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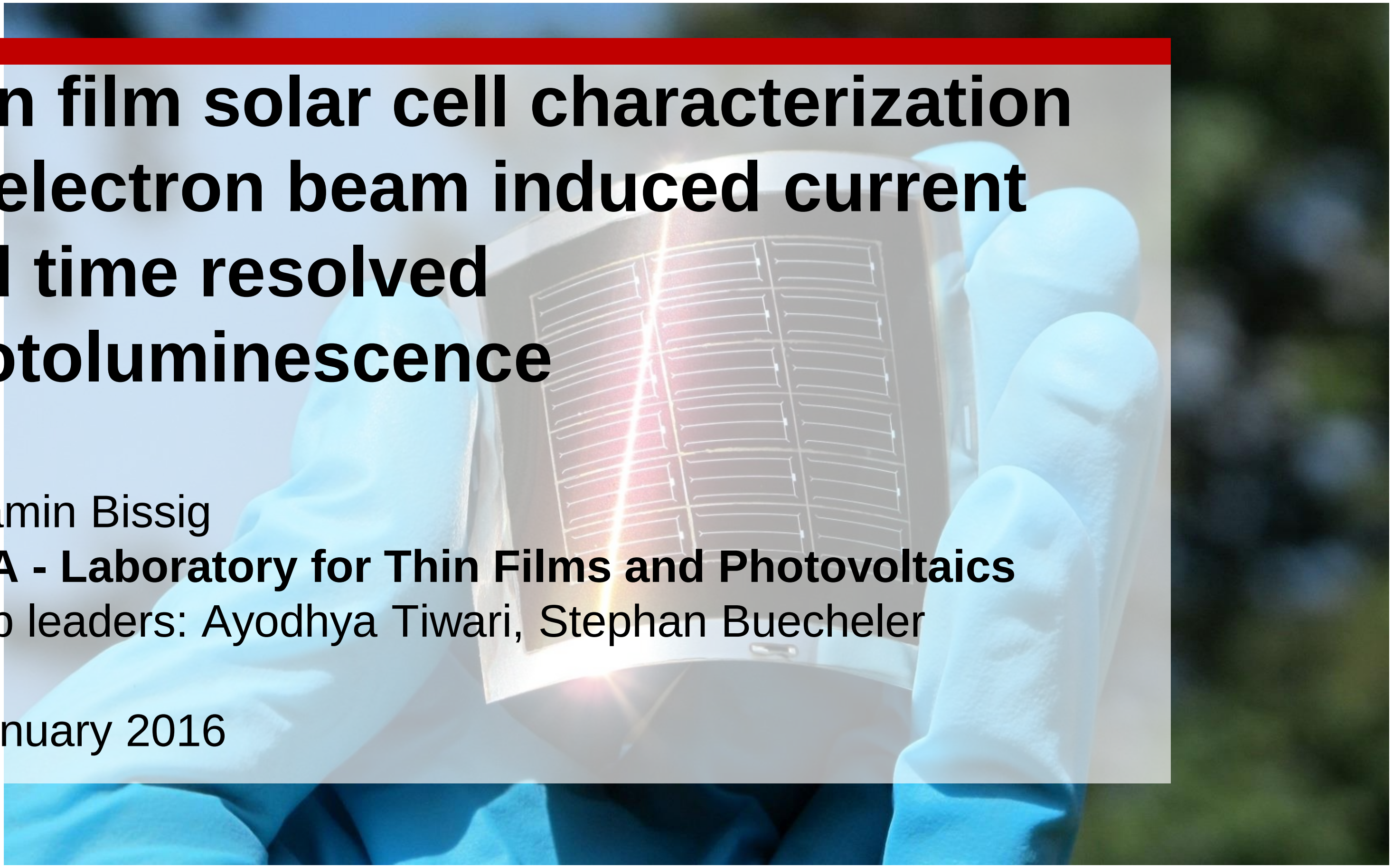
Materials Science & Technology



Thin film solar cell characterization by electron beam induced current and time resolved photoluminescence

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14 January 2016

Outline

Electron beam induced current (EBIC):

- **Principle & information content**
- **Experimental setup**
- **Limitations and artefacts**
- **Examples**
- **References**

Time resolved photo luminescence (TRPL)

- **Principle & information content**
- **Experimental setup**
- **Limitations and artefacts**
- **Examples**
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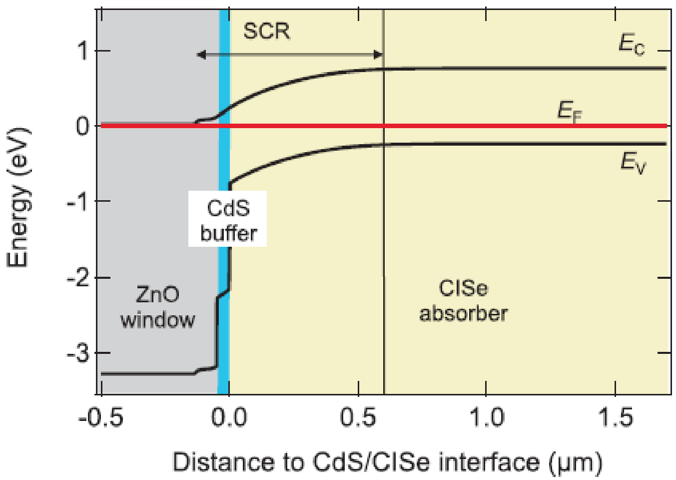
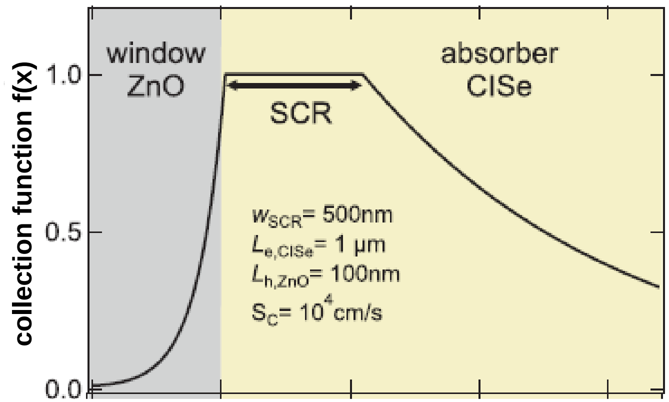
Conclusion

Cross section EBIC: priniciple & information

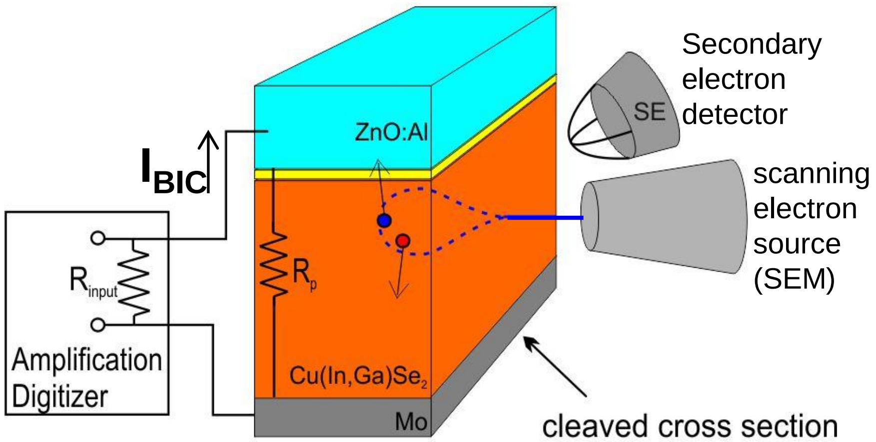
Collection function *f(x)* – a property of TFSC device:

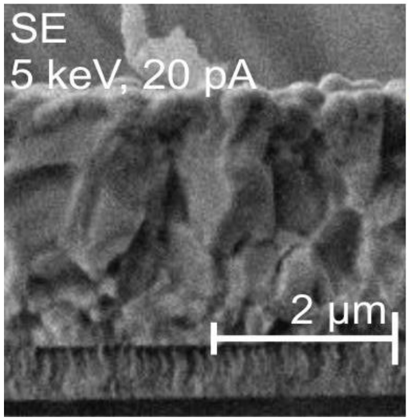


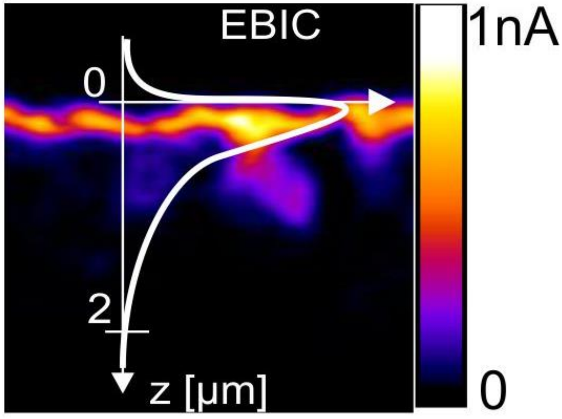


2013, Nichterwitz, JAP 114, 134504

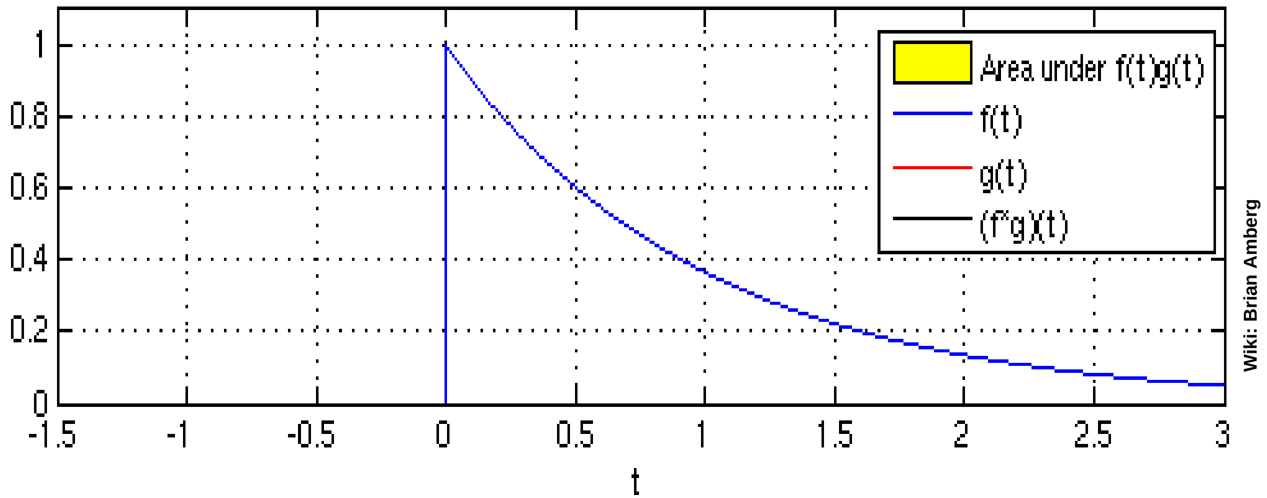
EBIC attempts to access *f(x)*:







EBIC Cross section EBIC: prinicipile & information



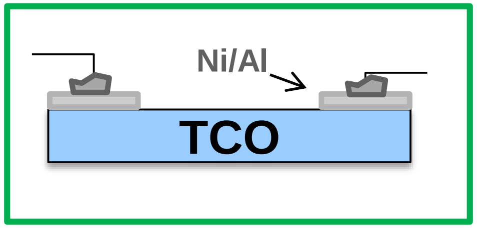
$$EBIC(x) = \int_0^t f(x') * g(x, x')\, dx',$$

EBIC:

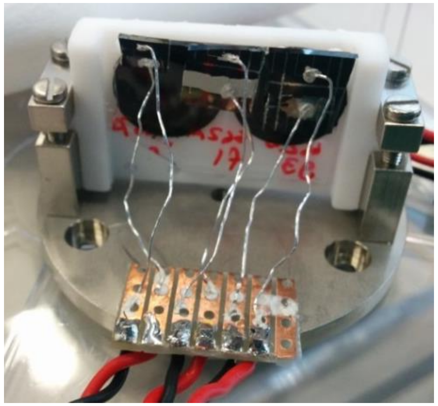
- simulatenous recording of SE and induced current
- Typical BIC curret ~ I_{inj}*E_b/E_g
- Convolutes generation- *g(x)* and collection function *f(x)*

EBIC Experimental procedure:

- ✓ **cleaving…** (sample age!)
- ✓ **contacting:** In wires & Ag paint on Ni/Al contact



- ✓ **mounting**

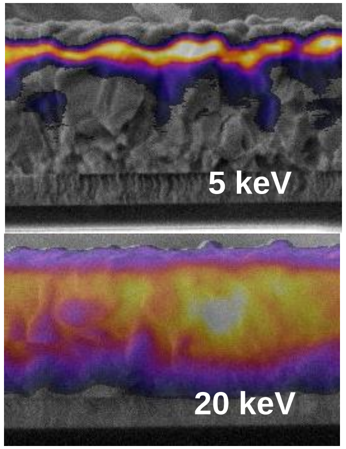


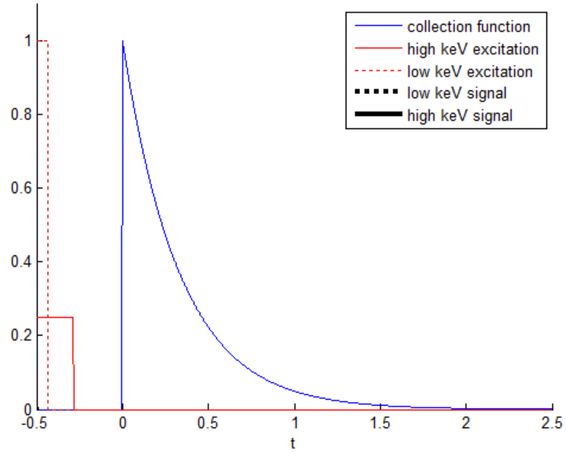
- multi line feedthrough
- mechanical bridge
- rotation stage

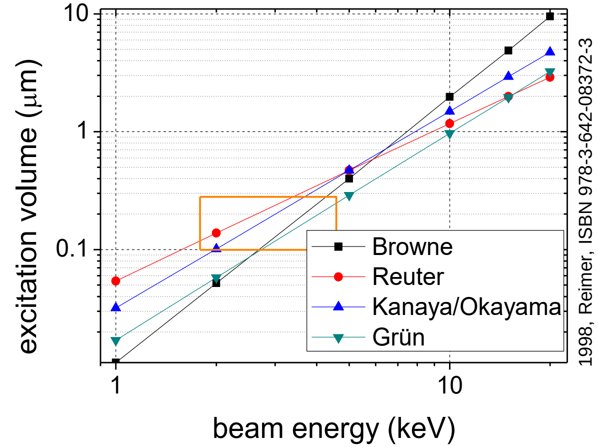
- ✓ **SEM**
- ✓ **amplifier → digitizer (commercial or quick&dirty: use SEM digitizer)**

Limitations & Artefacts

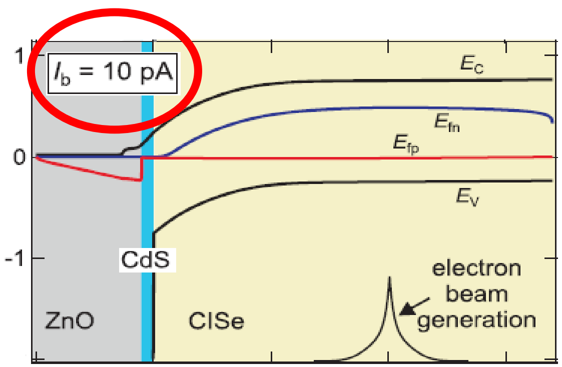
- **Lateral resolution: beam energy ~ generation volume**

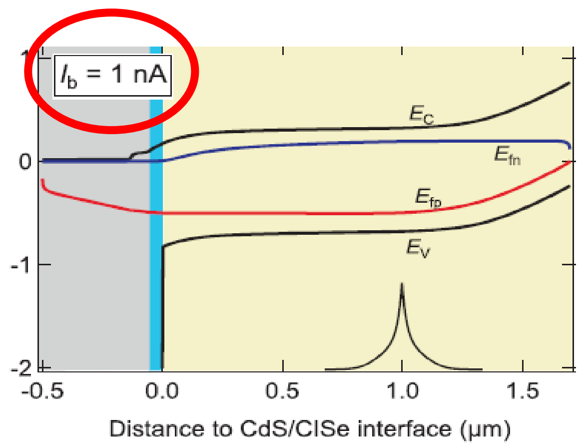


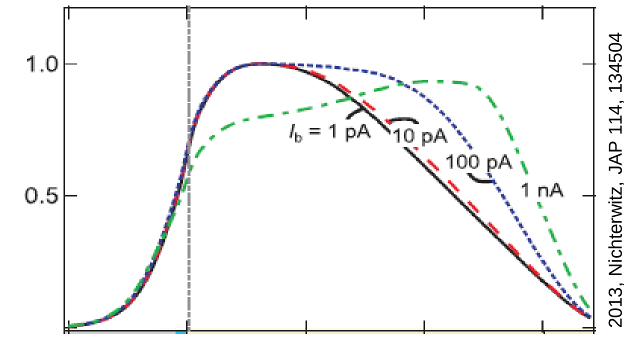




- **Injection current**



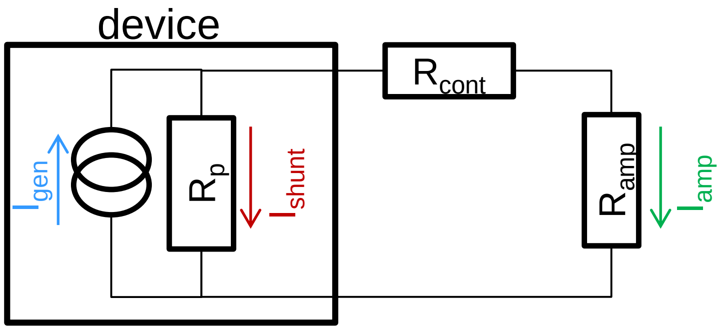




Low injection: $p_0 > N_{e,h} = \dfrac{E_b I_b \tau_{e,h}}{e E_{eh} L_{e,h}^3}$ condition

Limitations & Artefacts

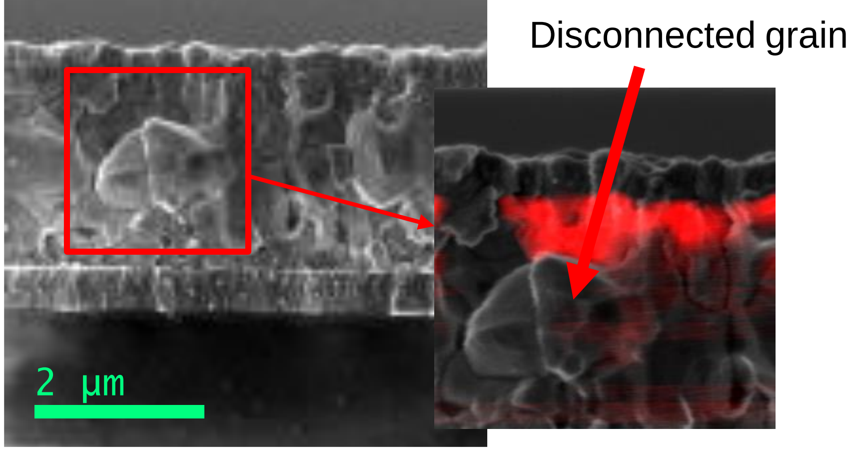
- **Shunt resistance: absolute comparison of different samples**



$$\frac{I_{amp}}{I_{gen}} = \frac{1}{1 + \frac{R_{cont} + R_{amp}}{R_p}}$$

Similar R_p or rescaling necessary for direct signal comparison

- **Surface & Morphology**

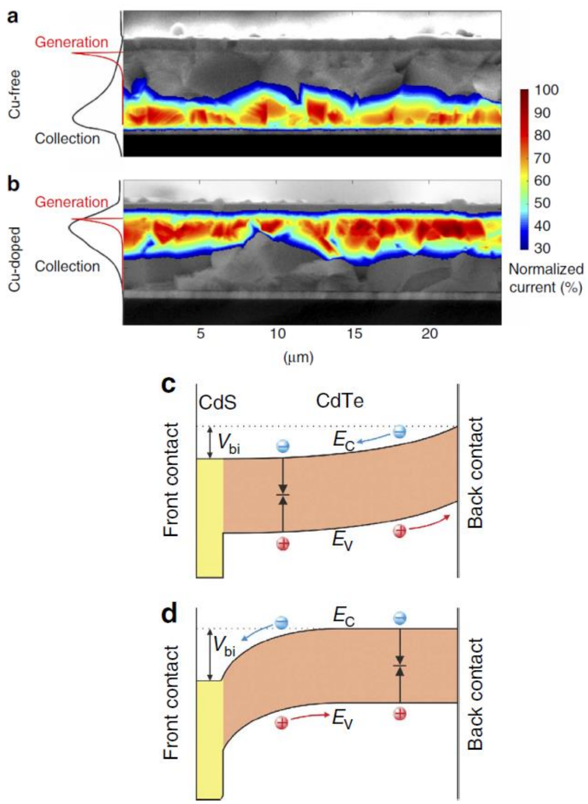


Focused ion beam polish can help, however:

- Ga ions, unknown effect on absorber
- Decreased R_p observed

EBIC Examples

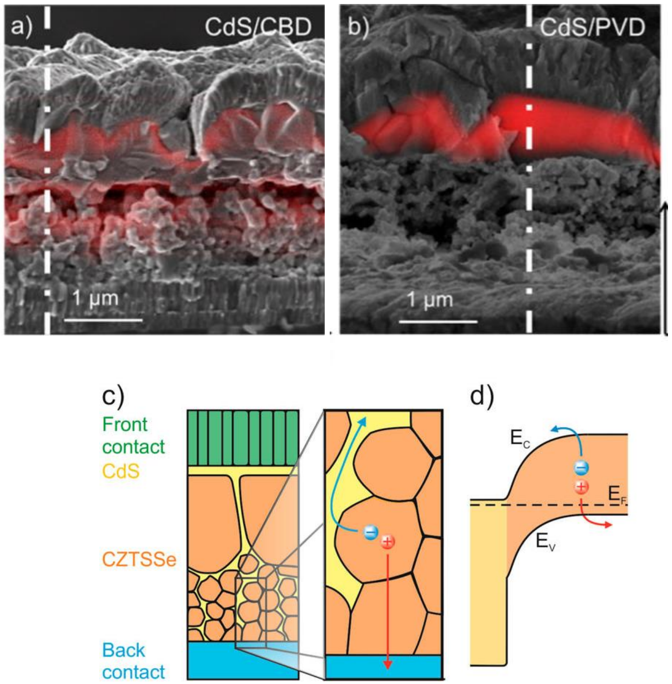
Cu doping of CdTe



Cu doping increases doping and leads to pn junction formation.

2013, Kranz, Nature Comm., 4:2306

Enhanced collection in $Cu(Zn,Sn)(S,Se)_2$



CdS indifussion into granular kesterite leads to enhanced collection.

2015, Werner, ACS Mat & Interf.
DOI: 10.1021/acsami.5b02435

EBIC References

Textbook introduction:

- 1998, Reimer, Springer-Berlin, "Scanning electron microscopy", ISBN 978-3-642-08372-3

Fundamental EBIC theory:

- 1982, Leamy, JAP 53, "Charge collection scanning electron microscopy"
- 1983, Donalto, JAP 54, "Theory of beam induced current characterization…"

Chalcogenide related:

Artefacts (energy, current, surface):

- 2009, Kniese, TSF 517, "Evaluation of electron beam…."
- 2013, Nichterwitz, JAP 114, "Numerical simulaton of cross section electron…"
- 2000, Rechid, TSF 361-362, "Characterising superstrate CIS solar cells with…"

Case studies:

Combination with EBSD:

- 2011, Abou-Ras, SolEnMat&SolCells 1452-1462, "Analysis of CIGS thin film …"

Effect of GB:

- 2014, Kavalakkatt, JAP 115, "Electron beam induced current at absorber back.."

Diffusion length from top-view EBIC:

- 2010, Brown, APL 96, "Determination of the minority carrier diffusion length…"

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Time resolved photo luminescence (TRPL)

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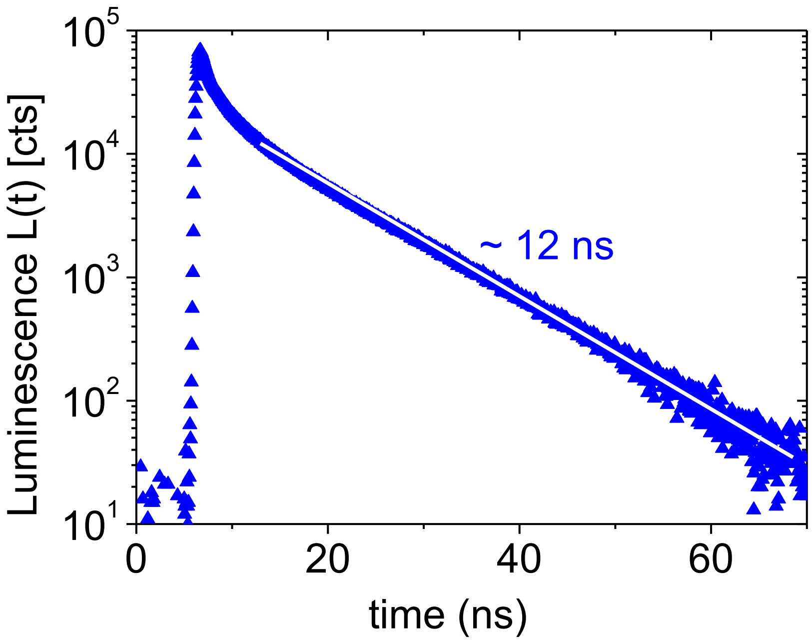
Conclusion

Priniciple & information

i) Excess carrier injection $\Delta n(t=0)$ (e.g. laser pulse)
ii) Time resolved detection of luminescent recombination signal L(t)



$$L(t) \propto \Delta n(t)$$

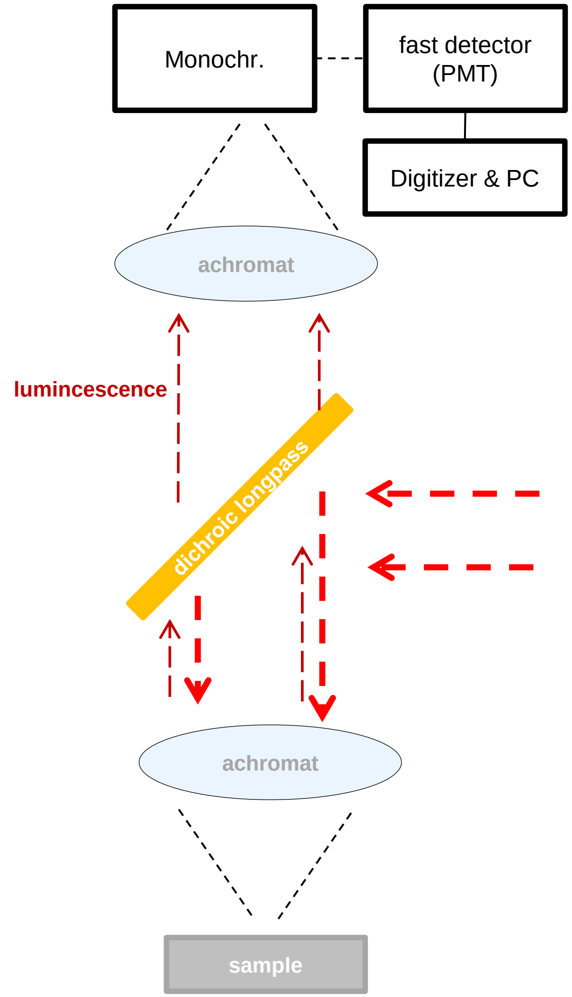
$$\Delta n(t) = \Delta n(t=0)e^{-t/\tau_n}$$

From Shockley read hall statistics and under low injection

Decay timescale of luminescence should reflect minority carrier «lifetime».

*neglecting Auger, after instantaneous injection of Δn

TRPL Methodology – time correlated single photon counting*

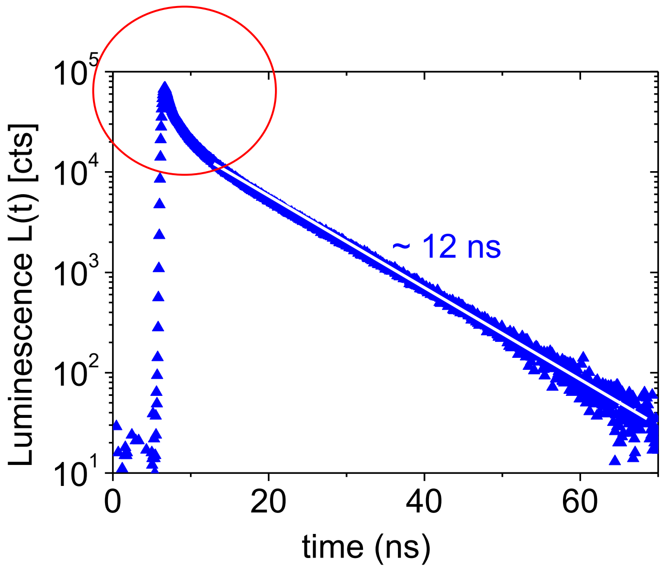


Excitation

- **MHz pulsed**
- **100 ps width**

Non idealities – **Non linear transients**

- ... due high injection density:



low injection ($\Delta n < p_0$):

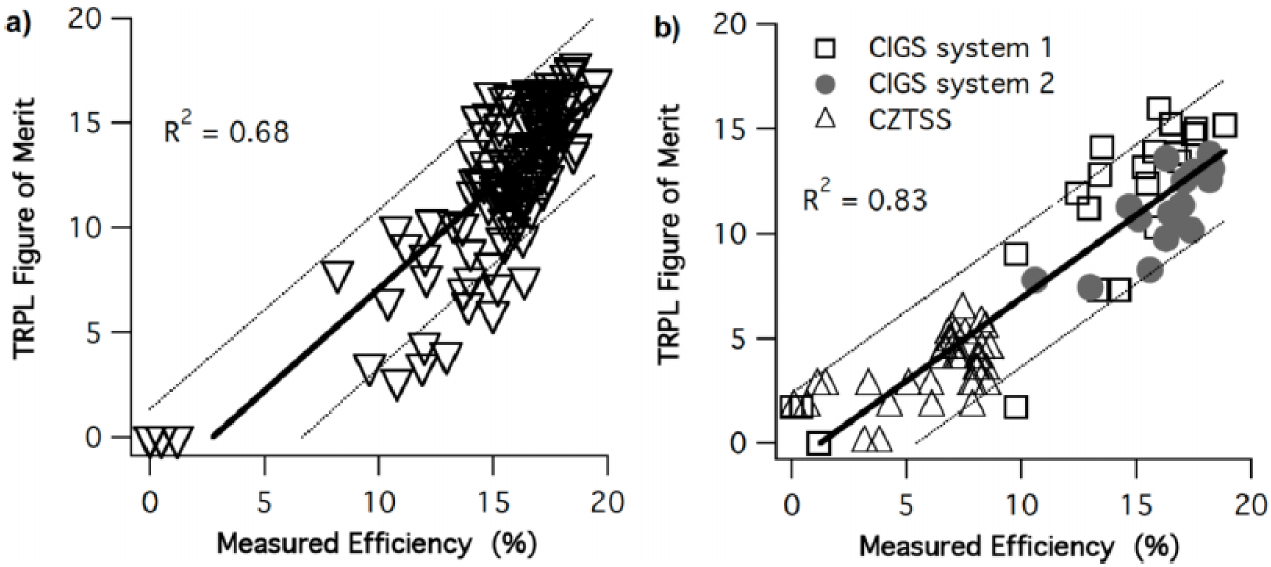
$$\dot{\Delta n} \sim -\frac{\Delta n}{\tau_n}$$

high injection ($\Delta n < p_0$):

$$\dot{\Delta n} \sim -\Delta n^2$$

- ...due trapping, junctions, surface effects, introducing non trivial dynamics!!
- Sample bleaching and aging additionally effect the transients

Predictive power of TRPL



Repins, Rev. Sci. Instr. 86, 013907, 2015.

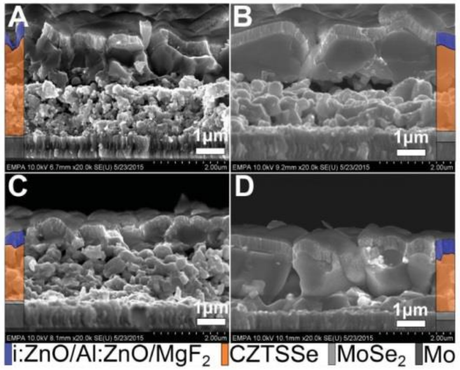
FIG. 2. TRPL figure of merit (y-axis) as measured on bare absorber versus completed-device efficiency (x-axis), for excitation with (a) 670-nm and (b) 905-nm laser. Line is least-squares linear fit to data, with the gray dashed lines showing 90% prediction intervals.

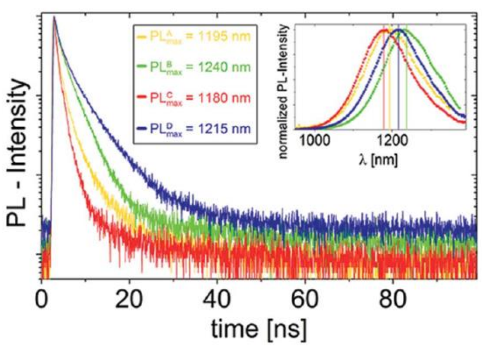
- Statistically, TRPL lifetime* is a predictive parameter for the device efficiency
- More difficult for one single device due:
  - Surfaces
  - Gradings
  - Shunts
  - **…** (see Repins, Rev. Sci. Instr. 86, 013907, 2015.)
  -

* here it is a figure of merit t*Yield(t=0), measured on bare absorbers

EBIC Examples

Highly efficient kesterite 11.2 %

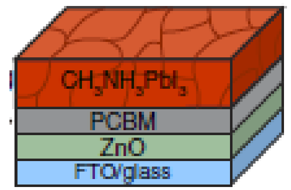


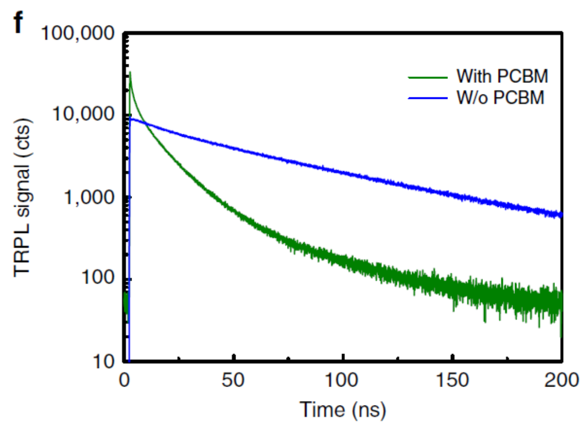


Improvements in absorber morphology are well reflected in lifetime.

2015, Haass, Adv. En. Mat, 1500712

PCBM as electron extractor on PbI_2:MA

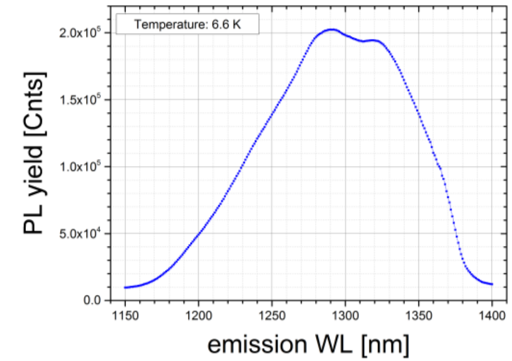


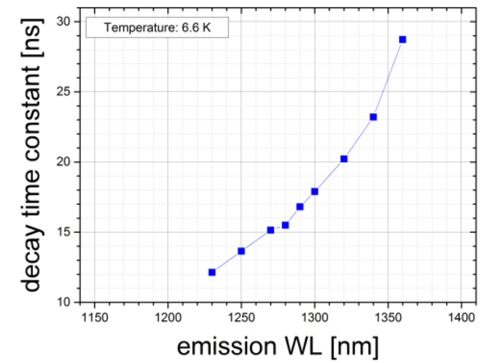


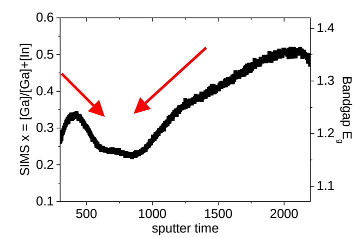
Initial non linear decay is understood as fast extraction of generated carriers → compare extraction efficiency.

2015, Fu, Nature Comm.
DOI: 10.1038

Effect of bandgap grading







E_g grading leads to additional kinetics.

TRPL References

Textbooks on semiconductor recombination:

- Dieter K. Schroder, Semiconductor Material and Device Characterization, Chapter 5 “Defects”, John Wiley & Sons, Inc., 2006.

TRPL techniques:

- Wolfgang Becker, Advanced Time-Correlated Single Photon Counting Techniques, ISBN 978-3-540-28882-4

Understanding curved transients:

- M. Maiberg, Theoretical study of time-resolved luminescence in semiconductors. I. Decay from the steady state, JAP 116, 2014.
- M. Maiberg, Theoretical study of time-resolved luminescence in semiconductors. II. Pulsed exciation, JAP 116, 2014.
- M. Maiberg, Theoretical study of time-resolved luminescence in semiconductors. III. Trap states in the bandgap, JAP 118, 2015.

...similar for CdTe

- A . Kanevce, The role of drift, diffusion, and recombination in timeresolved photoluminescence of CdTe solar cells determined through numerical simulation, PiP, 2013.

One illustrative case study on CIGS:

- W. Metzger, Long lifetimes in high efficency CIGS solar cells, APL 93, 2008.

On the predictive power of TRPL (i.e. Device efficiency):

- Repins, Fiber fed time resolved PL for reduced process feedback time on thin film PV, Rev. Sci. Instr. 86, 013907, 2015.

Conclusion

- EBIC and TRPL allow to **probe minority carrier recombination** processes:
  - EBIC offers sub µm resolution on carrier collection properties
  - TRPL is a highly sensitive probe for sources of non radiative recombination and minority carrier dynamics

- To avoid artefacts, both techniques require precisely controlled probing conditions, especially the injection level

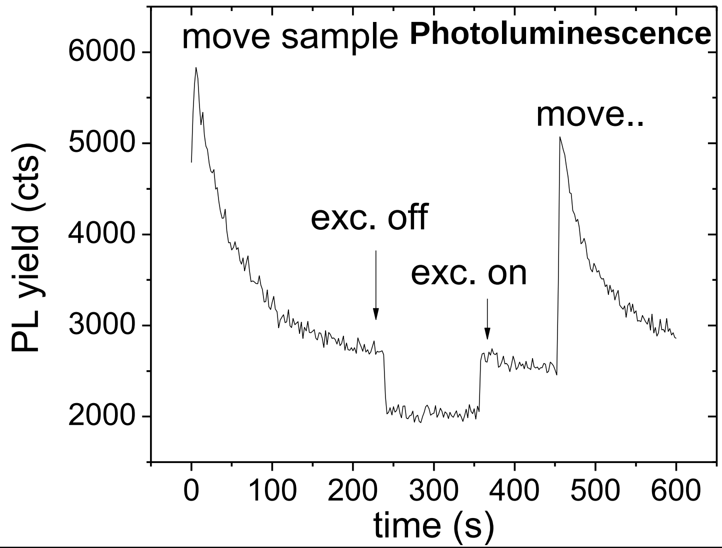
- Both are affected by fields, junctions, surfaces... which can make straightforward interpretation difficult but allows investigations of respective phenomena

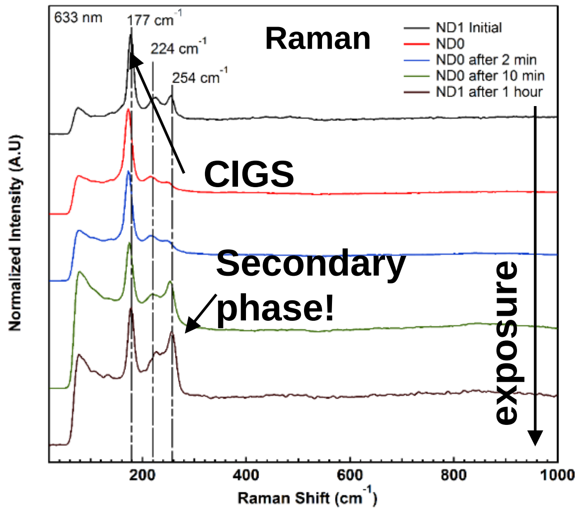
- TRPL provides a **statistically significant predictor** for device efficiency

BACKUP

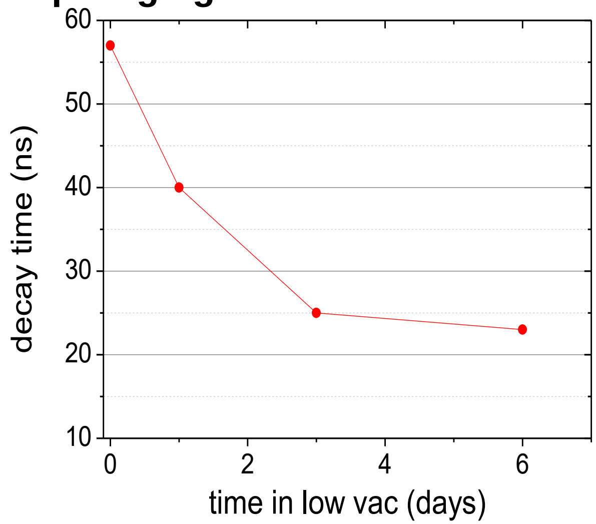
TRPL Other effects

PL bleaching – irradiation damage



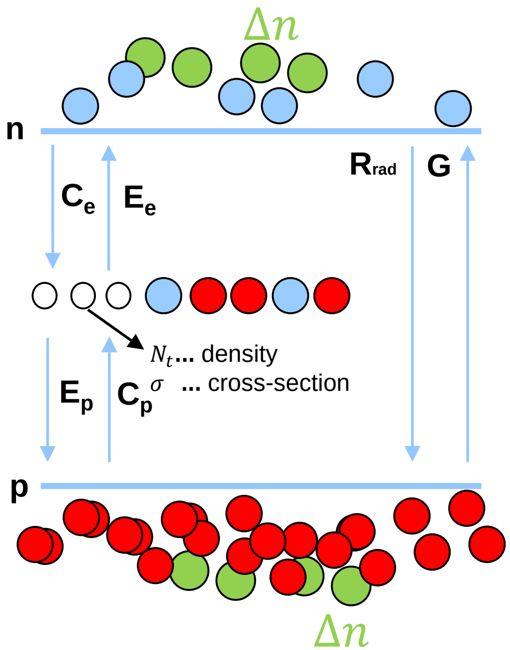


Sample aging



More details

3 level model:



Analytical expressions for excess carrier recombination dynamics*:

$$\dot{\Delta n} = -(R_{rad} + R_{SRH})$$

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

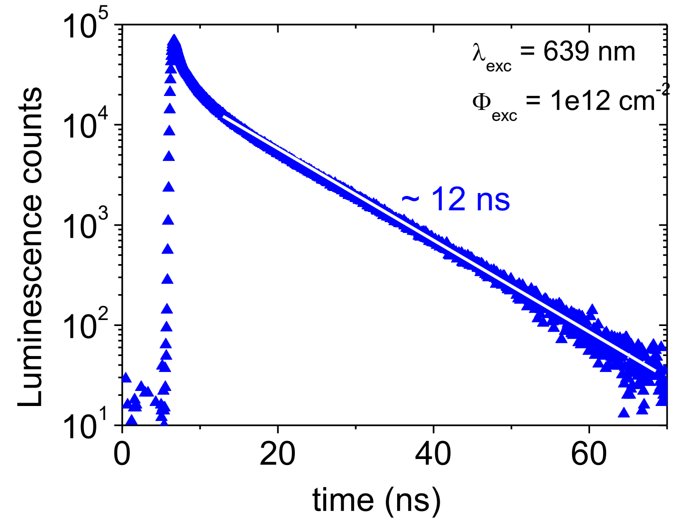
$$R_{SRH} = \frac{pn - p_0 n_0}{\tau_p(n+n^*) + \tau_n(p+p^*)}, \tau_n \propto 1/\sigma N_t$$

- For p-type and low injection $\Delta n << p_0$

$$\dot{\Delta n} \sim -R_{SRH} = -\frac{\Delta n}{\tau_n}$$

$$\Delta n(t) = \Delta n_0 e^{-t/\tau_n}$$

A typical measurement:



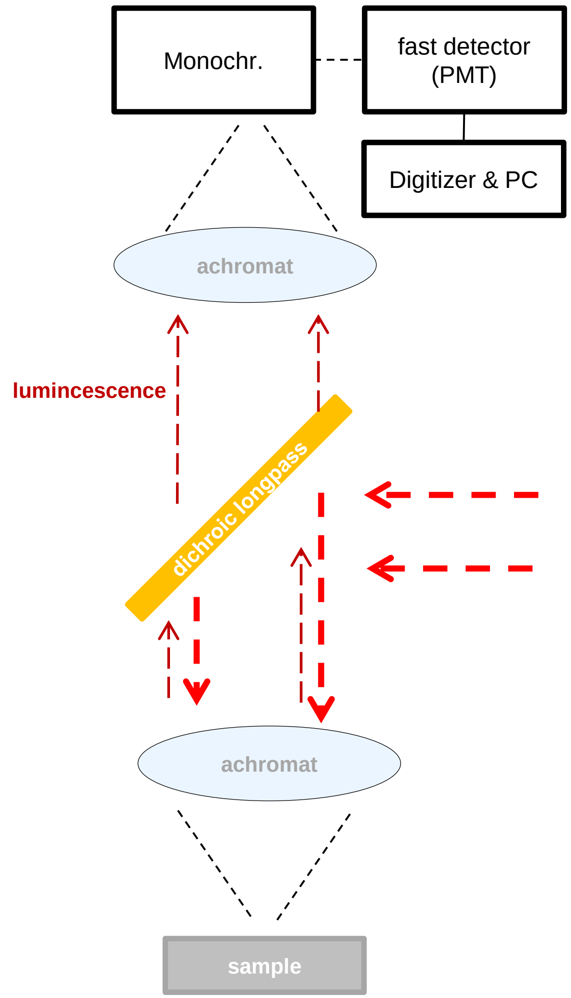
i) (instantaneous) excess carrier injection (e.g. laser pulse)
ii) time resolved detection of luminescent recombination signal L(t)

$$\log(L(t)) \propto log(\Delta n(t)) \propto const - t/\tau_n$$

Linear decay timescale on log-plot should reflect minority carrier «lifetime».

*neglecting Auger, after instantaneous injection of Δn

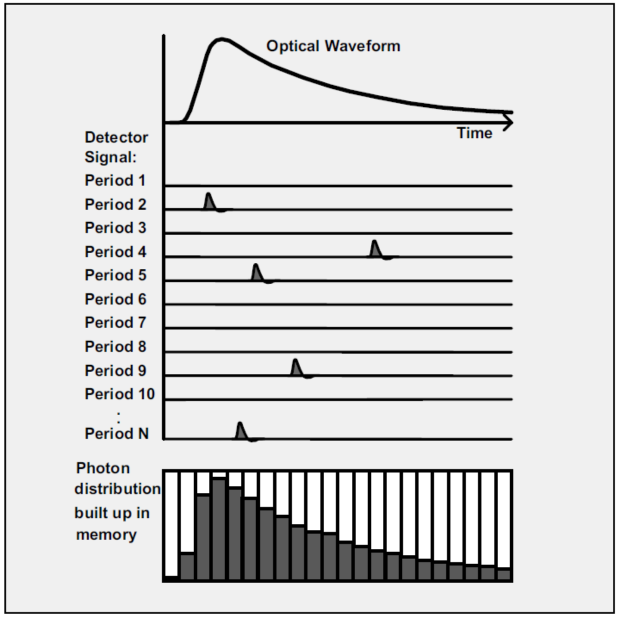
Experimental procedure



Time correlated single photon counting (TCSPC)

Excitation

- **MHz pulsed**
- **100 ps width**



Wolfgang Becker, ISBN 978-3-540-28882-4

Fig. 2.12 General principle of time-correlated single photon counting

TRPL Non idealities – **Non linear transients**

- ... due high injection density:

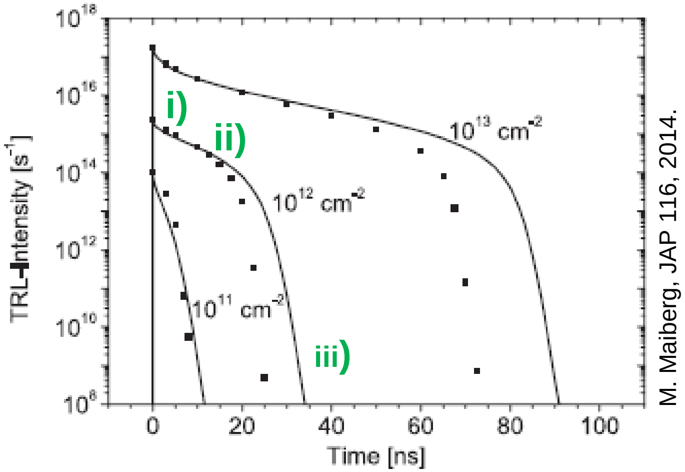
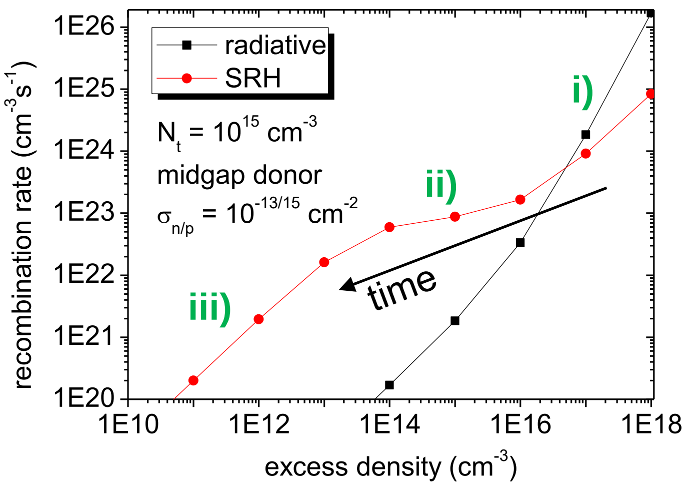


FIG. 6. TRL-transients for $N_d = 10^{15}\,cm^{-3}$ and different n_γ. The solid lines represent simulated data, the dots represent approximated data.



- ...due trapping, junctions, surface effects...

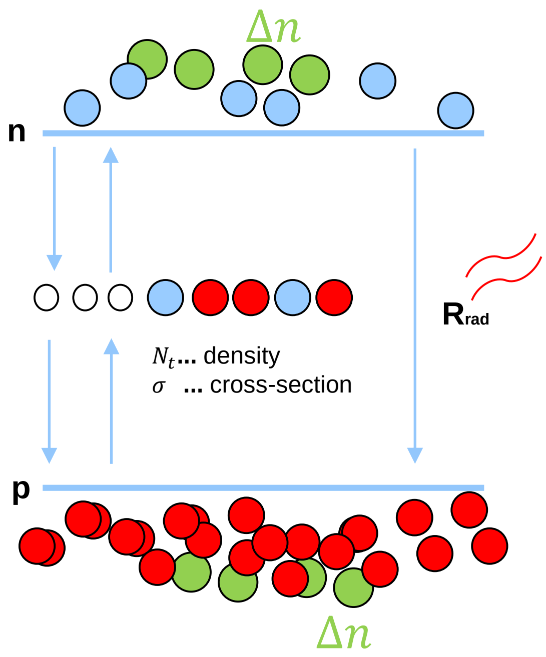
Radiative recombination: Band-band recombination

$$p = p_0 + \Delta p$$
$$n = n_0 + \Delta n$$
$$\Delta n = \Delta p$$

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

$$R_{rad} = \underbrace{B(n_0 + p_0)\Delta n}_{\text{"excess e–p finds host p–e"}} + \underbrace{B\Delta n^2}_{\text{"excess e–p finds excess p–e"}}$$

2 level model



$$\frac{dn}{dt} = -C_e + E_e + G - R_{rad}$$

$$\frac{dn_t}{dt} = C_e - E_e - C_p + E_p$$

$$\frac{dp}{dt} = -C_p + E_p + G - R_{rad}$$

Model: Defect recombination

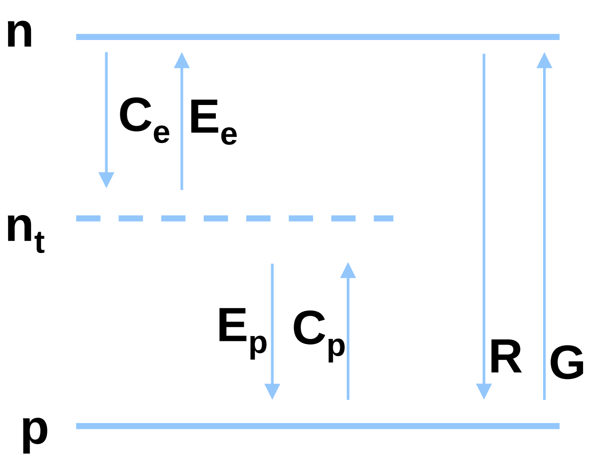
$$C_e = n\,(N_t - n_t)\,\sigma_n\,v_t$$

$$E_e = n_t\,N_C\;e^{-(EC-Ed)/kT}\,\sigma_n\,v_t$$

$$C_p = p\,n_t\,\sigma_p\,v_t$$

$$E_p = (N_t - n_t)\,N_V\;e^{-(ET-EV)/kT}\,\sigma_p\,v_t$$

- **dynamic trap XS =! equilibrium trap XS**
- **ready to simulate!**
- **where is SRH?**



Link to Shockley-Read-Hall expression:

- **recombination event <-> net electron capture on defect (steady state)**

$$R_{SRH} = C_e - E_e$$
$$C_e = n\,(N_t - n_t)\,\sigma_n\,v_t$$
$$E_e = n_t\,N_C\;e^{-(EC-ET)/kT}\,\sigma_n\,v_t$$

- **find defect occupation**
- **assume steady state (not therm eq.)*: Ce-Ee=Cp-Ep**

$$\rightarrow n_t = N_t f_t = \frac{C_n n + C_p p}{C_n(n+n^*) + C_p(p+p^*)}$$

$$\boldsymbol{R_{SRH} = \frac{pn - p_0 n_0}{\tau_p(n+n^*) + \tau_n(p+p^*)}}$$

$$n* = \quad N_C\;e^{-(EC-ET)/kT}$$