Recombination and lifetime
Main question

Will this wafer make a good solar cell?
Where are we?

\[ J_n(x) \rightarrow G_n(x) \rightarrow U_n(x) \rightarrow J_n(x + dx) \]

\[ dV \]

\[ dx \]
Continuity equation

- Assuming uniform generation and no net charge transport (disregarding surface recombination) within the semiconductor:

\[
\frac{d\Delta n(t)}{dt} = G(t) - U_{\text{eff}} = G(t) - \frac{\Delta n}{\tau_{\text{eff}}}
\]

- Solving for \( \tau_{\text{eff}} \) yields:

\[
\tau_{\text{eff}}(\Delta n) = \frac{\Delta n(t)}{G(t) - \frac{d\Delta n(t)}{dt}}
\]

More generally, see: Nagel et al, “Generalized analysis of quasi-steady-state…”, JAP, 1999
Continuity equation – steady state

• The photoluminescence intensity is detected with constant excitation over a long time, so we can assume steady state.

• In steady state ($d\Delta n/dt=0$), the generation rate $G$ and recombination rate $U$ are balanced:

$$G = U_{eff} = \frac{n}{eff} \Rightarrow eff = \frac{n}{G}$$

• Need to know $\Delta n$ and $G$ to determine the effective lifetime.
Recombination processes

$U_n(x)$

- **RADIATIVE (BAND-TO-BAND)**
- **SHOCKLEY-REED-HALL**
- **AUGER**
Bulk recombination – simplified equations

\[ U_{\text{rad}} \]
\[ U_{p,\text{rad}} = \frac{\Delta n}{\tau_{p,\text{rad}}} \]
\[ \tau_{p,\text{rad}} = \frac{1}{(B_{\text{rad}} \cdot N_a)} \]

\[ U_{\text{Aug}} \]
\[ U_{p,\text{Aug}} = \frac{\Delta n}{\tau_{p,\text{Aug}}} \]
\[ \tau_{p,\text{Aug}} = \frac{1}{(A_p \cdot N_a^2)} \]

\[ U_{\text{SRH}} \]
\[ U_{p,\text{SRH}} = \frac{\Delta n}{\tau_{p,\text{SRH}}} \]
\[ \tau_{p,\text{SRH}} = \frac{1}{(B_{p,\text{SRH}} \cdot N_t)} \]
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

\[
(\tau_{\text{eff}})^{-1} = (\tau_{\text{mech1}})^{-1} + (\tau_{\text{mech2}})^{-1} + (\tau_{\text{mech3}})^{-1} + \ldots
\]

- 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

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

\[ U_{\text{surf}} \]

\[ U_{p,\text{surf}} \cdot \delta x = S_p \cdot \Delta n \]

\[ S_p = B_n \cdot N_t \]
Surface recombination current

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

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

\[ J_{n,\text{surf}} = -q \cdot \int U_{n,\text{surf}} \cdot \, dx = q \cdot S_n \cdot \Delta n \]
Surface recombination and lifetime

- Surface recombination must be considered when measuring lifetime.

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surf}}}
\]

- If \( S \) is too high compared with \( \tau_{\text{bulk}} \), \( \tau_{\text{eff}} \) will be determined only by the surface recombination.
Surface recombination and lifetime
Surface recombination and lifetime

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

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

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

Rein: “Lifetime spectroscopy”
Surface recombination and lifetime

- For low values of $S$ ($S \cdot d/D_n < 1/4$)

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + (2 \cdot S/d)
\]

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

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
    - $\text{SiO}_2$, $\text{a-SiN}_x: \text{H}$, $\text{a-Si:H}$, $\text{a-Al}_x\text{O: H}$...
  - Measure the lifetime
Diffusion length and lifetime

- The diffusion length ($L$) is defined as follows:
  \[ L = (D \cdot \tau)^{1/2} \]

- $L$ 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.
Diffusion length and solar cell performance

\[ L_n \geq W \]

\[ L_n < W \]

\[ L_n \ll W \]
The Einstein relation

- The Einstein relation relates minority carrier mobilities and diffusivities

\[ \frac{kT}{q} = \frac{D}{\mu} \]

- Electrons
  - \( \mu = 1450 \text{ cm}^2/\text{V} \cdot \text{s} \)
  - \( D = 37.7 \text{ cm}^2/\text{s} \)
- Holes
  - \( \mu = 500 \text{ cm}^2/\text{V} \cdot \text{s} \)
  - \( D = 13.0 \text{ cm}^2/\text{s} \)
Diffusion length and lifetime

Diffusion length versus lifetime

Measured data from Wacker Siltronics
Lifetime measurements

- How do we measure the lifetime?
  - Photoconductance \((\sigma \sim \Delta n)\)
  - Photoconductance decay \((d\sigma/dt \sim d(\Delta n)/dt)\)
  - Radiative recombination \((I_{PL} \sim \Delta n)\)
  - IR-absorption by excited charge \((I_{fca} \sim \Delta n)\)
Lifetime measurements

• Which methods do we use to 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
Quasi-Steady State PhotoConductance

\[
\frac{d\Delta n(t)}{dt} = G(t) - U_{\text{eff}} = G(t) - \frac{\Delta n}{\tau_{\text{eff}}} = 0
\]

\[
\tau_{\text{eff}} = G(t) / \Delta n
\]
QSSPC

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

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

\[ \tau_{\text{eff,QSSPC}} = \frac{\Delta n}{g_E} \]

- Excess carrier density linked to conductivity

\[ \Delta n = \frac{\Delta \sigma(t)}{q(\mu_n + \mu_p)} W \]
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
Microwave **photoconductance decay**

\[ \frac{d\Delta n(t)}{dt} = G(t) - U_{\text{eff}} = G(t) - \frac{\Delta n}{\tau_{\text{eff}}} \]

\[ \tau_{\text{eff}} = \frac{\Delta n}{\left( \frac{d\Delta n(t)}{dt} - G(t) \right)} = \frac{\Delta n}{\left( \frac{d\Delta n(t)}{dt} \right)} \]
μ-PCD

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

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

- Change in photoconductivity measured as microwave reflection

\[ \frac{\Delta n}{(d\Delta n(t)/dt)} = \frac{\Delta \sigma(t)}{q(\mu_n + \mu_p)Wd\Delta n(t)/dt} \]
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
PhotoLuminescence imaging

\[ \frac{d\Delta n(t)}{dt} = G(t) - U_{\text{eff}} = G(t) - \frac{\Delta n}{\tau_{\text{eff}}} = 0 \]

\[ \tau_{\text{eff}} = G(t) / \Delta n \]
PL imaging

- **Method**
  - Relate measured luminescence signal from radiative recombination to $\Delta n$
  - Extract effective lifetime from ratio of $\Delta n$ to generation rate $G$

\[
U_{rad} = B_{rad}(np - ni^2)
\]

\[
B_{rad} \Delta n (\Delta n + Na)
\]

\[
\tau_{eff} = \Delta n / G
\]
Generation rate

- Simple!
- Assume all photons entering the wafer are absorbed, and create an electron-hole-pair:

\[ G = \frac{laser (1 - R_{808nm})}{W} \]

- Photon flux: \(10^{17}\text{cm}^{-2}\text{s}^{-1}\)
- Reflectance at excitation wavelength
- Thickness of wafer, assumed uniform distribution
Relation to excess charge carrier density

- Radiative recombination in (p-type) silicon:

\[ R_{rad} = B_{rad} np \approx B_{rad} \left( N_A \cdot n + n^2 \right) \]

\[ n \approx \int_0^z n(z) dz \]

- Including \( B_{rad} \), the effect of camera, filters, surface morphology in a calibration factor \( C \):

\[ I_{\text{camera}}(n) \approx C \left( N_A \cdot n + n^2 \right) \]
Luminescence spectrum of silicon

- Band to band luminescence around 1000-1100nm
- Radiative (and non-radiative) defects yield dark signal since luminescence is outside detection limit (long-wavelength IR)
- High band-to-band luminescence signal means defects do not dominate
- Camera filters designed to filter out reflected laser light (~800 nm), and detect only band-to-band luminescence
Quasi-steady-state photoconductance

pvcdrom.pveducation.org

Bentzen: PhD thesis
Calibration of luminescence intensity to excess carrier density

- QSSPC measures conductivity and yields free carrier density given a mobility model
- Intensity vs. free carrier density
- Determines calibration constant $C$

$$I_{\text{camera}}(n) \approx C(N_A n + n^2)$$

Low injection, high doping

$$\approx CN_A n$$

- Now we can measure the PL intensity to get a map of $\Delta n$!
Complications

- Need to know doping – preferably have uniform doping…
  - Inhomogeneously doped wafers can show large variations in luminescence intensity
  - Minor effect on the conversion from conductivity to excess carrier density, due to mobility model
- QSSPC calibration over large area
  - Mobility models – compensated silicon
  - Need to take care for mc-silicon, averaged intensity
- Compensated silicon
  - Mobility model (as far as I know…) for QSSPC measurements still under discussion
  - Net doping variations will dominate the image
Complications

- Luminescence from emitters is usually neglected
- Reabsorption of luminescence photons
  - weak effect in the detected spectral range
- Uniformity of reflectance
  - Lifetime scales with reflectance
- Blurring if diffusion length is much longer than a pixel size (160 \text{um})
  - Small effect in solar grade silicon, limited to a few pixels
- Radiative recombination coefficient decreases at high injection level, screening effect
- Diffuse surfaces cause blurring
Effect of reflectance

- The generation rate $G$ is not constant over the wafer
- Misinterpreted as lower lifetime, but also an actual decrease in passivation quality? Thickness?
- Partly corrected by having a laterally varying generation rate $G$
High-resolution PL of multicrystalline silicon

- As-cut wafer
  - Same surface treatment (except for a-Si deposition)
  - Blurring due to longer diffusion length?

- Passivated wafer
  - $L = \sqrt{D}$

Electrons:
- $D = 37.7 \text{ cm}^2/\text{s}$
- $\tau \sim 15 \text{ us}$
- $L \sim 200 \text{ um}$
Slip lines in monocrystalline silicon

- Slip lines
  - Crystal defects during growth
  - Can lead to breakage during wafering
Compensated silicon

- UMG material
- See large effects of doping, also an issue for QSSPC calibration
- Research ongoing to adapt technique for compensated material

Haunschild et al., 35th PVSEC, 20
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

\[ \Delta \sigma(t) = q(\mu_n \Delta n + \mu_p \Delta p)W + qn_t \mu_n W \]

• This effect will lead to an \textbf{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:

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

- Scattering cross section ($\sigma_t$)
- Thermal velocity of electrons ($v_{th}$)
- Concentration of defects ($N_t$)

- If the lifetime is dominated by one defect with a known $\sigma_t$, 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 $\text{Fe}_i$ 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 ($\text{Fe}_i^+$) is a common “lifetime killer” in Si
- In p-Si, $\text{Fe}_i^+$ tends to pair up with B acceptors ($\text{B}_s^-$) forming so-called Fe-B pairs (FeB)
- FeB pairs can be split up by illumination into $\text{B}_s^-$ and $\text{Fe}_i^+$
Case 3: Determining Fe\(_i\) concentration in Si

- Before illumination
  \[
  (\tau_{\text{before}})^{-1} = (\tau_{\text{surf}})^{-1} + (\tau_{\text{FeB}})^{-1}
  \]

- After illumination and pair separation
  \[
  (\tau_{\text{after}})^{-1} = (\tau_{\text{surf}})^{-1} + (\tau_{\text{Fe_i}})^{-1}
  \]

- Difference
  \[
  (\tau_{\text{after}})^{-1} - (\tau_{\text{before}})^{-1} = (\tau_{\text{Fe_i}})^{-1} - (\tau_{\text{FeB}})^{-1}
  \]