Distinguishing Bulk and Surface Recombination By Measuring and Modeling Ultrafast Carrier Dynamics

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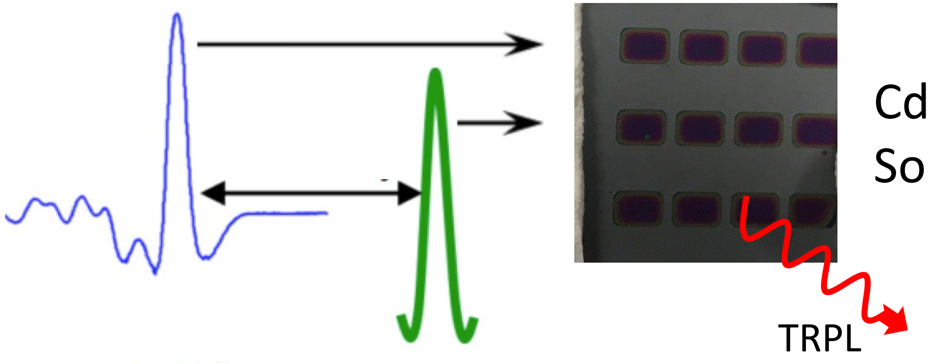
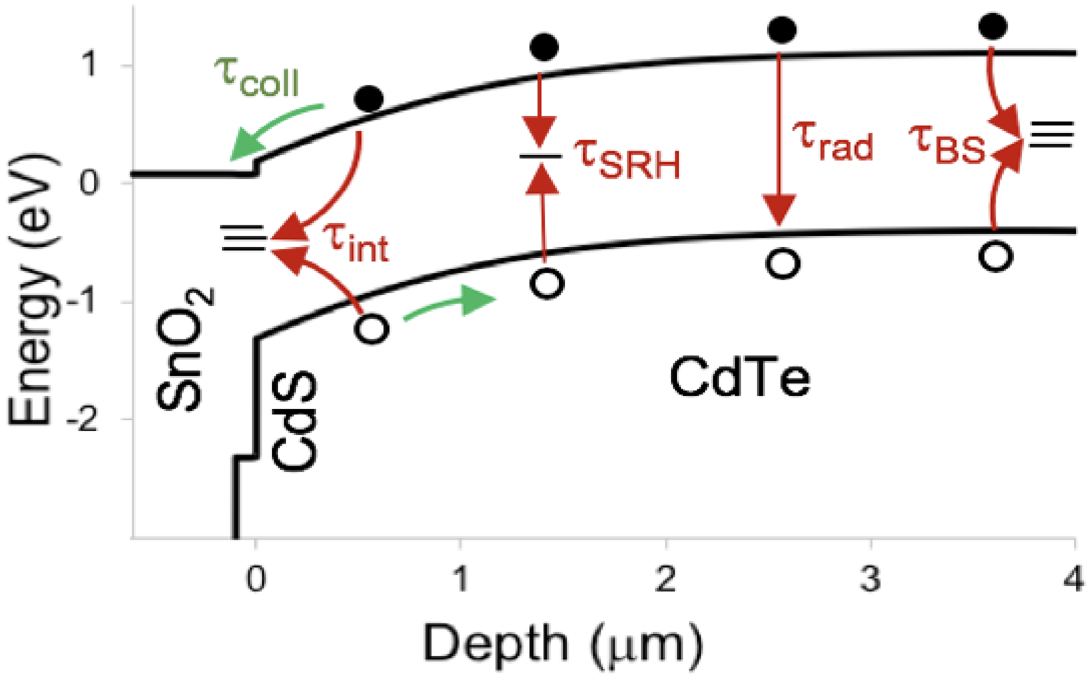
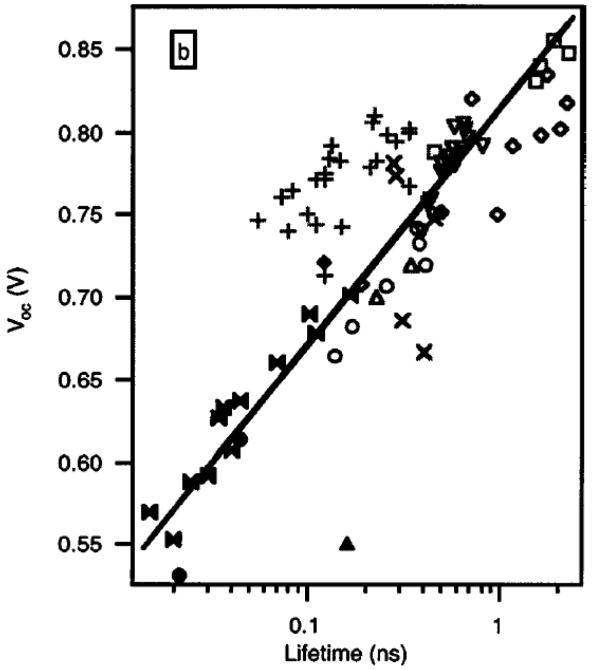


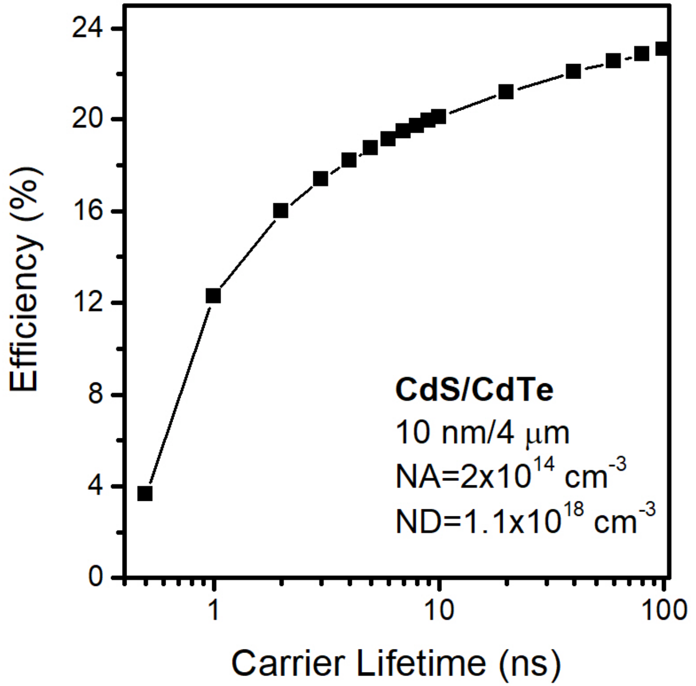
CdTe Thin Films and Solar Cells

Identifying Sources of Recombination to Inform Device Design & Processing





Metzger et al., JAP (2003)



Simulations with SCAPS

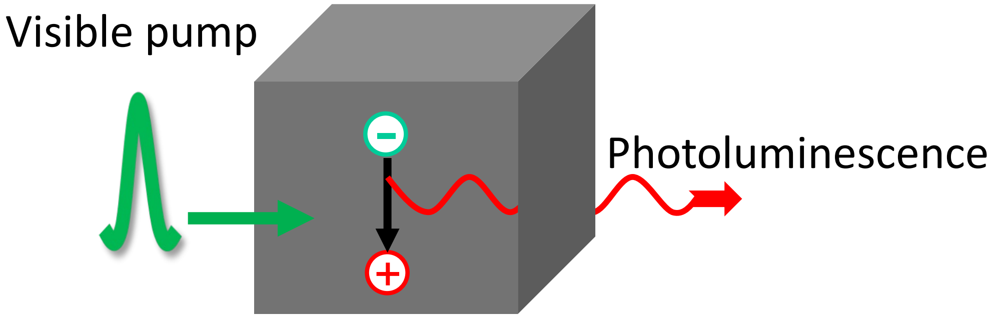
What is the photoexcited carrier lifetime?

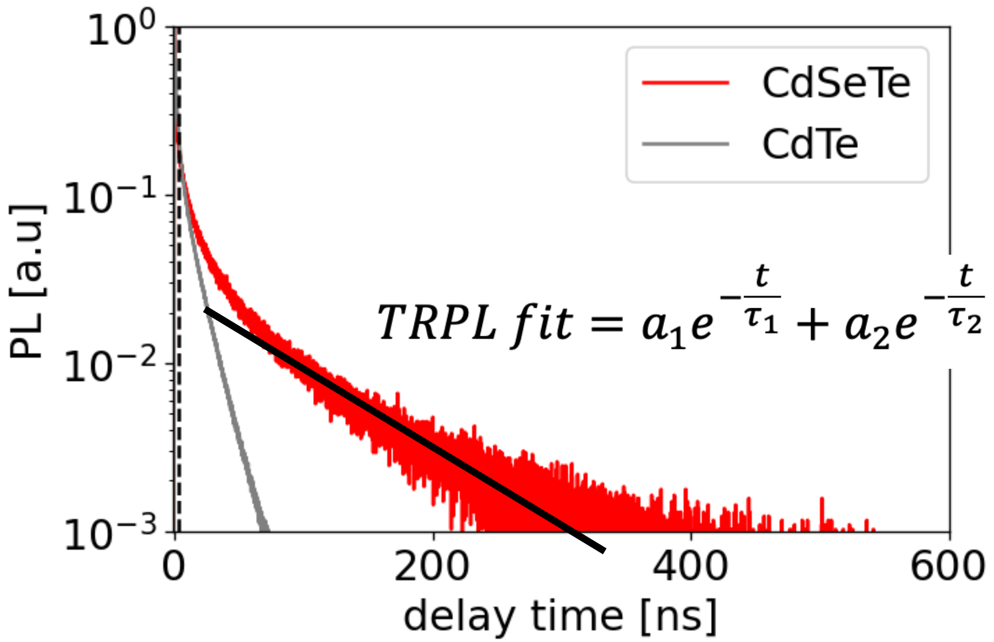
Which recombination mechanisms, bulk or surface/interface, are limiting?

How can we answer these questions?

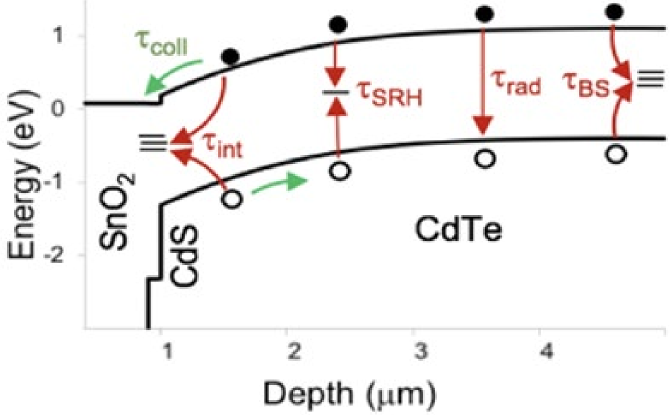
Conventional Approach: τ_2 from Time-Resolved Photoluminescence (TRPL)

TRPL probes photoluminescence from radiative recombination





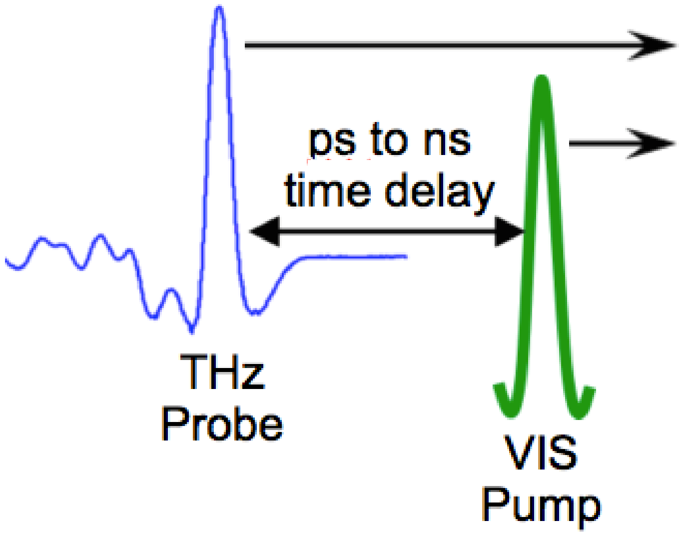
$$TRPL\ fit = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}}$$



- Often assumed that long time constant τ_2 is associated with the bulk lifetime.
- Early dynamics from carrier redistribution and surface recombination.
- Charge storage in the junction and de-trapping can also influence dynamics.
- This approach can lead to incomplete and sometimes incorrect understanding, as described by Hages, *Adv. Mater.* 2017; Moseley, *J. Appl. Phys.* 2021; Taheri, *J. Appl. Phys.* 2021; Hages, *Joule* 2022.

Our Approach: Combined Dynamics and Modeling

Time-Resolved Photoluminescence &
THz Spectroscopy



Data

Modeling

Carrier Lifetimes
Recombination Mechanisms
Carrier Density
Mobility

Feedback

Design materials to
increase PV efficiency

Transport Models Reveal Transient Carrier Density Profiles

Continuity equations for electrons and holes:

$$\nabla . J_n = -q\left(G - R - \frac{\partial n}{\partial t}\right)$$

$$\nabla . J_p = q\left(G - R - \frac{\partial p}{\partial t}\right)$$

with G=0

pn-n_i^2

$$\boxed{R_{SRH}} = \tau_p \frac{\sigma_n\sigma_p v_{th} N_t (pn - n_i^2)}{\sigma_n\left[n+n_i \exp\frac{E_t-E_i}{kT}\right] + \tau_n \sigma_p\left[p+n_i \exp\frac{E_i-E_t}{kT}\right]}$$

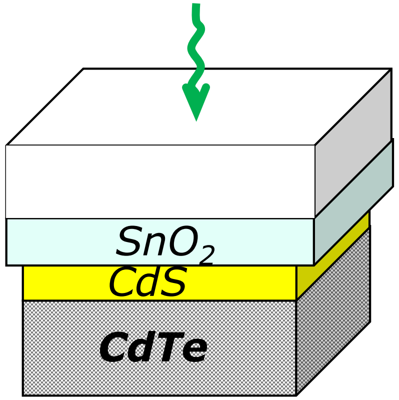
$$R_{rad} = B_{rad}(np - n_0 p_0)$$

Poisson's equation:

$$\nabla^2 V = -\frac{q}{\varepsilon}(p - n + N_d - N_a)$$

Initial condition (pulsed light, Beer's law):

$$N_{photon\ flux} = N_0 \exp(-x\alpha_i)$$



CdS/CdTe Interface:

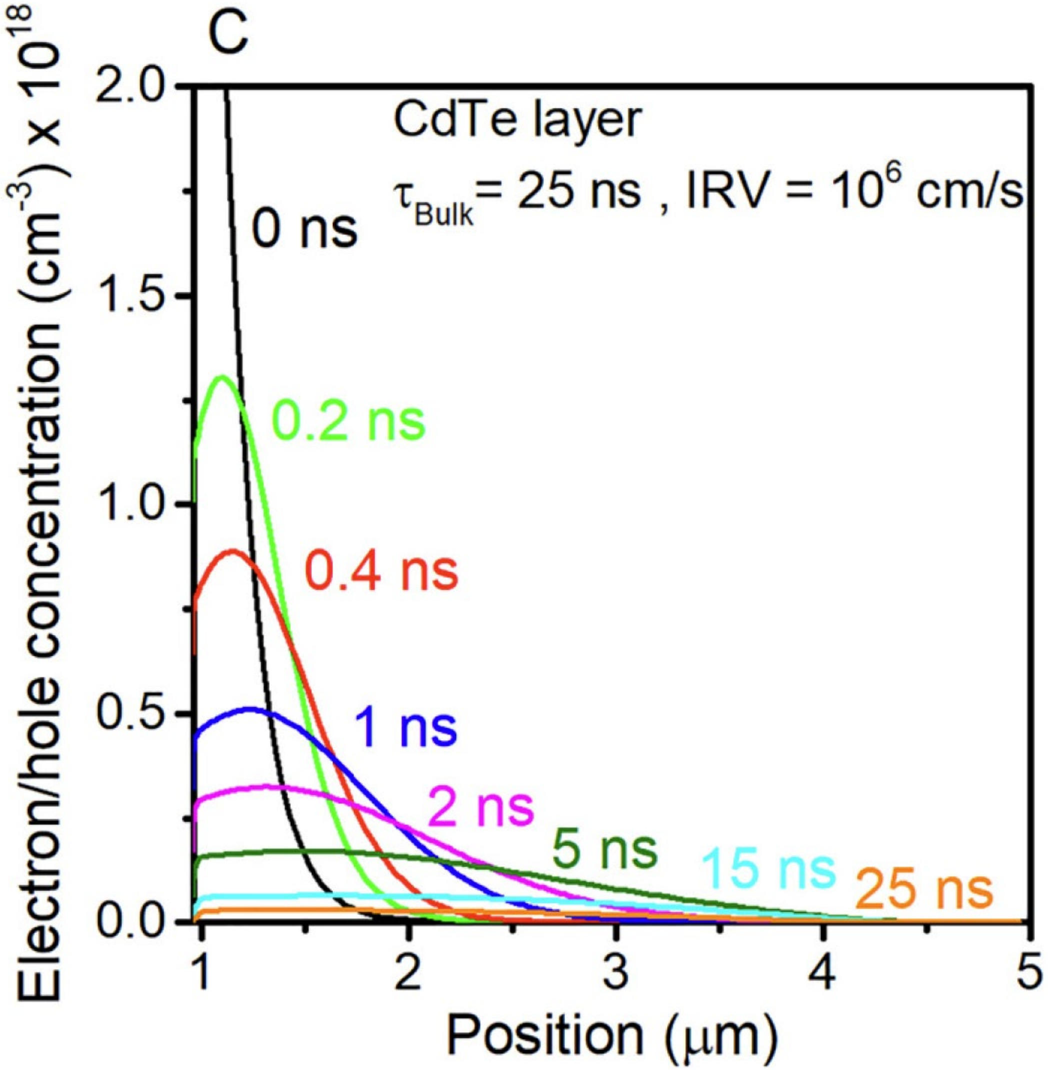
$$\frac{dn}{dx} = \boxed{\frac{IRV}{D_n}} n(0,t)$$

$$\frac{dp}{dx} = \frac{IRV}{D_p} p(0,t)$$

CdTe Back Surface:

$$\frac{dn}{dx} = \boxed{\frac{BSRV}{D_n}} n(L,t)$$

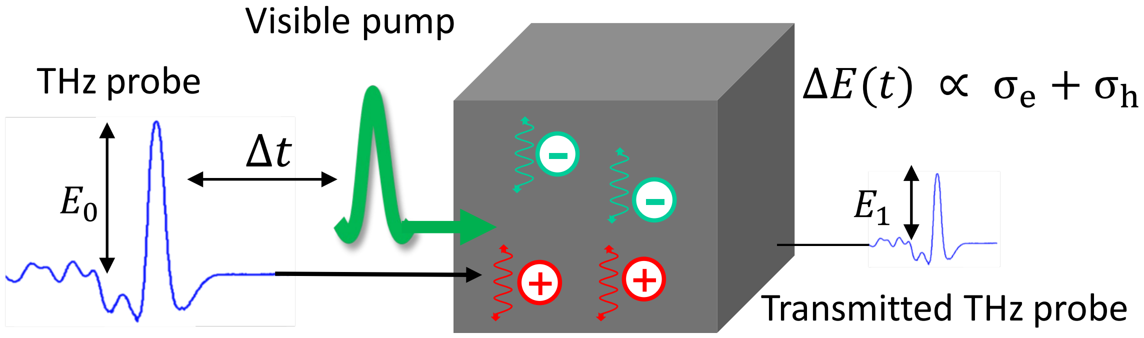
$$\frac{dp}{dx} = \frac{BSRV}{D_p} p(L,t)$$



Solved using COMSOL

Complementary Time-Resolved Terahertz Spectroscopy (TRTS)

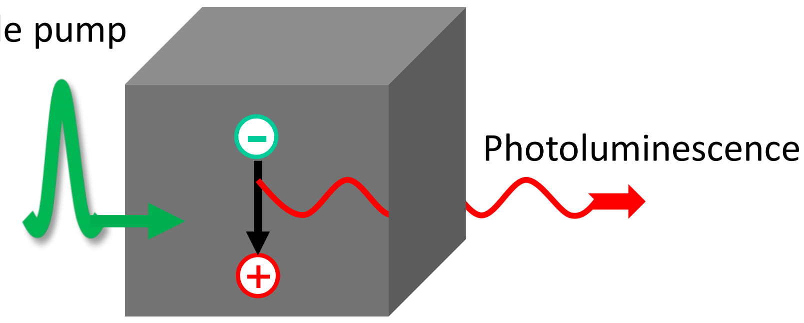
Time-resolved terahertz spectroscopy:



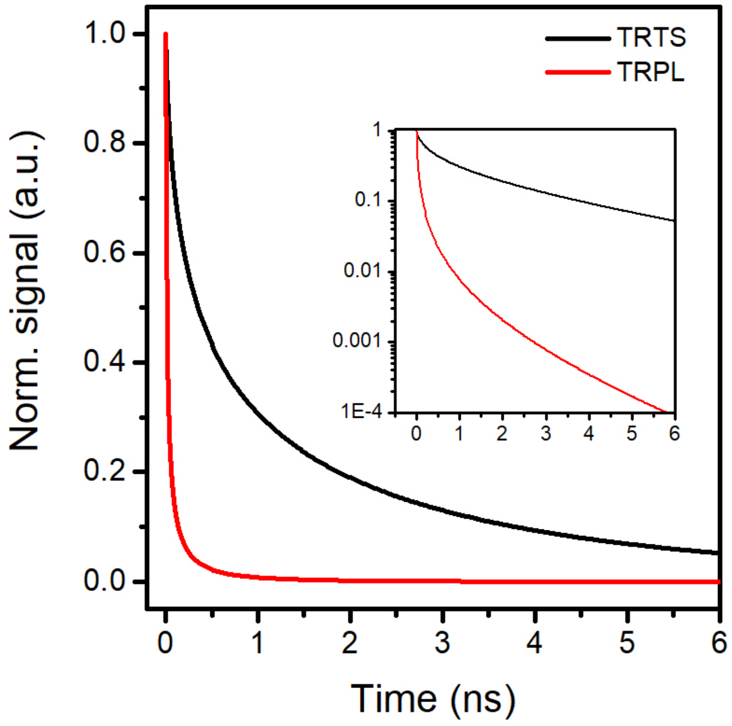
$$\Delta E(t) \propto \sigma_e + \sigma_h$$

TRTS probes the photoconductivity induced by electrons and holes (Terahertz pulse: 0.2 - 2 THz, or 0.8 - 8 meV, or 6.6 - 66 cm^{-1})

Time-resolved photoluminescence:



TRPL probes photoluminescence from radiative recombination



$$\Delta E(t) \propto \sigma_e(t) + \sigma_h(t)$$

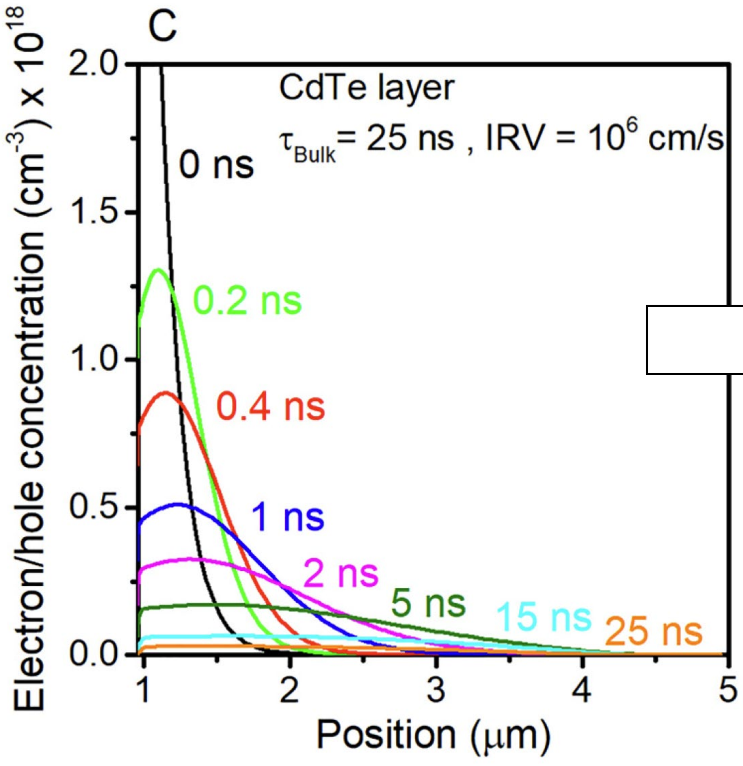
$$\propto q\mu_e \Delta n(t) + q\mu_h \Delta p(t)$$

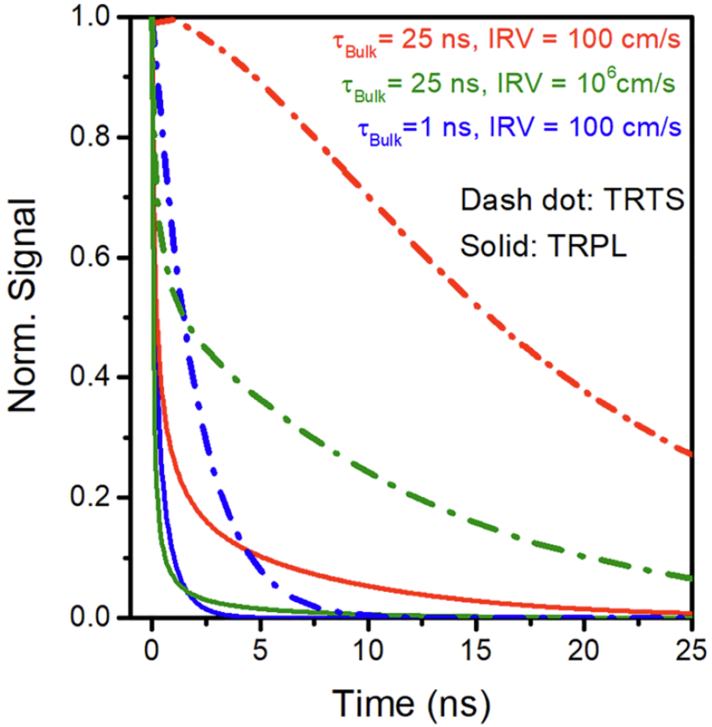
Δn: Electron concetration
Δp: Hole concetration
μ_e: Electron mobility
μ_h: Hole mobility
q: Elementary charge constant

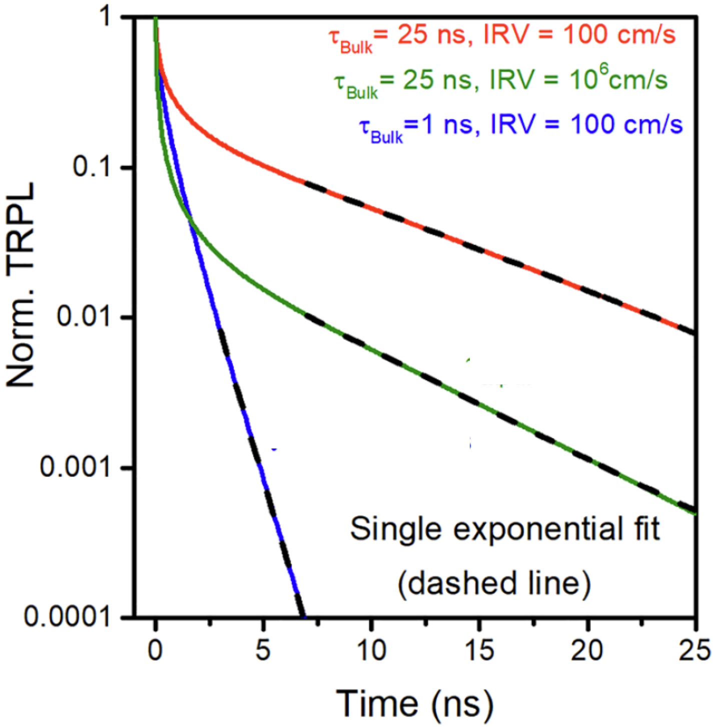
Simulation of TRTS and TRPL Signals

$$TRTS(t) \propto \int (\mu_e \Delta n(x,t) + \mu_h \Delta p(x,t))dx$$

$$TRPL(t) \propto \int (np - n_0 p_0)dx$$

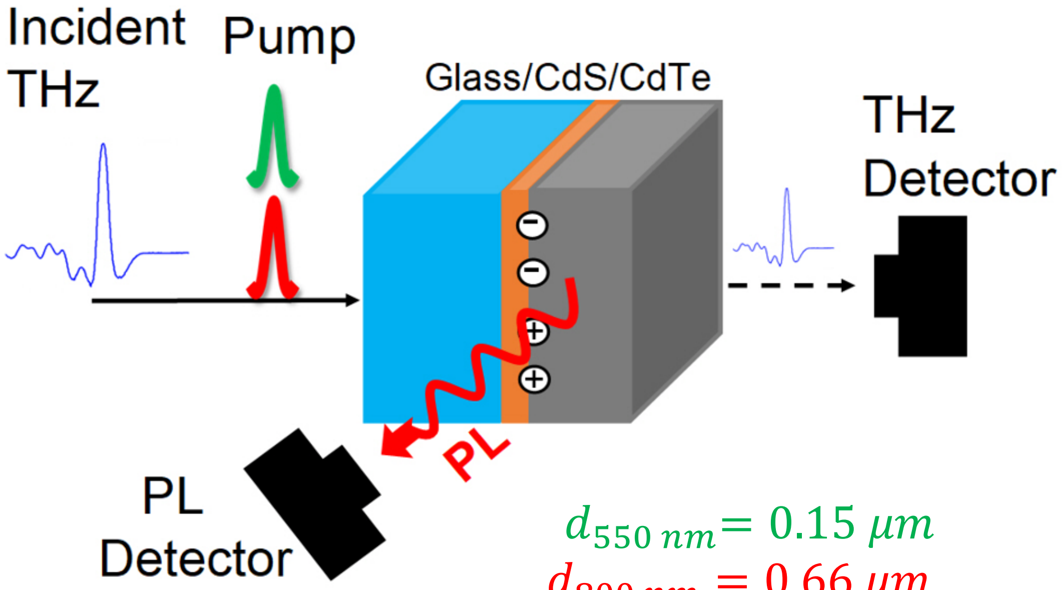




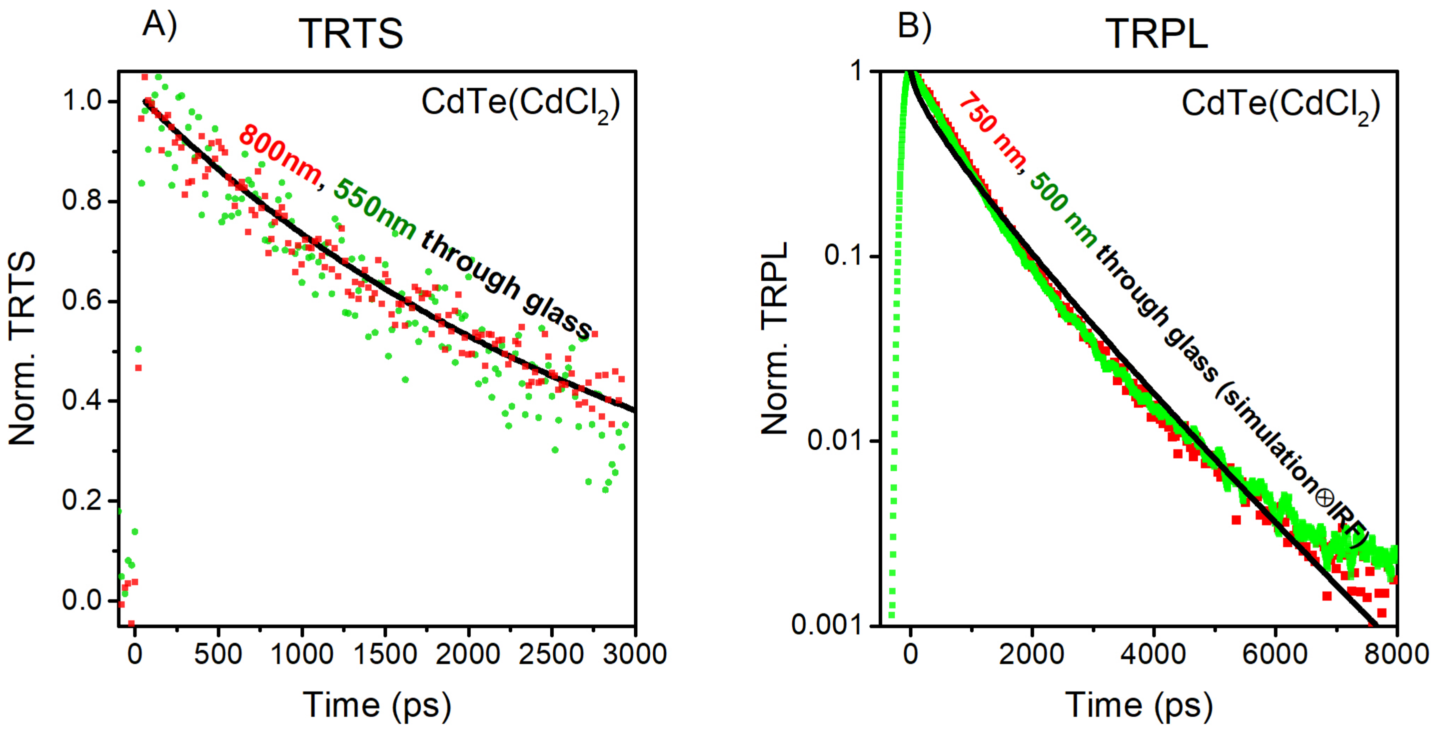


Taheri, JAP (2021)

Extracting Recombination Parameters from Fits to Data



$d_{550\ nm} = 0.15\ \mu m$
$d_{800\ nm} = 0.66\ \mu m$



Use of multiple pump wavelength simplifies differentiation between surface and the bulk recombination.

Comparable dynamics when excited from glass side for Green vs Red excitation.

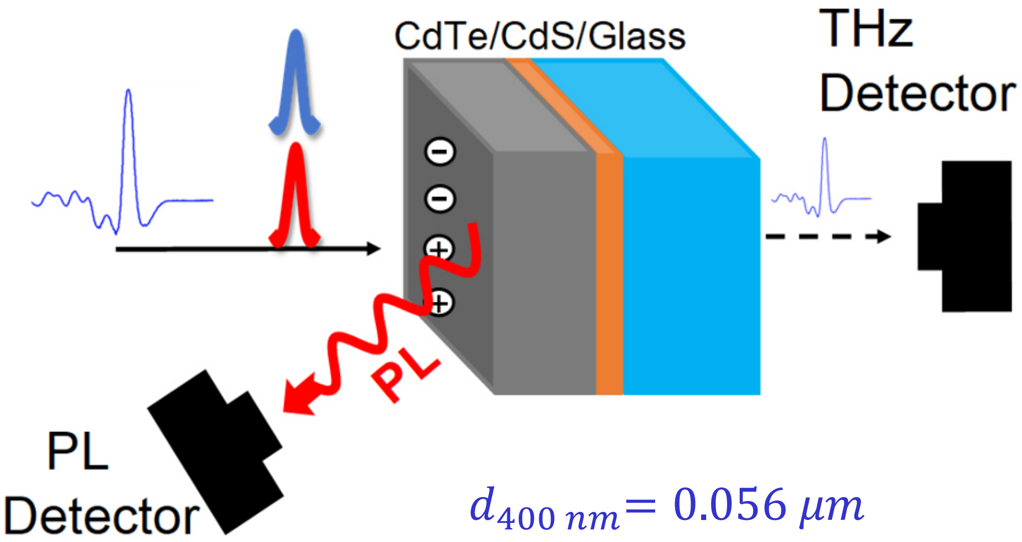
Negligible/suppressed IR (<2x10^4 $\frac{cm}{s}$)

Bulk lifetime of 1.7 ns

VTD of CdTe on CdS with CdCl$_2$
from U. Delaware IEC

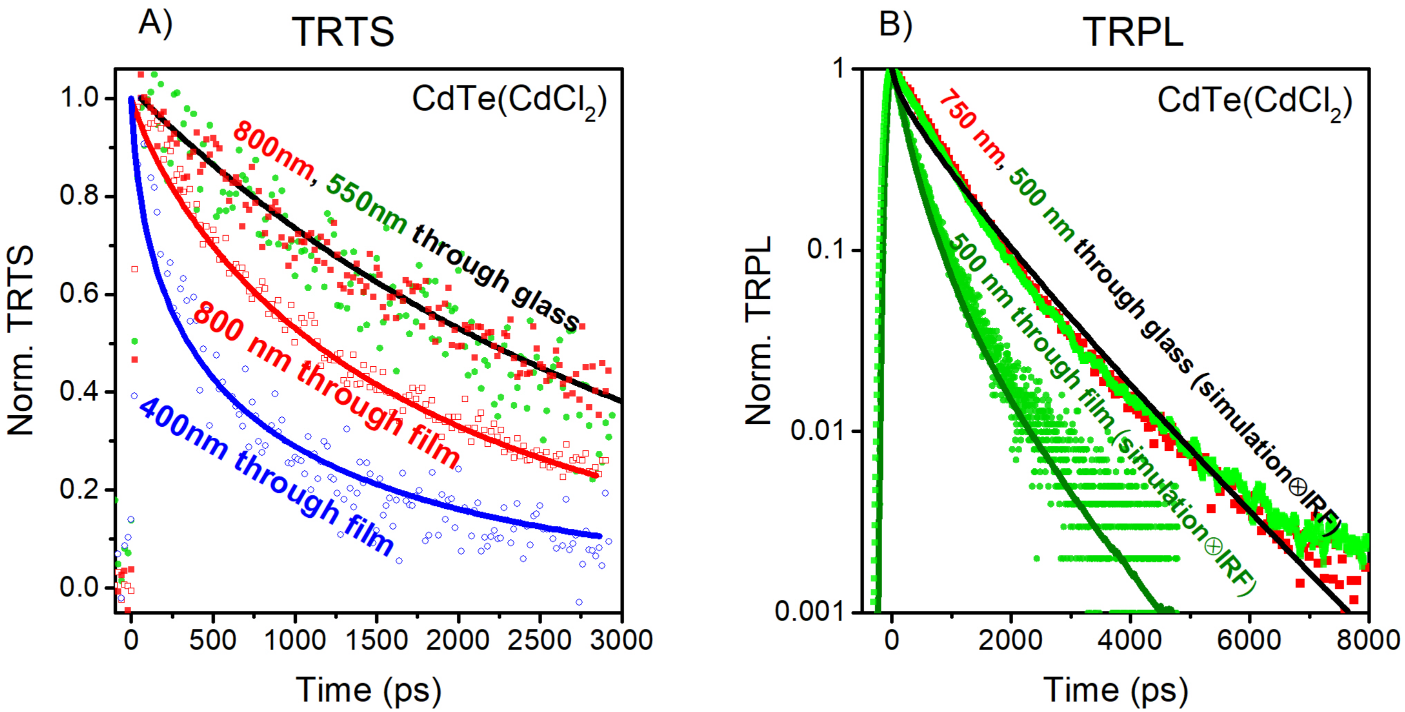
Taheri, JAP (2021)

Evaluating Back Surface Recombination



$d_{400\ nm} = 0.056\ \mu m$

$d_{800\ nm} = 0.66\ \mu m$



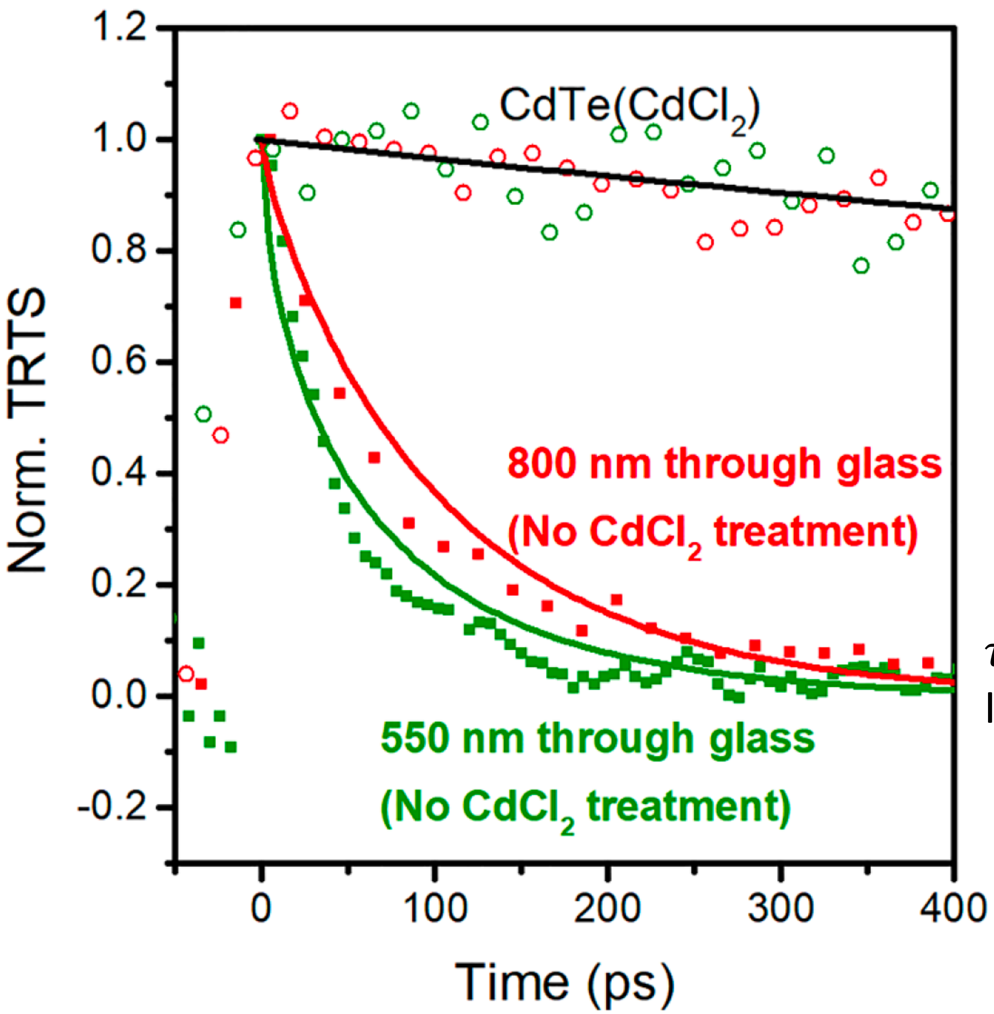
Dynamics are faster with Blue than Red excitation when excited from film side.

→ **Need to consider back surface recombination in addition to bulk recombination**

BSRV: $6 \times 10^4 \frac{cm}{s}$

Bulk lifetime: 1.7 ± 0.3 ns

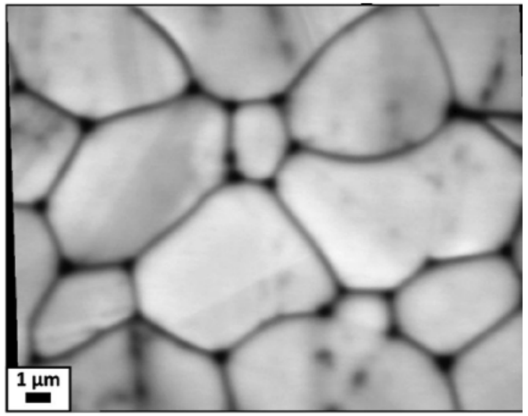
$CdCl_2$ Treatment of CdTe Films Improves Bulk and Interface

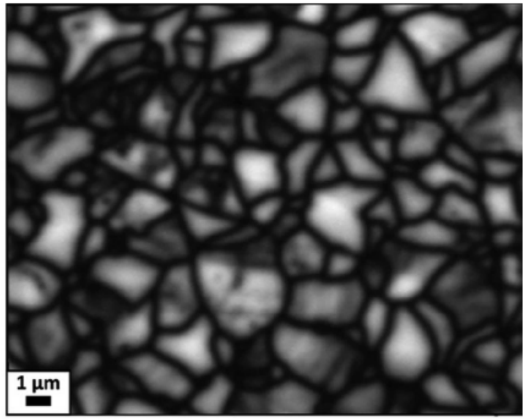


$\tau_{bulk} = 1.7 \pm 0.3\ ns$
IRV: Negligible interface recombination ($<2x10^4$ cm/s)

$\tau_{bulk} = 53 \pm 7\ ps$
IRV = 1×10^8 cm/s

After $CdCl_2$, larger grains

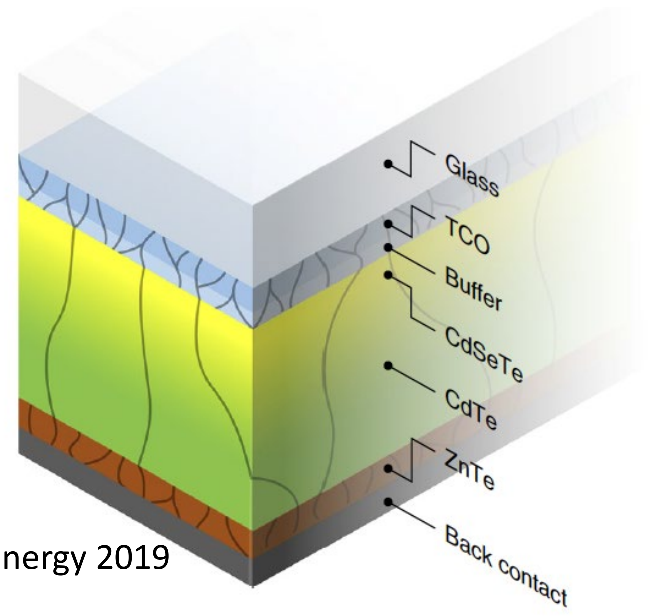




Before $CdCl_2$, many grain boundaries

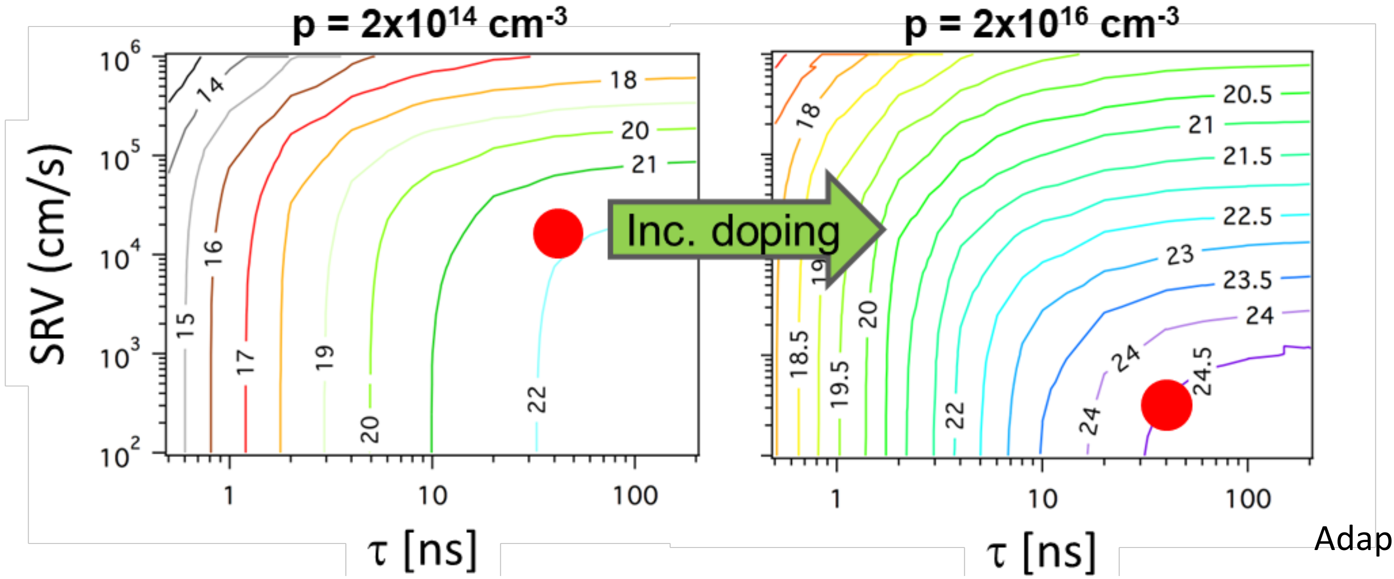
*Adapted from M. Amarasinghe et al., Adv. Energy Mater.,2018.

Next Steps Toward Improving CdTe PV Performance



Metzger,
Nature Energy 2019

State-of-the-art devices from First Solar use:
- Wide bandgap buffer layer
- CdSeTe/CdTe graded absorber and Cu/As doping
- ZnTe or alternative back contact

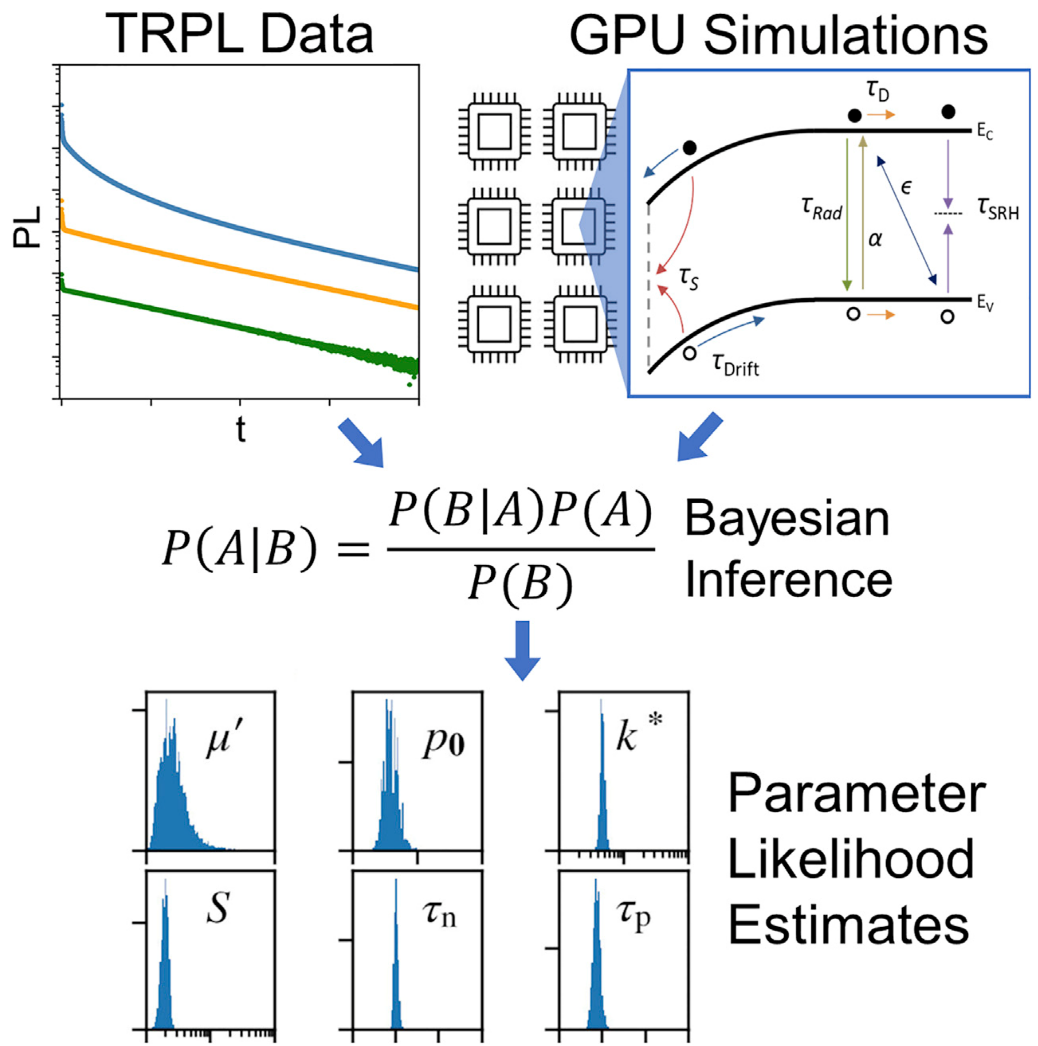


Adapted from Kanevce, JAP (2017)

New collaborative DOE project led by Univ. of Delaware aims to use Sb doping to increase V_{oc} and efficiency. Will require long bulk lifetimes and slow surface recombination.

Next Steps with Method: Parameter Extraction with Bayesian Inference

- COMSOL model is accurate but slow
  - ~30 min per TRPL or TRTS simulation
  - Limits the number of simulated parameter sets compared to experimental data
- Prof. Chuck Hages (U. Florida) has developed a new Python model to solve the semiconductor equations in an absorber film on GPUs that can test simulated parameter sets ~10^4x faster
  - *Joule* 2022
- Bayesian inference enables extraction of best fit parameters upon comparison to experimental data



TRPL Data

GPU Simulations

$$P(A|B) = \frac{P(B|A)P(A)}{P(B)}$$

Bayesian Inference

Parameter Likelihood Estimates

Example Iterated Bayesian Inference

- Multiparameter $(\boldsymbol{k}, \boldsymbol{n_0}, \boldsymbol{p_0}, \boldsymbol{\tau_n}, \boldsymbol{\tau_p}, \boldsymbol{\mu_n}, \boldsymbol{\mu_p}, \boldsymbol{\epsilon}, \boldsymbol{S_f}, \boldsymbol{S_b})$ Bayesian inference allows for decoupling regimes with overlapping contributions

- Experimental data is compared to simulated data sets to compute likelihood values

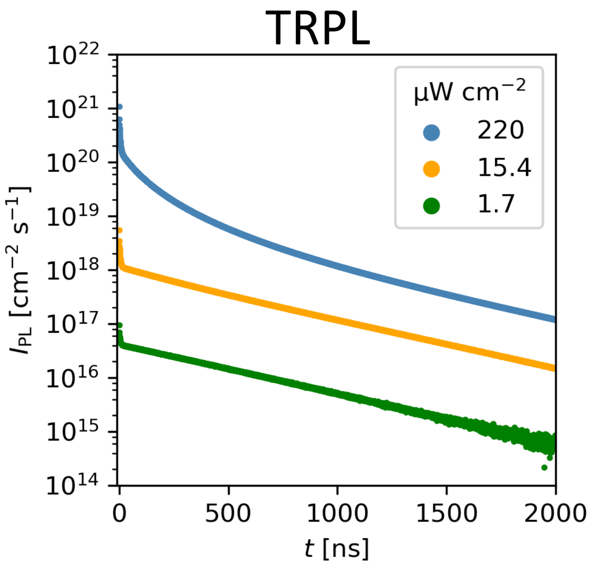
$$P(\Omega|y_n) = \frac{P(\Omega|y_{n-1})P(y_n|\Omega)}{P(y_n)}$$

Bayes Theorem

$$P(y_n|\Omega) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{\left(y_n - y_n^*(\Omega)\right)^2}{2\sigma^2}}$$

Likelihood

Example Inference on Perovskite Film

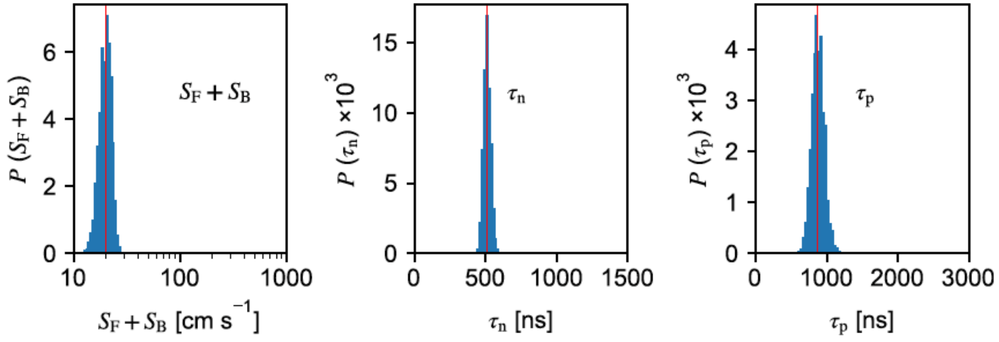


Parameter	Input	Inferred
μ_n (cm^2 V^{-1} s^{-1})	20	$\mu' = 22 \pm 0.2$
μ_p (cm^2 V^{-1} s^{-1})	20	
$k^\star/10^{-11}$ (cm^3 s^{-1})	4.8	4.8 ± 0.05
$p_0/10^{15}$ (cm^{-3})	3	3.0 ± 0.03
τ_n (ns)	511	511 ± 0.9
τ_p (ns)	871	878 ± 3.1
S_F (cm s^{-1})	10	$(S_F + S_B) = 19.8 \pm 0.1$
S_B (cm s^{-1})	10	

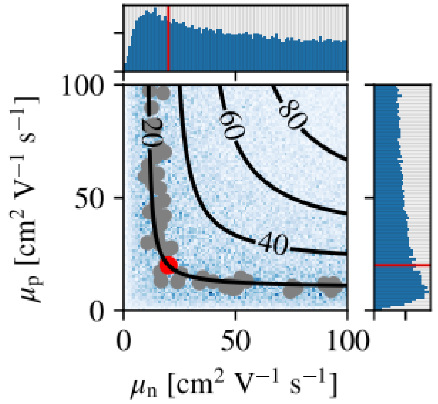
1. **Improved output information density**

   Analytical solutions rely on approximations and decoupled physics in asymptotic regimes

2. **Better data** (probability histograms)

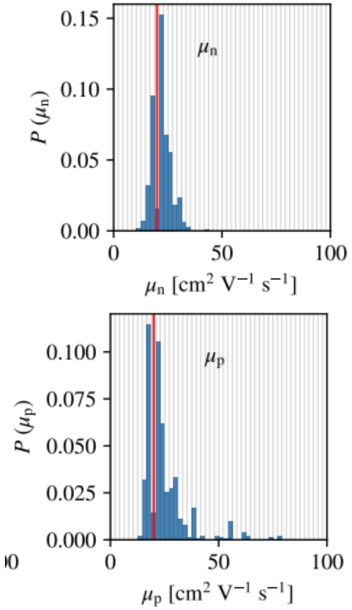


3. **Parameter correlations**



4. **Experimental Design**

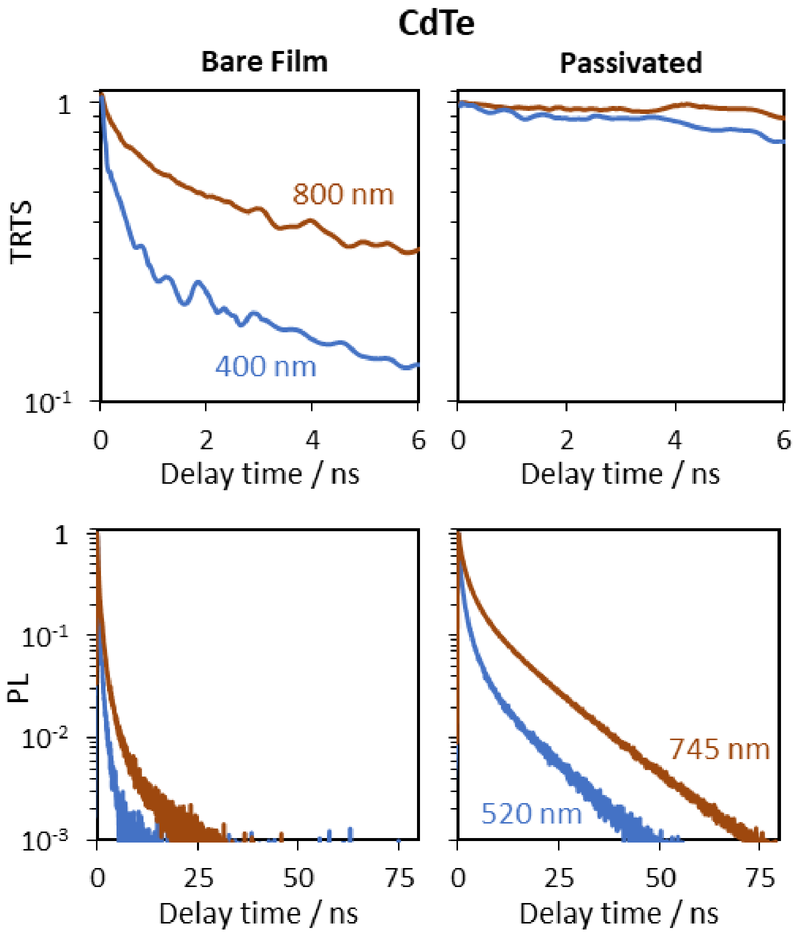
   Use large data sets of (millions of simulations) to design experiments to improve inferred parameter confidence

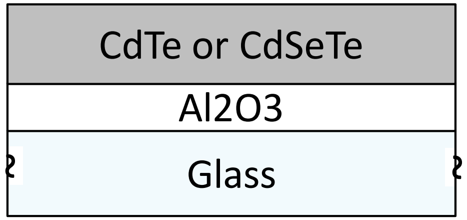


Fai, Ladd, Hages, *Joule*, **6**, 1-27 (2022)

Test Case: Uniform $CdSe_xTe_{1-x}$ Absorber from NREL

Combined TRTS & TRPL:





CdTe or CdSeTe

Al2O3

Glass

Carrier Diffusion (μ’)

← Surface Recombination (S_F or S_B) →

Bulk Recombination (k, τ_{SRH})

Bulk Recombination

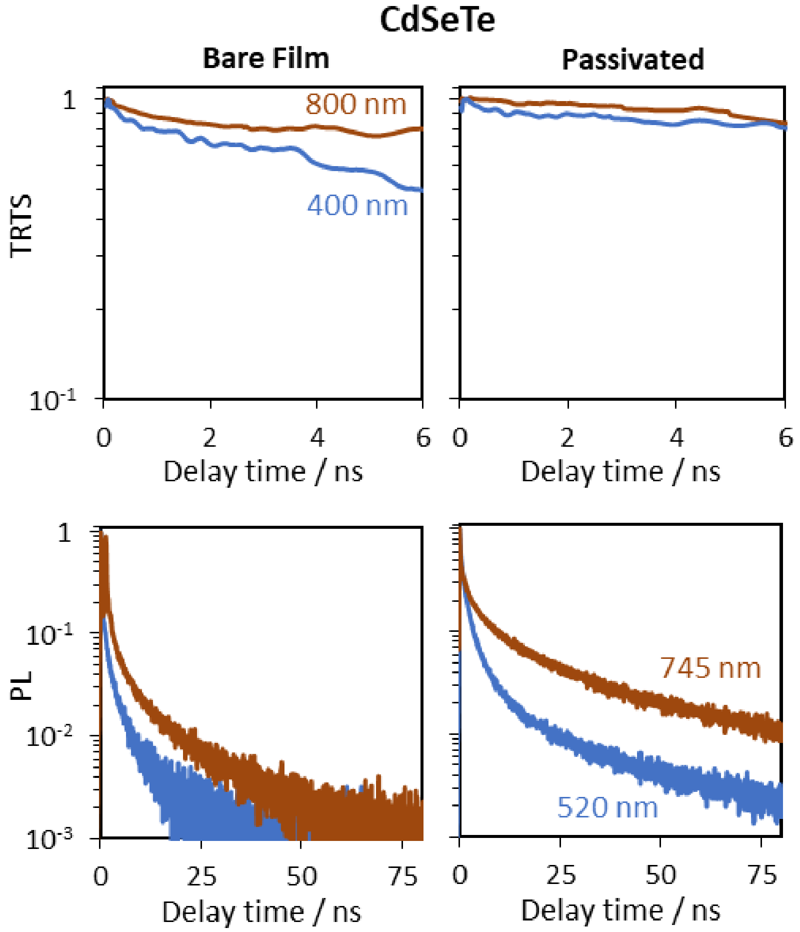
High Injection: k, $\tau_n + \tau_p$

← *Low Injection:* τ_n →

Surface Recombination

High Injection: $S_F + S_B$, μ'

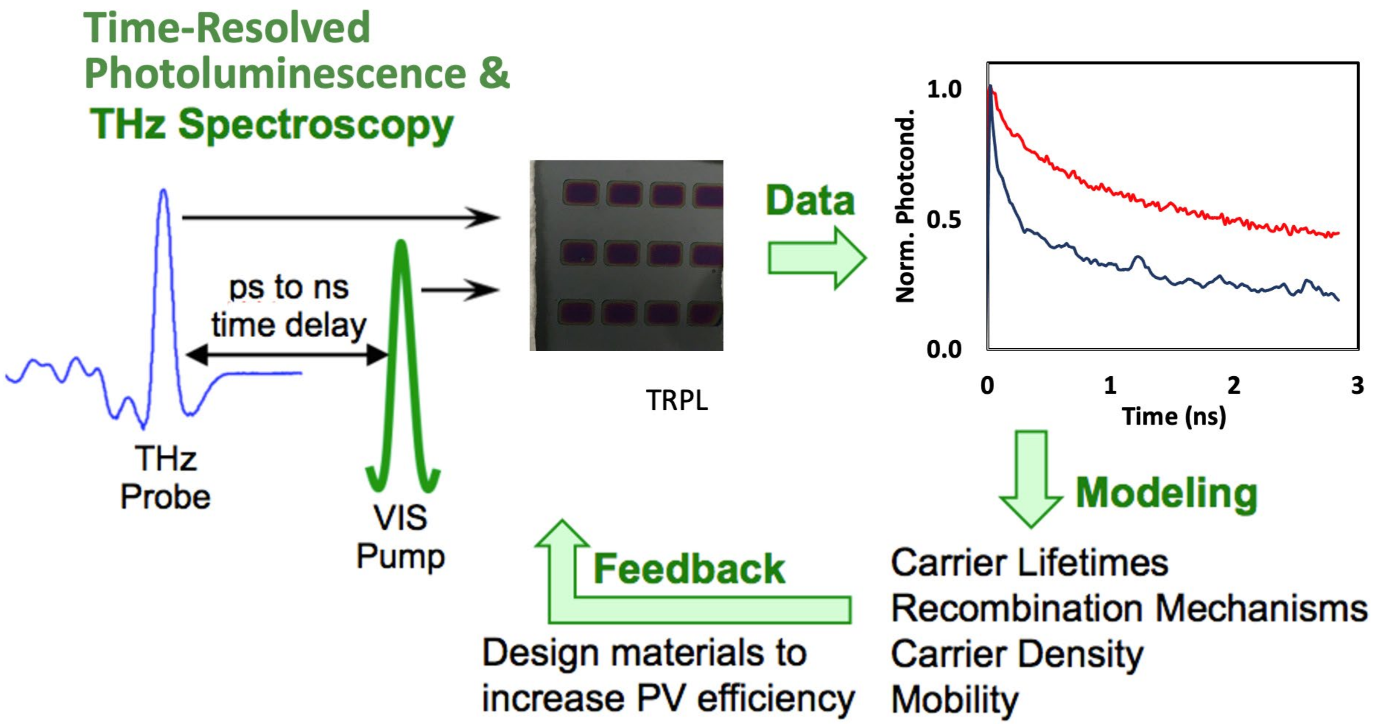
Low Injection: $S_F + S_B$, μ_n



Reduced surface (and bulk?) recombination with Se

Samples from Matt Reese and Deborah McGott

Conclusions and Next Steps



Time-Resolved Photoluminescence & THz Spectroscopy

Carrier Lifetimes
Recombination Mechanisms
Carrier Density
Mobility

Design materials to increase PV efficiency

The combination of modeling with TRTS and TRPL under multiple excitation conditions improves accuracy and precision of parameter estimation.

Ultrafast carrier dynamics can link materials, processing, and device performance to direct the design of more efficient solar cells.

Next steps: Expanding the Python simulations and Bayesian inference to handle full devices and combined TRPL and TRTS data for fast and accurate parameter estimation.

- In-depth evaluation of the front interface to minimize recombination
- Understanding the effects of dopant atom and activation methods on bulk recombination
- Recombination vs charge transfer with passivated/selective transparent back contacts to enable bifacial / tandem cells

Acknowledgements

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Calvin Fai
Prof. Tony Ladd

Taheri...Baxter, *J. Appl. Phys.*, 163104 (2021)
Fai...Hages, *Joule* (2022)

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DOE SETO DE-EE0009344

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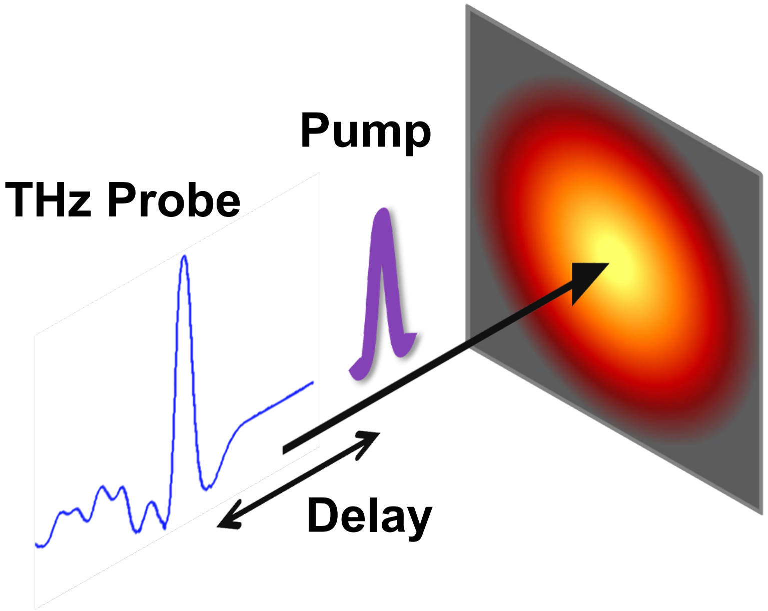
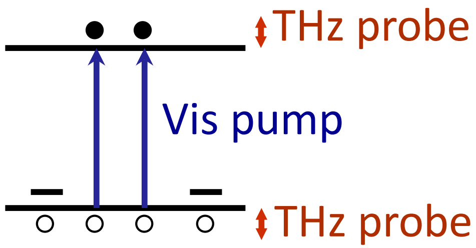
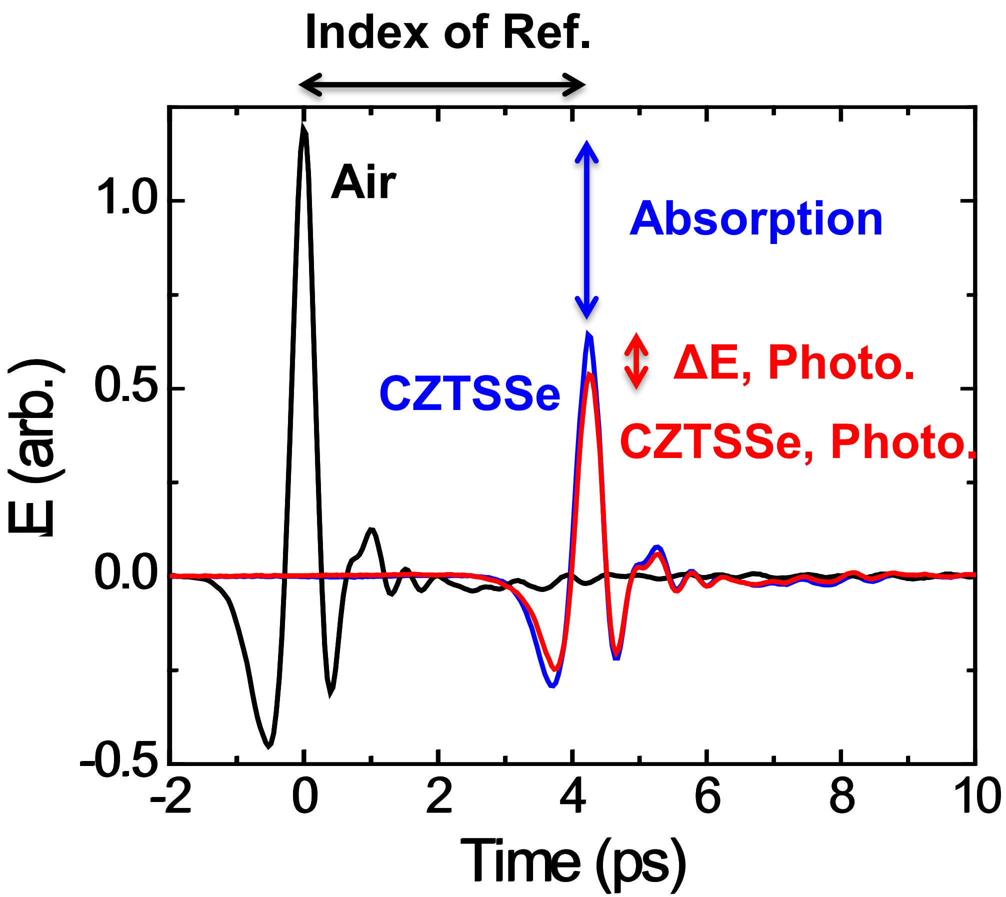
THz Spectroscopy: Probing Mobile Carriers

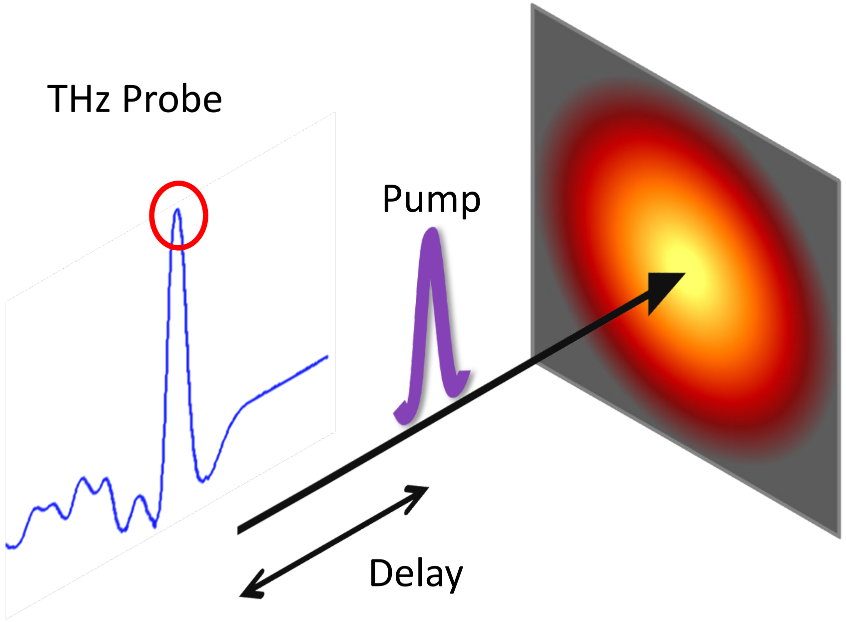


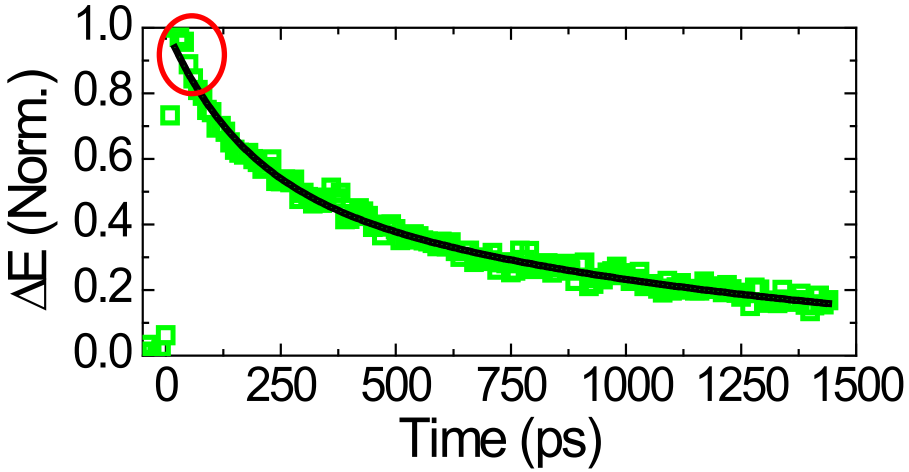




- Fourier Transform to find frequency-resolved conductivity (1 THz = 33 cm^{-1} = 4 meV)
- Pump-probe for transient photoconductivity

Transient Photoconductivity from TRTS





$$\sigma(t_p) = -\frac{\Delta E(t_P)}{E_{ref}} \times \frac{2n_{eff}c\varepsilon_0}{d(t_p)}$$

$$\Delta E(t) \propto q\mu_e\left(\boxed{\Delta n(t)}\right) + q\mu_h\left(\boxed{\Delta p(t)}\right)$$

Time-resolved, average far-IR (THz) response integrated through the film thickness.

Diffusion-Recombination Model

Model photoexcited carrier density, N(x,t), using the diffusion-recombination equation

Initial condition (from pump pulse):

$$N(x,0) = N_0 \exp(-\alpha x)$$

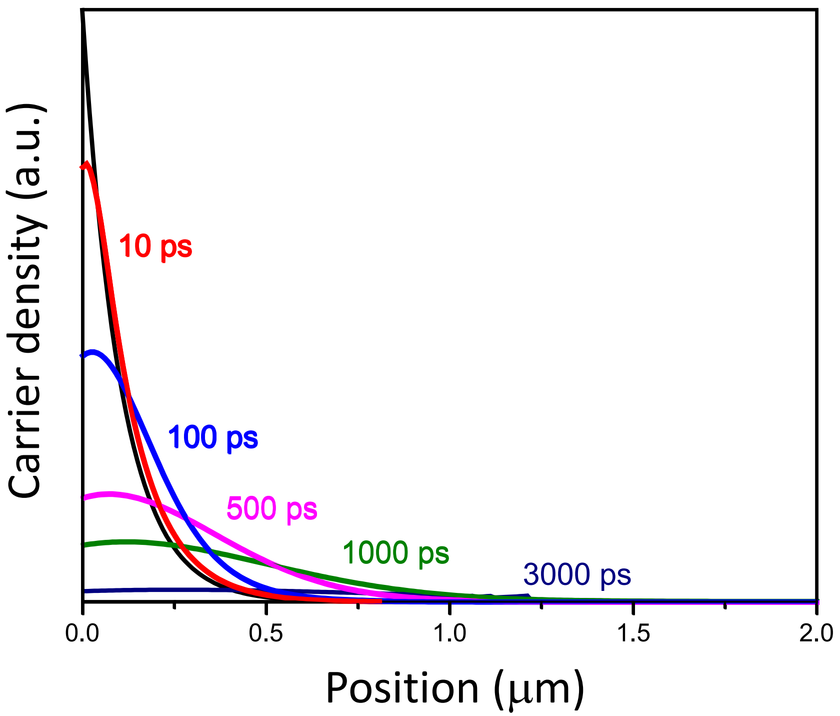
Continuity equation:

$$\frac{\partial N(x,t)}{\partial t} = D\frac{\partial^2 N}{\partial x^2} - \frac{N}{\boxed{\tau_{SRH}}}$$

Boundary conditions:

$$\frac{\partial N(0,t)}{\partial x} = \frac{\boxed{S}}{D} N(0,t)$$

$$N(L,t)=0$$



THz signal, ΔR(t), proportional to $\int N(x,t)dx$