Toward a 1D Device Model Part 2: Material Fundamentals

Lecture 8 – 10/4/2011
MIT Fundamentals of Photovoltaics
2.626/2.627 – Fall 2011
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2.626/2.627 Roadmap

You Are Here

Fundamentals
Every photovoltaic device must obey:

Conversion Efficiency \( (\eta) \equiv \frac{\text{Output Energy}}{\text{Input Energy}} \)

For most solar cells, this breaks down into:

\[
\eta_{\text{total}} = \eta_{\text{absorption}} \times \eta_{\text{excitation}} \times \eta_{\text{drift/diffusion}} \times \eta_{\text{separation}} \times \eta_{\text{collection}}
\]
Liebig’s Law of the Minimum

\[ \eta_{\text{total}} = \eta_{\text{absorption}} \times \eta_{\text{excitation}} \times \eta_{\text{drift/diffusion}} \times \eta_{\text{separation}} \times \eta_{\text{collection}} \]


Rough Depiction of Interrelated Materials & Device Effects

Devices

- Solar Cell Efficiency ($\eta$)
  \[ \eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{\Phi} \]

- Open-Circuit Voltage ($V_{oc}$)

- Short-Circuit Current ($J_{sc}$)
  \[ J_{sc} = q \int IQE(\lambda) \cdot p(\lambda) \cdot d\lambda \]

- Fill Factor ($FF$)

- Internal Quantum Efficiency ($IQE$)

Materials

- Built-In Voltage ($V_o$)
  \[ V_o = \frac{kT}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right) \]

- Surface Fermi-Level Pinning

- Absorption Coefficient ($\alpha$)

- Diffusion Length ($L_{diff}$)
  \[ L_{diff} = \sqrt{D(\mu) \cdot \tau_{bulk}} \]

- Shunt Resistance ($R_{sh}$)

- Surface Density Of States

- Im[Dielectric Constant] ($\varepsilon_2$)

- Series Resistance ($R_s$)

- Carrier Concentration ($N_A, N_D, n_i$)

- Lifetime ($\tau$)

- Mobility ($\mu$)

Source: T. Buonassisi, unpublished.

Buonassisi (MIT) 2011
Learning Objectives: Toward a 1D Device Model

1. Describe what minority carrier diffusion length is, and calculate its impact on $J_{sc}$, $V_{oc}$. Describe how minority carrier diffusion length is affected by minority carrier lifetime and minority carrier carrier mobility.

2. Describe how minority carrier diffusion length is measured.

3. Lifetime:
   - Describe basic recombination mechanisms in semiconductor materials.
   - Calculate excess carrier concentration as a function of carrier lifetime and generation rate. Compare to background (intrinsic + dopant) carrier concentrations.

4. Mobility:
   - Describe common mobility-limiting mechanisms (dopants, temperature, ionic semiconductors).
Minority Carrier Diffusion Length

**Definition:** Minority carrier diffusion length is the average distance a minority carrier moves before recombining.

**Importance to a Solar Cell:** Photoexcited carriers must be able to move from their point of generation to where they can be collected. Longer diffusion lengths generally result in better performance.
Minority Carrier Diffusion Length

Definition: The average distance a minority carrier moves before recombining.

Importance to a Solar Cell: Carriers must be able to move from their point of generation to where they can be collected.

Cross section of solar cell made of high-quality material
Minority carrier diffusion length ($L_{\text{diff}}$) is LARGE.
Solar cell current output ($J_{\text{sc}}$) is large.

Most electrons diffuse through the solar cell uninhibited, contributing to high photon-to-electron (quantum) efficiencies.
Minority Carrier Diffusion Length

**Definition:** The average distance a minority carrier moves before recombining.

**Importance to a Solar Cell:** Carriers must be able to move from their point of generation to where they can be collected.

Cross section of solar cell made of **defect-ridden** material
Minority carrier diffusion length ($L_{\text{diff}}$) is small.
Solar cell current output ($J_{\text{sc}}$) is small.

Electrons generated closer to the surface make it to the contacts, but those in the bulk are likely to “recombine” (lose their energy, e.g., at bulk defects, and not contribute to the solar cell output current).
Mathematical Formalism

Recall that the current produced in an illuminated pn-junction device, is limited by the minority carrier flux at the edge of the space-charge region.

\[ J_{sc} \approx qG L_{diff} \]

\[ J_{sc} \propto L_{diff} \]

From Eq. 4.44 in Green.

\( J_{sc} = \) illuminated current = \( J_L \)

\( G = \) carrier generation rate
Mathematical Formalism

Note that the voltage is also affected by $L_{\text{diff}}$.

$$V_{\text{oc}} = \frac{k_B T}{q} \ln \left( \frac{J_{\text{sc}}}{J_o} + 1 \right)$$

From Eq. 4.45 in Green.

$V_{\text{oc}}$ = open-circuit voltage

$J_o$ = saturation current density

$$J_o \approx \frac{q D n_i^2}{L_{\text{diff}} N}$$

From Eq. 4.37 in Green.

$D$ = minority carrier diffusivity

$N$ = majority carrier dopant concentration

$n_i$ = intrinsic carrier concentration

$$V_{\text{oc}} \propto \ln \left( L_{\text{diff}}^2 \right) \propto 2 \ln \left( L_{\text{diff}} \right) \propto \ln \left( L_{\text{diff}} \right)$$
Mathematical Formalism

Assuming a weak dependence of FF on $L_{\text{diff}}$, we have the following relationship:

$$\eta \propto J_{\text{sc}} V_{\text{oc}} \propto L_{\text{diff}} \ln(L_{\text{diff}})$$
Mathematical Formalism

Assuming a weak dependence of FF on $L_{\text{diff}}$, we have the following relationship:

$$\eta \propto J_{sc} V_{oc} \propto L_{\text{diff}} \ln(L_{\text{diff}})$$

**Diagram:**

- **Device Efficiency vs. Diffusion Length**
- $L_{\text{diff}} \ll$ device thickness.
- $L_{\text{diff}} \gg$ device thickness.
Minority Carrier Diffusion Length

When your material has short minority carrier diffusion length relative to absorber thickness, two engineering options:

*Reduce absorber layer thickness (if light management permits)* or
*increase diffusion length.*
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Collection Probability

- Collection probability is the probability that a light generated carrier will reach the depletion region and be collected.
- Depends on where it is generated compared to junction and other recombination mechanisms, and the diffusion length.

![Collection Probability Diagram](image)

With high surface recombination, the collection probability at the surface is low.

Courtesy of Christiana Honsberg. Used with permission.
Collection Probability

Collection probability is low further than a diffusion length away from junction.

Active region for current collection falls approximately within a diffusion length of the junction.

Courtesy of Christiana Honsberg. Used with permission.
Collection Probability

\[ J_{sc} \text{ determined by generation rate and collection probability} \]

\[ J_L = q \int_0^W G(x)CP(x)dx \]

Courtesy of Christiana Honsberg. Used with permission.
Spectral Response (Quantum Efficiency)

A reduction of the overall QE is caused by reflection and a low diffusion length.

The red response is reduced due to rear surface passivation, reduced absorption at long wavelengths and low diffusion lengths.

Blue response is reduced due to front surface recombination.

No light is absorbed below the band gap and so the QE is zero at long wavelengths.

\[ \lambda = \frac{hc}{E_g} \]

Standards: IEC 60904-3 and 60904-8

Courtesy of PVCDROM. Used with permission.
Minority Carrier Diffusion Length

At each point…

\[ \text{IQE}^{-1} = 1 + \alpha^{-1} \cos \theta \]

\[ \frac{1}{\text{IQE}} = \frac{1}{\alpha} + \frac{\cos \theta}{L_{\text{eff}}} \]

Mapped over an entire sample…

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What Limits Diffusion Length?
What Limits the Minority Carrier Diffusion Length?

**Quick answer:** Recombination-active defects, intrinsic mobility limitations, or absence of percolation pathways.

Thin films: Effect of bulk defects (GBs) on $\eta$. Nanostructured: Effect of morphology on $\eta$.

Please see lecture video for visuals.

Mathematical Formalism

Diffusion length is governed by “lifetime” and “mobility”

\[ L_{\text{diff}} = \sqrt{D \tau_{\text{bulk}}} \]

- \( L_{\text{diff}} \): bulk diffusion length
- \( D \): diffusivity
- \( \tau_{\text{bulk}} \): bulk lifetime

\[ D = \frac{k_B T}{q \mu} \]

- \( k_B \): Boltzmann coefficient
- \( T \): temperature
- \( q \): charge
- \( \mu \): mobility

For carriers in an electric field

Definition of “bulk lifetime”: The average time an excited carrier exists before recombining. (i.e., temporal analogy to diffusion length.)

Units = time.

- \( \tau_{\text{bulk}} \) of µs to ms is typical for indirect bandgap semiconductors, while \( \tau_{\text{bulk}} \) of ns to µs is typical of direct bandgap semiconductors.

Definition of “mobility”: How easily a carrier moves under an applied field. (i.e., ratio of drift velocity to the electric field magnitude.)

Expressed in units of cm\(^2\)/(V*s).

Mobilities of 10-100’s cm\(^2\)/Vs typical for most crystalline semiconductors. Can be orders of magnitude lower for organic, amorphous, and ionic materials.
Mathematical Formalism

Diffusion length is governed by “lifetime” and “mobility”

\[
L_{\text{diff}} = \sqrt{D \tau_{\text{bulk}}}
\]

- \(L_{\text{diff}}\) = bulk diffusion length
- \(D\) = diffusivity
- \(\tau_{\text{bulk}}\) = bulk lifetime

\[
D = \frac{k_B T}{q \mu}
\]

- \(k_B\) = Boltzmann coefficient
- \(T\) = temperature
- \(q\) = charge
- \(\mu\) = mobility

Definition of “bulk lifetime”: The average time an excited carrier exists before recombining. (i.e., temporal analogy to diffusion length.)

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- \(\tau_{\text{bulk}}\) of \(\mu s\) to ms is typical for indirect bandgap semiconductors, while \(\tau_{\text{bulk}}\) of ns to \(\mu s\) is typical of direct bandgap semiconductors.

Definition of “mobility”: How easily a carrier moves under an applied field. (i.e., ratio of drift velocity to the electric field magnitude.)

Expressed in units of \(\text{cm}^2/(\text{V} \cdot \text{s})\).

Mobilities of 10-100’s \(\text{cm}^2/\text{Vs}\) typical for most crystalline semiconductors. Can be orders of magnitude lower for organic, amorphous, and ionic materials.
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Excess Electron Carrier Concentration

\[ n = n_0 + \Delta n \]

\[ \Delta n = G \tau \]

**Excess Electron Carrier Density**
- \( n \) [carriers/cm\(^3\)]

**Generation rate**
- \( G \) [carriers/cm\(^3\) \cdot sec]

**Excited Carrier Lifetime**
- \( \tau \) [sec]

*Generally equal to doping concentration*
Minority, Majority Carriers in Silicon Under AM1.5G

\[ \Delta n = G \tau = 10^{11} \text{cm}^{-3} \]

\[ \Delta n = \Delta p = 10^{11} \text{cm}^{-3} \]

\[ n_i = 10^{10} \text{cm}^{-3} \]

\[ \Delta n = \Delta p > n_i \]

Excited Carrier Lifetime

\(~10\mu\text{s}\)

if :

\[ N_D = 10^{16} \text{cm}^{-3} \]

then :

\[ \Delta p \gg p_0 = \frac{n_i^2}{N_D} = 10^4 \text{cm}^{-3} \]

\[ N_D \gg \Delta n \]
Carrier Lifetime and Recombination

Bulk Minority Carrier Lifetime:

\[ \tau = \frac{\Delta n}{R} \]

\( \Delta n = \) Excess minority carrier concentration
\( R = \) Recombination rate

*First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.*

More Detailed Calculation:

\[ \frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{rad}}} \]

Radiative recombination, can be derived from thermodynamics: 
\([\varepsilon = \alpha]\)

p-type silicon

Minority Carrier

Majority Carrier
Carrier Lifetime and Recombination

**Bulk Minority Carrier Lifetime:**

\[ \tau = \frac{\Delta n}{R} \]

\( \Delta n = \) Excess minority carrier concentration

\( R = \) Recombination rate

First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

**More Detailed Calculation:**

\[ \frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Auger}}} \]

Dominant under very high injection conditions

\[ \tau_{\text{Auger}} = \frac{1}{CN_A^2} \]
Carrier Lifetime and Recombination

**Bulk Minority Carrier Lifetime:**

\[ \tau = \frac{\Delta n}{R} \]

- \( \Delta n \) = Excess minority carrier concentration
- \( R \) = Recombination rate

*First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.*

**More Detailed Calculation:**

\[ \frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}} \]

Defect level-mediated recombination

*p-type silicon*
Radiative Recombination

\[ R = G = Bnp = Bn_i^2 \]

\[ R = B \left( np - n_i^2 \right) \]

\[ n = n_0 + \Delta n \]
\[ p = p_0 + \Delta p \]

\[ \tau_{rad} = \frac{1}{B \left( N_A + \Delta n \right)} \]
\[ \tau_{rad} = \frac{1}{B \left( N_D + \Delta p \right)} \]

Under equilibrium dark conditions

Net Recombination non-equilibrium 
= \( R - G_{equilibrium} \)

n-type (where \( n_0=N_D \))

p-type (where \( p_0=N_A \))
Radiative recombination is very slow in silicon, and is rarely the limiting lifetime in silicon-based solar cells. However, radiative recombination is often the lifetime-limiting recombination pathway for high-quality “thin-film” materials, including GaAs.

\[
\tau_{rad, Si} = \frac{1}{\left(2 \times 10^{-15}\right)\left(10^{16}\right)} = 100\text{ms}
\]
Defects and Carrier Recombination: $\tau_{SRH}$

Defects can form in semiconductors. Defect formation energy ($\Delta E_A$) determines equilibrium concentration at a given temperature.

Defects can introduce midgap stages. Midgap states are characterized by their energy level(s) ($E_D$) and capture cross sections for electrons and holes ($\sigma_e$, $\sigma_h$)


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Defects and Carrier Recombination: $\tau_{SRH}$

\[ \tau_{SRH} = \frac{\tau_{n0}(n_0 + p_1 + \Delta n) + \tau_{p0}(p_0 + n_1 + \Delta n)}{n_0 + p_0 + \Delta n} \]

\[ n_1 = N_c = e^{\left(\frac{E_T - E_c}{kT}\right)} \]

\[ p_1 = N_v = e^{\left(\frac{E_v - E_T}{kT}\right)} \]

\[ \tau_{p0} = \frac{1}{N_{vth}\sigma_p} \]

\[ \tau_{n0} = \frac{1}{N_{vth}\sigma_n} \]

\[ N = \text{trap density} \]

\[ \sigma = \text{capture cross-section} \]
Defects and Carrier Recombination: $\tau_{SRH}$

With deep traps (i.e. mid-gap) and low-injection conditions:

$$\tau_{SRH, \ n-type} = \tau_p = \frac{1}{N_{vth}\sigma_p}$$

$$\tau_{SRH, \ p-type} = \tau_n = \frac{1}{N_{vth}\sigma_n}$$

Deep traps and high-injection conditions:

$$\tau_{SRH} = \tau_n + \tau_p$$
Localized Defects Create Efficient Recombination Pathway

Direct Bandgap Semiconductor

Indirect Bandgap Semiconductor

Recombination efficient (no phonon required) \( \tau \sim \text{ns to \( \mu \text{s} \)} \)

Recombination inefficient (phonon required) \( \tau \sim \text{ms} \)

Image by MIT OpenCourseWare.
Localized Defects Create Efficient Recombination Pathway

Recombination efficient (no phonon required) $\tau \sim \text{ns to } \mu\text{s}$

Efficient recombination via defect level! $\tau < \mu\text{s}$ with high defect concentrations

Image by MIT OpenCourseWare.
Defects Impact Minority Carrier Lifetime

Impurity Point Defects (c-Si)

Dislocations (c-Si)

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Effect of Defects on Minority Carrier $\tau$, $L_{\text{diff}}$

The distribution of defects matters as much as their total concentration!


Surfaces Introduce Many Mid-Gap States

Mid-gap surface states provide additional pathway for recombination. They are often formed by dangling bonds on the surface.

\[
\tau_{surf} \approx \frac{W}{2S} + \frac{1}{D} \left( \frac{W}{\pi} \right)^2
\]

Sample thickness

Surface recombination velocity

Carrier diffusivity

Proper Passivation Reduces Surface Recombination

Proper surface passivation ties up dangling bonds, reduces density of trap states.

“Perfect” passivation yields:

\[ S \rightarrow 0, \quad \tau_{surf} \rightarrow \infty \]

Practically, \( S \) approaching 1 cm/s have been achieved on silicon.
Measuring Surface Recombination Velocity

1. Measure lifetime of samples of varying thickness, but with same bulk and surface properties. (The lifetime will be affected by both bulk and surface conditions, thus measurement will reveal an “effective” lifetime, or \( \tau_{\text{eff}} \).)

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

2. Any variation in lifetime should be due to a changing \( \tau_{\text{surf}} \), per below:

\[
\tau_{\text{surf}} \approx \frac{W}{2S} + \frac{1}{D} \left( \frac{W}{\pi} \right)^2
\]


3. With >2 lifetime measurements (sample thicknesses), can solve for \( \tau_{\text{surf}} \)!
Auger Recombination, $\tau_{\text{Auger}}$

\[ R_{n\text{-type}} \sim pn^2 \]

\[ \tau_{n\text{-type}} \approx \frac{1}{Cn^2} \]

\[ R_{p\text{-type}} \sim np^2 \]

\[ \tau_{p\text{-type}} \approx \frac{1}{Cp^2} \]

*Above equations true at sufficiently high doping densities ($\geq 10^{18}\text{cm}^{-3}$ in silicon)
Auger Recombination in $n$-type silicon

\[ R_{n\text{-type}} \sim pn^2 \]

\[ \tau_{n\text{-type}} \approx \frac{1}{Cn^2} \]

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Auger Recombination in $n$-type silicon

\[ \frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{band}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}} \]

Courtesy of Daniel Macdonald. Used with permission.

Daniel MacDonald thesis “Recombination and Trapping in Multicrystalline Silicon Solar Cells,” The Australian National University (May 2011)
Recall that

\[
\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}}
\]

If defect-mitigated recombination is dominant, band-to-band radiative recombination will be suppressed:

\[
\frac{1}{\tau_{\text{rad}}} \gg \frac{1}{\tau_{\text{SRH}}}
\]

or

\[
\tau_{\text{rad}} \ll \tau_{\text{SRH}}
\]

In fact, band-to-band (radiative recombination) and defect-mitigated (non-radiative recombination) are inversely proportional.

By imaging the band-to-band (radiative) recombination using a very sensitive CCD camera, we are able to quantitatively extract the minority carrier lifetime.
Photoluminescence Imaging (PLI)

Experimental Setup

Measurement of Wafer


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Temperature Changes $\sigma_0$

Trapped carriers are more likely to be (re-)emitted at higher thermal energies ($k_bT$). At lower T, trapped carriers reside in traps longer, facilitating recombination.


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Effect of Reduced Mobility on Solar Cell Performance

Low carrier mobility can reduce device efficiency by several tens of percent relative (as big of an impact as lifetime!)

\[ L_{\text{diff}} = \sqrt{D\tau_{\text{bulk}}} \]

\[ D = \frac{k_B T}{q} \mu \]

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What Limits Mobility?

1. Defect Scattering
2. Trapping at stretched bonds
3. Incomplete percolation pathways
4. Phonon Scattering

Example of carrier trapping
L. Wagner et al., *PRL* 101, 265501 (2008)

Example of complex percolation pathway

Diagrams removed due to copyright restrictions.
See lecture video.
Increased concentration of ionized dopant atoms increases conductivity, but can reduce carrier mobility (due to scattering).
Percolation Pathways

Both $\mu$ and $\tau$ play a role in determining $L_{\text{diff}}$, and hence efficiency, for various device architectures.

Table removed due to copyright restrictions. See lecture video.

F. Yang et al., ACS Nano 2, 1022 (2008)
Simple Example

1. Well-behaved inorganic semiconductor (no effect of trapping at stretched bonds and incomplete percolation pathways).
2. Defect scattering dominant $\rightarrow$ ionized dopants inside sample scatter carriers.
Demo: Conductivity of Heated Intrinsic and Doped Silicon

![Diagram showing a circuit with a heat source and a resistor labeled 'silicon'.]
Demo Explained

\[ n = n_0 + \Delta n \approx N_D + \Delta n \]

For intrinsic Si, \( \Delta n \gg N_D \).
For highly doped Si, \( \Delta n \ll N_D \).

\[ \sigma = \frac{1}{\rho} = q \mu n \]

Conductivity is the product of \( \mu \) and \( n \).