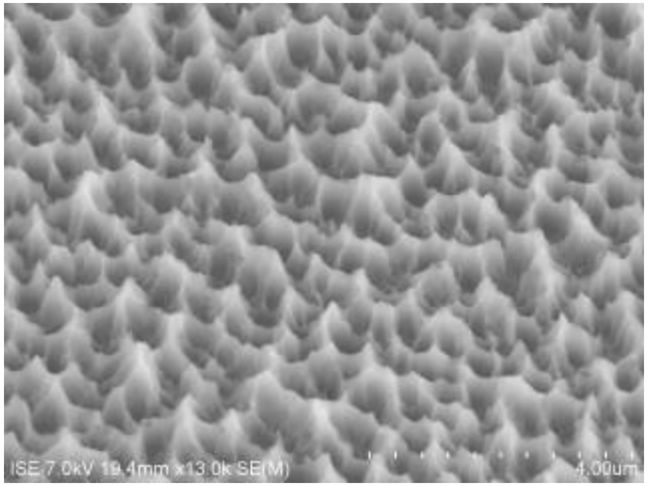
Recombination and lifetime

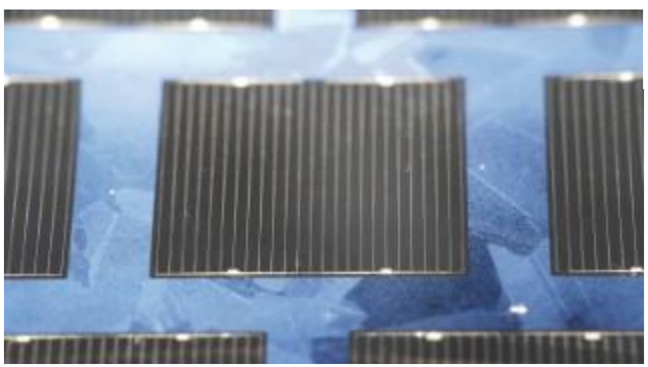
UNIK 4450/9450 – Schedule

- 30/8 Solar cell fundamentals
- 6/9 Solar cell efficiency
- 13/9 Semiconductor theory
- 20/9 Generation
- 27/9 Recombination and lifetime
- 4/10 Silicon
- 11/10 Junctions
- 18/10 Solar cells
- 25/10 Silicon solar cells I (@IFE)
- 1/11 Silicon solar cells II
- 8/11 Light management
- 15/11 Alternative solar cells
- 29/11 Solar modules & systems
- 6/12 Q&A

- Oral exam (Week 50)

Cool concept of the week



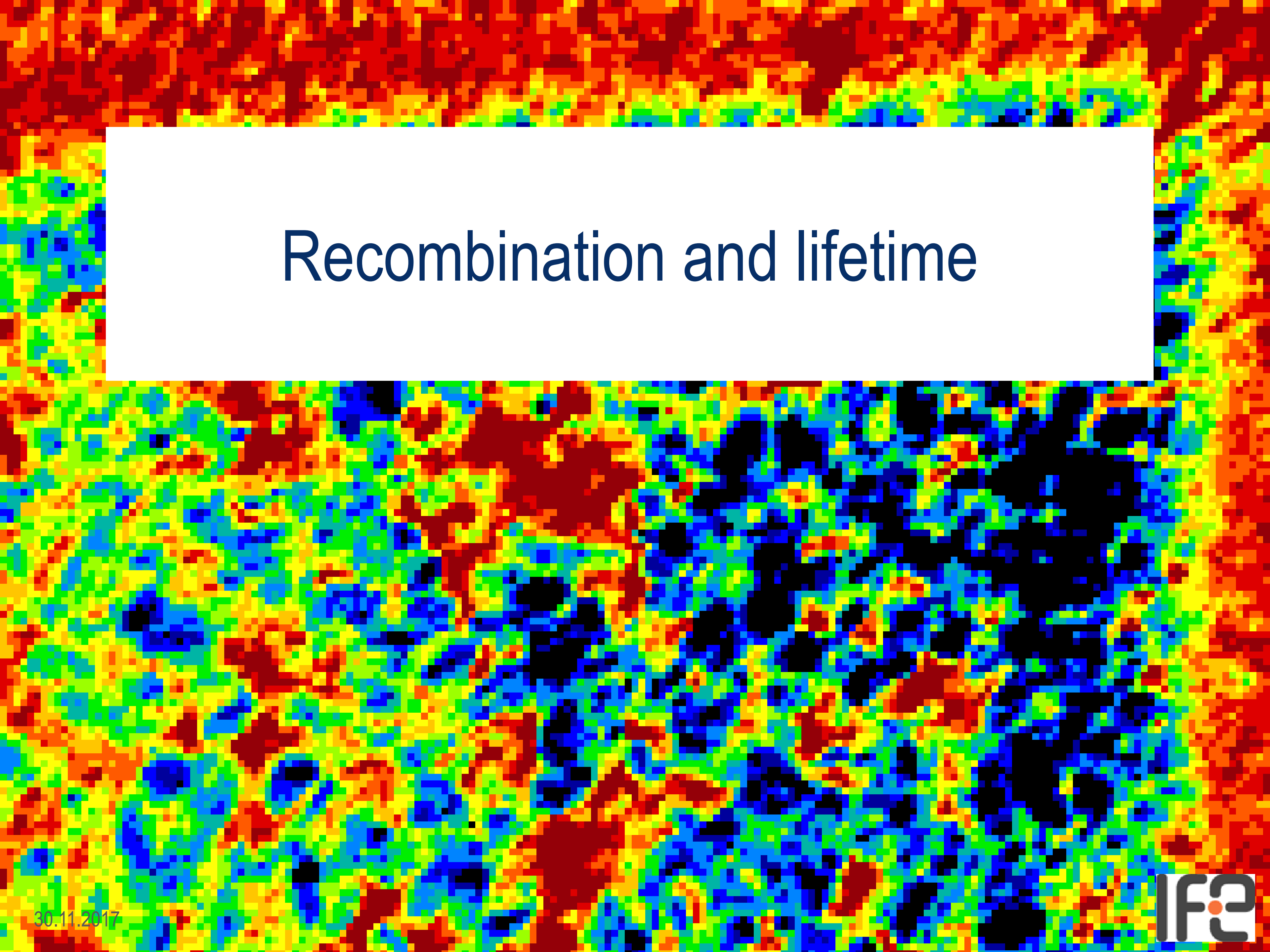


FRAUNHOFER-INSTITUT FÜR SOLARE ENERGIESYSTEME ISE

PRESSEINFORMATION

Fraunhofer ISE steigert Weltrekord für multikristalline Siliciumsolarzelle auf 22,3 Prozent

Weltweit arbeiten Forschung und Industrie an der weiteren Senkung des Solarstrompreises. Die deutsche Forschung spielt dabei eine führende Rolle. Das Fraunhofer-Institut für Solare Energiesysteme ISE hat jetzt seinen erst vor wenigen Monaten erzielten Weltrekordwirkungsgrad für multikristalline Siliciumsolarzellen weiter verbessert. Die Rekordsolarzelle wandelt 22,3 Prozent des Sonnenlichts in elektrische Energie um.



Recombination and lifetime

Main question

Will this wafer become a good solar cell?

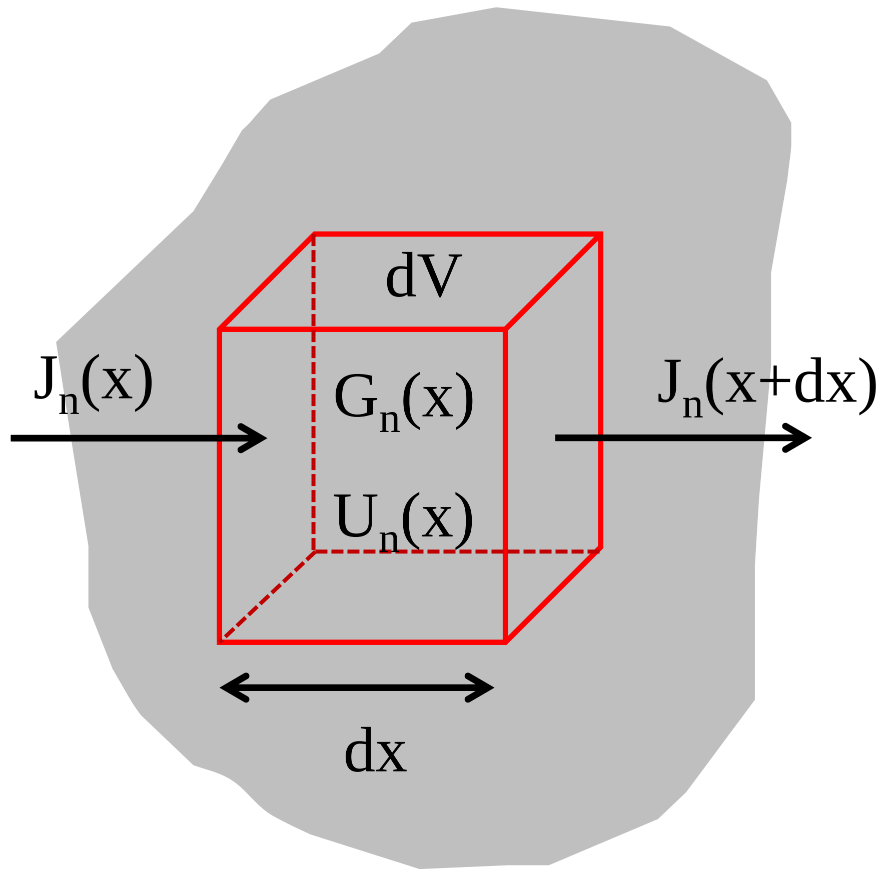
Overview

- Brief recollection of prior events…
- Recombination theory
- Bulk recombination mechanisms
  - Theoretical description
  - The case of moderate doping: decoupling p and n
- Surface recombination
- Lifetime measurements
  - Quasi-steady state photoconductance (QSSPC/«Sinton»)
  - Microwave detected photoconductance decay (μ-PCD)
  - Photoluminescence imaging (PL)
  - Carrier density imaging (CDI)

Transport in semiconductors

- Solar cell device operation:

  1. The number of charge carriers must be conserved
  2. The electrostatic potential $\varphi(x)$ obeys Poisson's equation



$$\delta n/\delta t = 1/q \cdot \delta/\delta x(J_n(x)) + G_n(x) - U_n(x)$$

Transport in steady state

$$\delta n/\delta t = 1/q \cdot \delta/\delta x(J_n(x)) + G_n(x) - U_n(x) = 0$$

$$\delta p/\delta t = 1/q \cdot \delta/\delta x(J_p(x)) + G_p(x) - U_p(x) = 0$$

$$(\delta/\delta x)^2\varphi(x) = (q/\varepsilon_0\varepsilon_s)(-Q_{fixed} + n - p)$$

The transport problem

Electrons in the (neutral) p-region:

$$(\delta^2/\delta x^2)n + (qE/kT)(\delta/\delta x)n + G_n(x)/D_n - U_n(x)/D_n = 0$$

Holes in the (neutral) n-region:

$$(\delta^2/\delta x^2)p + (qE/kT)(\delta/\delta x)p + G_p(x)/D_p - U_p(x)/D_p = 0$$

Today's topic

$$(\delta^2/\delta x^2)n + (qE/kT)(\delta/\delta x)n + G_n(x)/D_n - \mathbf{U_n(x)}/D_n = 0$$

$$(\delta^2/\delta x^2)p + (qE/kT)(\delta/\delta x)p + G_p(x)/D_p - \mathbf{U_p(x)}/D_p = 0$$

Challenge

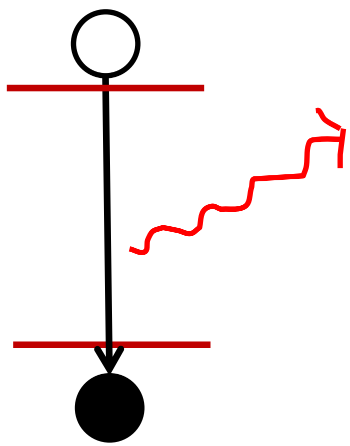
$$\delta n/\delta t = 1/q \cdot \delta/\delta x(J_n(x)) + G_n(x) - U_n(x)$$

$U \sim n \cdot p$

$$\delta p/\delta t = 1/q \cdot \delta/\delta x(J_p(x)) + G_p(x) - U_p(x)$$

$$(\delta/\delta x)^2 \varphi(x) = (q/\varepsilon_0 \varepsilon_s)(-Q_{fixed} + n - p)$$

Recombination processes



RADIATIVE
(BAND-TO-BAND)

Microscopic description

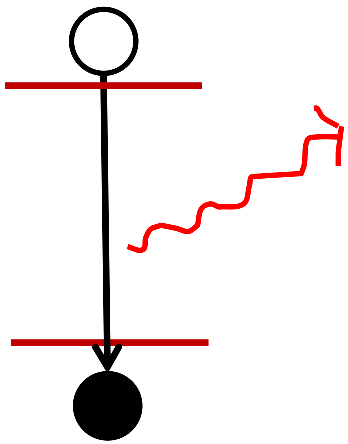
f_c

$\mathbf{H_{cv}}$

f_v

Radiative recombination

Spontaneous emission



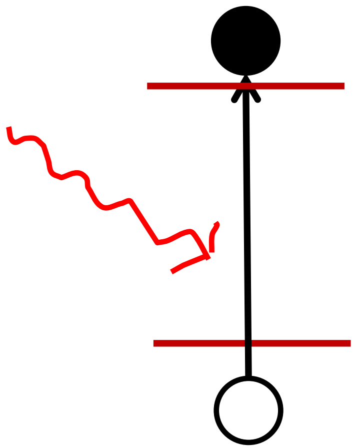
- Process depends on f_c, f_v and the magnitude of $\mathbf{H}_{cv}{}^2$.
- Rate of spontaneous emission:

$$r_{sp} = \frac{2\pi}{h} \mathbf{H}_{cv}{}^2 \, f_c(1-f_v)$$

Radiative recombination

Absorption

- Process depends on $f(E)$, f_c, f_v and the magnitude of $\mathbf{H}_{cv}{}^2$.
- Rate of absorption:



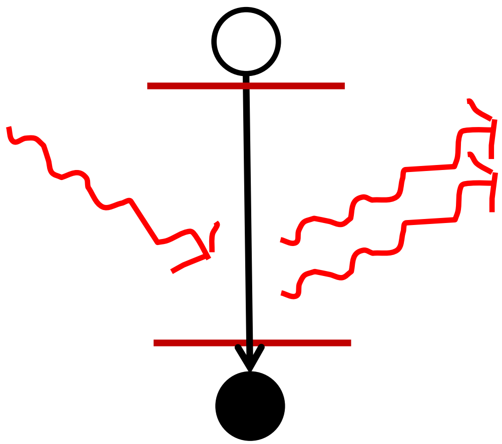
$$r_{abs} = \frac{2\pi}{h}\mathbf{H}_{cv}{}^2\, f(E)\, f_v(1-f_c)$$

Radiative recombination

Stimulated emission

- Process depends on $f(E)$, f_c, f_v and the magnitude of $\mathbf{H}_{cv}{}^2$.
- Rate of stimulated emission:

$$r_{abs} = \frac{2\pi}{h}\mathbf{H}_{cv}{}^2\, f(E)\, f_c(1\text{-}f_v)$$



Radiative recombination

Radiative recombination

- We now want to calculate the radiative recombination rate, U_{rad}.
- The net rate of absorption (absorption – stimulated emission) is given by

$$r_{abs} = \frac{2\pi}{h} \mathbf{H}_{cv}{}^2 \, f(E) \, [f_v - f_c]$$

- The rate of spontaneous emission is given by

$$r_{sp} = \frac{2\pi}{h} \mathbf{H}_{cv}{}^2 \, f_c \, [1 - f_c]$$

Radiative recombination

- At quasi thermal equilibrium, the following is valid:

$$r_{abs} = r_{sp}$$

$$\frac{2\pi}{h} \mathbf{H}_{cv}{}^2 \, f(E) \, [f_v - f_c] = \frac{2\pi}{h} \mathbf{H}_{cv}{}^2 \, f_c \, [1 - f_c]$$

$$f(E) = f_c \, [1 - f_c]/[f_v - f_c]$$

- Which, after a bit of gymnastics, becomes

$$f(E) = (e^{(E-\Delta\mu)/kT} - 1)^{-1}$$

Radiative recombination

- Away from equilibrium, we can write:

$$r_{abs}(E) = rs_p(E) f_{eq}(E) / f(E)$$

- We know that the following must hold

$$\mathrm{f(E)} = \frac{n_{ph(E)}}{g_{ph(E)}}$$

Radiative recombination

- Therefore

$$r_{sp}(E) = rab_s(E)f\,(E)/feq(E)$$

$$r_{sp}(E) = rab_s(E)\frac{n_{ph(E)}}{g_{ph(E)}}/feq(E)$$

Radiative recombination

- We also know that

$$n_{ph(E)} = U_E/E$$

and:

$$g_{ph(E)} = \frac{8\pi n s^3}{h^3 c^3} \frac{E^2}{}$$

- Based on this information, we eventually get:

$$r_{sp(E)} = f(E)_{eq}(E) \frac{2\pi n_s^{\ 2}}{h^3 c^2} \frac{\propto(E)E^2}{exp^{(E-\Delta\mu)/kT} - 1}$$

Radiative recombination

- This can be simplified to the following form:

$$r_{sp}(E) = be(E, \Delta\mu)\ \alpha(\mathrm{E})$$

- Here,

$$\mathrm{b_e(E, \Delta\mu)} = \mathrm{F_a} \frac{2}{\mathrm{h^3c^2}} \frac{\mathrm{E^2}}{\mathrm{exp}^{(\mathrm{E}-\Delta\mu)/\mathrm{kT}} - 1}$$

Radiative recombination

- Total radiative recombination:

$$U_{rad,\ tot} = \int b_e(E, \Delta\mu)\ \alpha(E)\ dE$$

- Net radiative recombination:

$$U_{rad,\ net} = \int b_e(E, \Delta\mu)\ \alpha(E)\ dE - \int be(E,0)\ \alpha(E)\ dE$$

- Which we further simplify to:

$$\boxed{U_{rad,\ net} = Brad(np - ni^2)}$$

Coupled equation

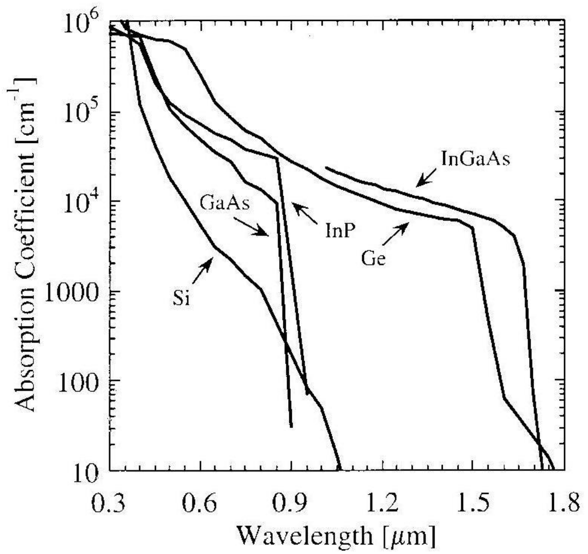
- Unfortunately, this general expression couples n and p

$$\mathrm{U}_{rad, net} = Brad(np - ni^2)$$

- Fortunately, things change when we look at relevant parameters

Comment

- Strong absorption also results in strong radiative recombination!
  - Direct band semiconductors: radiative recombination can matter
    - GaAs, …
  - Indirect band semiconductors: other recombination mechanisms dominate
    - Si, Ge, …



Handbook of Optical Constants of Solids, edited by Edward D. Palik, (1985), Academic Press NY.

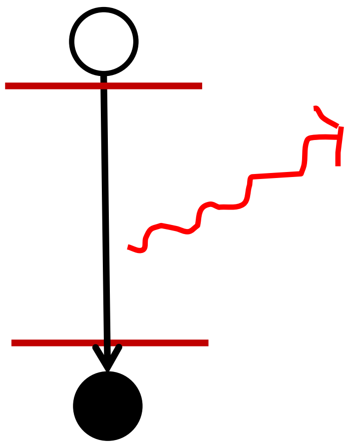
Radiative recombination

- Doping levels, p-type material

$$n = n_0 + \Delta n = \frac{n_i^{\,2}}{N_a} + \Delta n$$

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

$$n_i^2 = n_0 p_0$$



- Assumptions:

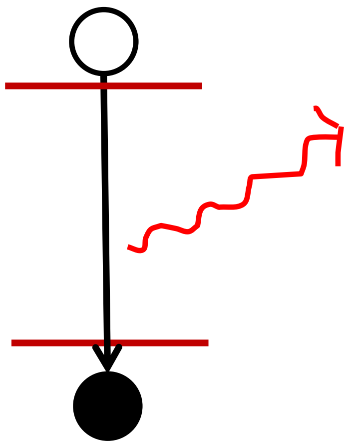
$$n_0 << \Delta n \ll p_0$$

Radiative recombination

- The equations become

$$U_{rad} = \mathrm{Brad}(np - ni^2)$$

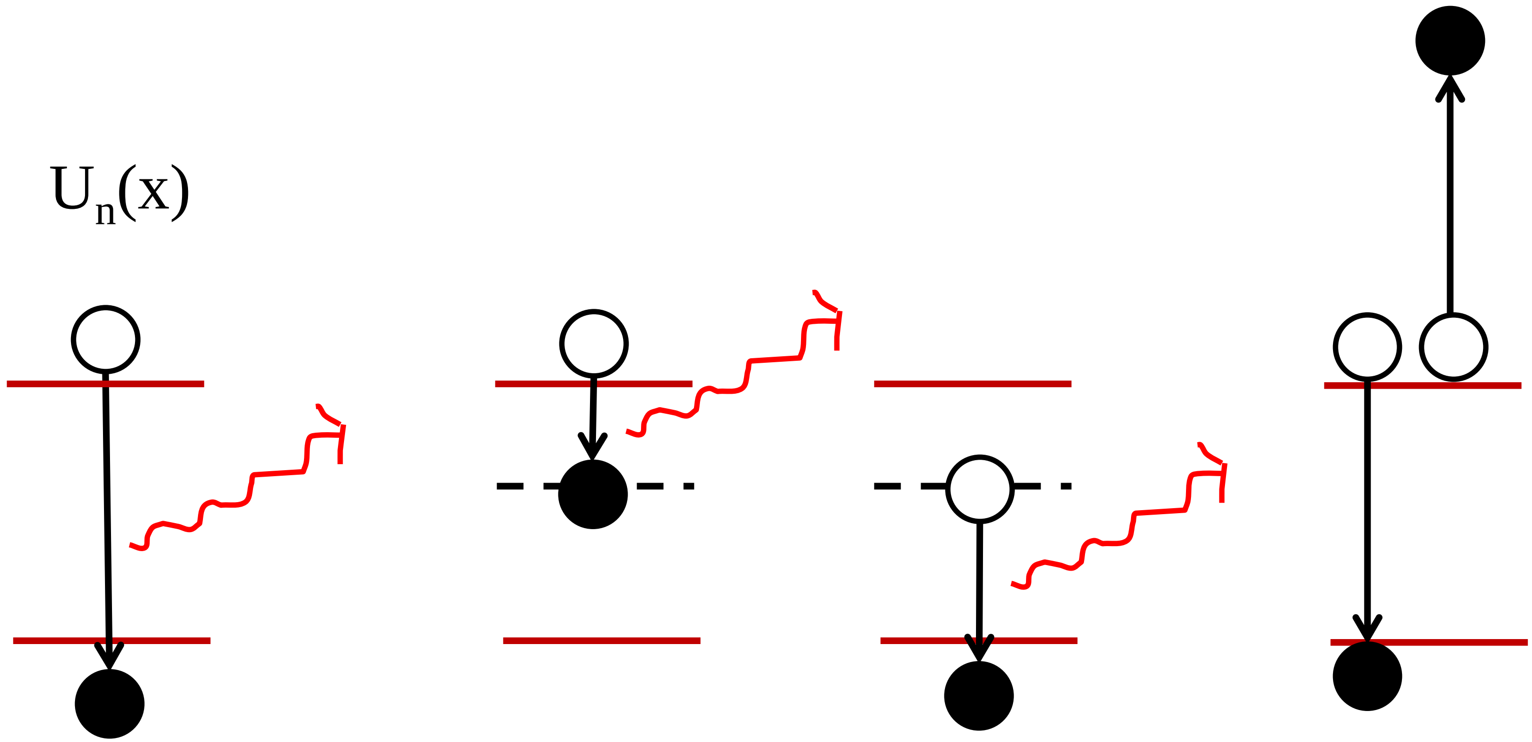
$$\sim \mathrm{Brad}(\Delta n N_a)$$



- We define lifetime

$$U_{rad} = \Delta n/\tau_{rad}$$

Recombination processes



RADIATIVE
(BAND-TO-BAND)

SHOCKLEY-REED-
HALL

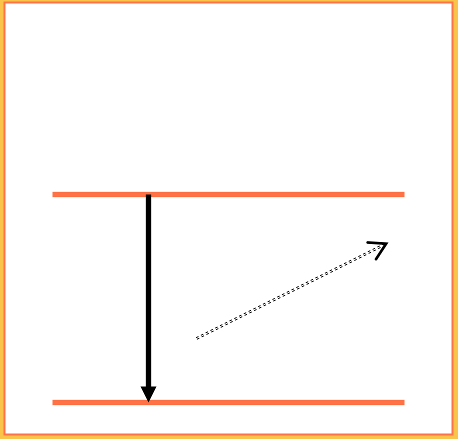
AUGER

Bulk recombination – simplified equations

U_{rad}

$U_{p,rad} = \Delta n/\tau_{p,rad}$

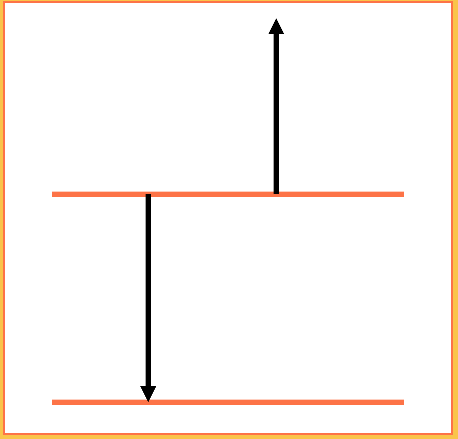
$\tau_{p,rad} = 1/(B_{rad} \cdot N_a)$



U_{Aug}

$U_{p,Aug} = \Delta n/\tau_{p,Aug}$

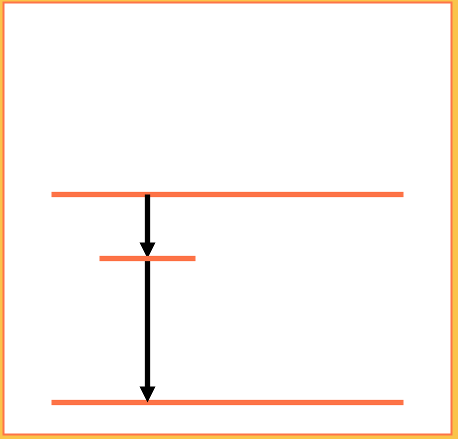
$\tau_{p,Aug} = 1/(A_p \cdot N_a{}^2)$



U_{SRH}

$U_{p,SRH} = \Delta n/\tau_{p,SRH}$

$\tau_{p,SRH} = 1/(B_{p,SRH} \cdot N_t)$



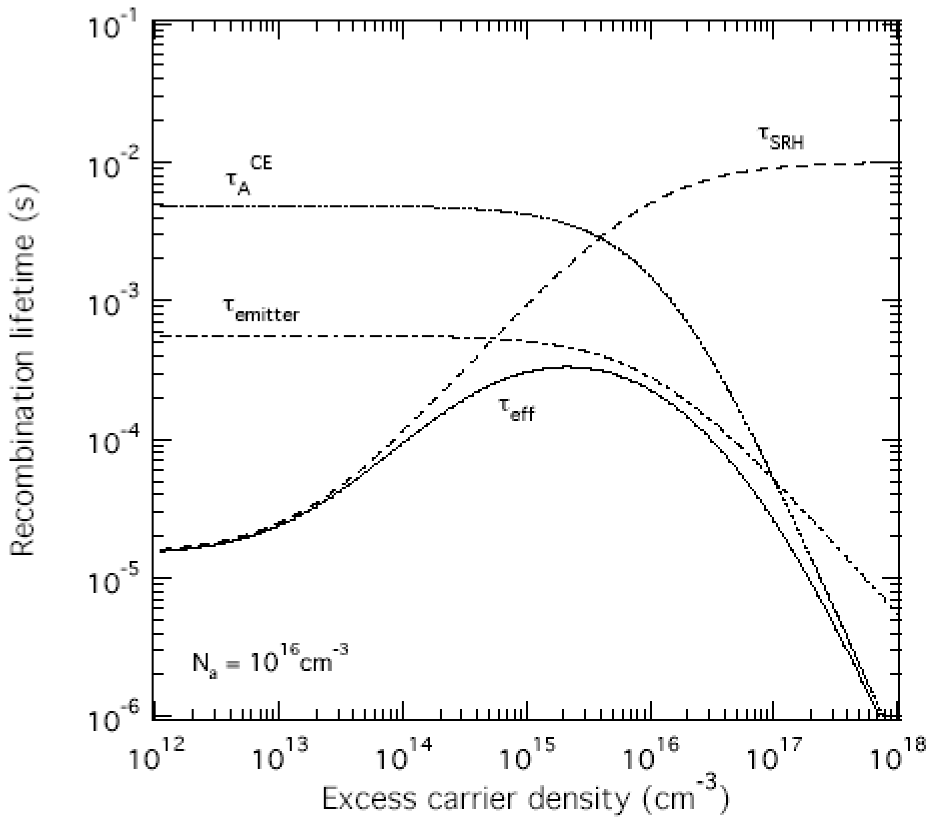
Effective lifetime

- Several recombination mechanisms will occur simultaneously in any given material
- The total effective lifetime is given by the inverse sum of the separate lifetime contributions

$$(\tau_{eff})^{-1} = (\tau_{mech1})^{-1} + (\tau_{mech2})^{-1} + (\tau_{mech3})^{-1} + \dots$$

- Mostly, one or a few recombination processes with low associated lifetimes will dominate

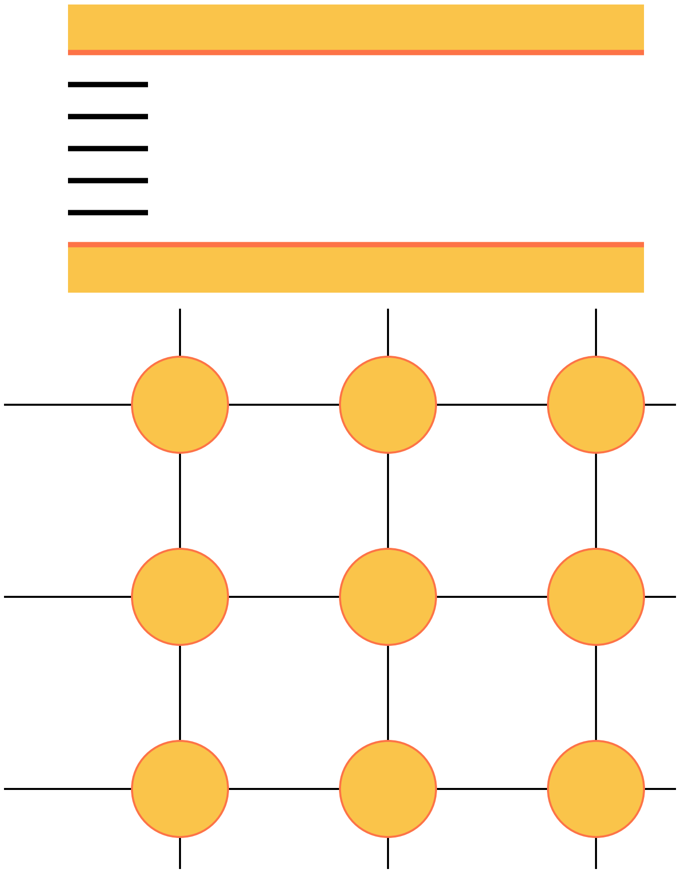
Bulk lifetime in silicon



Bentzen: PhD thesis

Surface recombination

- A surface is an extended defect
  - Introduces states in the band gap
  - Dangling bonds
  - Impurities
- Most often described using a surface recombination velocity (S) and a recombination flux
- Formalism analogous to SRH



Surface recombination

U_{surf}

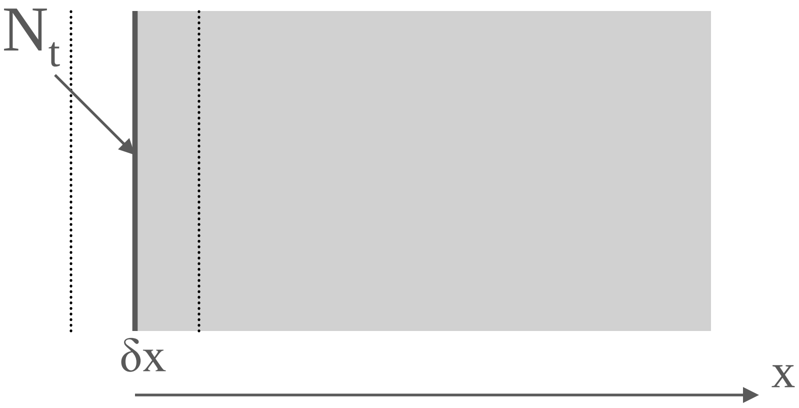
$$U_{surf} \cdot \delta x = \frac{n_{surf} p_{surf} - n_i^2}{(1/S_n)(p_{surf} + p_t) + (1/S_p)(n_{surf} + n_t)}$$

Surface recombination

U_{surf}

$$U_{p,surf} \cdot \delta x = S_p \cdot \Delta n$$

$$S_p = B_n \cdot N_t$$



Surface recombination current

- Surface recombination will contribute to the current densities at the surface

$$J_{p,surf} = q \cdot \int U_{p,surf} \cdot dx = q \cdot S_p \cdot \Delta n$$

$$J_{n,surf} = -q \cdot \int U_{n,surf} \cdot dx = q \cdot S_n \cdot \Delta n$$

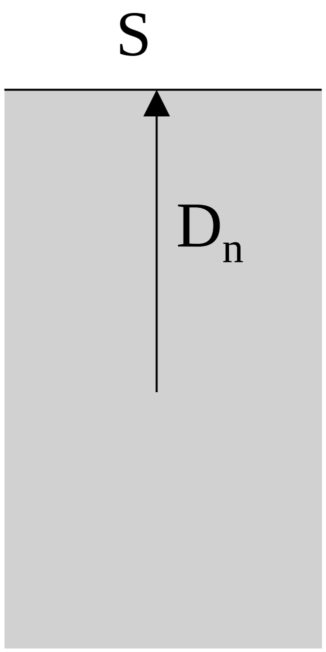
Surface recombination and lifetime

- Surface recombination must be considered when measuring lifetime

$$(1/\tau_{eff}) = (1/\tau_{bulk}) + (1/\tau_{surf})$$

- If S is too high compared with τ_{bulk}, τ_{eff} will be determined only by the surface recombination

Surface recombination and lifetime

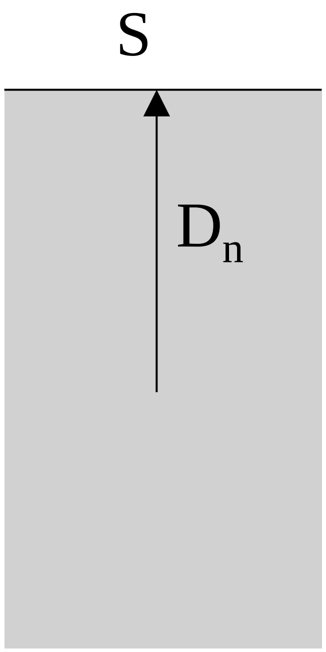


Surface recombination and lifetime

- For high values of S ($S \cdot d/D_n > 100$)

$$(1/\tau_{eff}) = (1/\tau_{bulk}) + D_n(\pi/d)^2$$

  - All charge reaching the surface recombines
    - Exact value of S no longer important
    - Diffusion towards surface becomes limiting factor
  - Validity of equation:
    - Diffusion constant (D_n) $\approx 30\ cm^2/s$
    - Wafer thickness (d) $\approx 300\ \mu m$
    - Equation valid within ~ 5% as long as $S > 100\ 000\ cm/s$



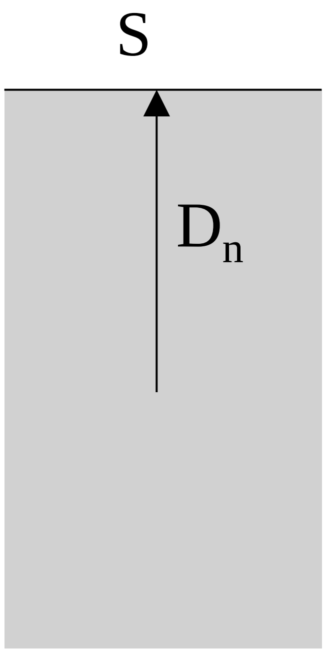
Rein: "Lifetime spectroscopy"

Surface recombination and lifetime

- For low values of S ($S \cdot d/D_n < ¼$)

$$(1/\tau_{eff}) = (1/\tau_{bulk}) + (2 \cdot S/d)$$

  - Limited by recombination at surface
  - Validity of equation:
    - Diffusion constant (D_n) $\approx 30\ cm^2/s$
    - Wafer thickness (d) $\approx 300\ \mu m$
    - Equation valid within ~ 5% as long as S $< 250\ cm/s$

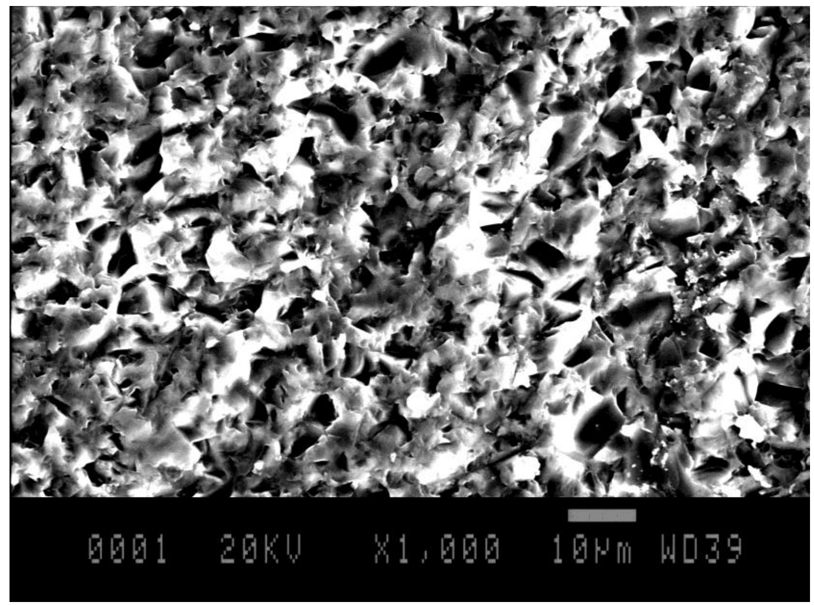


Rein: "Lifetime spectroscopy"

Surface passivation

- Abrupt semiconductor surfaces: large S
- For lifetime measurements, low S is required
  - High quality bulk material

- Recipe
  - Remove surface damage
  - Clean surface thoroughly
  - Apply a suitable passivating film
    SiO_2, a-SiN_x:H, a-Si:H, a-Al_xO:H…
  - Measure the lifetime



IFE

Diffusion length and lifetime

- The diffusion length (L) is defined as follows:

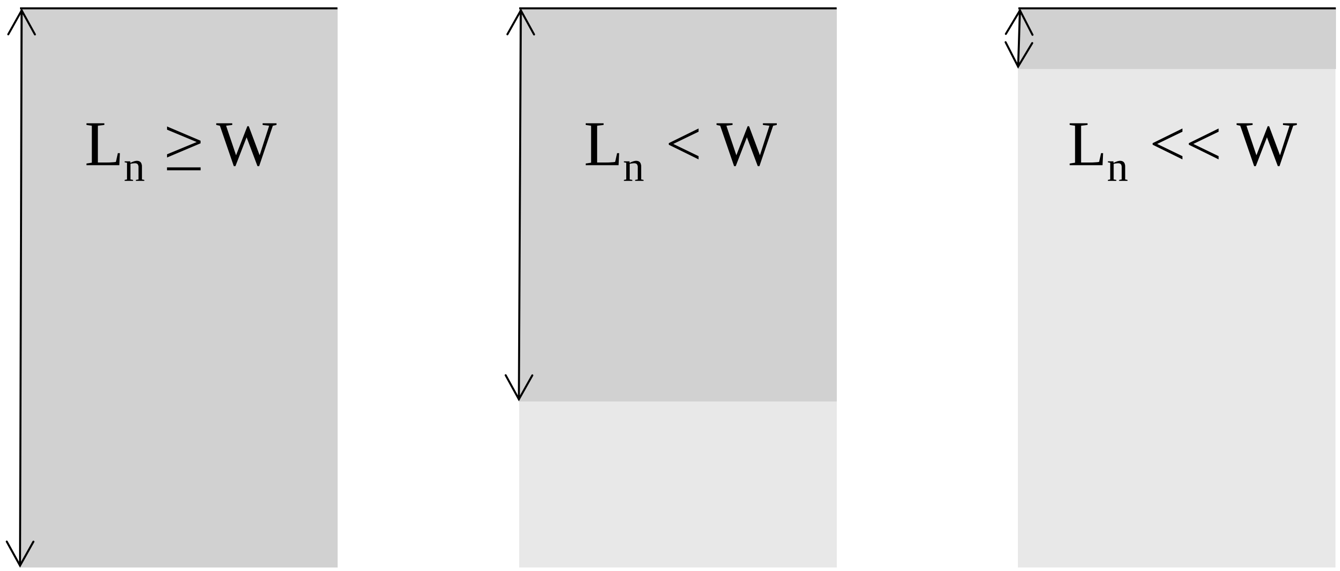
$$\boxed{L = (D \cdot \tau)^{1/2}}$$

- L is a measure of the average distance a minority charge carrier is able to move without recombining
- L is important in determining which solar cell structures can be realized from a given material

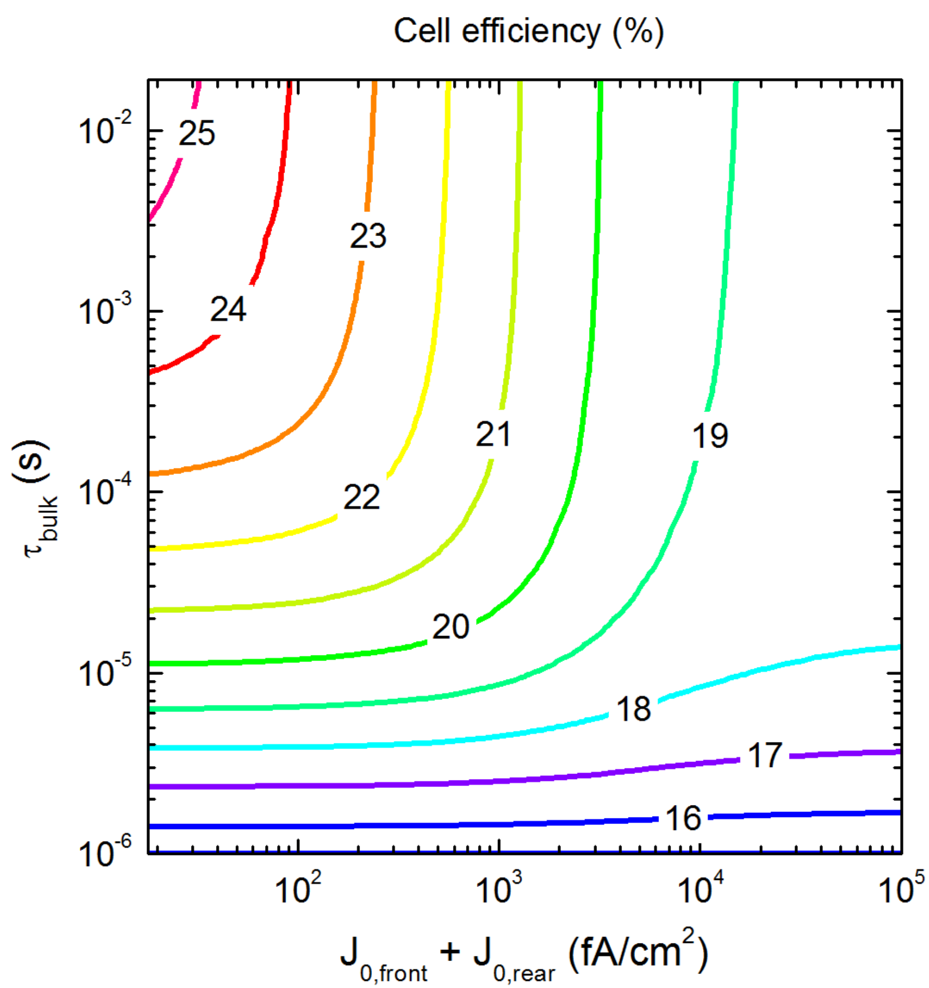
Clever student question:

”Why do I care?”

Diffusion length and solar cell performance



Lifetime and surface recombination



PV LIGHTHOUSE

H. Haug et al (IFE, 2014)

IFE

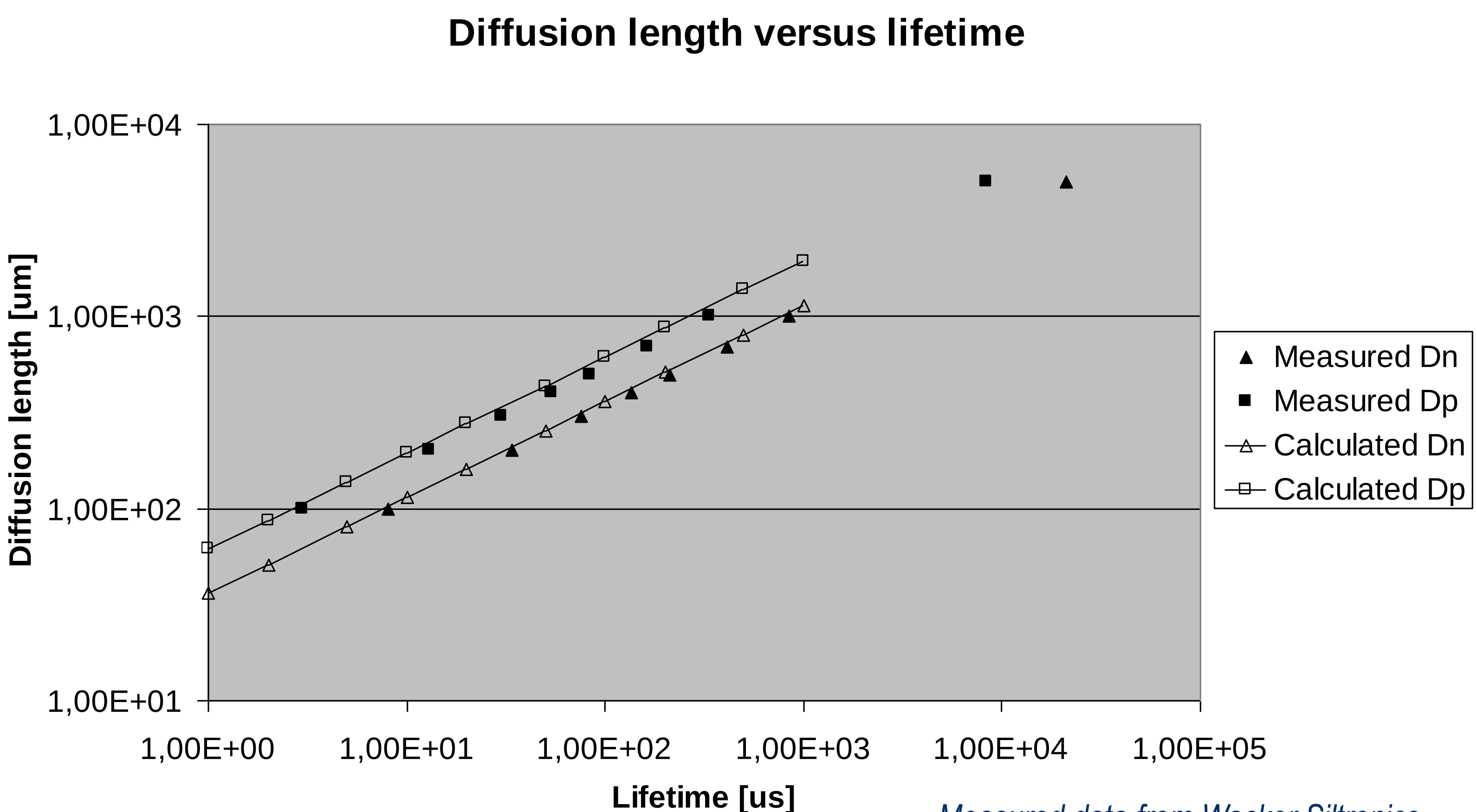
The Einstein relation

- The Einstein relation relates minority carrier mobilities and diffusitivities

$$k_B T/q = D/\mu$$

- Electrons
  - $\mu = 1450\ cm^2/V \cdot s$
  - $D = 37{,}7\ cm^2/s$
- Holes
  - $\mu = 500\ cm^2/V \cdot s$
  - $D = 13{,}0\ cm^2/s$

Diffusion length and lifetime



Measured data from Wacker Siltronics

Clever student question (refined):

”How can I measure lifetime?”

Transient vs steady state

$$\tau_{eff} = \frac{\Delta n(t)}{G(t) - d\Delta n(t)/dt}$$

$$\tau_{eff} = \frac{-\Delta n(t)}{d\Delta n(t)/dt}$$

TRANSIENT

$$\tau_{eff} = \frac{\Delta n(t)}{G(t)}$$

STEADY STATE

Lifetime measurements

- How do we measure the lifetime?
  - Quasi-steady state photoconductance (QSSPC/«Sinton»)
  - Microwave detected photoconductance decay (µ-PCD)
  - Photoluminescence imaging (PL)
  - Carrier density imaging (CDI)

- Artifacts of lifetime measurements
  - Trapping

- Applications of lifetime measurements

QSSPC

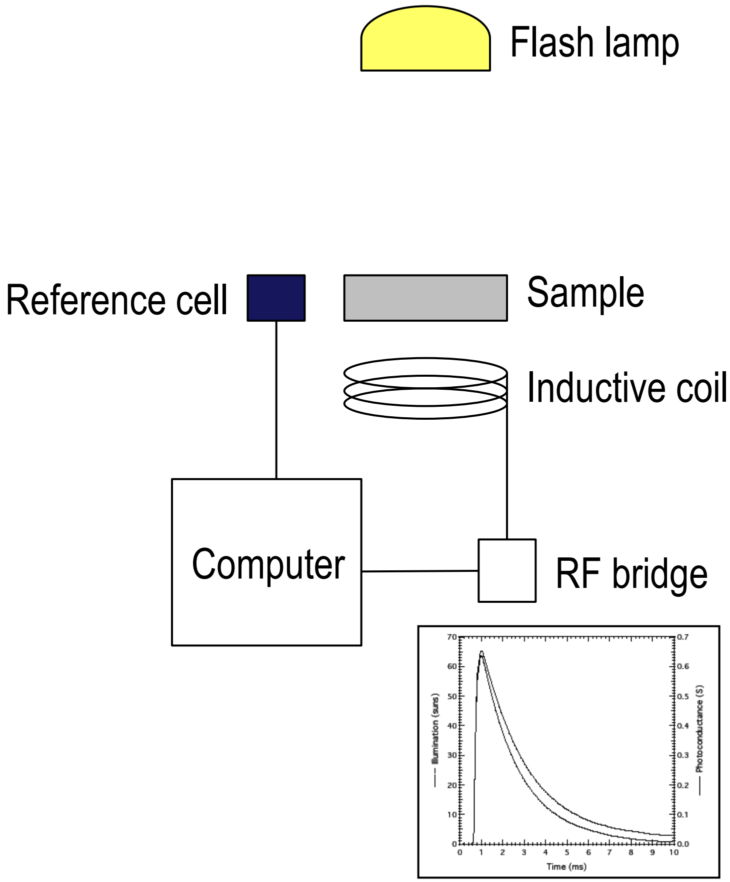
- Quasi-steady state: flash decay slow compared to lifetime

- Lifetime determined from excess carrier density in quasi-steady state

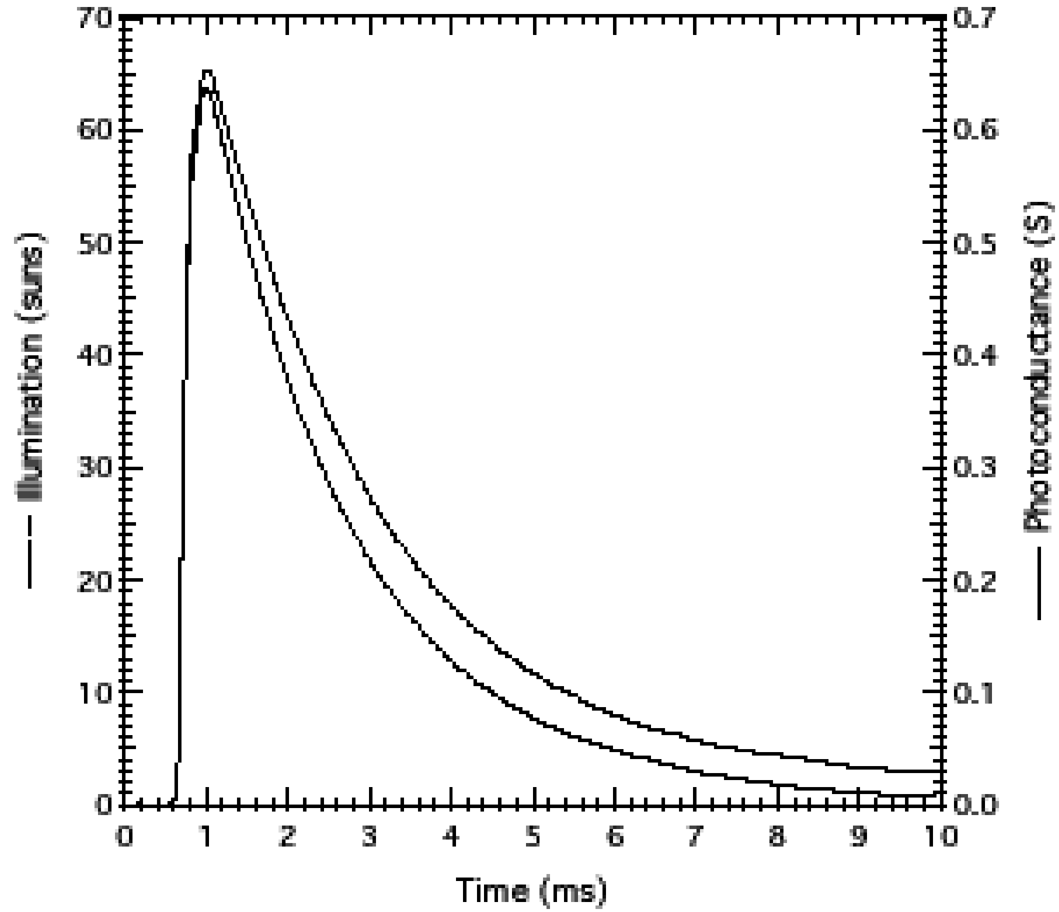
$$\tau_{eff,QSSPC} = \Delta n / g_E$$

- Excess carrier density linked to conductivity

$$\Delta n = \Delta\sigma(t)/q(\mu_n + \mu_p)W$$



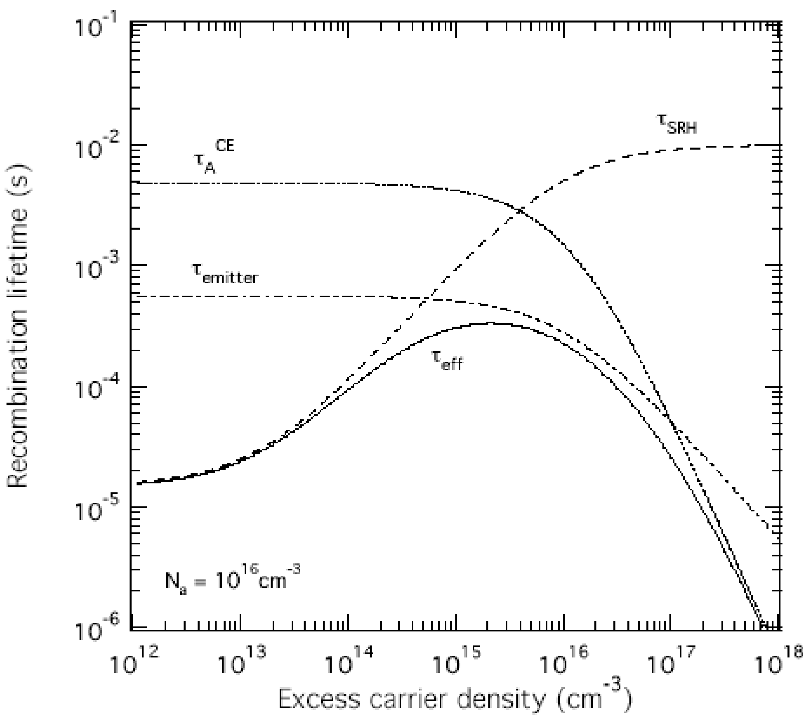
QSSPC



Bentzen: PhD thesis

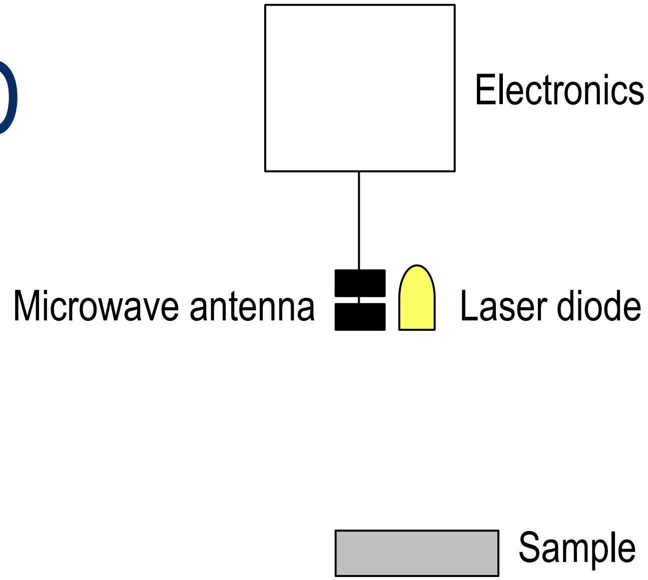
QSSPC

- Advantage
  - Measures lifetime as a function of injection level
  - Robust physical models
  - True lifetimes can be extracted
- Disadvantage
  - Usually measures across large area



Bentzen: PhD thesis

μ-PCD



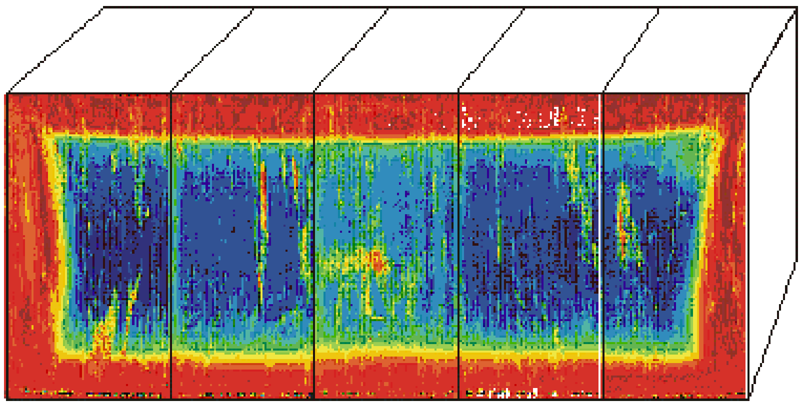
- Very short pulse applied to sample
  - Measures $d\Delta n(t)/dt$, not the steady state generation rate g_E

$$\tau_{eff,u\text{-}PCD} = \Delta n/(d\Delta n(t)/dt)$$

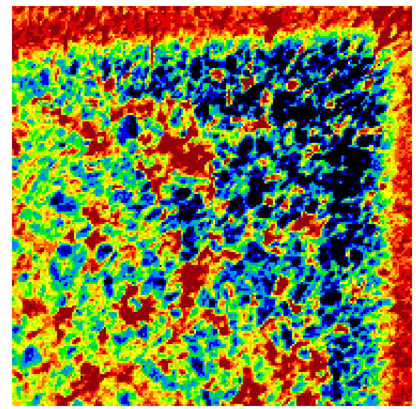
- Change in photoconductivity measured as microwave reflection

$$\Delta n/(d\Delta n(t)/dt)$$
$$=$$
$$\Delta\sigma(t)/(q(\mu_n + \mu_p)Wd\Delta n(t)/dt)$$

u-PCD – measurement examples



- When measuring thick samples, such as blocks, a long wavelength can be used
- Photogeneration far from surface
- Surface passivation not critical



- On wafers, surfaces are always close at hand
- A surface passivation is required
- Without passivation, the maximal measured lifetime only is a few µs

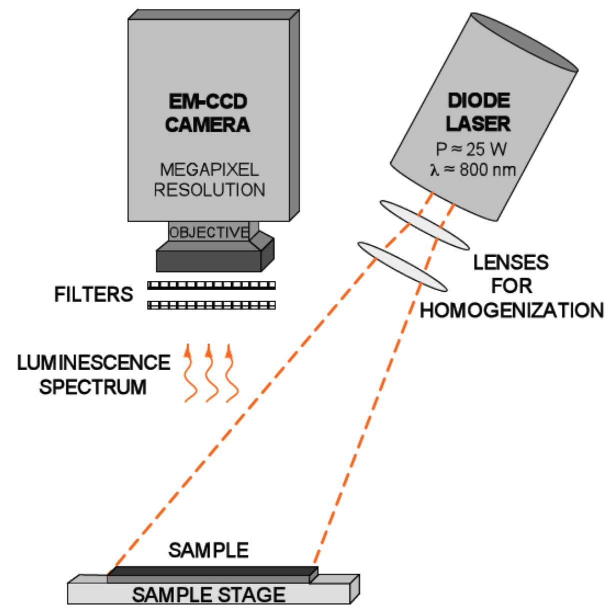
u-PCD

- Advantage
  - High spatial resolution obtainable

- Disadvantages
  - No implicit knowledge of injection level
  - Lifetime versus injection level requires adjustments of bias light

PL imaging

- Method
  - Relate measured luminescence signal from radiative recombination to Δn
  - Extract effective lifetime from ratio of Δn to generation rate G



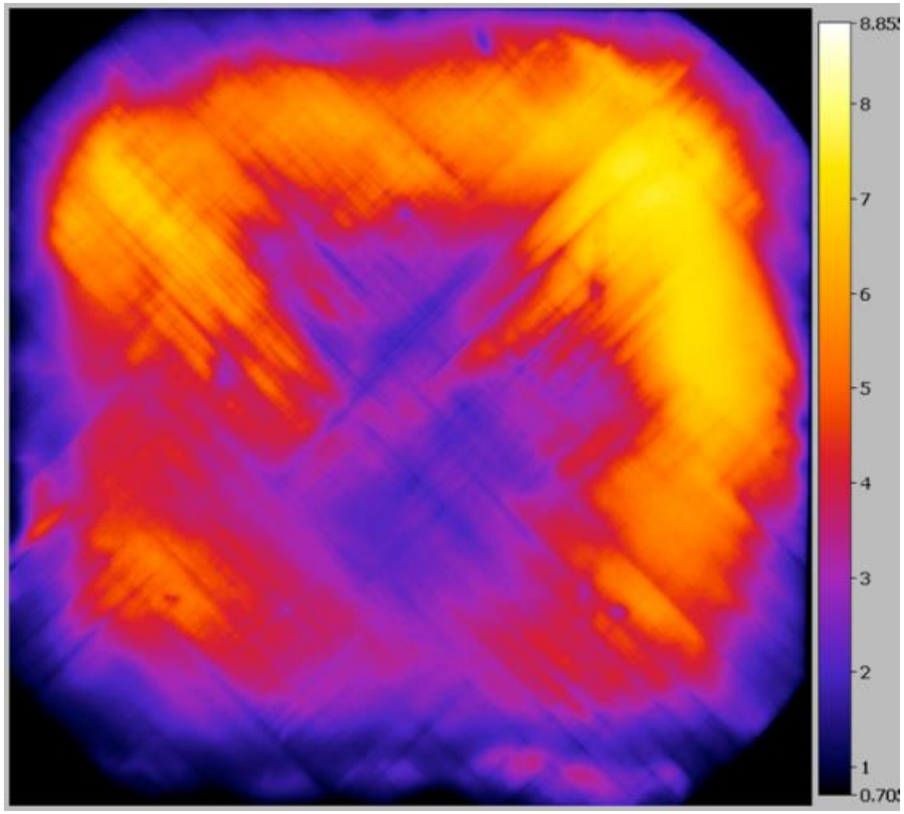
$$U_{rad} = \ Brad(np \ - ni^2)$$

$$B_{rad}\,\Delta n(\tilde{\Delta} n + Na)$$

$$\tau_{eff} = \Delta n/G$$

Angelskår

PL imaging – measurement example



PL

- Advantage
  - High spatial resolution obtainable
  - Potentially super-fast
- Disadvantages
  - Calibration required, but can be implemented easily
  - Doping level knowledge required, but can be implemented easily

The effect of non-recombinative traps

- Charge neutrality requires that

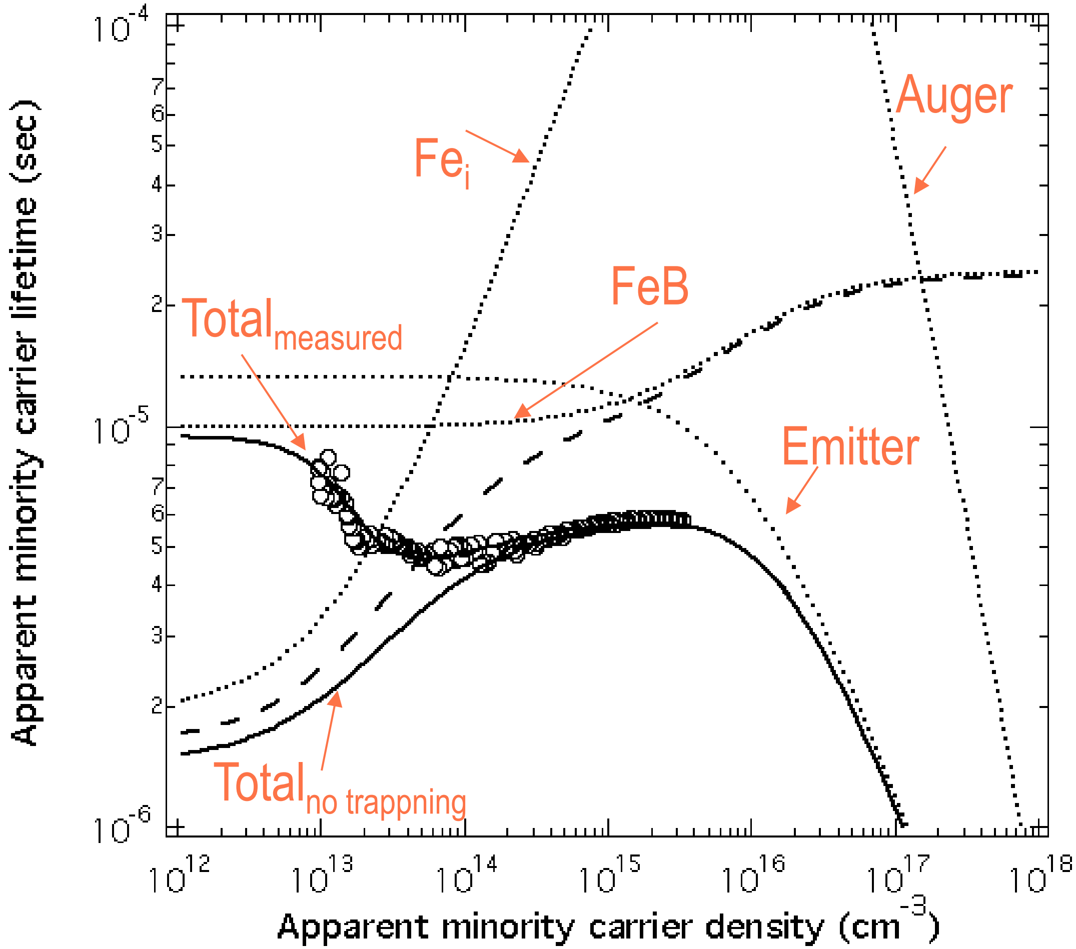
$$\Delta n = \Delta p$$

- Certain traps only store charge carriers for some time before re-releasing them to the nearest energy band
- With a number of electron traps (n_t), the conductivity becomes

$$\Delta\sigma(t) = q(\mu_n \Delta n + \mu_p \Delta p)W + q n_t \mu_n W$$

- This effect will lead to an **apparent** increase in lifetime

Trapping – calculated example



Bentzen: PhD thesis

Case 1: Counting dissolved impurities

- A lifetime determined by dissolved impurities can be described as follows:

$$1/\tau = \sigma_t v_{th} N_t$$

  - Scattering cross section (σ_t)
  - Thermal velocity of electrons (v_{th})
  - Concentration of defects (N_t)
- If the lifetime is dominated by one defect with a known σ_t, the defect concentration can be estimated

Case 2: Counting precipitates

- A lifetime determined by precipitates can be described by the following empirical equation:

$$L = 0.7 \cdot (N_p)^{-1/3}$$

  - Precipitate density (N_p)
- Hard in principle, lifetime usually limited by other factors

Luque & Hegedus: "PV Handbook"

Case 3: Determining Fe_i concentration in Si

- Fe is an important defect in mc-Si technology
- The concentration of Fe in B-doped Si can be determined by lifetime measurements
- Interstitially dissolved Fe (Fe_i^+) is a common “lifetime killer” in Si
- In p-Si, Fe_i^+ tends to pair up with B acceptors (B_s^-) forming so-called Fe-B pairs (FeB)
- FeB pairs can be split up by illumination into B_s^- and Fe_i^+

Case 3: Determining Fe_i concentration in Si

- Before illumination

$$(\tau_{before})^{-1} = (\tau_{surf})^{-1} + (\tau_{FeB})^{-1}$$

- After illumination and pair separation

$$(\tau_{after})^{-1} = (\tau_{surf})^{-1} + (\tau_{Fe\_i})^{-1}$$

- Difference

$$(\tau_{after})^{-1} - (\tau_{before})^{-1} = (\tau_{Fe\_i})^{-1} - (\tau_{FeB})^{-1}$$