

## 5. Recombination

### Recombination processes

We assumed that adjustment of carrier concentrations to their equilibrium values could be characterized by a lifetime. We need to identify the relevant recombination processes to identify the influences on lifetime. Three distinct bulk recombination mechanisms are identified in the following sections.

### Band-to-band optical processes (I)

Consider electronic transitions in a two-state system. In the context of semiconductors, we consider these to be the CB and VB edges. In a direct-gap material, the transition may occur by absorption or emission of photons with energy  $E_{\text{ph}} = E_C - E_V = E_g$ . The probabilities for the transitions are proportional to the "effective" densities and occupation probabilities of initial and final states. Using the Fermi functions in quasi-equilibrium:

$$f_C = f(E_C - E_{F_n}) = \frac{1}{e^{(E_C - E_{F_n})/kT} + 1}$$

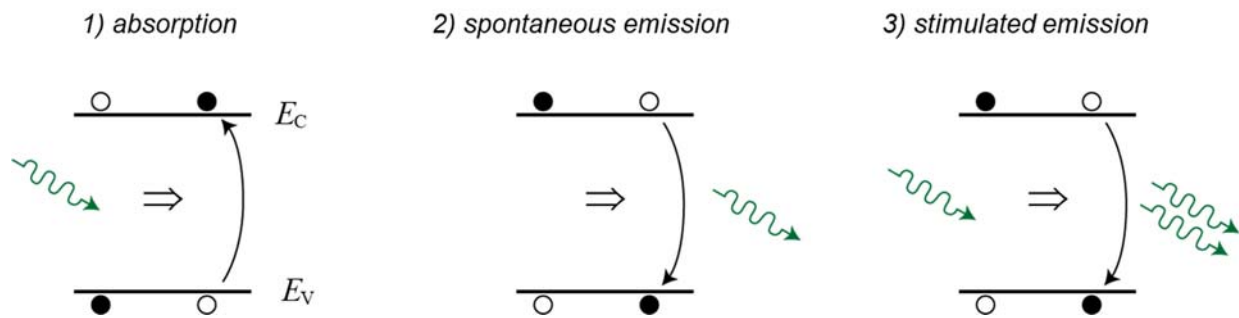
$$1 - f_V = f(E_{F_p} - E_V) = \frac{1}{e^{(E_{F_p} - E_V)/kT} + 1}$$

the probabilities for occupation  $P$  or vacancy  $\bar{P}$  of an electron state in the CB, or a hole state in the VB are:

$$P_{\text{electron}} = f_C \quad P_{\text{hole}} = 1 - f_V$$

$$\bar{P}_{\text{electron}} = 1 - f_C \quad \bar{P}_{\text{hole}} = f_V$$

Einstein realized that three energy conserving processes should be considered. These are absorption, spontaneous emission, and stimulated emission:



The rates for these processes 1,2, and 3 depend on rate constants  $A$ ,  $B$ , and  $C$ , and the probability  $f_{\text{ph}}$  that a photon of energy  $E_g$  is present:

$$r_1 = A \cdot f_{\text{ph}} \cdot f_V \cdot (1 - f_C)$$

$$r_2 = B \cdot (1 - f_V) \cdot f_C$$

$$r_3 = C \cdot f_{\text{ph}} \cdot (1 - f_V) \cdot f_C$$

### Band-to-band optical processes (II)

If the two-state system is in equilibrium with the radiation field, we must have equal rates for absorption and emission:  $r_1 = r_2 + r_3$ . This occurs for a particular value of  $f_{\text{ph}}$ :

$$f_{\text{ph}} = \frac{B \cdot (1 - f_{\text{v}}) \cdot f_{\text{c}}}{A \cdot f_{\text{v}} \cdot (1 - f_{\text{c}}) - C \cdot (1 - f_{\text{v}}) \cdot f_{\text{c}}} = \frac{B}{A} \cdot \left[ \frac{1}{\left( \frac{1}{f_{\text{c}}} - 1 \right) - \frac{C}{A}} \right]$$

Defining  $\Delta\mu = E_{F_n} - E_{F_p}$

$$f_{\text{ph}} = \frac{B/A}{e^{(E_g - \Delta\mu)/kT} - C/A}$$

### Band-to-band optical processes (III)

Consider our two state system to be enclosed in the cavity. Recall, for blackbody-cavity in equilibrium to its enclosed radiation field

$$f_{\text{ph}} \rightarrow \frac{1}{e^{E/kT} - 1}$$

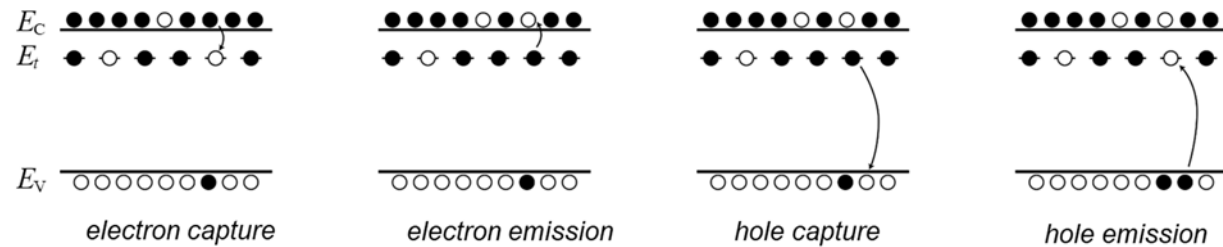
This form must be recovered when the two-state system is absent. This implies that  $A = B = C$ , and that the two-state system modifies the blackbody spectrum by the substitution  $E \rightarrow E - \Delta\mu$ . So, in the presence of a two-state system (e.g., a semiconductor), the correct distribution function for photons is:

$$f_{\text{ph}} = \frac{1}{e^{(E_g - \Delta\mu)/kT} - 1}$$

The radiation field is altered by the semiconductor by the introduction of a “photon chemical potential”, equal to the quasi-Fermi-level splitting.

### Shockley-Read-Hall recombination (I)

Consider localized trap levels having density  $N_t$  within the bandgap at energy  $E_t$ . Note that isolated states such as these will not form a continuous band without electronic coupling between the states. We can imagine transitions involving exchange of carriers between the trap states and the CB and VB edges.



Expressions for the transition rates can then be written based on the carrier concentrations at each level. Using the distribution function  $f_t$  for the trap level, we have the rates of electron capture from the CB into an empty trap state, as well as hole capture, i.e., annihilation of a hole by the emission of an electron from a filled trap state into an empty VB state:

$$U_n = B_n \cdot N_t \cdot n \cdot (1 - f_t), \quad U_p = B_p \cdot N_t \cdot p \cdot f_t$$

The rates for electron emission from a filled trap state to the CB, and hole emission, that is excitation of an electron into an empty trap state from the VB are:

$$G_n = \frac{N_t \cdot f_t}{\tau_{n,\text{esc}}}, \quad G_p = \frac{N_t \cdot (1 - f_t)}{\tau_{p,\text{esc}}}$$

The capture rates are related to the trap density:

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$$\frac{1}{\tau_n} = B_n \cdot N_t, \quad \frac{1}{\tau_p} = B_p \cdot N_t$$

Where the coefficients depend on the thermal velocity and capture cross sections

$$B_n = v_n \cdot \sigma_n, \quad B_p = v_p \cdot \sigma_p$$

### Shockley-Read-Hall recombination (II)

We can determine the escape lifetimes in equilibrium, knowing that  $G_n = U_n$  and  $G_p = U_p$ :

$$B_n \cdot \cancel{N_t} \cdot n_0 \cdot (1 - f_t) = \frac{\cancel{N_t} \cdot f_t}{\tau_{n,esc}}, \quad B_p \cdot \cancel{N_t} \cdot p_0 \cdot f = \frac{\cancel{N_t} \cdot (1 - f_t)}{\tau_{p,esc}}$$

These lead to

$$\frac{1}{\tau_{n,esc}} = B_n \cdot n_0 \cdot \left( \frac{1}{f_t} - 1 \right), \quad \frac{1}{\tau_{p,esc}} = B_p \cdot p_0 \cdot \left( \frac{1}{f_t} - 1 \right)$$

It is readily shown that

$$\frac{1}{f_t} - 1 = e^{(E_t - E_F)/kT}, \quad \frac{1}{\frac{1}{f_t} - 1} = e^{(E_F - E_t)/kT}$$

The equilibrium carrier concentrations are

$$n_0 = n_i \cdot e^{(E_F - E_i)/kT}, \quad p_0 = p_i \cdot e^{(E_i - E_F)/kT}$$

Using the electron and hole densities when  $E_F = E_t$

$$n_t \doteq n_0 \cdot e^{(E_t - E_F)/kT} = n_i \cdot e^{(E_t - E_i)/kT}, \quad p_t \doteq p_0 \cdot e^{(E_F - E_t)/kT} = n_i \cdot e^{(E_i - E_t)/kT}$$

we can write

$$\frac{1}{\tau_{n,esc}} = B_n \cdot n_t, \quad \frac{1}{\tau_{p,esc}} = B_p \cdot p_t$$

The electron and hole emission rates are then

$$G_n = N_t \cdot f_t \cdot B_n \cdot n_t, \quad G_p = N_t \cdot (1 - f_t) \cdot B_p \cdot p_t$$

We know that

$$\frac{1}{\tau_n} = B_n \cdot N_t, \quad \frac{1}{\tau_p} = B_p \cdot N_t$$

Thus, the emission rates are

$$G_n = \frac{n_t \cdot f_t}{\tau_n}, \quad G_p = \frac{p_t \cdot (1 - f_t)}{\tau_p}$$

### Shockley-Read-Hall recombination (III)

Assuming charge neutrality, the SRH recombination rate is:

$$U_{SRH} = U_n - G_n = U_p - G_p$$

This tells us that

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$$\frac{n \cdot (1 - f_t)}{\tau_n} - \frac{N_t \cdot f_t}{\tau_{n,esc}} = \frac{p \cdot f_t}{\tau_p} - \frac{N_t \cdot (1 - f_t)}{\tau_{p,esc}}$$

From the preceding analysis

$$\frac{n \cdot (1 - f_t)}{\tau_n} - \frac{n_t \cdot f_t}{\tau_n} = \frac{p \cdot f_t}{\tau_p} - \frac{p_t \cdot (1 - f_t)}{\tau_p}$$

Regrouping

$$\left( \frac{p + p_t}{\tau_p} + \frac{n + n_t}{\tau_n} \right) \cdot f_t = \frac{n}{\tau_n} + \frac{p_t}{\tau_p}$$

A little algebra gives the probability that a trap state is filled

$$f_t = \frac{\frac{n}{\tau_n} + \frac{p_t}{\tau_p}}{\frac{p + p_t}{\tau_p} + \frac{n + n_t}{\tau_n}} = \frac{n \cdot \tau_p + p_t \cdot \tau_n}{(n + n_t) \cdot \tau_p + (p + p_t) \cdot \tau_n}$$

or that a trap state is empty

$$1 - f_t = \frac{n_t \cdot \tau_p + p \cdot \tau_n}{(n + n_t) \cdot \tau_p + (p + p_t) \cdot \tau_n}$$

### Shockley-Read-Hall recombination (IV)

Solving for  $f_t$ , after some algebra we have the SRH recombination rate:

$$U_{SRH} = U_p - G_p (= U_n - G_n) = \frac{p \cdot f_t}{\tau_p} - \frac{p_t \cdot (1 - f_t)}{\tau_p} = \frac{n \cdot p - n_t \cdot p_t}{(n + n_t) \cdot \tau_p + (p + p_t) \cdot \tau_n}$$

Recall that

$$n \cdot p = n_i^2 e^{\Delta\mu/kT}, \quad n_t \cdot p_t = n_i^2$$

We can then write

$$U_{SRH} = \frac{n_i^2 \cdot (e^{\Delta\mu/kT} - 1)}{(n + n_t) \cdot \tau_p + (p + p_t) \cdot \tau_n}$$

Consider deviations from equilibrium  $n = n_0 + \Delta n$ ,  $p = p_0 + \Delta p$ . The numerator is

$$n \cdot p - n_t \cdot p_t = n \cdot p - n_i^2 = n \cdot p - n_0 \cdot p_0 \approx n_0 \cdot \Delta p + p_0 \cdot \Delta n$$

Now

$$U_{SRH} = \frac{n_0 \cdot \Delta p + p_0 \cdot \Delta n}{(n_0 + \Delta n + n_t) \cdot \tau_p + (p_0 + \Delta p + p_t) \cdot \tau_n}$$

Consider moderately doped material. Typically

$$\begin{aligned} n_0 &\gg p_0, & // \text{n-type} \\ p_0 &\gg n_0, & // \text{p-type} \end{aligned}$$

Let's assume the capture lifetimes  $\tau_n$  and  $\tau_p$  are of comparable magnitude to each other. If the trap is a deep level, then  $n_0 \gg (n_t, p_t)$  (n-type), or  $p_0 \gg (n_t, p_t)$  (p-type). In this case, at low injection [ $(\Delta n, \Delta p)$  small], the SRH rate is independent of dopant concentration:

$$U_{\text{SRH}} = \begin{cases} \frac{\Delta p}{\tau_p}, & //\text{n-type} \\ \frac{\Delta n}{\tau_n}, & //\text{p-type} \end{cases}$$

### Shockley-Read-Hall recombination (V)

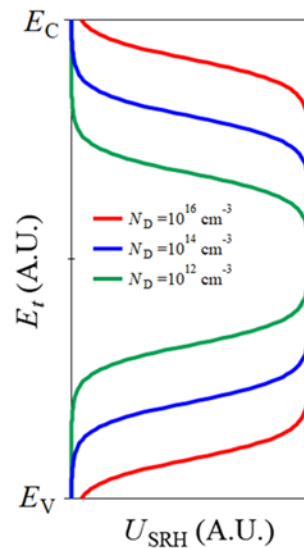
Consider n-type material with  $n_0 = N_D$ . Let's examine how the SRH recombination rate varies with position of the trap level within the gap. As before, we assume  $\tau_n$  and  $\tau_p$  are comparable. With low-injection, i.e.,  $N_D \gg (\Delta n, \Delta p)$ . Analytically,

$$U_{\text{SRH}} = \frac{N_D \cdot \Delta p + \left(\frac{n_i^2}{N_D}\right) \cdot \Delta n}{(N_D + \cancel{\Delta n} + n_i) \cdot \tau_p + \left(\frac{n_i^2}{N_D} + \Delta p + \frac{n_i^2}{n_i}\right) \cdot \tau_n}$$

$$\approx \frac{N_D \cdot n_i \cdot \Delta p}{n_i^2 \cdot \tau_p + (N_D \cdot \tau_p + \cancel{\Delta p} \cdot \tau_n) \cdot n_i + n_i^2 \cdot \tau_n}$$

$$U_{\text{SRH}} \approx \frac{\Delta p}{\tau_p + (n_i \cdot \tau_p + p_i \cdot \tau_n) / N_D}$$

As the doping level increases, the trap energy becomes less important, and the recombination rate is approximately  $\Delta p / \tau_p$ . We generally expect deep levels to have the biggest effect on recombination.



### Shockley-Read-Hall recombination (VI)

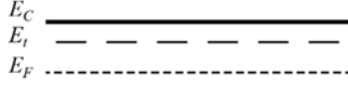
Let's look at the n-type case more carefully. Regardless of the trap position,  $U_{\text{SRH}}$  is proportional to the excess hole concentration,  $\Delta p$ . When the trap is a shallow level near the CB edge, the lifetime increases to  $n_i \cdot \tau_p / N_D$ . In this case, hole emission limits the recombination rate. When the trap is a deep level, the

lifetime is just the hole capture lifetime,  $\tau_p$ . When the trap is shallow, near the VB edge, the lifetime increases to  $p_t \cdot \tau_n / N_D$ . In this case, electron capture limits recombination.

1) Shallow electron trap  
(near CB edge):

$$E_t > E_F$$

$$n_t \gg N_D$$



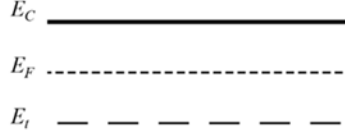
$$U_{\text{SRH}} = \frac{N_D \cdot \Delta p}{n_t \cdot \tau_p}$$

$$\frac{1}{\tau} = \frac{N_D}{n_t \cdot \tau_p} \left( \ll \frac{1}{\tau_p} \right)$$

2) Deep level (mid-gap):

$$E_t < E_F$$

$$N_D \gg n_t$$

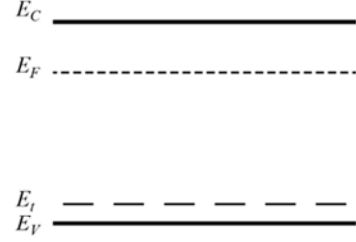


$$U_{\text{SRH}} = \frac{\Delta p}{\tau_p}$$

3) Shallow hole trap  
(near VB edge):

$$E_t < E_F$$

$$p_t \gg N_D$$



$$U_{\text{SRH}} = \frac{N_D \cdot \Delta p}{p_t \cdot \tau_n}$$

$$\frac{1}{\tau} = \frac{N_D}{p_t \cdot \tau_n} \left( \ll \frac{1}{\tau_p} \right)$$

### Auger recombination

Auger processes involve the intraband exchanges of energy. For example, a photon spontaneously emitted by an electron during recombination with hole can be absorbed by another electron, which is elevated above the CB edge, with the absorbed energy eventually being lost as heat during thermalization back to the band edge. We can anticipate the parametric dependence of the recombination rates:

$$U_{p,\text{Aug}} = A_p \cdot (n^2 \cdot p - n_0^2 \cdot p_0), \quad U_{n,\text{Aug}} = A_n \cdot (n \cdot p^2 - n_0 \cdot p_0^2)$$

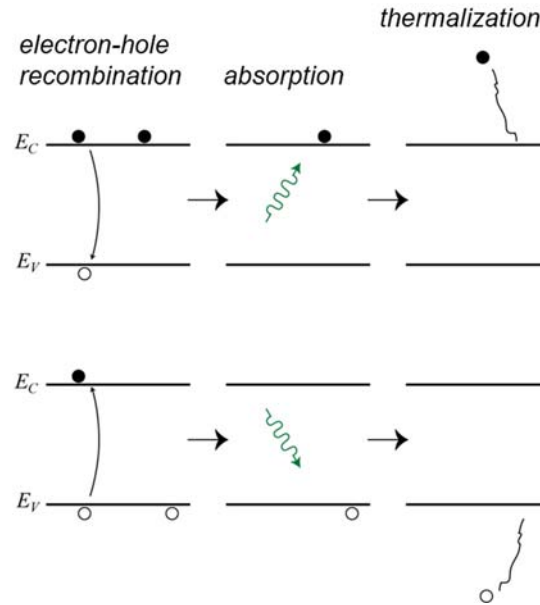
Due to the quadratic dependence on one carrier concentration, the disparity in Auger recombination rates between minority and majority carriers is even more exaggerated than for other mechanisms. Consider a p-type material with  $p = N_a$ . The Auger recombination rate for electrons is:

$$U_{n,\text{Aug}} = A_n \cdot [(n_0 + \Delta n) \cdot N_A^2 - n_0 \cdot p_0^2]$$

$$\approx A_n \cdot N_A^2 \cdot \Delta n = \frac{\Delta n}{\tau_{n,\text{Aug}}}$$

where we have identified the Auger lifetime:

$$\frac{1}{\tau_{n,\text{Aug}}} = A_n \cdot N_A^2$$



### Net Lifetime

At any particular carrier concentration, the combined effects of the various recombination mechanisms can be combined into a single lifetime. Consider an n-type material. The excess hole concentration varies as:

$$\Delta p(t) = \Delta p(0) \cdot e^{-t/\tau_{p,SRH}} \cdot e^{-t/\tau_{p,rad}} \cdot e^{-t/\tau_{p,Aug}} = \Delta p(0) \cdot e^{-t/\tau_p}$$

The net lifetime is given by:

$$\frac{1}{\tau_p} = \frac{1}{\tau_{p,SRH}} + \frac{1}{\tau_{p,rad}} + \frac{1}{\tau_{p,Aug}} = B_p \cdot N_t + B_{rad} \cdot N_D + A_{p,Aug} \cdot N_D^2$$

Similarly, for electrons in a p-type material:

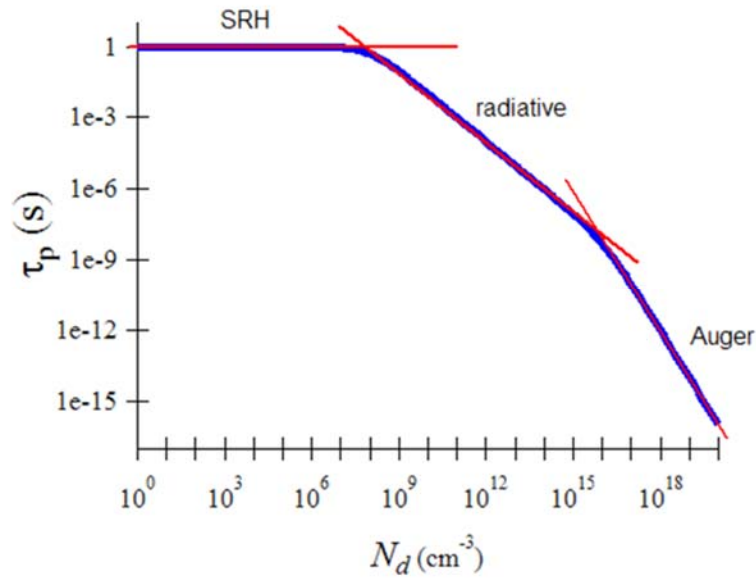
$$\frac{1}{\tau_n} = \frac{1}{\tau_{n,SRH}} + \frac{1}{\tau_{n,rad}} + \frac{1}{\tau_{n,Aug}} = B_n \cdot N_t + B_{rad} \cdot N_A + A_{n,Aug} \cdot N_A^2$$

In the context of the orders-of-magnitude variations in doping concentrations, we can summarize these mechanisms as follows:

intrinsic (no doping): SRH dominates

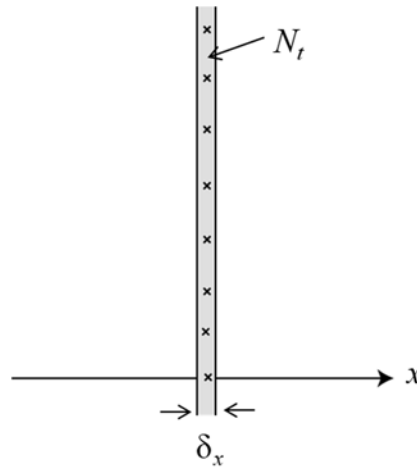
moderate doping: radiative dominates

high doping: Auger dominates



### Surface Recombination (I)

Consider SRH centers localized within a thin layer of width  $\delta_x$  at a 2-D interface.



The areal SRH recombination rate is

$$U_{\text{SRH}} \cdot \delta_x = \frac{n \cdot p - n_i^2}{\frac{1}{S_n} \cdot (p + p_t) + \frac{1}{S_p} \cdot (n + n_t)}$$

using the surface recombination “velocities” ( $[S_n] = [S_p] = \frac{\text{cm}}{\text{s}}$ ):

$$S_n = \frac{\delta_x}{\tau_n}, \quad S_p = \frac{\delta_x}{\tau_p}$$

The areal density of traps is  $N_s = N_t \cdot \delta_x$ , where  $[N_s] = \text{cm}^{-2}$ . The electron and hole capture rates are then:



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$$S_n = B_n \cdot N_s, S_p = B_p \cdot N_s$$

$$U_{\text{SRH}} \cdot \delta_x = \frac{n \cdot p - n_i^2}{\frac{1}{S_n} \cdot (p + p_t) + \frac{1}{S_p} \cdot (n + n_t)}$$

### Surface Recombination (II)

Consider an acceptor-doped material with  $p_0 = N_A$  ( $\gg n, n_i$ ). With  $n = n_0 + \Delta n$  and  $p \approx p_0 = N_A$ , we have

$$n \cdot p - n_i^2 \approx (n_0 + \Delta n) \cdot p_0 - n_i^2 = \Delta n \cdot N_A$$

At an interface

$$\frac{1}{S_n} \cdot (p + p_t) + \frac{1}{S_p} \cdot (n + n_t) \approx \frac{N_A}{S_n}$$

so  $U \cdot \delta_x \rightarrow S_n \cdot \Delta n$ . Continuity in steady state gives

$$\frac{\partial n}{\partial t} = 0 = \frac{1}{q} \cdot \frac{dJ_n}{dx} + G_n - U_n$$

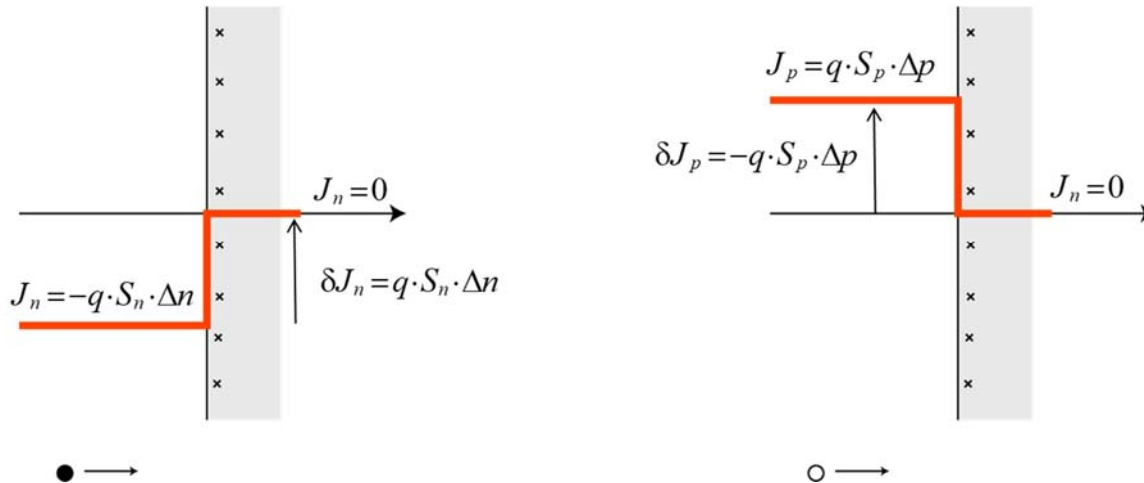
$$\frac{dJ_n}{dx} = q \cdot (U_n - G_n)$$

Generation is not localized, so  $G_n \cdot \delta x \rightarrow 0$ . There is a discontinuity across the interface in the current density

$$\delta J_n = q \cdot S_n \cdot \Delta n$$

Similarly, for an n-type material, we would have

$$\delta J_p = -q \cdot S_p \cdot \Delta p$$



When a current abruptly vanishes at a surface, the magnitude of the discontinuity equals that of the current itself. For example, in an n-type material, a current that vanishes due to recombination at the surface of an n-type material must satisfy:

$$J_n = -\delta J_n = -q \cdot S_n \cdot \Delta n$$

If there is no drift contribution ( $E = 0$ ), the current is diffusion only.

$$J_n|_{\text{interface}} = q \cdot D_n \cdot \frac{dn}{dx} = q \cdot D_n \cdot \frac{d(\Delta n)}{dx} = -q \cdot S_n \cdot \Delta n$$

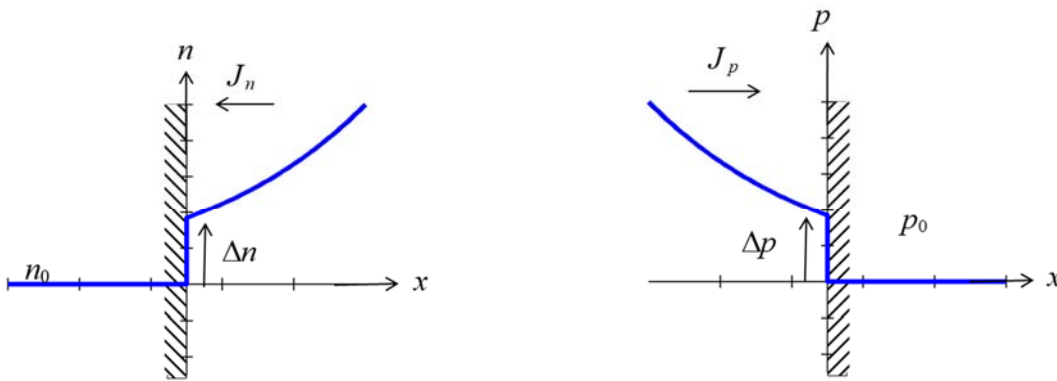
$$\frac{d(\Delta n)}{dx} = -\frac{S_n}{D_n} \cdot \Delta n$$

Similarly, for p-type:

$$J_p|_{\text{interface}} = -q \cdot D_p \cdot \frac{dp}{dx} = -q \cdot D_p \cdot \frac{d(\Delta p)}{dx} = q \cdot S_p \cdot \Delta p$$

$$\frac{d(\Delta p)}{dx} = -\frac{S_p}{D_p} \cdot \Delta p$$

The derivative and the value of the excess carrier concentrations are proportional. This presents a boundary condition that can allow determination of the concentration elsewhere.



### Diffusion length (with generation)

Start with the continuity equation for holes in steady state

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \cdot \frac{\partial J_p}{\partial x} + G_p - U_p (= 0)$$

which becomes

$$\frac{dJ_p}{dx} = q \cdot (G_p - U_p)$$

Take the recombination rate to be

$$U_p(x) = \frac{p(x) - p_0}{\tau_p}$$

If the region is neutral and has no electric field

$$J_p = -q \cdot D_p \cdot \frac{dp}{dx}$$

The generated hole density is

$$p_g = G_p \cdot \tau_p$$

This gives

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$$D_p \cdot \frac{d^2 p}{dx^2} = U_p - G_p$$

This gives

$$\frac{d^2 p}{dx^2} = \frac{p(x) - p_0 - p_g}{L_p^2}$$

using the diffusion length for holes

$$L_p = \sqrt{D_p \cdot \tau_p}$$

Solutions have the form

$$p(x) = p_0 + p_g + \Delta p(x)$$

Then

$$\frac{d^2 (\Delta p)}{dx^2} = \frac{\Delta p}{L_p^2}$$

Now the excess (excluding generation) carrier concentrations have the form

$$\Delta p(x) = A \cdot e^{x/L_p} + B \cdot e^{-x/L_p}$$

**“Effective” surface-recombination velocity**

Let’s take a semi-infinite slab

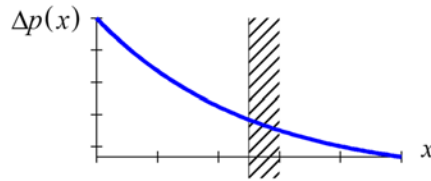
$$\lim(x \rightarrow \infty)[\Delta p(x)] = 0$$

This gives  $A = 0$ , so

$$\Delta p(x) = \Delta p(0) \cdot e^{-x/L_p}$$

The diffusion current at any point is

$$J_p(x) = -q \cdot D_p \cdot \frac{d(\Delta p)}{dx} = \frac{q \cdot D_p}{L_p} \cdot \Delta p(0) \cdot e^{-x/L_p} = \frac{q \cdot D_p}{L_p} \cdot \Delta p(x)$$



This has the form of a surface recombination current

$$J_p(x) = q \cdot S_{\text{eff}} \cdot \Delta p(x)$$

where the “effective” surface-recombination velocity at any point is

$$S_{\text{eff}} = \frac{D_p}{L_p} = \sqrt{\frac{D_p}{\tau_p}}$$

**Surface recombination: Example 1**

Our general form is

$$p(x) = p_0 + p_g + \Delta p(x)$$

Assume that we know  $\Delta p(0)$  and  $\Delta p(w)$ . Then

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$$\Delta p(x) = A \cdot e^{x/L_p} + B \cdot e^{-x/L_p}$$

So,

$$\Delta p(0) = A + B \text{ and } \Delta p(w) = A \cdot e^{w/L_p} + B \cdot e^{-w/L_p}$$

Now

$$\Delta p(x) = \frac{\Delta p(0) \cdot \sinh[(w-x)/L_p] + \Delta p(w) \cdot \sinh(x/L_p)}{\sinh(w/L_p)}$$

and

$$J_p(x) = -q \cdot D_p \cdot \frac{d(\Delta p)}{dx} = \frac{q \cdot D_p}{L_p} \left[ \frac{\Delta p(0) \cdot \cosh[(w-x)/L_p] - \Delta p(w) \cdot \cosh(x/L_p)}{\sinh(w/L_p)} \right]$$

### Surface recombination: Example 2

Assume, instead, we know  $\Delta p(0)$  and  $J_p(w) = q \cdot S_p \cdot \Delta p(w)$ . We can say  $\Delta p(0) = p(0) - p_0$

$$\frac{q \cdot D_p}{L_p} \cdot \left[ \frac{\Delta p(0) - \Delta p(w) \cdot \cosh(w/L_p)}{\sinh(w/L_p)} \right] = q \cdot S_p \cdot \Delta p(w)$$

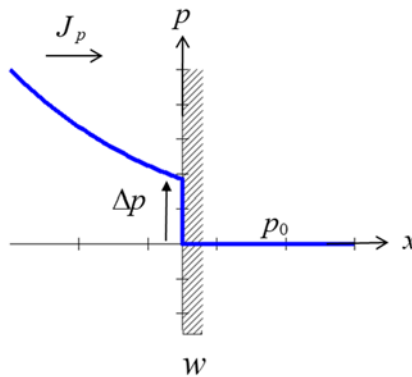
Define  $r = \frac{S_p \cdot L_p}{D_p}$

$$\Delta p(w) = \frac{\Delta p(0)}{\cosh(w/L_p) + r \cdot \sinh(w/L_p)}$$

$$\Delta p(x) = \frac{\Delta p(0) \cdot \{ \cosh[(w-x)/L_p] + r \cdot \sinh[(w-x)/L_p] \}}{\cosh(w/L_p) + r \cdot \sinh(w/L_p)}$$

$$J_p(x) = -q \cdot D_p \cdot \left. \frac{d(\Delta p)}{dx} \right|_x$$

$$= \frac{q \cdot D_p}{L_p} \cdot \frac{\{ \sinh[(w-x)/L_p] + r \cdot \cosh[(w-x)/L_p] \}}{\cosh(w/L_p) + r \cdot \sinh(w/L_p)} \cdot \Delta p(0)$$



### Surface recombination: Example 3

For a p/n junction solar cell, we will find that

$$\Delta p(0) = p_0 \cdot (e^{qV/kT} - 1) - p_g$$

Recombination at the back-surface ( $x = w$ ) contact gives a hole current of



