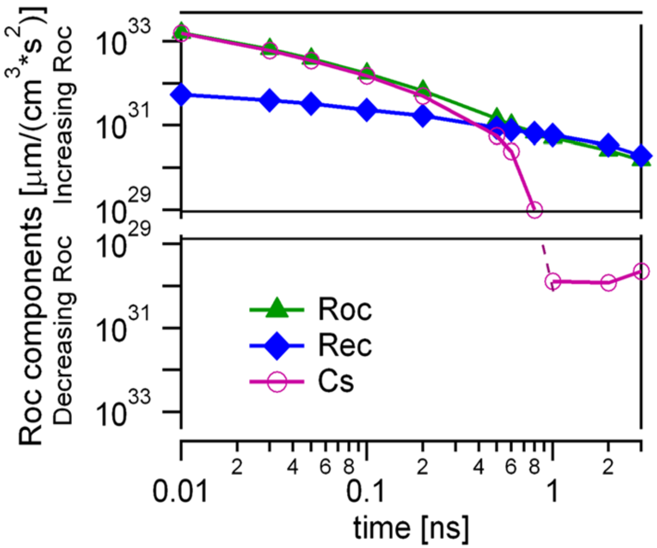
- Combine diffusion and drift into carrier motion

$$R_{oc} = C_k + R_{ec}$$

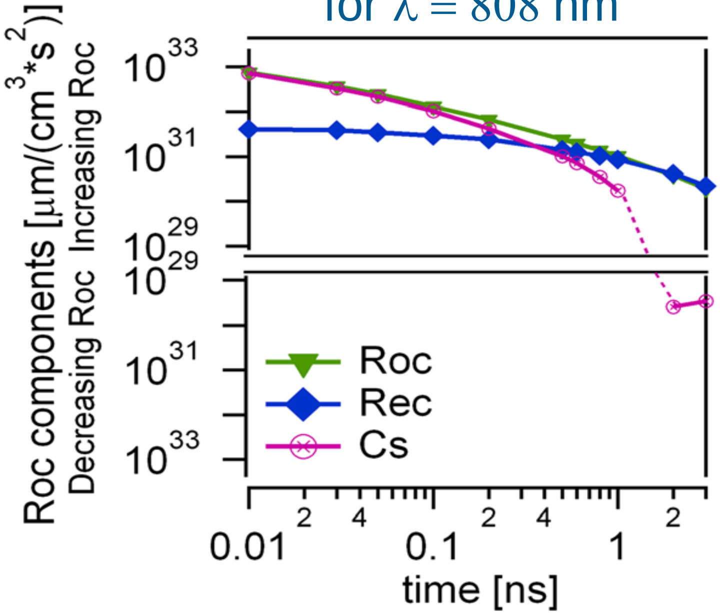
- During the faster part of the decay (τ_1) the carrier motion dominates the decay
- At later times (τ_2) the recombination is dominant



2 factor analysis for $\lambda = 635$ nm



2 factor analysis for $\lambda = 808$ nm



Summary (part 2)

- A mathematical method can be used to separate contributions from different mechanisms on the TRPL decay
- The TRPL decay can be dissected into diffusion, drift and recombination terms
- Under the conditions studied, simulations show that during the fast initial part of the decay, the slope of the TRPL curve is dominated by drift and diffusion of carriers
- Hence, information about recombination within the absorber material or at the heterointerface is not easily obtained from this section of the curve
- The latter, slower part of the decay provides best information about the material quality
- For CdTe absorbers with significantly lower mobilities or significantly faster recombination, these relationships could change

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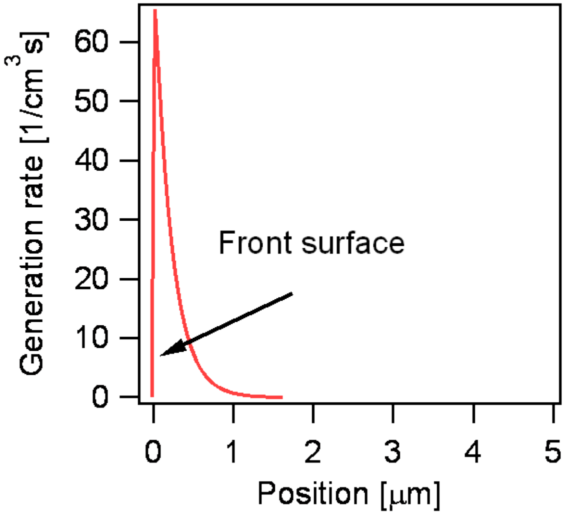
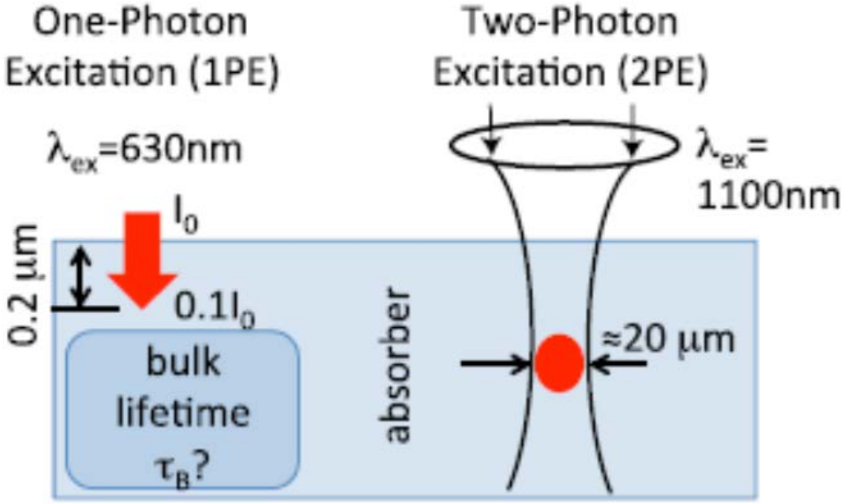
- Spatial distribution of generated carriers in CdTe absorbers

Spatial generation of carriers

- CdTe has a high absorption coefficient
- Most of the light is absorbed next to the interface
- It might be impossible to distinguish interface vs. bulk recombination with a single measurement
- With 2 photon excitation (2PE), the laser beam can be focused at different places in the material and hopefully provide information about bulk and interface separately

$$\frac{1}{\alpha(630nm)} = 200\ nm$$



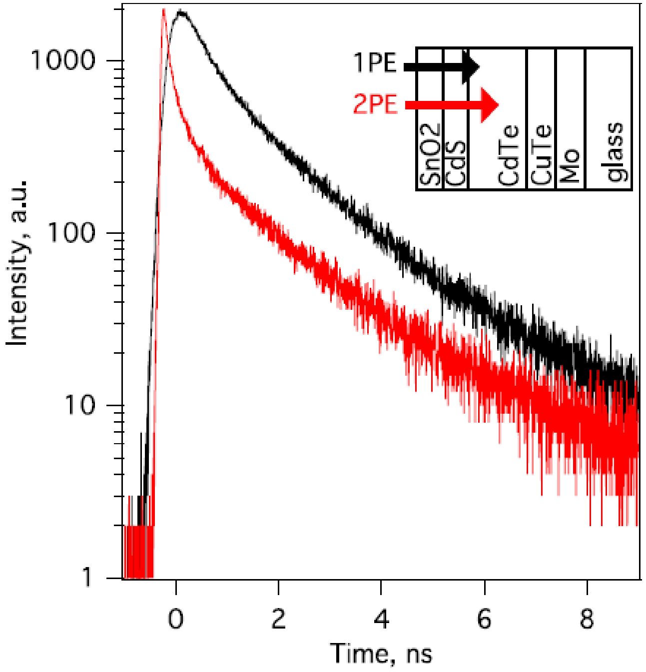


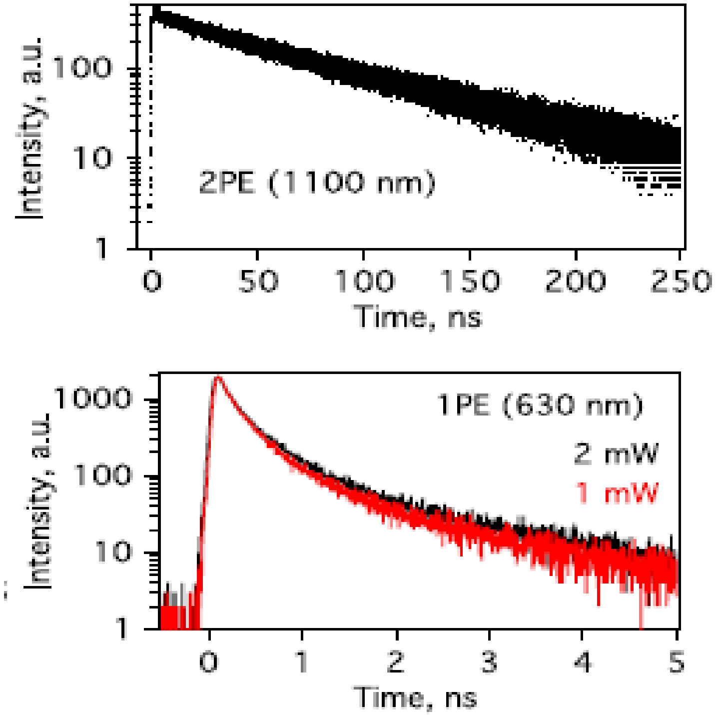
Kuciauskas et al, JPV (2013)

Experimental 1PE and 2PE decays

- 1PE and 2PE measurement on a px- CdTe device with a substrate structure
- Lifetime values determined from decays are similar

- 1PE and 2PE measurement on an undoped single crystal CdTe
- Decay times are orders of magnitude different

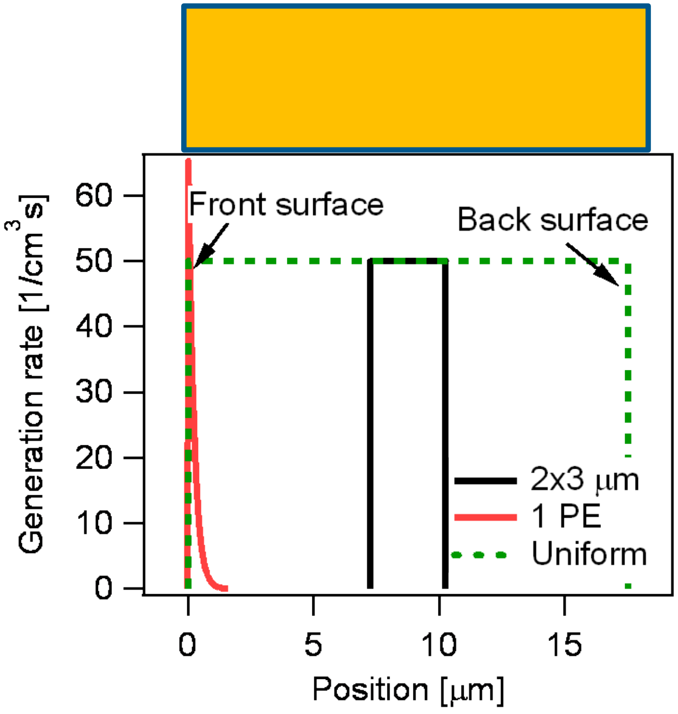




Kuciauskas et al, JPV (2013)

Understand the 2PE measurement

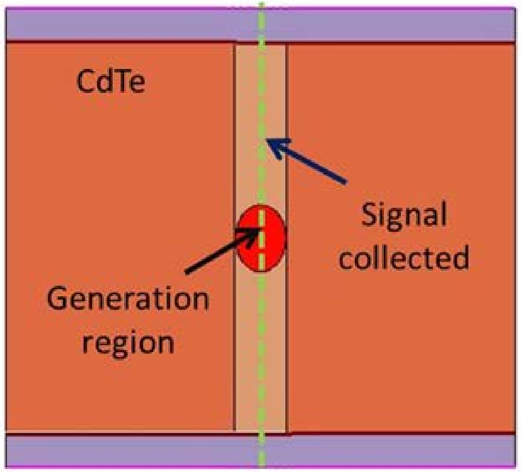
- Can one separate surface and bulk using a small spot 2PE measurement?
- Under which conditions?
- Or by using a combination of measurements?
  - Compare 1PE and 2PE
  - Small spot size and uniform generation
- For good quality materials that have a long diffusion length, does diffusion of carriers interfere with the measurement?

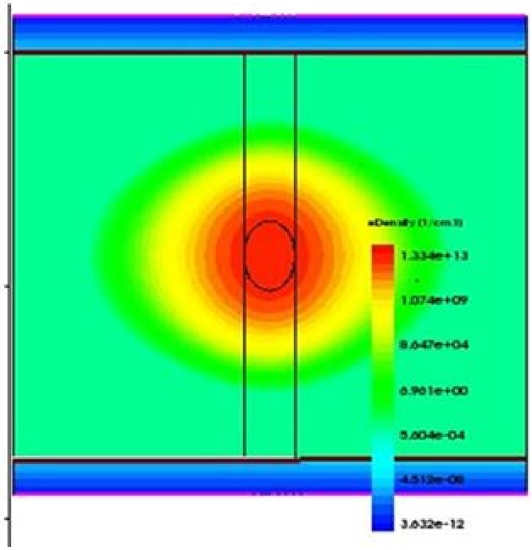


Different spatial generation

A 2D model

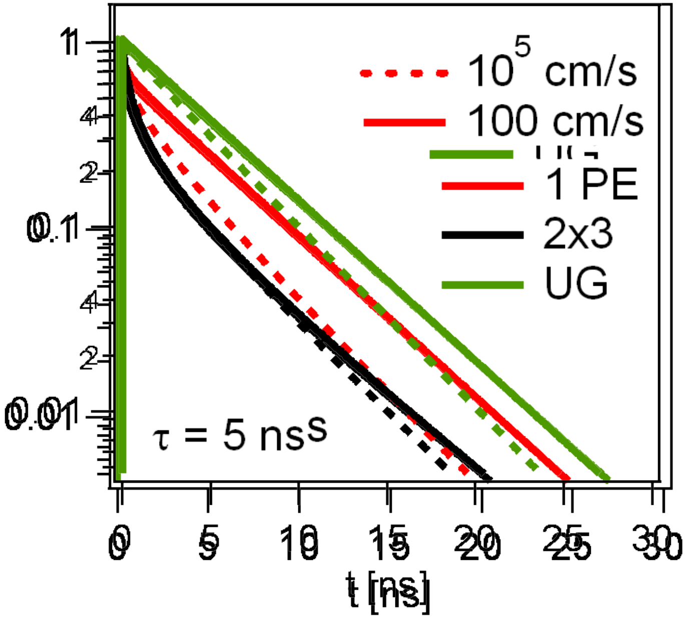
- A 17.5 microns thick CdTe absorber is illuminated by a 2PE signal
- Generation profile is shown with an ellipse in the middle of the sample
- Generation within the ellipse is uniform
- Radiative recombination rate is integrated over a cylinder shown with lighter orange color





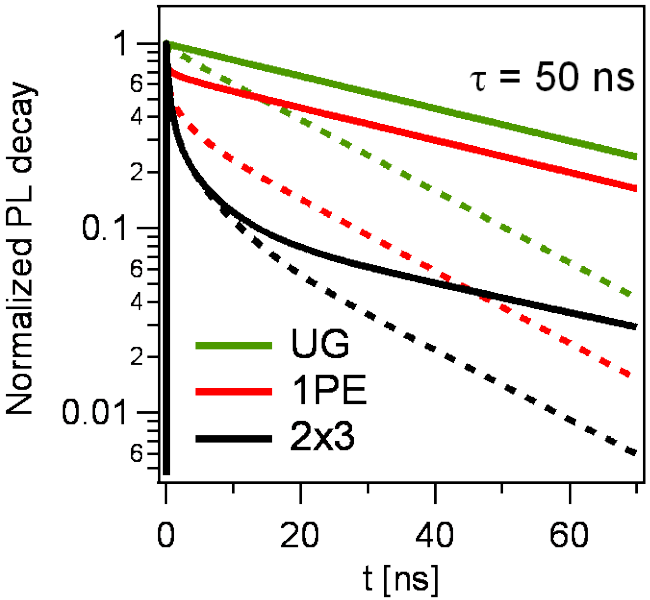
Different spatial generation

- Simulated TRPL decay for 1PE excitation, uniform generation, and small spot excitation
- Slower slopes (τ_2) are equivalent in all measurements
- They contain information about both bulk and interface



τ = 5 ns; L = 2.8 μm

S = 100 cm/s



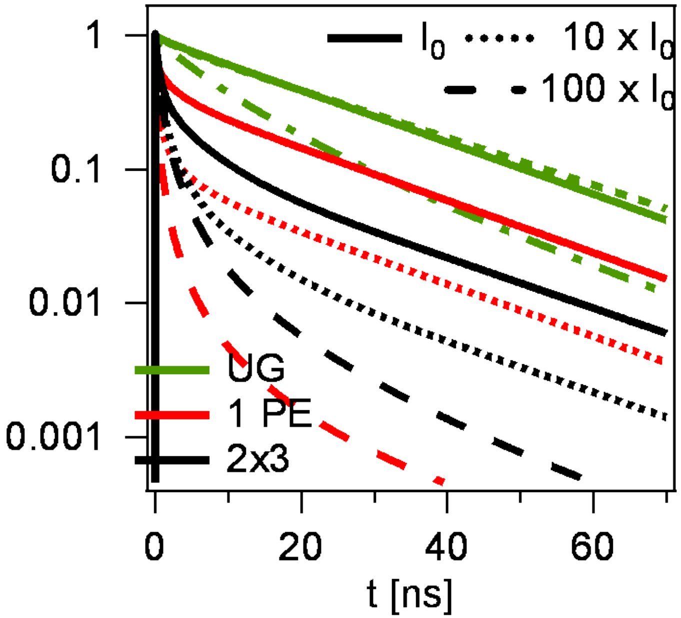
τ = 50 ns

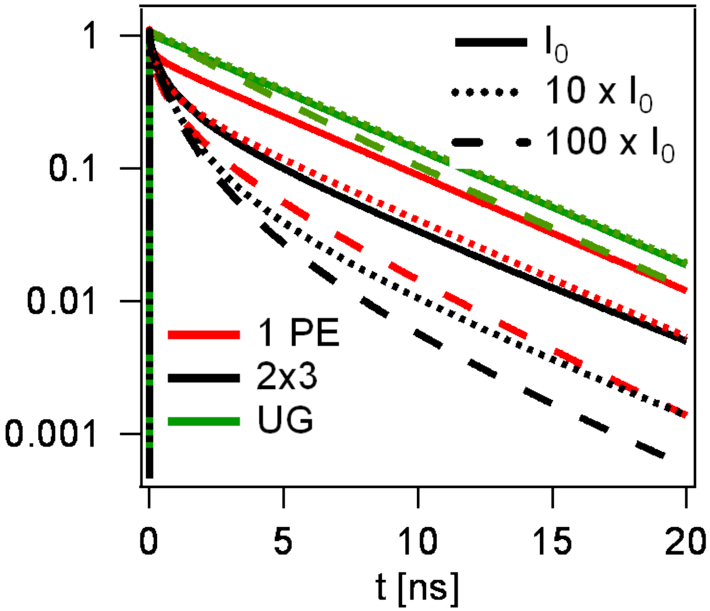
L = 8.8 μm

Injection dependence

- τ = 50 ns, S =10^5 cm/s
- Surface recombination dominates

- τ = 5 ns, S = 100 cm/s
- Bulk recombination dominates





- In both cases, similar behavior is observed
- τ_2 becomes smaller as we increase injection intensity
- For τ_b = 50 ns this change with intensity is larger, because of larger diffusion length

Summary (part 3)

- By altering the spatial generation of carriers, it might be possible to deconvolute surface and bulk recombination
- A combination of measurements might offer a possibility to estimate carrier mobility in addition to lifetime

Thank you for your attention