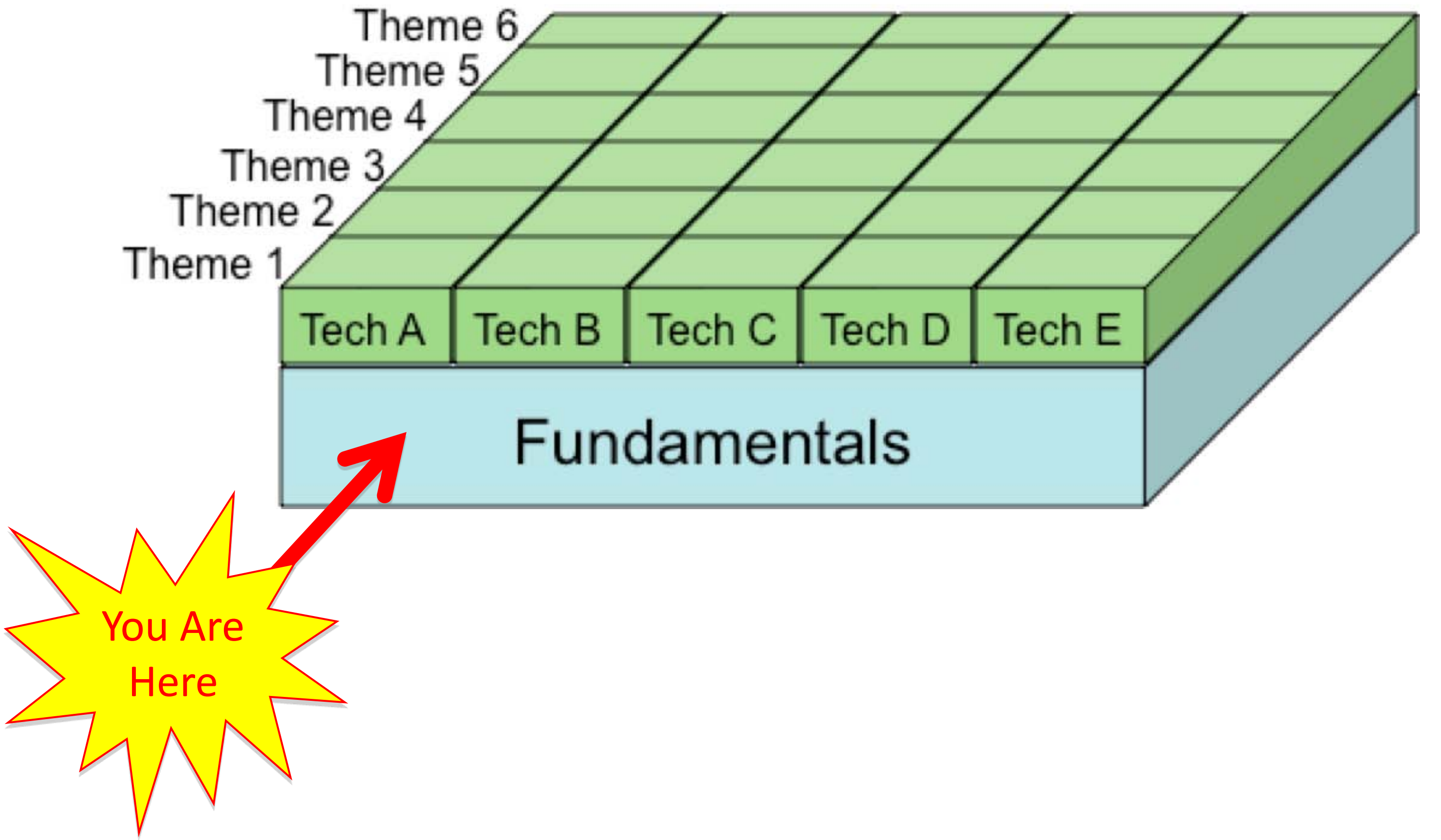
Toward a 1D Device Model Part 2: Material Fundamentals

Lecture 8 – 10/4/2011

MIT Fundamentals of Photovoltaics 2.626/2.627 – Fall 2011

Prof. Tonio Buonassisi

2.626/2.627 Roadmap



2.626/2.627: Fundamentals

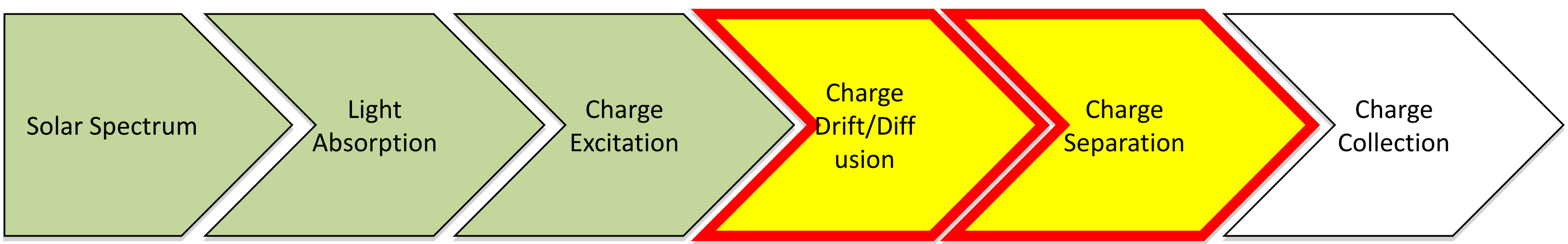
Every photovoltaic device must obey:

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

For most solar cells, this breaks down into:

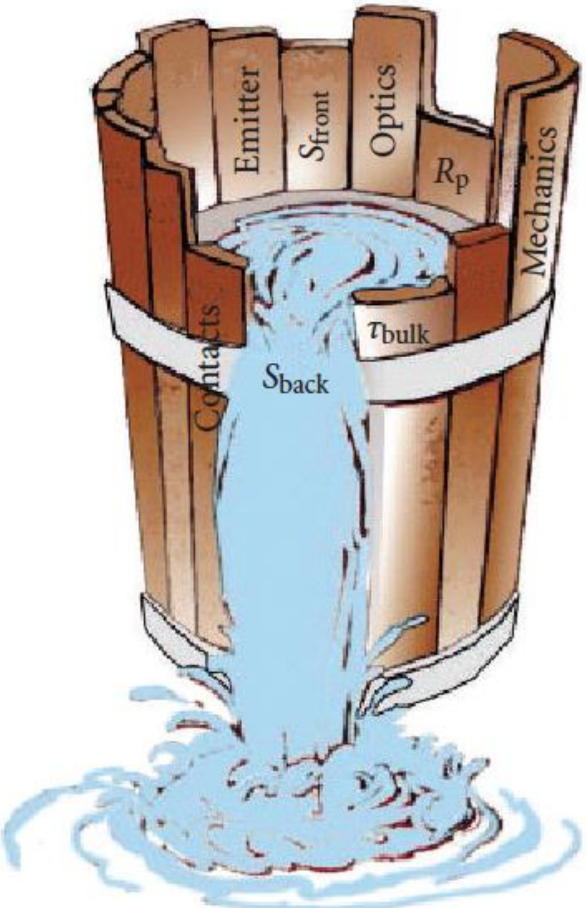
Inputs

Outputs



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

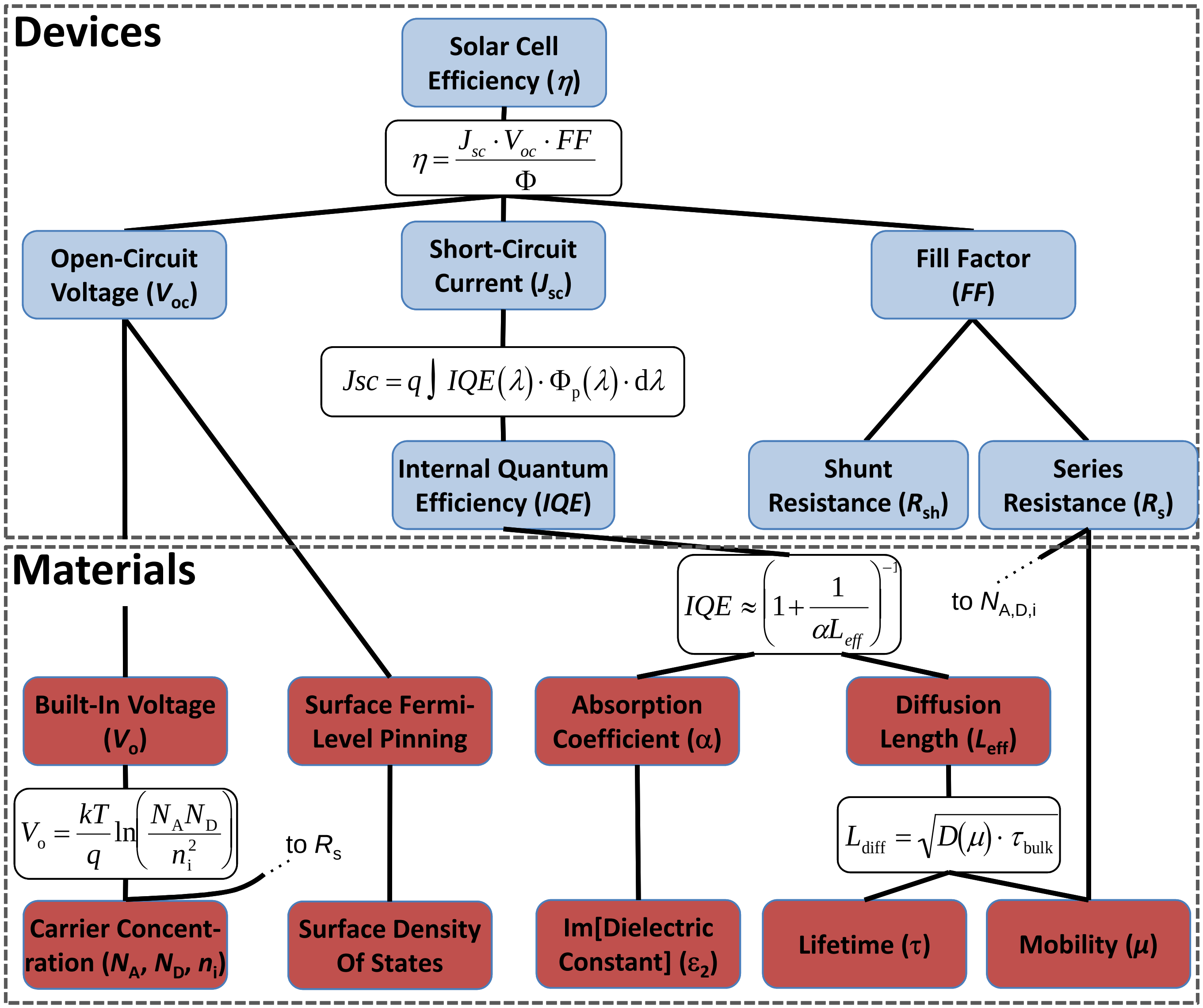
Liebig's Law of the Minimum



S. Glunz, *Advances in Optoelectronics* 97370 (2007)

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

Rough Depiction of Interrelated Materials & Device Effects



Source: T. Buonassisi, unpublished.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 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.

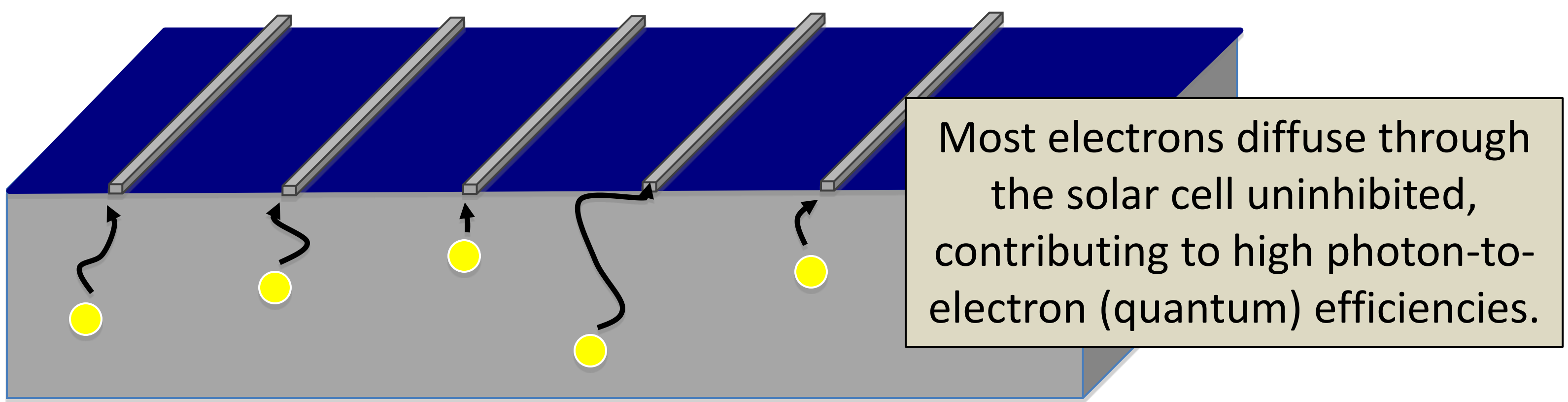
Importance to a Solar Cell: Photoexcited carriers must be able to move from their point of generation to where they can be collected. Longer diffusion lengths generally result in better performance.

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 <u>high-quality</u> material
Minority carrier diffusion length (L_{diff}) is LARGE.
Solar cell current output (J_{sc}) is large.

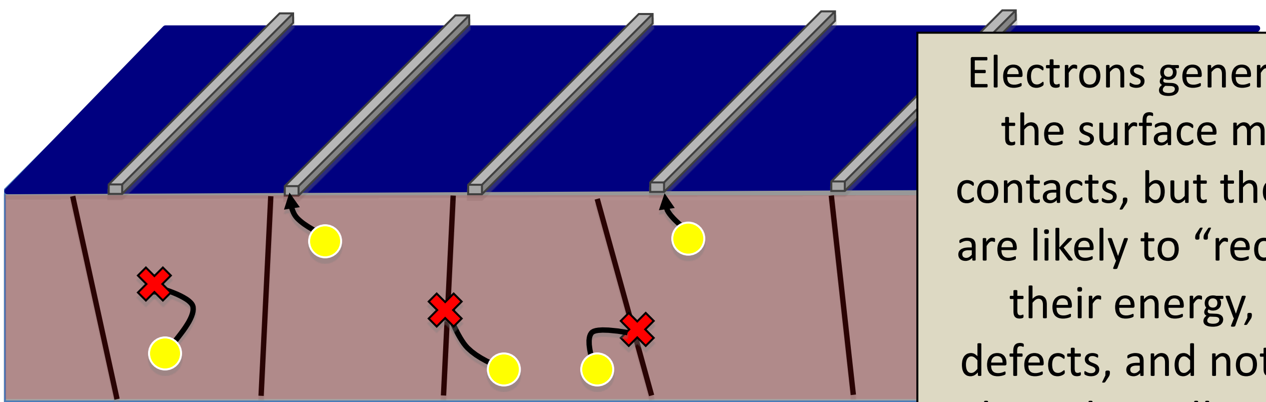


Minority Carrier Diffusion Length

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 <u>defect-ridden</u> material
Minority carrier diffusion length (L_{diff}) is small.
Solar cell current output (J_{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 illumianted pn-junction device, is limited by the minority carrier flux at the edge of the space-charge region.

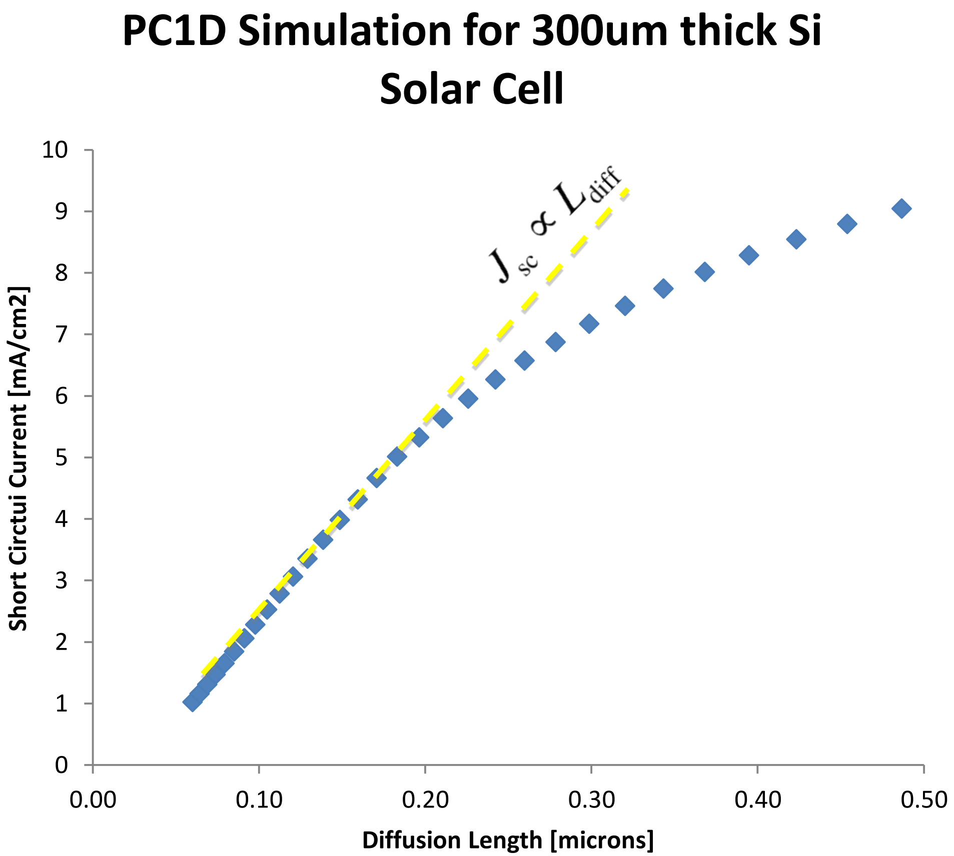
$$J_{sc} \approx qGL_{diff}$$

$$J_{sc} \propto L_{diff}$$

From Eq. 4.44 in Green.

J_{sc} = illuminated current = J_L

G = carrier generation rate



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Mathematical Formalism

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

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

From Eq. 4.45 in Green.
V_{oc} = open-circuit voltage
J_o = saturation current density

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

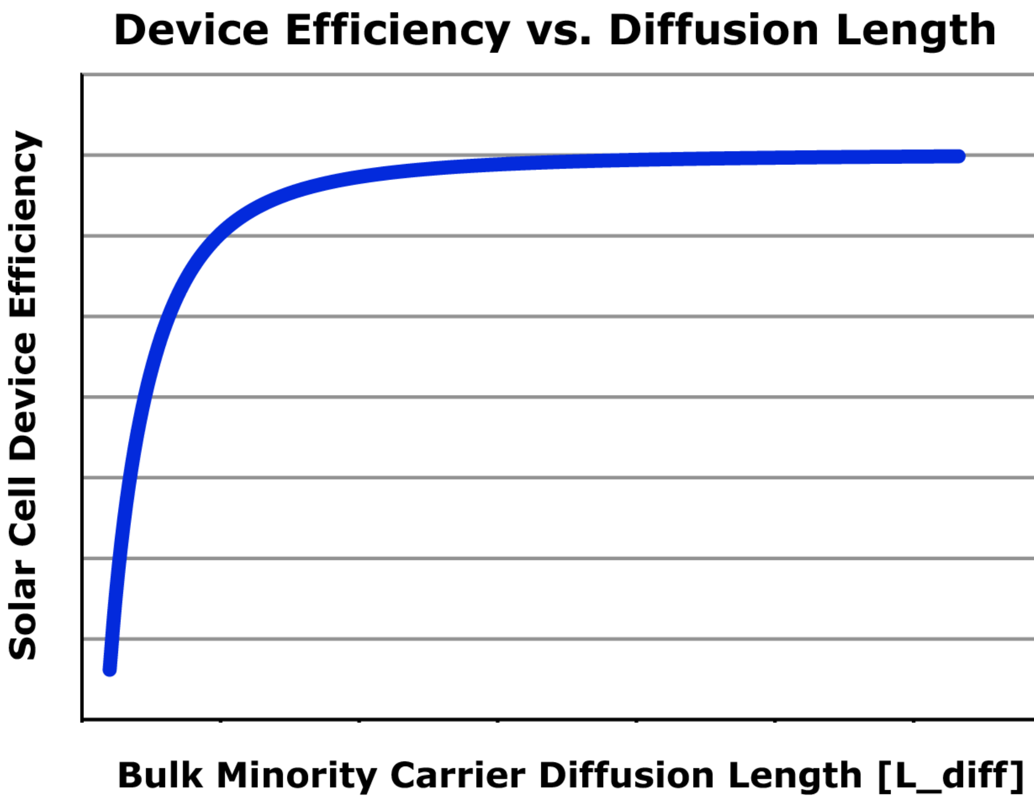
From Eq. 4.37 in Green.
D = minority carrier diffusivity
N = majority carrier dopant concentration
n_i = intrinsic carrier concentration

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

Mathematical Formalism

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

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



Mathematical Formalism

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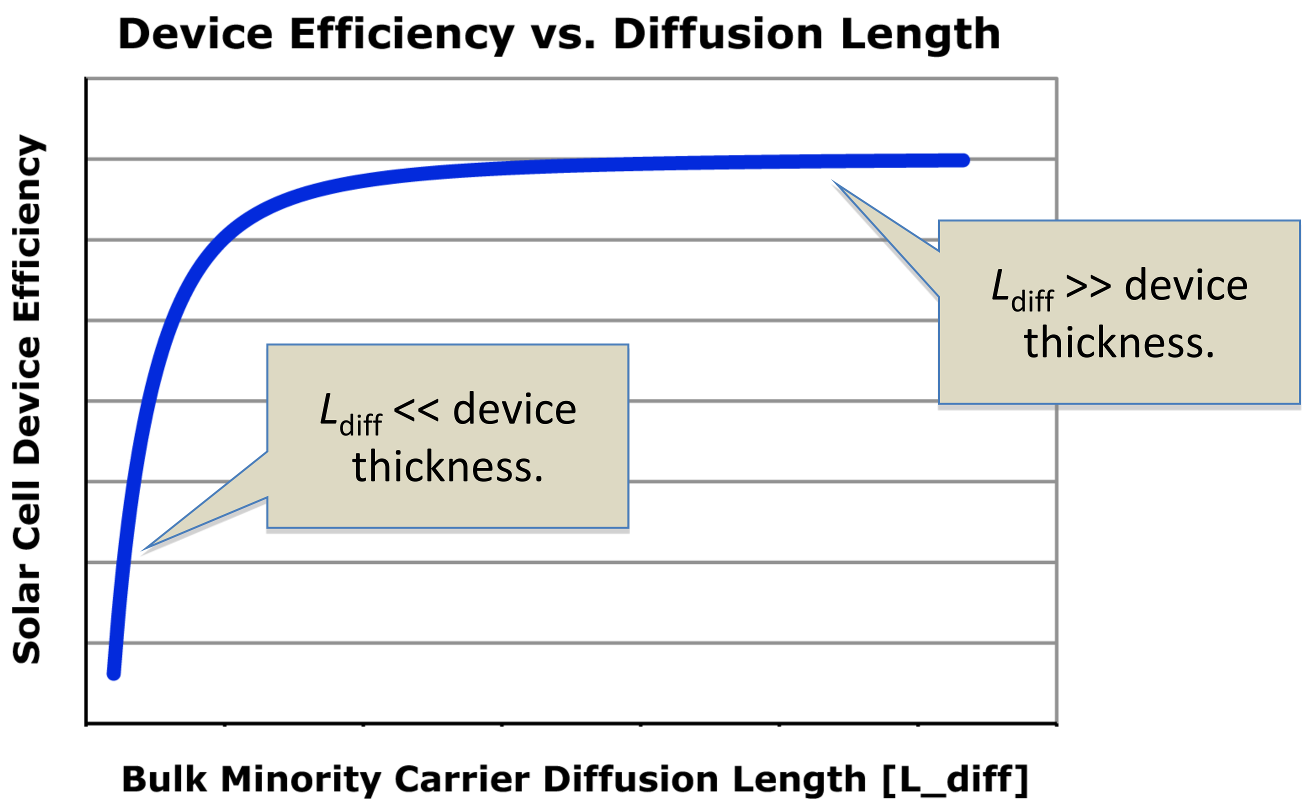
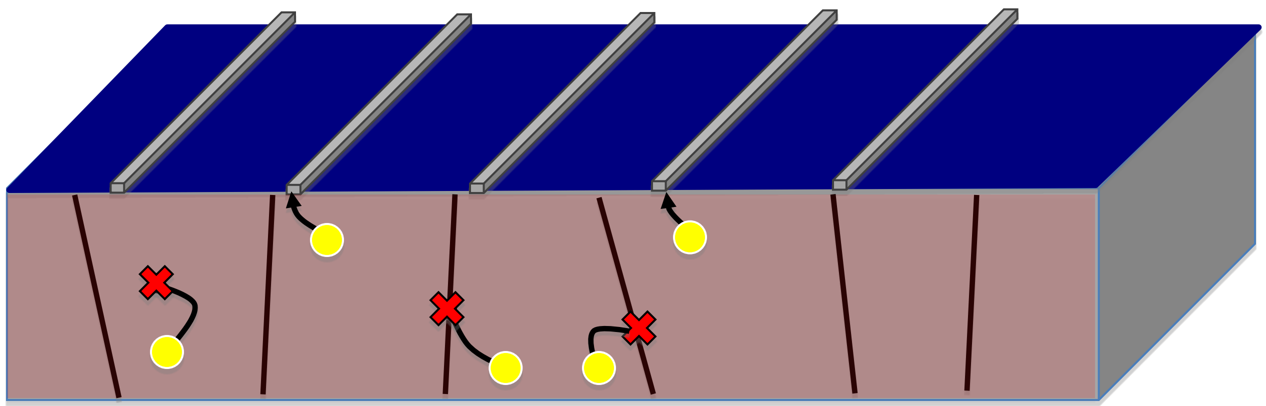


Minority Carrier Diffusion Length

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.



Learning Objectives: Toward a 1D Device Model

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   - Describe basic recombination mechanisms in semiconductor materials.
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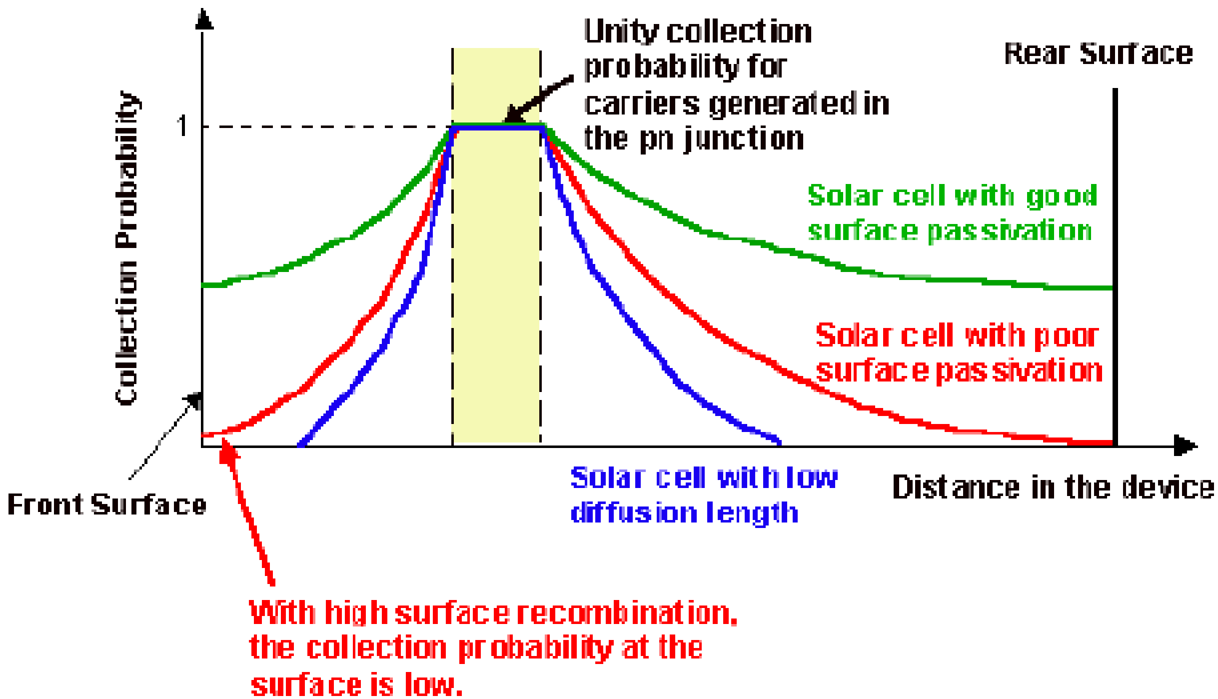
4. Mobility:
   - Describe common mobility-limiting mechanisms (dopants, temperature, ionic semiconductors).

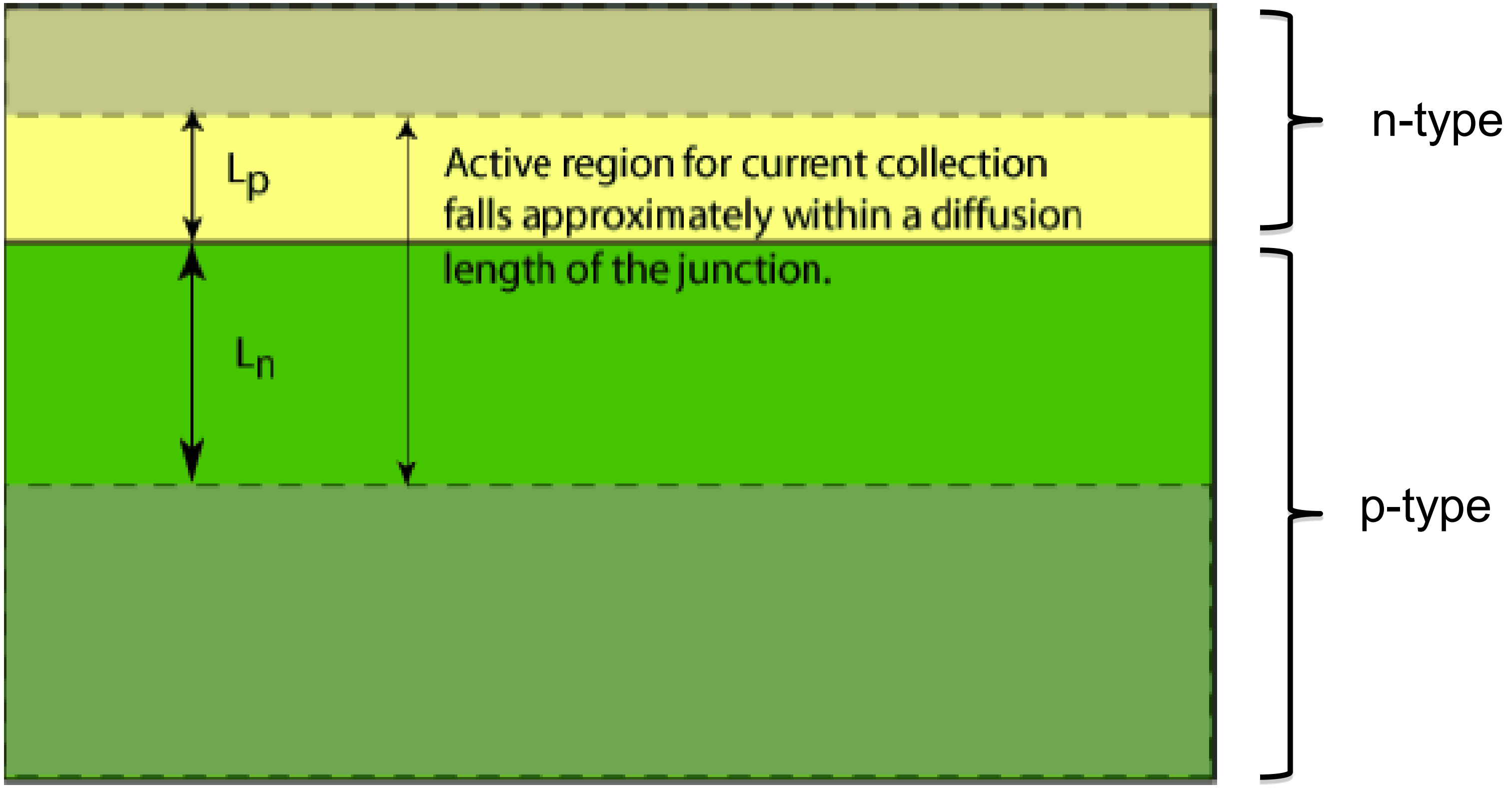
Collection Probability

- 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.



Courtesy of Christiana Honsberg. Used with permission.

Collection Probability



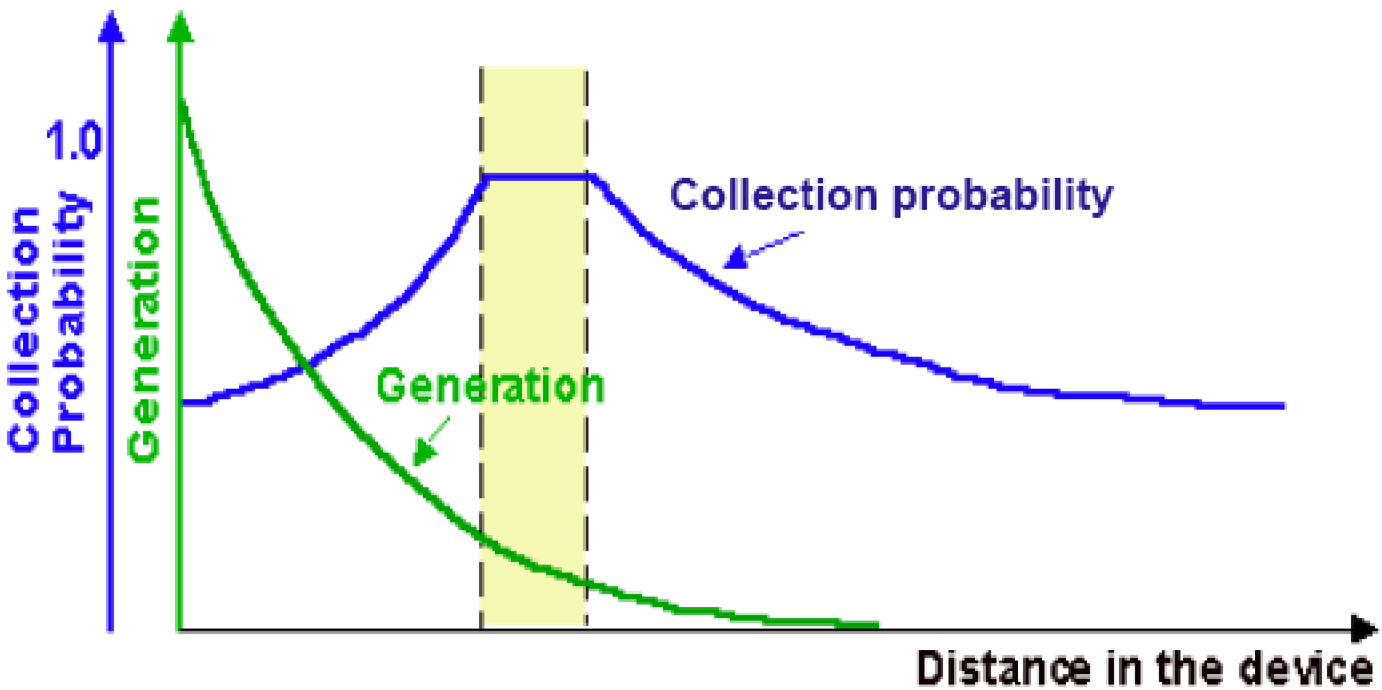
Collection probability is low further than a diffusion length away from junction

From PV CDROM

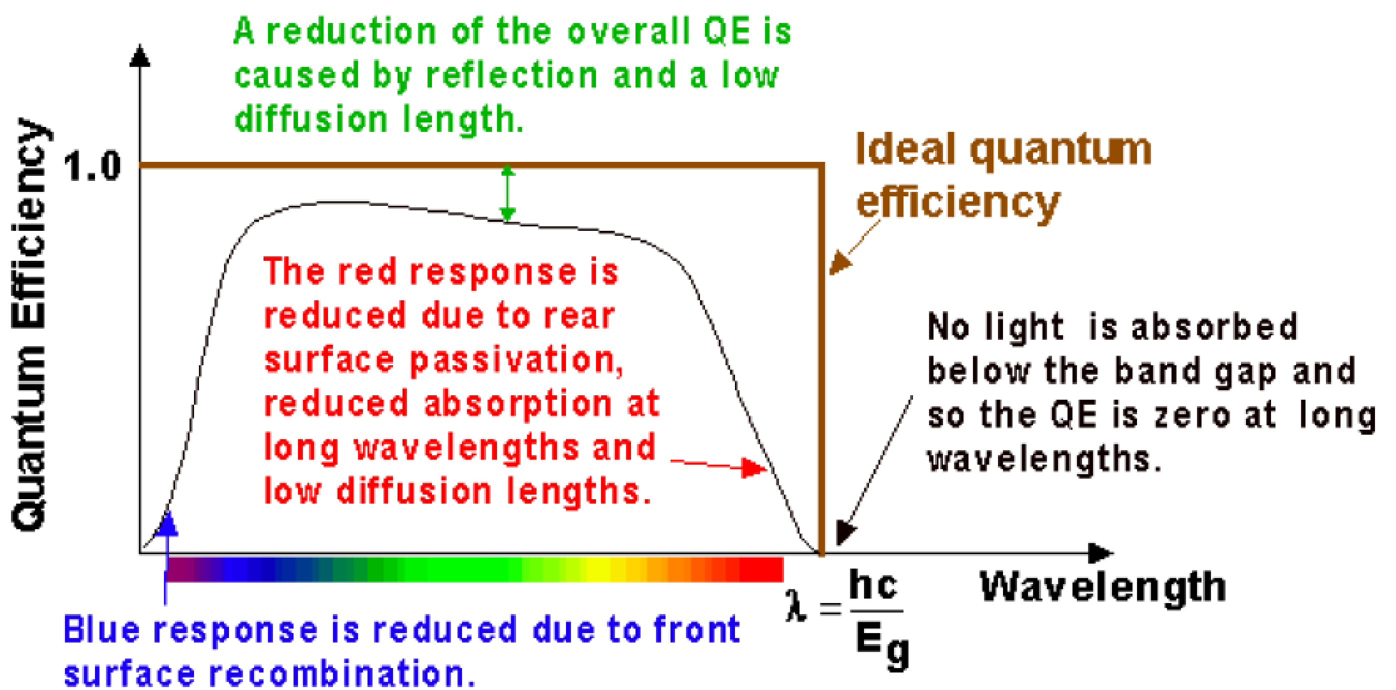
Collection Probability

J_{sc} determined by generation rate and collection probability

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



Spectral Response (Quantum Efficiency)



Courtesy of PVCDROM. Used with permission.

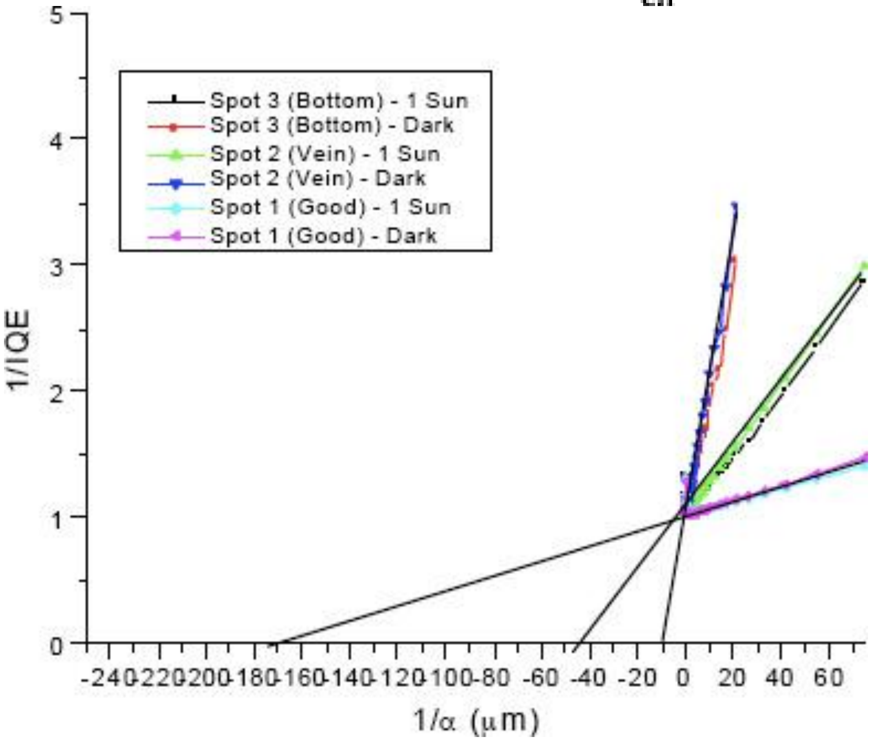
Standards: IEC 60904-3 and 60904-8

from PVCDROM

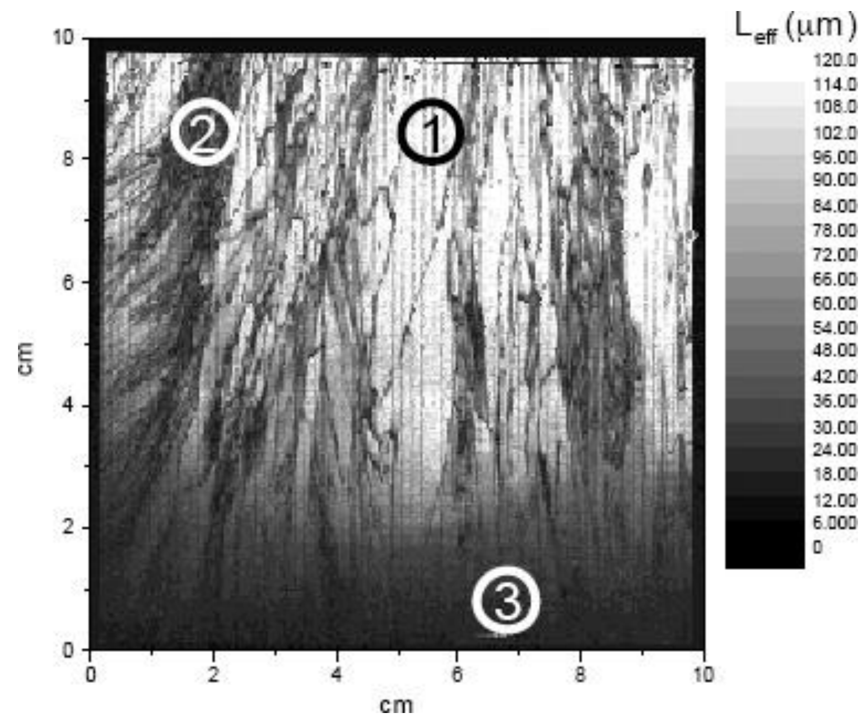
Minority Carrier Diffusion Length

At each point…

$$\mathrm{IQE}^{-1} = 1 + \alpha^{-1}\frac{\cos\,\theta}{L_{\mathrm{eff}}}$$



Mapped over an entire sample…



See: P. A. Basore, *IEEE Trans. Electron. Dev*. **37**, 337 (1990).

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 <u>bulk defects</u> (GBs) on η.

Nanostructured: Effect of <u>morphology</u> on η.

Please see lecture video for visuals.

R.B. Bergmann, *Appl. Phys. A* **69**, 187 (1999)

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

Mathematical Formalism

Diffusion length is governed by "lifetime" and "mobility"

$$L_{\mathrm{diff}} = \sqrt{D\tau_{\mathrm{bulk}}}$$

$$D = \frac{k_B T}{q}\mu$$

L_{diff} = bulk diffusion length
D = diffusivity
τ_{bulk} = bulk lifetime

For carriers in an electric field
k_B = Boltzmann coefficient
T = temperature
q = charge
μ = mobility

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

Units = time.

τ_{bulk} of µs to ms is typical for indirect bandgap semiconductors, while τ_{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"

$$L_{\text{diff}} = \sqrt{D\tau_{\text{bulk}}}$$

$$D = \frac{k_B T}{q}\mu$$

Carrier Lifetime

Carrier Mobility

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D = diffusivity
τ_{bulk} = bulk lifetime

ers in an electric field

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Excess Electron Carrier Concentration

Generally equal to doping concentration

$$n = n_0 + \Delta n$$

$$\Delta n = G\tau$$

Excess Electron Carrier Density

$$\left[\frac{carriers}{cm^3}\right]$$

Generation rate

$$\left[\frac{carriers}{cm^3 \cdot \sec}\right]$$

Excited Carrier Lifetime

[sec]

Minority, Majority Carriers in Silicon Under AM1.5G

$$\Delta n = G\tau = 10^{11} cm^{-3}$$

AM1.5G ~ 10^{16}

$$\left[\frac{carriers}{cm^3 \cdot \sec}\right]$$

Excited Carrier Lifetime

~10µs

$$\Delta n = \Delta p = 10^{11} cm^{-3}$$

$$n_i = 10^{10} cm^{-3}$$

$$\Delta n = \Delta p > n_i$$

$if:$

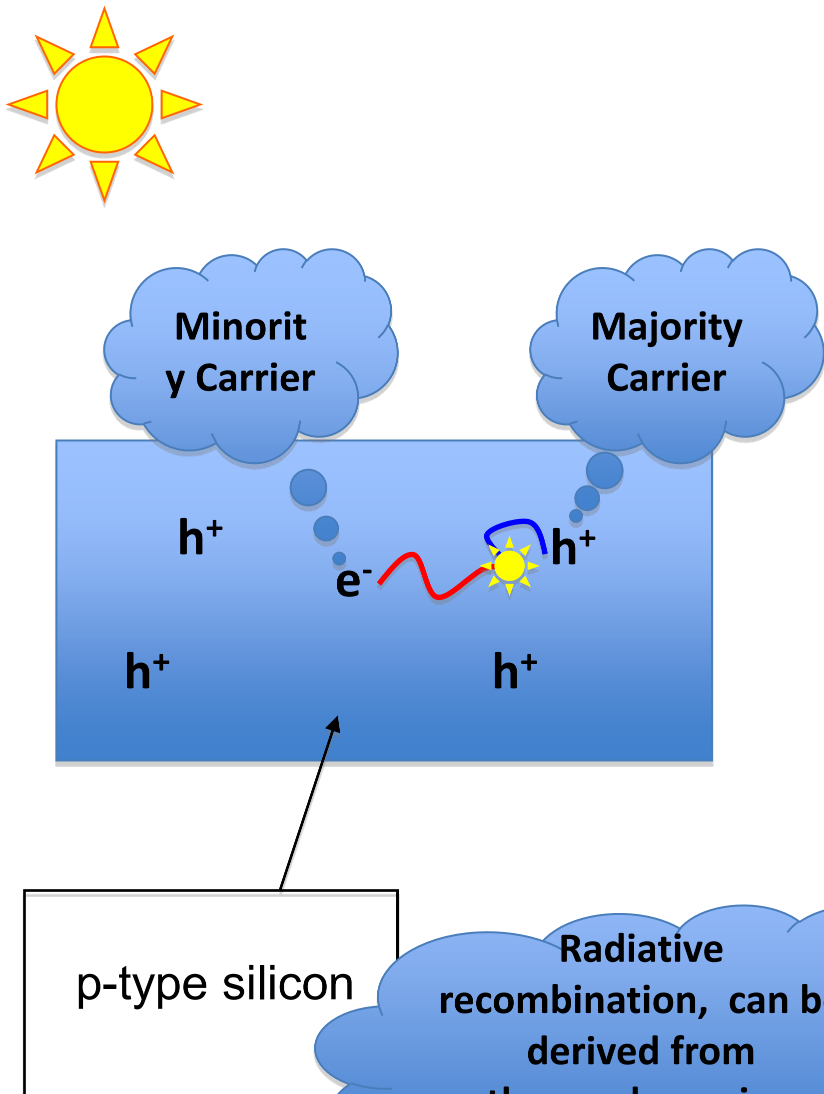
$$N_D = 10^{16} cm^{-3}$$

$then:$

$$\Delta p >> p_0 = \frac{n_i^2}{N_D} = 10^4 cm^{-3}$$

$$N_D >> \Delta n$$

Carrier Lifetime and Recombination



Bulk Minority Carrier Lifetime:

$$\tau = \frac{\Delta n}{R}$$

Δn = Excess minority carrier concentration

R = Recombination rate

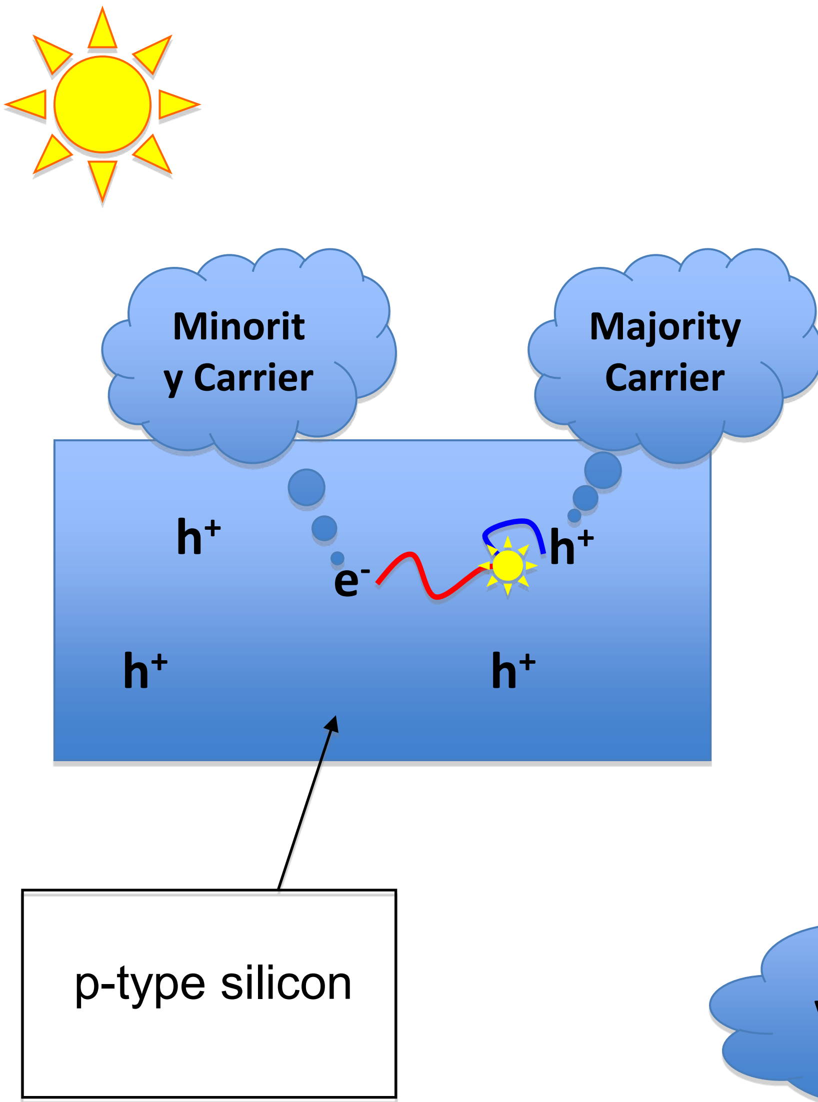
First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

More Detailed Calculation:

$$\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{rad}}}$$

Radiative recombination, can be derived from thermodynamics: [ε=α]

Carrier Lifetime and Recombination



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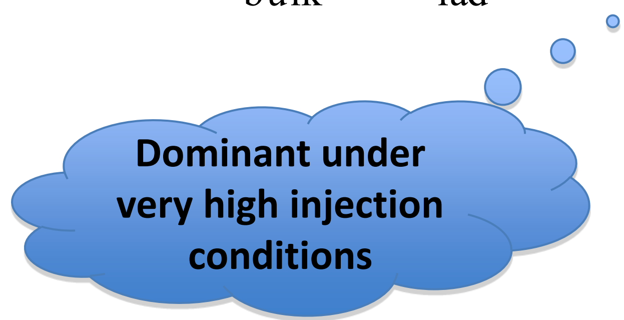
First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

More Detailed Calculation:

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



$$\tau_{\text{Auger}} = \frac{1}{CN_A^2}$$

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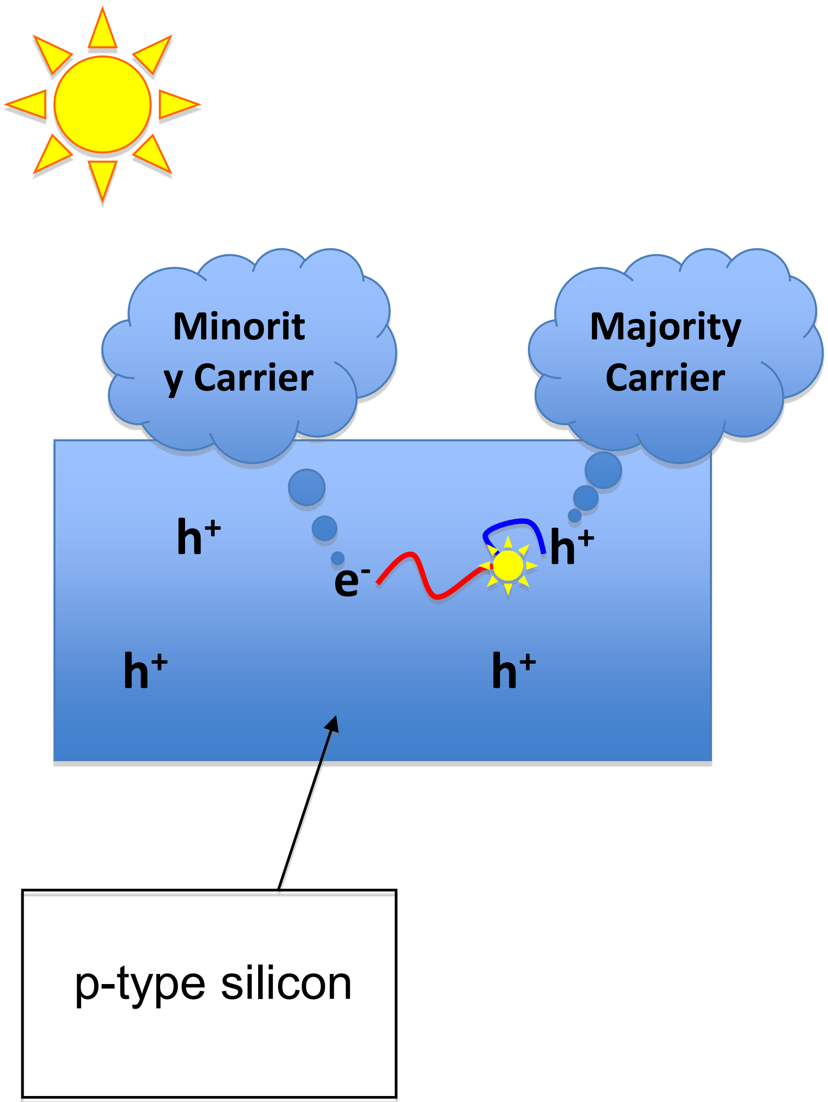
Carrier Lifetime and Recombination



Bulk Minority Carrier Lifetime:

$$\tau = \frac{\Delta n}{R}$$

Δn = Excess minority carrier concentration

R = Recombination rate

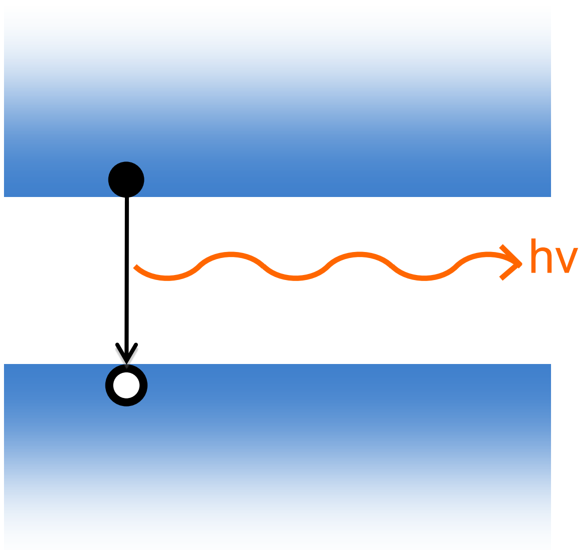
First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

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

Radiative Recombination



$$R = G = Bnp = Bn_i^2$$

Under equilibrium dark conditions

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

Net Recombination non-equilibrium $= R\text{-}G_{equilibrium}$

$$n = n_0 + \Delta n$$

$$p = p_0 + \Delta p$$

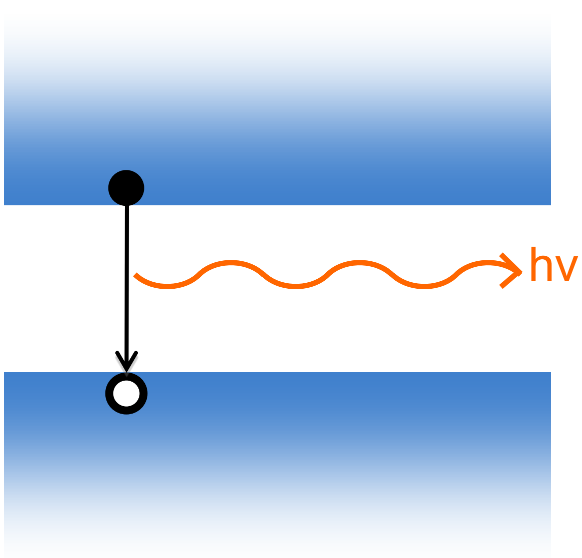
$$\tau_{rad} = \frac{1}{B\left(N_A + \Delta n\right)}$$

n-type (where $n_0 = N_D$)

$$\tau_{rad} = \frac{1}{B\left(N_D + \Delta p\right)}$$

p-type (where $p_0 = N_A$)

Radiative Recombination



$$\tau_{rad,\ Si} = \frac{1}{\underbrace{(2 \times 10^{-15})}_{B}\underbrace{(10^{16})}_{n}} = 100ms$$

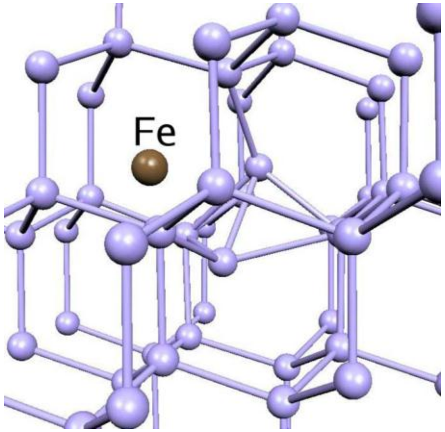
Radiative recombination is very slow in silicon, and is rarely the limiting lifetime in silicon-based solar cells. *However, radiative recombination is often the lifetime-limiting recombination pathway for high-quality "thin-film" materials, including GaAs.*

Defects and Carrier Recombination: τ_{SRH}

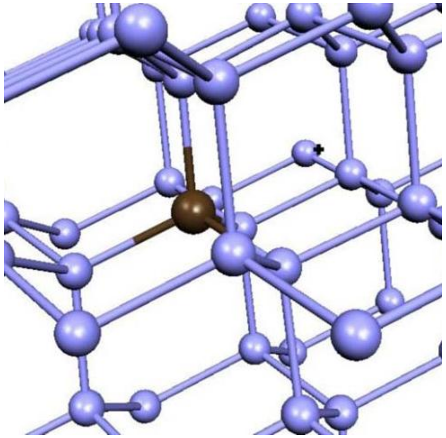
Defects can form in semiconductors.

Defect formation energy (ΔE_A) determines equilibrium concentration at a given temperature.

Interstitial Iron (Fe_i)



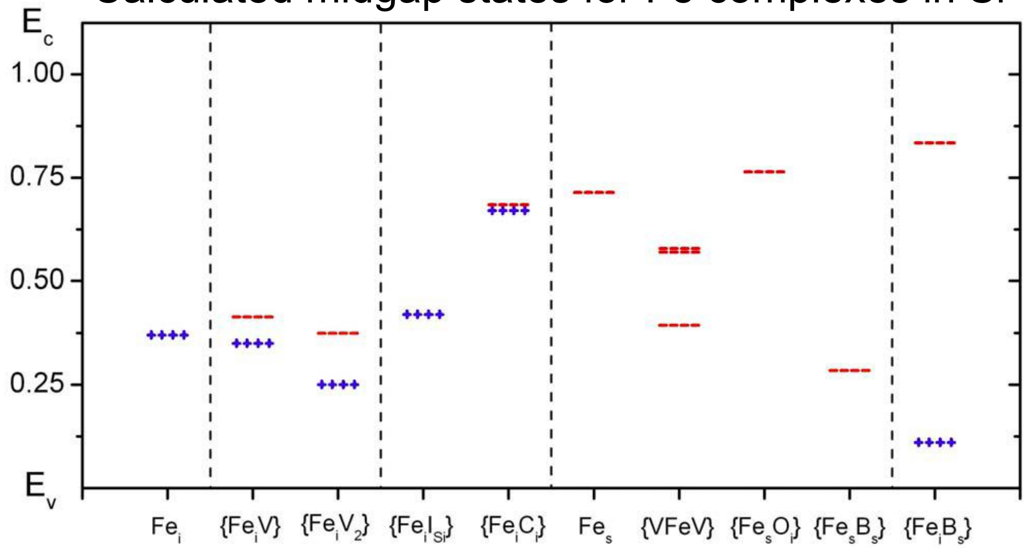
Substitutional Iron (Fe_s)



Defects can introduce midgap stages.

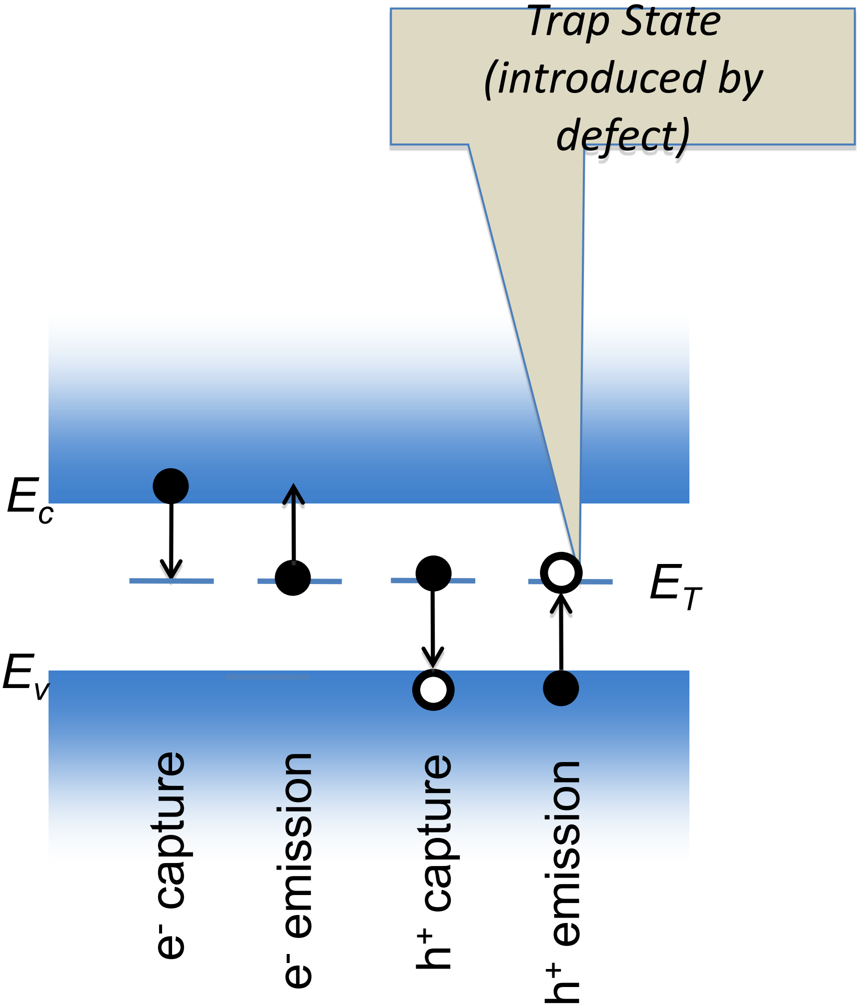
Midgap states are characterized by their energy level(s) (E_D) and capture cross sections for electrons and holes (σ_e, σ_h)

Calculated midgap states for Fe complexes in Si



S.K. Estreicher *et al.*, *Phys. Rev. B* **77**, 125214 (2008).

Defects and Carrier Recombination: τ_{SRH}



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

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

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

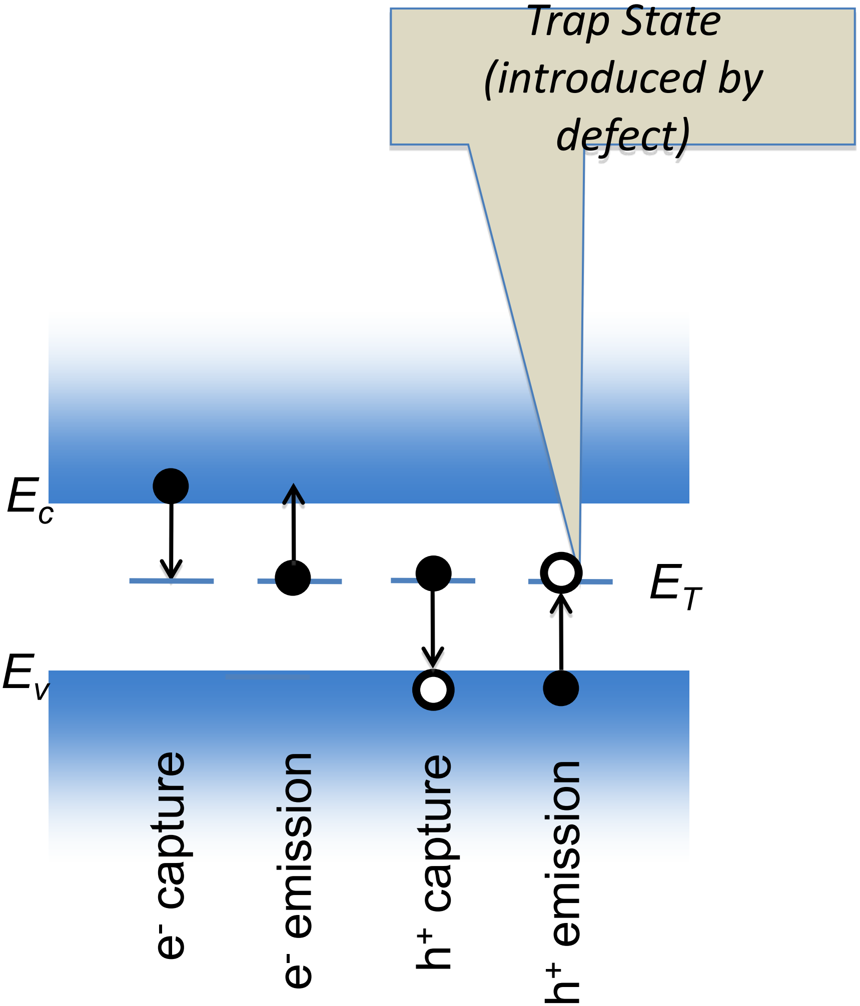
$$\tau_{p0} = \frac{1}{N v_{th} \sigma_p}$$

$$\tau_{n0} = \frac{1}{N v_{th} \sigma_n}$$

$N = trap\ density$

$\sigma =$ ***capture cross-section***

Defects and Carrier Recombination: τ_{SRH}



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

$$\tau_{SRH,\ n-type} = \tau_{p0} = \frac{1}{N v_{th} \sigma_p}$$

$$\tau_{SRH,\ p-type} = \tau_{n0} = \frac{1}{N v_{th} \sigma_n}$$

Deep traps and high-injection conditions:

$$\tau_{SRH} = \tau_{n0} + \tau_{p0}$$

Localized Defects Create Efficient Recombination Pathway

Direct Bandgap Semiconductor

Indirect Bandgap Semiconductor

Recombination efficient
(no phonon required)
τ ~ ns to μs

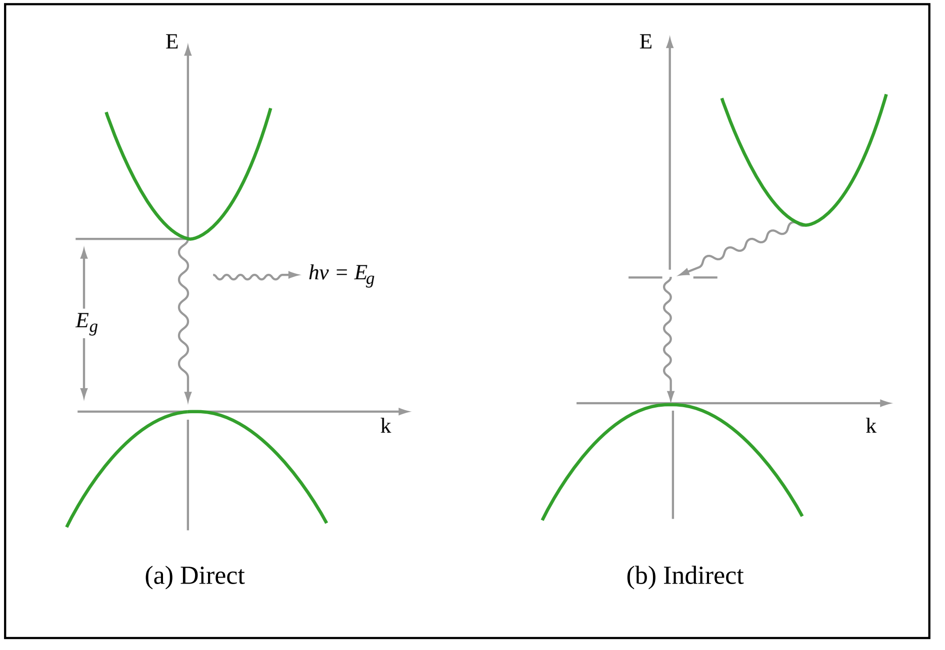


Image by MIT OpenCourseWare.

Recombination inefficient
(phonon required)
τ ~ ms

Localized Defects Create Efficient Recombination Pathway

Direct Bandgap Semiconductor

Indirect Bandgap Semiconductor

Recombination efficient
(no phonon required)
τ ~ ns to μs

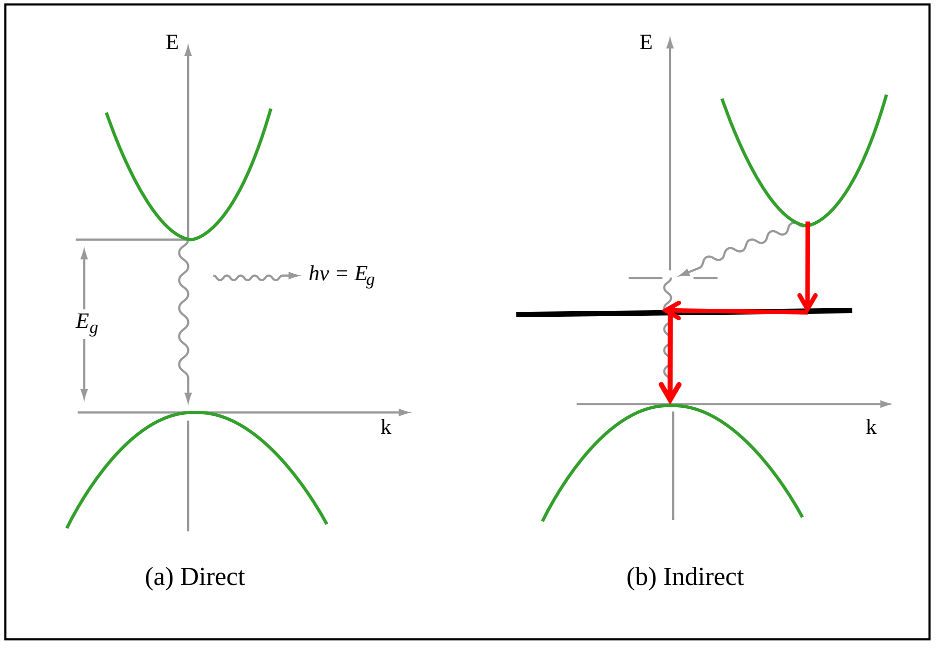
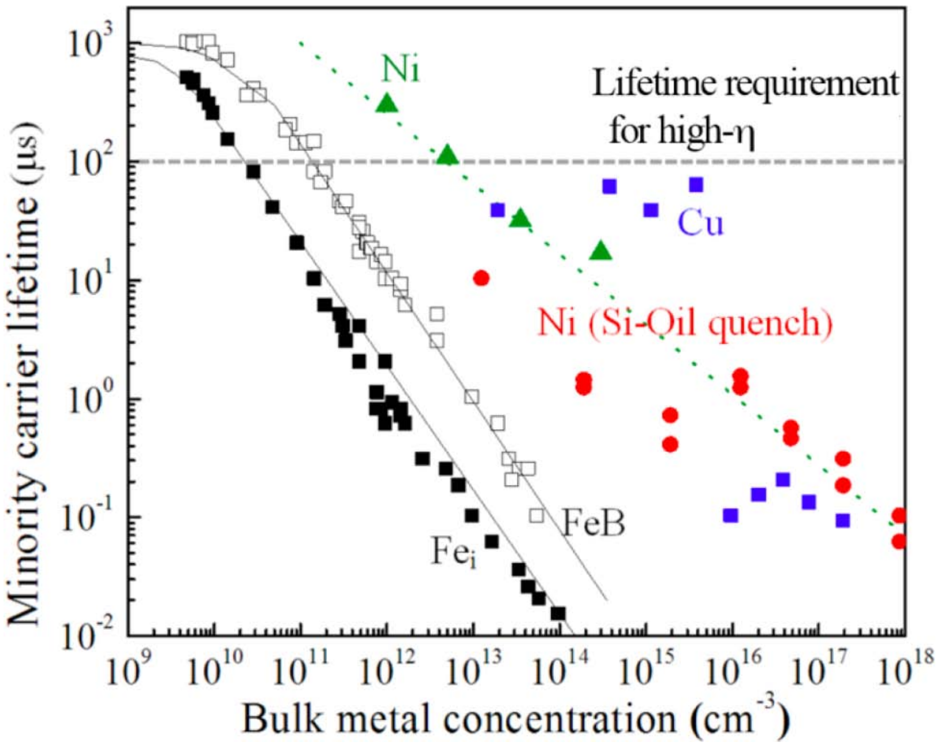


Image by MIT OpenCourseWare.

Efficient recombination via defect level!
τ < μs with high defect concentrations

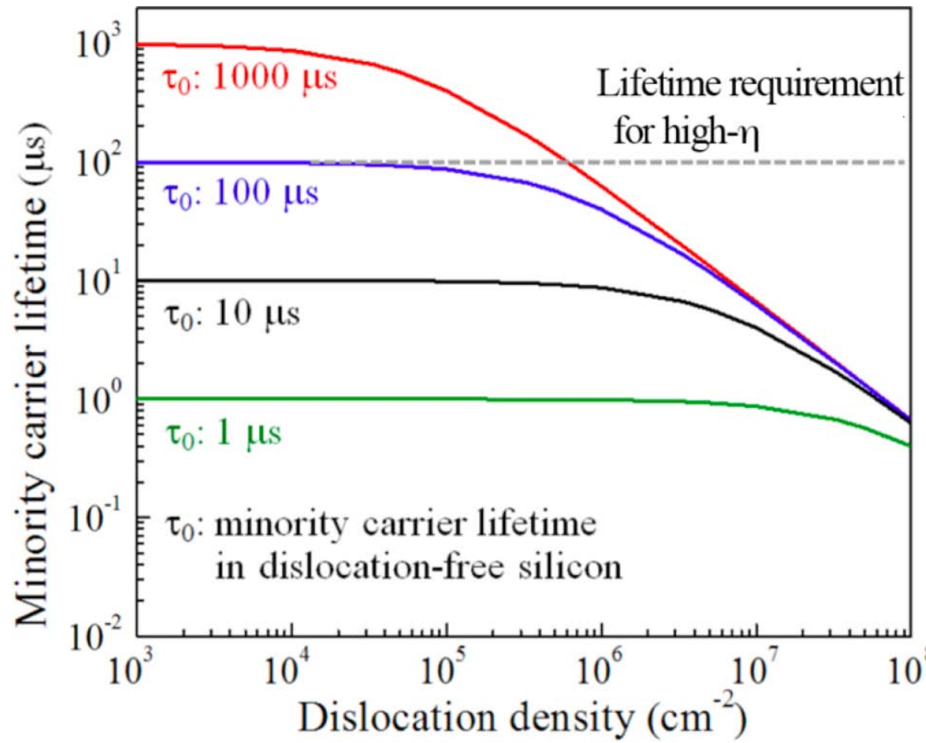
Defects Impact Minority Carrier Lifetime

Impurity Point Defects (c-Si)



Courtesy of Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

Dislocations (c-Si)



A.A. Istratov, *Materials Science & Engineering B*, **134**, 282 (2006)
C. Donolato, *Journal of Applied Physics* **84**, 2656 (1998)

Effect of Defects on Minority Carrier τ, L_{diff}

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

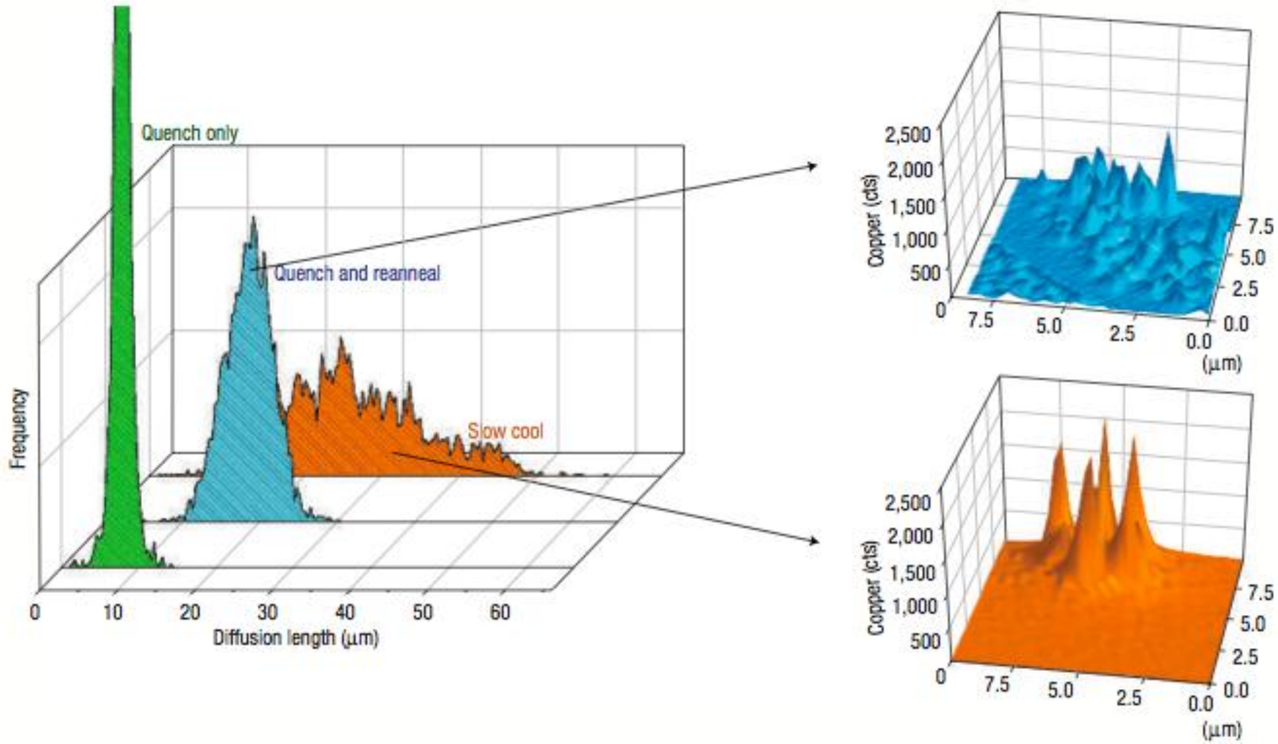


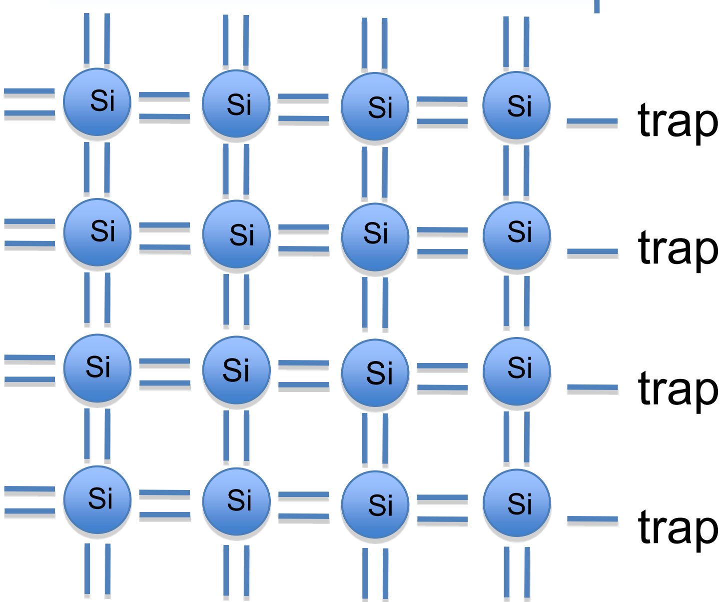
Figure 3 Effect of the distribution of metal defects on material performance. Material performance (minority-carrier diffusion length histograms, left) in three differently cooled samples (quench, quench and re-anneal, slow cool) is compared with size and spatial distributions of metal defects (high-resolution μ-XRF maps (right), XRF copper counts per second plotted against *x* and *y* coordinates in μm). The material with microdefects in lower spatial densities clearly outperforms materials with smaller nanodefects in higher spatial densities, despite the fact that all materials contain the same total amount of metals.

T. Buonassisi *et al.*, *Nature Mater.* **4**, 676 (2005)

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

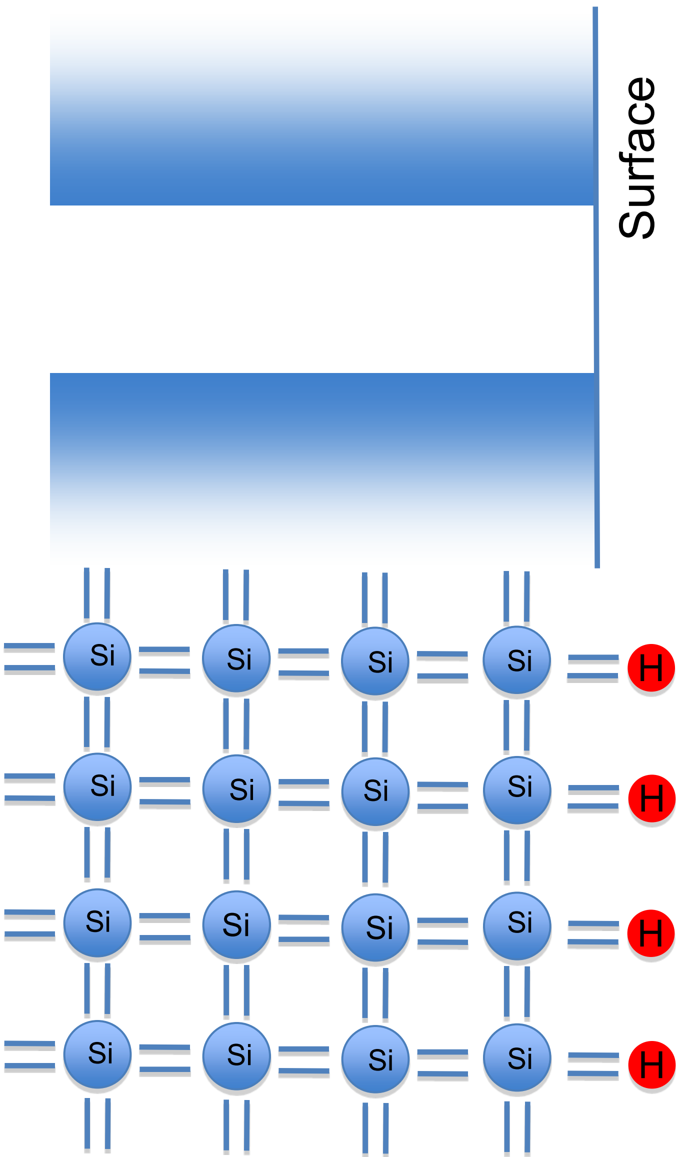
Surface recombination velocity

Carrier diffusivity

Ref: Horányi et al., *Appl. Surf. Sci.* **63**, 306 (1993)

http://pvcdrom.pveducation.org/CHARACT/surface.htm

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 τ_{eff}.)

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surf}}$$

2. Any variation in lifetime should be due to a changing τ_{surf}, per below:

Sample thickness

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

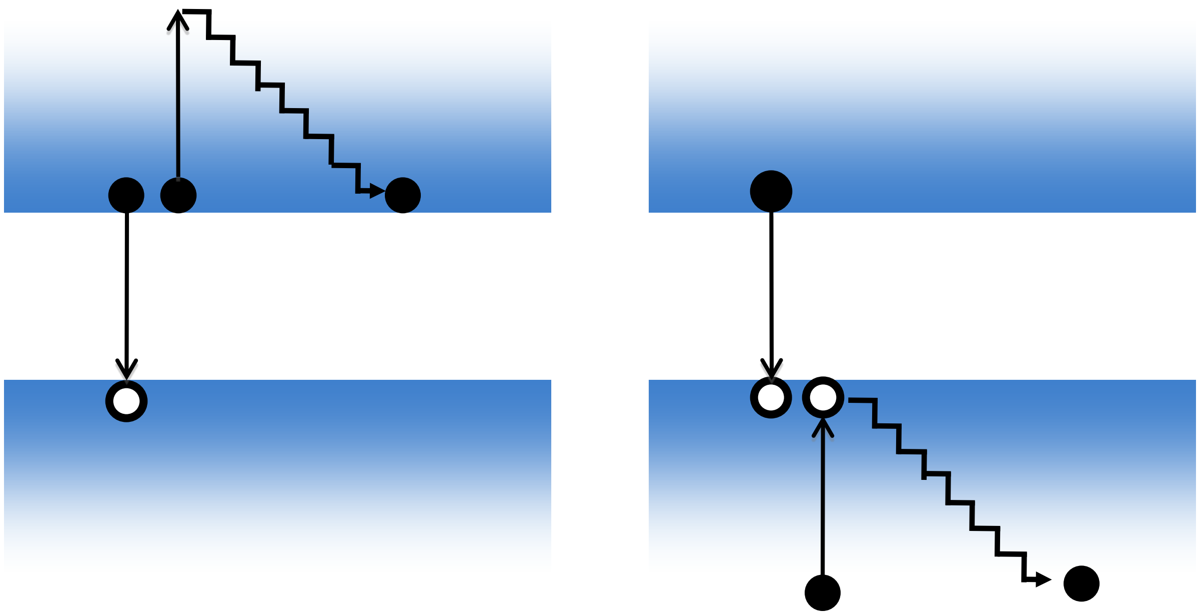
Surface recombination velocity

Carrier diffusivity

Ref: Horányi et al., *Appl. Surf. Sci.* **63**, 306 (1993)

3. With >2 lifetime measurements (sample thicknesses), can solve for τ_{surf}!

Auger Recombination, τ_{Auger}



$$R_{n-type} \sim pn^2$$

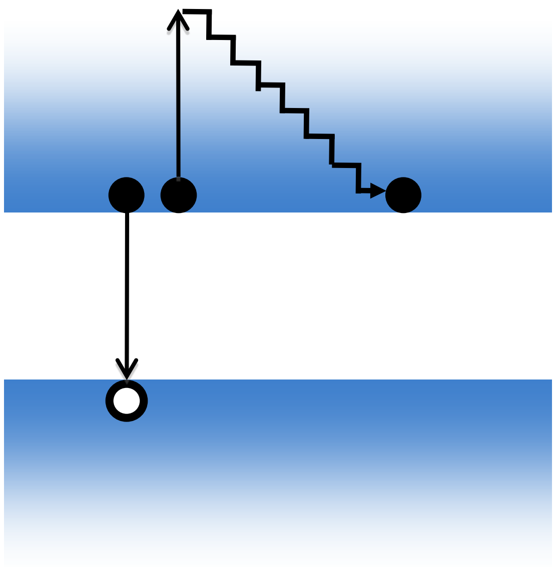
$$\tau_{n-type} \approx \frac{1}{Cn^2}$$

$$R_{p-type} \sim np^2$$

$$\tau_{p-type} \approx \frac{1}{Cp^2}$$

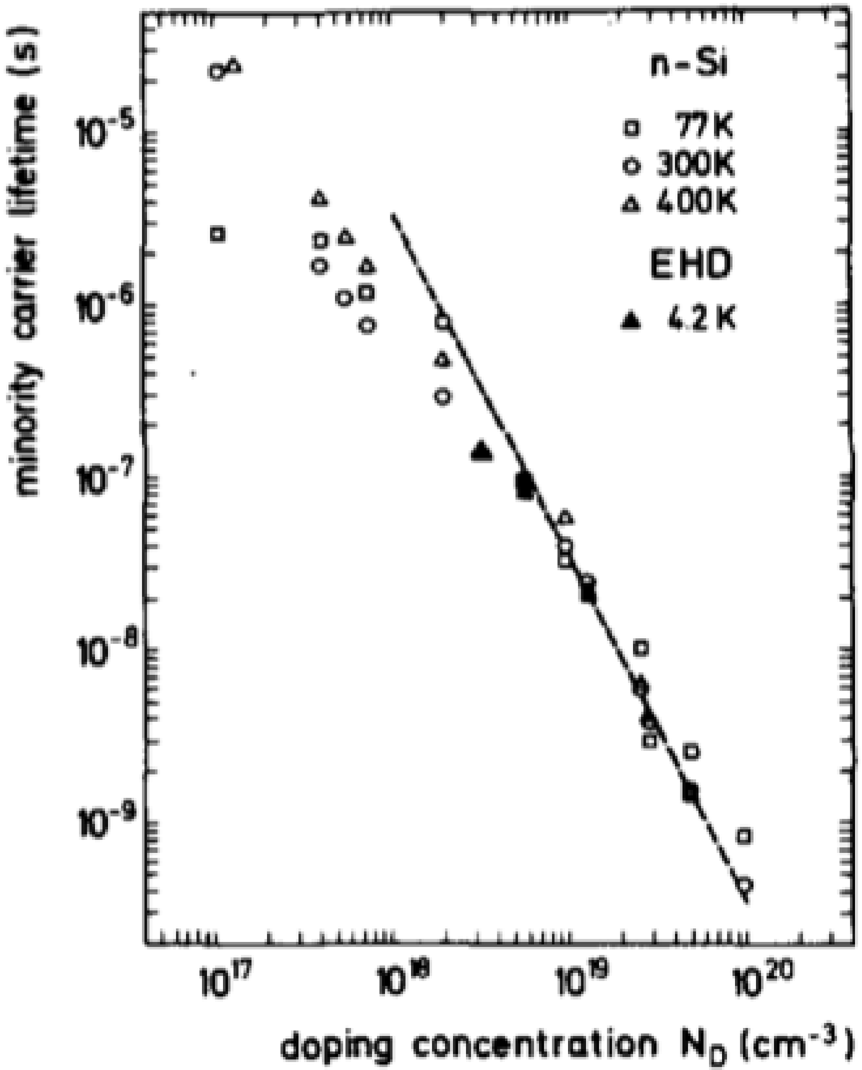
*Above equations true at sufficiently high doping densities (≥10^{18}cm^{-3} in silicon)

Auger Recombination in *n*-type silicon



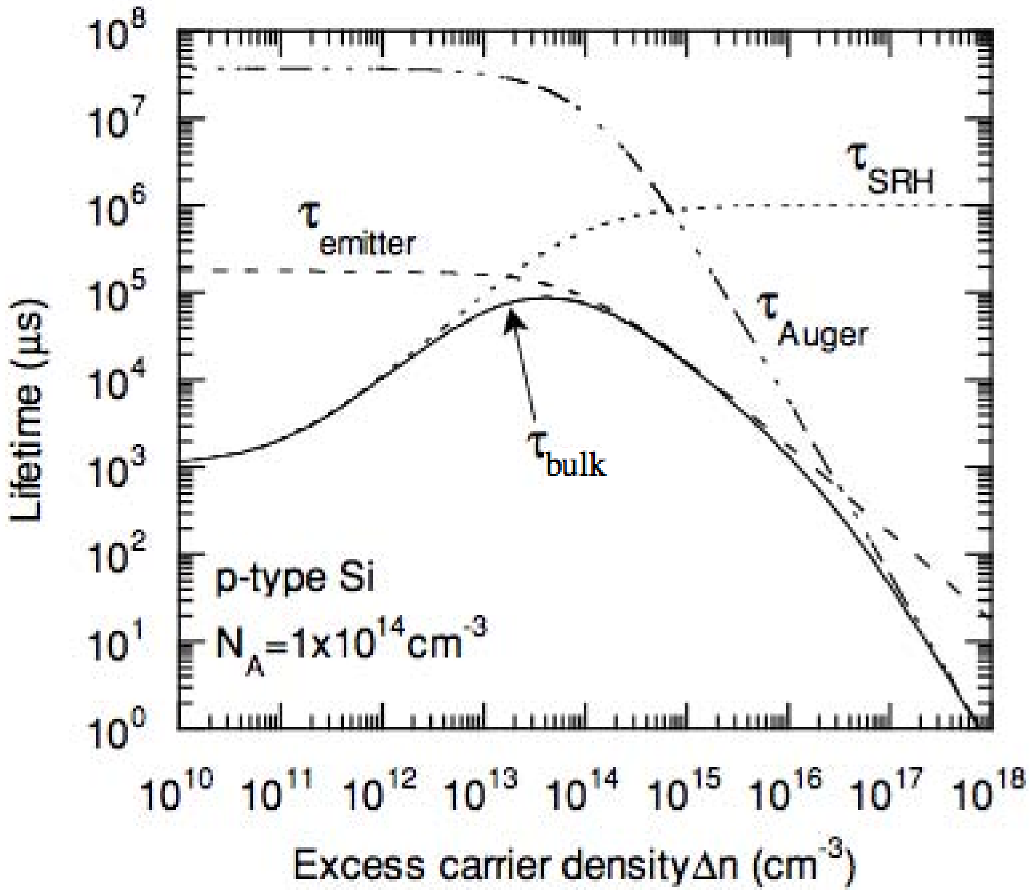
$$R_{n-type} \sim pn^2$$

$$\tau_{n-type} \approx \frac{1}{Cn^2}$$



J. Dziewior, W. Shmid, *Appl. Phys. Lett.*, **31**, p346 (1977)

Auger Recombination in *n*-type silicon



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

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

Measuring Minority Carrier Lifetime

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:

$$\frac{1}{\tau_{\text{rad}}} >> \frac{1}{\tau_{SRH}}$$

or

$$\tau_{\text{rad}} << \tau_{SRH}$$

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

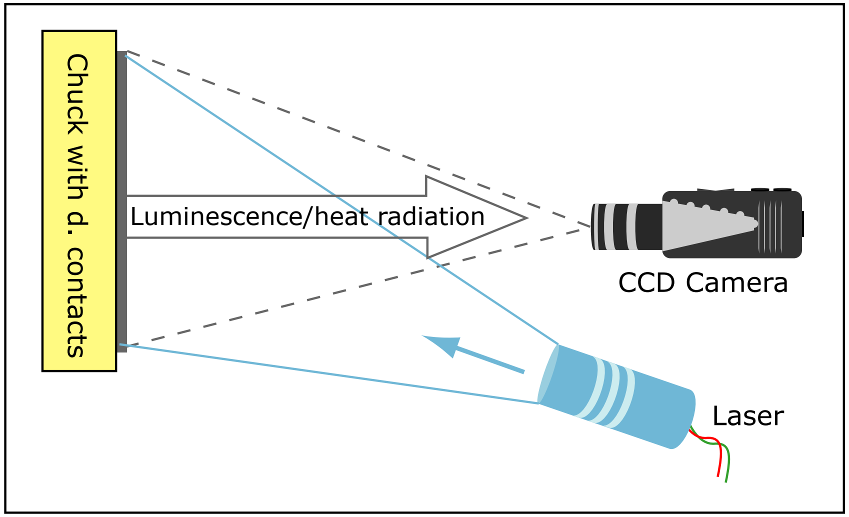


Image by MIT OpenCourseWare.

M. Kasemann *et al*., *Proc. IEEE PVSC,* San Diego, CA (2008).

Measurement of Wafer

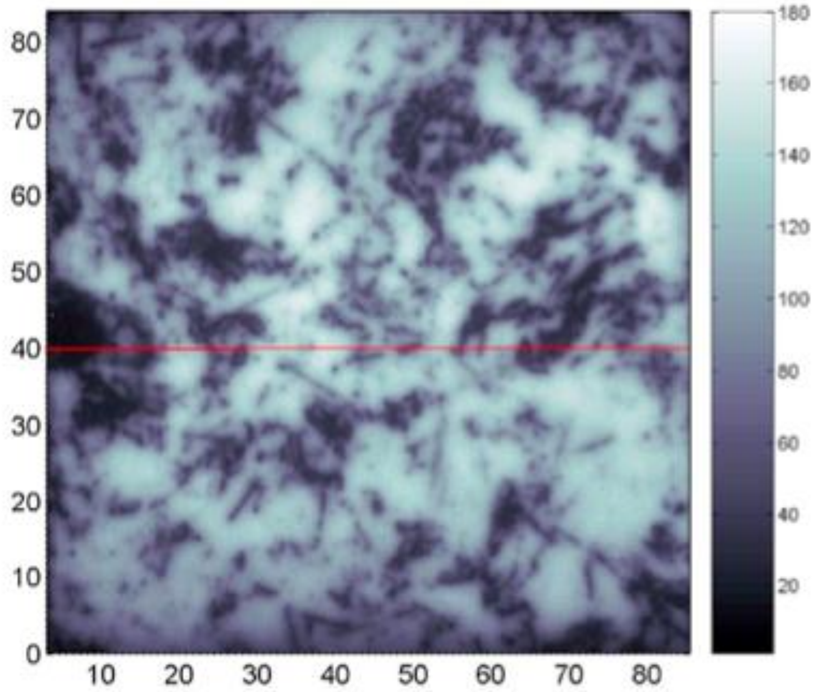
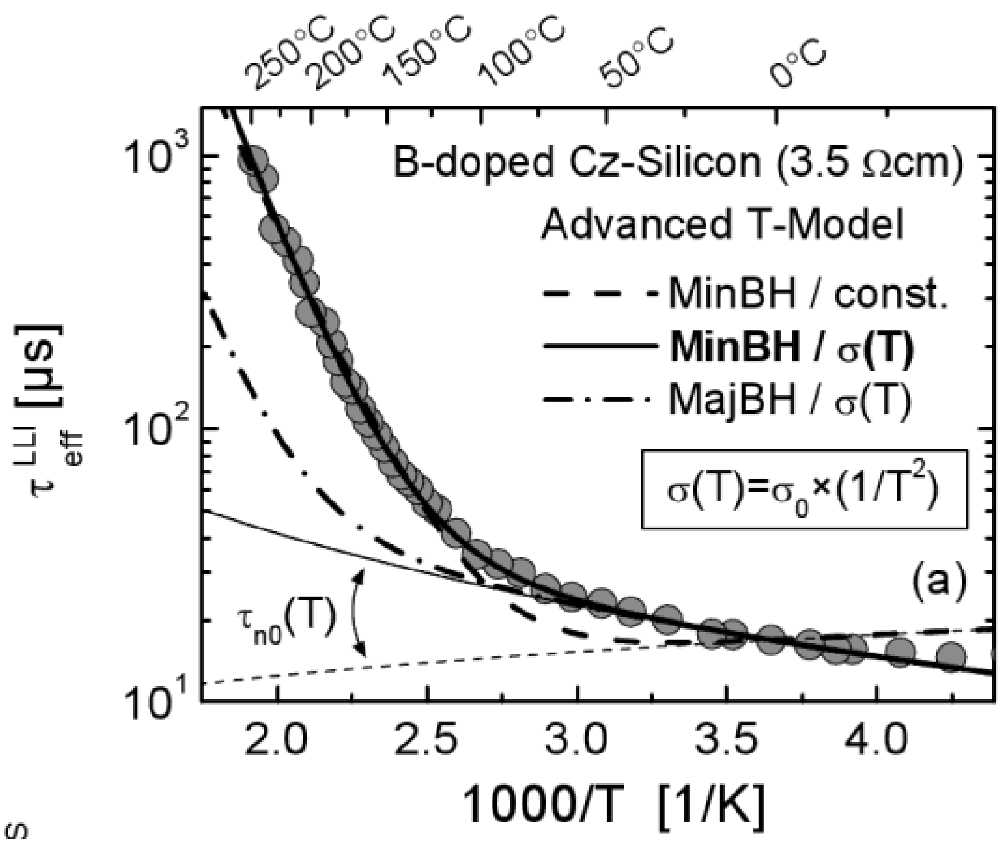
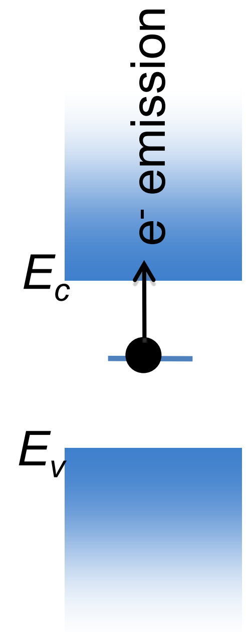


FIG. 1. (Color online) Lifetime distribution within an 8.5×8.5 cm^2 area of a 302 μm thick, 1.2 Ω cm, mc-Si, *p*-type wafer obtained from a PL image measured with a data acquisition time of 1.5 s and with a spatial resolution of 130 μm.

T. Trupke *et al*., *Appl. Phys. Lett.* **89**, 044107 (2006).

Temperature Changes σ_0





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

S. Rein, Lifetime spectroscopy. Springer-Verlag (Berlin, 2005). p. 430

Learning Objectives: Toward a 1D Device Model

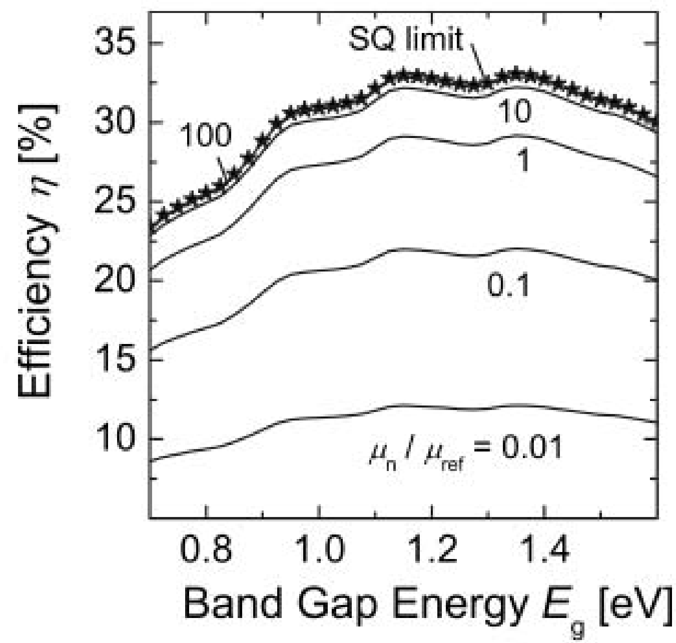
1. Describe what minority carrier diffusion length is, and calculate its impact on J_{sc}, V_{oc}. Describe how minority carrier diffusion length is affected by minority carrier lifetime and minority carrier mobility.
2. Describe how minority carrier diffusion length is measured.
3. Lifetime:
   - Describe 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).**

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!)*

$$L_{\mathrm{diff}} = \sqrt{D\tau_{\mathrm{bulk}}}$$

$$D = \frac{k_B T}{q}\mu$$



J. Mattheis *et al.*, *Phys. Rev. B.* **77**, 085203 (2008)

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)

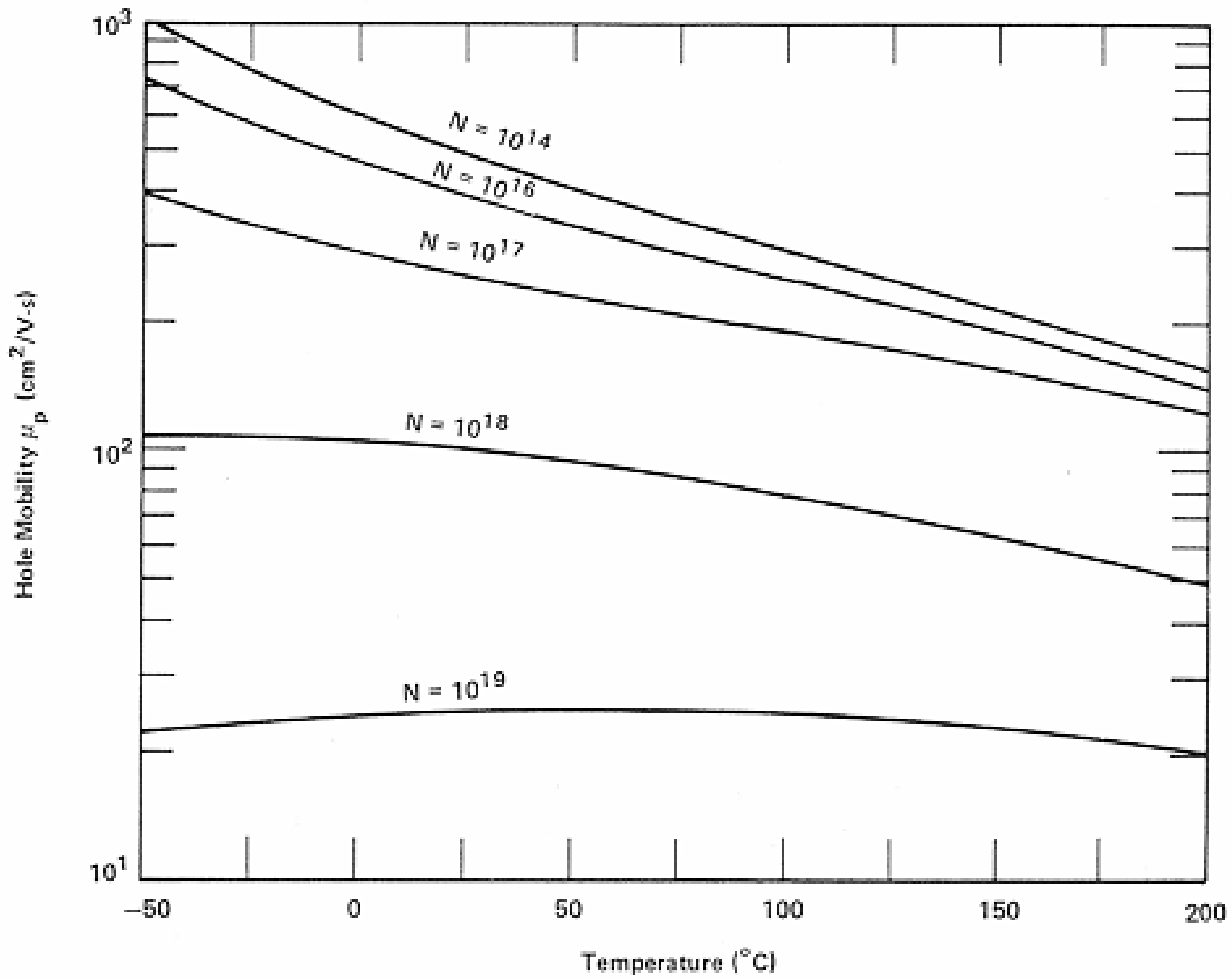
Example of complex percolation pathway

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

Diagrams removed due to copyright restrictions.
See lecture video.

Mobility and Carrier Concentration in Semiconductor

Increased concentration of ionized dopant atoms increases conductivity, but can reduce carrier mobility (due to scattering).



Buonassisi (MIT) 2011

Percolation Pathways

Both μ and τ play a role in determining L_{diff}, and hence efficiency, for various device architectures.

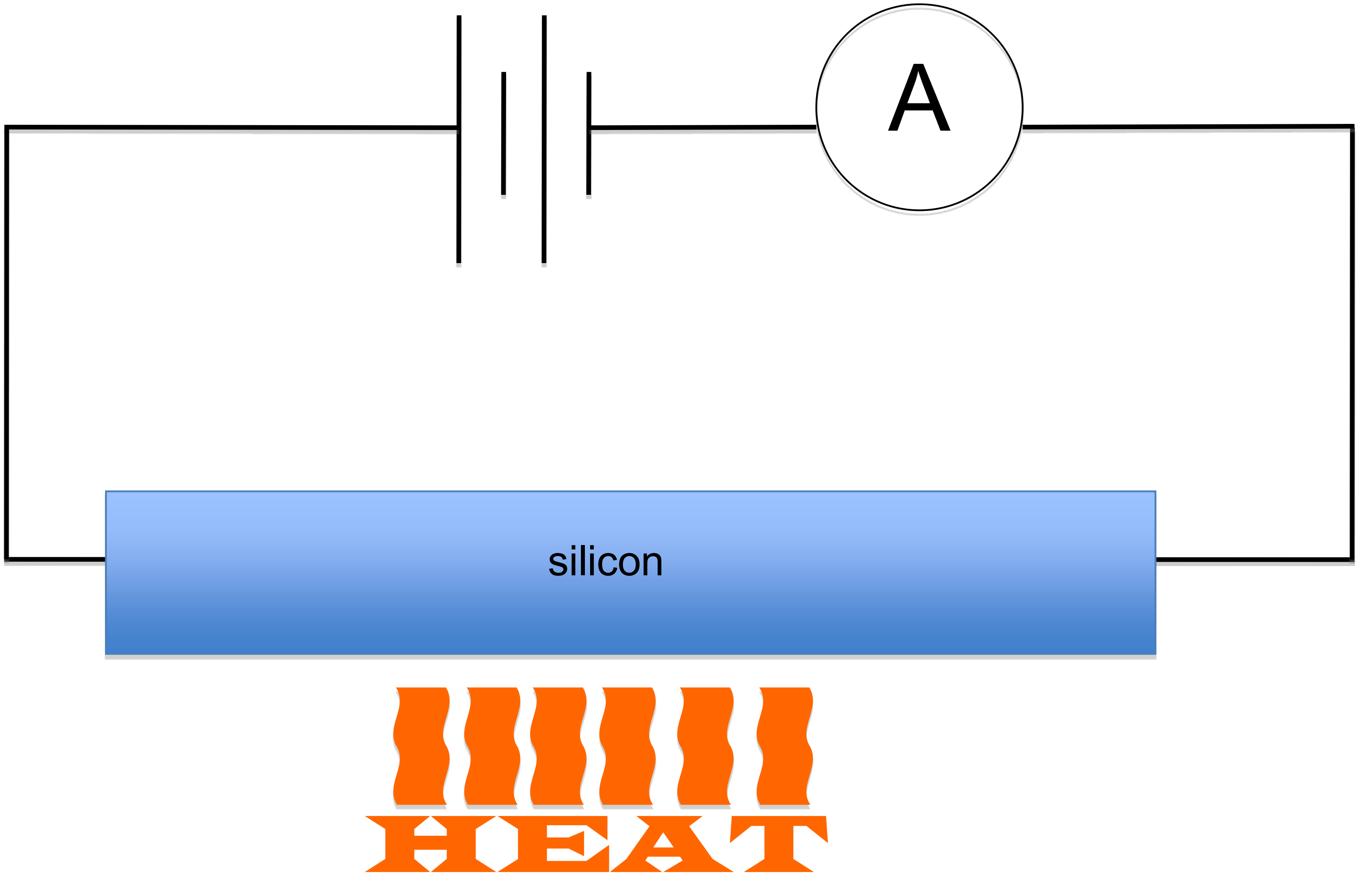
Table removed due to copyright restrictions.
See lecture video.

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 → ionized dopants inside sample scatter carriers.

Demo: Conductivity of Heated Intrinsic and Doped Silicon



Demo Explained

$$n = n_0 + \Delta n \approx N_D + \Delta n$$

For intrinsic Si, $\Delta n >> N_D$.
For highly doped Si, $\Delta n << N_D$.

$$\sigma = \frac{1}{\rho} = q\mu n$$

Conductivity is the product of μ and n.