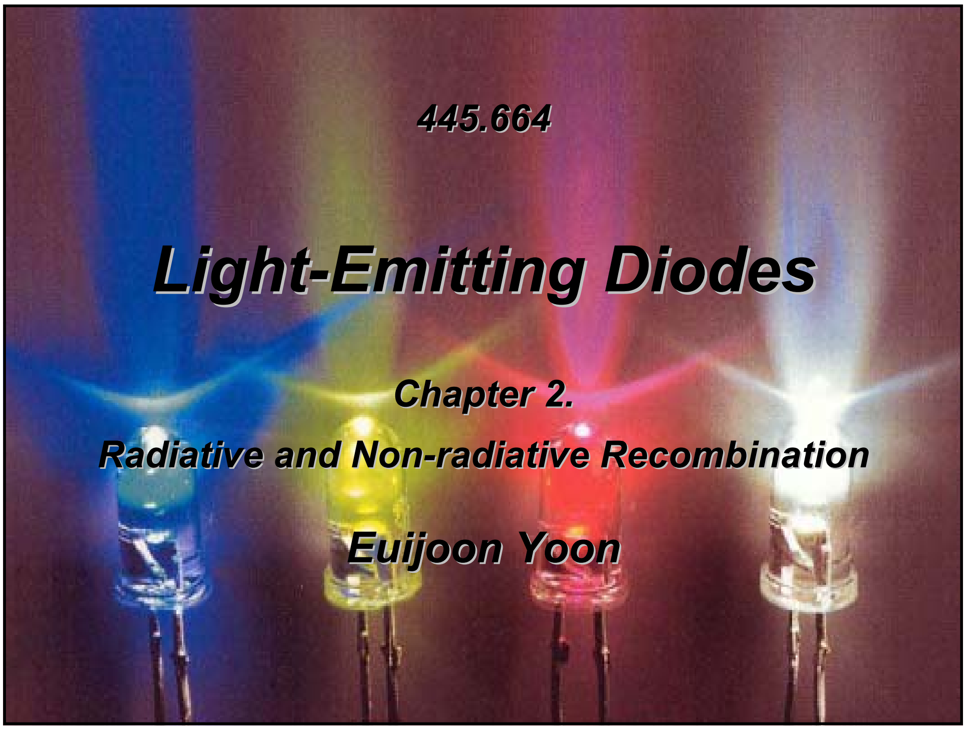

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# Light-Emitting Diodes

## Chapter 2.
## Radiative and Non-radiative Recombination

Euijoon Yoon

## Electron and Hole Concentrations

- Under equilibrium conditions,

Mass action law $n_0 \, p_0 = n_i^2$

| | |
|---|---|
| $n_0$ | equilibrium electron concentration |
| $p_0$ | equilibrium hole concentration |
| $n_i$ | intrinsic carrier concentration |

- Under excitation conditions,
(absorption of light, injection of current)

$$n = n_0 + \Delta n \quad \text{and} \quad p = p_0 + \Delta p$$

| | |
|---|---|
| $n$ | free electron concentration |
| $\Delta n$ | excess free electron concentration |
| $p$ | free hole concentration |
| $\Delta p$ | excess free hole concentration |

## Recombination of Carriers

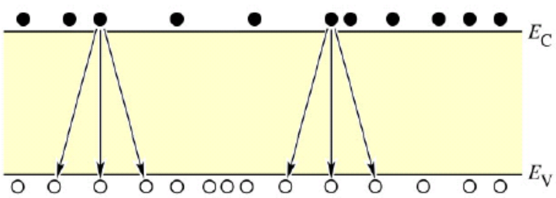



Fig. 2.1. Illustration of electron-hole recombination. The number of recombination events per unit time per unit volume is proportional to the product of electron and hole concentrations, *i. e.* $R \propto n\,p$.

- The number of recombination events will be proportional to the concentration of electrons and holes

Bimolecular rate equation $$R = -\frac{dn}{dt} = -\frac{dp}{dt} = Bnp$$

| | |
|---|---|
| $R$ | recombination rate |
| | ( $10^{-11} \sim 10^{-9}$ $cm^3/s$ for III-V semiconductors) |
| $B$ | bimolecular recombination coefficient |



## Radiative Recombination for Low-level Excitation

- Electrons and holes are generated and annihilated in pairs.

$$\Rightarrow \; \Delta n(t) = \Delta p(t) \quad \text{under steady - state}$$

- For the case of low-level excitation, the photogenerated carrier concentration is much smaller than the majority carrier concentration.

$$\Rightarrow \; \Delta n \ll n_0 \quad \text{and} \quad \Delta p \ll p_0$$

$$R = B[\, n_0 + \Delta n(t)\,][\, p_0 + \Delta p(t)\,] = Bn_i^2 + B(n_0 + p_0)\Delta n(t)$$
$$= R_0 + R_{excess}$$

| | |
|---|---|
| $R_0$ | equilibrium recombination rate |
| $R_{excess}$ | excess recombination rate |

$$\frac{dn(t)}{dt} = G - R = (G_0 + G_{excess}) - (R_0 + R_{excess})$$

| | |
|---|---|
| $G_0$ | equilibrium generation rate |
| $G_{excess}$ | excess generation rate |

## Carrier Concentration as a Function of Time

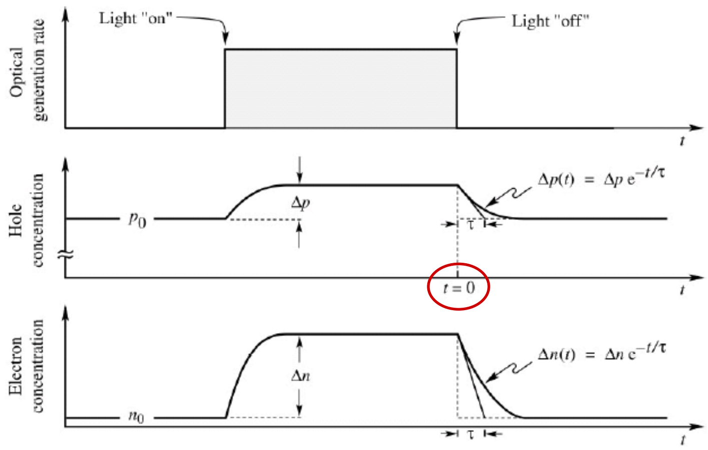



Fig. 2.2. Carrier concentration as a function of time before, during, and after an optical excitation pulse. The semiconductor is assumed to be p-type and thus it is $p_0 >> n_0$. Electrons and holes are generated in pairs, thus $\Delta p = \Delta n$. Under low-level excitation shown here, it is $\Delta n << p_0$. In most practical cases the equilibrium minority carrier concentration is extremely small so that $n_0 << \Delta n$.



## Carrier Lifetime

- **$t = 0$ (light off) ➔ $G_{excess} = 0$**
- **Equilibrium ➔ $G_0 = R_0$**

$$\Rightarrow \frac{d}{dt} n(t) = \frac{d}{dt}\left(n_0 + \Delta n(t)\right) = \frac{d}{dt}\Delta n(t) = -R_{excess} = -B\left(n_0 + p_0\right)\Delta n(t)$$

$$\Delta n(t) = \Delta n_0\, e^{-B(n_0 + p_0)t} = \Delta n_0\, e^{-\frac{t}{\tau}}$$

**carrier lifetime** $\tau = \left[B\left(n_0 + p_0\right)\right]^{-1}$

$$\tau = \frac{1}{B\, p_0} = \frac{1}{B\, N_A} \quad \text{for p-type semiconductors}$$

$$\tau = \frac{1}{B\, n_0} = \frac{1}{B\, N_D} \quad \text{for n-type semiconductors}$$

## Minority Carrier Lifetime

**Minority carriers**

- **Termination of photoexcitation**
  - ➔ **The carrier concentration decays exponentially with a characteristic time constant. (minority carrier lifetime, $\tau$ )**

**Majority carriers**

- **The carrier concentration also decays with the same time constant.**
- **However, only a very small fraction of the majority carriers disappear by recombination.**

***Carrier lifetime can be extracted from minority carrier concentrations.***

***p-type semiconductors ➔ electron carrier lifetime***
***n-type semiconductors ➔ hole carrier lifetime***



## Minority Carrier Lifetime of p-type GaAs

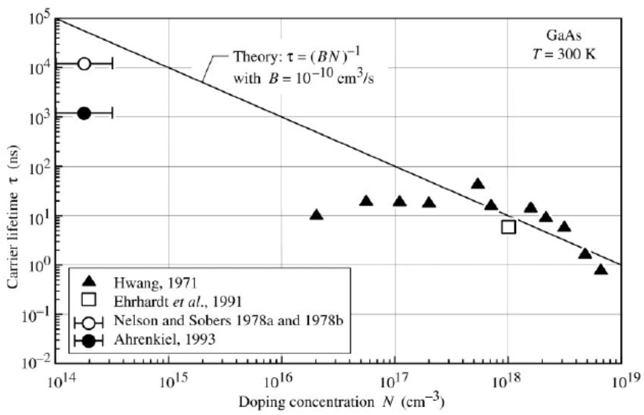



Fig. 2.3. Minority carrier lifetime as a function of doping concentration in GaAs at 300 K. The lifetime was inferred from luminescence decay mesurements. The data points of Nelson and Sobers (1978a and 1978b) and Ahrenkiel (1993) were measured on nominally undoped material with a doping concentration << $10^{15}$ $cm^{-3}$.

- **In nominally undoped materials, minority carrier lifetime as long as 15 μs have been measured in GaAs at room temperature.**

## Radiative Recombination for High-level Excitation

- Electrons and holes are generated and annihilated in pairs.

$$\Rightarrow \quad \Delta n(t) = \Delta p(t) \quad \text{under steady-state}$$

- For the case of high-level excitation, the photogenerated carrier concentration is larger than the equilibrium carrier concentration.

$$\Rightarrow \quad \Delta n \gg (n_0 + p_0)$$

$$R = B[\, n_0 + \Delta n(t)\,][\, p_0 + \Delta p(t)\,] = B\, n_i^2 + B\, \Delta n(t)^2$$

$$\Rightarrow \frac{d}{dt}\Delta n(t) = -B\, \Delta n(t)^2$$

$$\Delta n(t) = \frac{1}{B\,t + \Delta n_0^{-1}} \qquad (\Delta n(0) = \Delta n_0)$$

➔ non-exponential carrier decay



## Carrier Lifetime for High-level Excitation

Low-level excitation

$$\Delta n(t) = \Delta n_0\, e^{-\frac{t}{\tau(t)}}$$

$$\frac{d\Delta n(t)}{dt} = \Delta n_0\, e^{-\frac{t}{\tau}}\left(-\frac{1}{\tau(t)}\right) = \Delta n(t)\left(-\frac{1}{\tau(t)}\right)$$

$$\tau(t) = -\frac{\Delta n(t)}{\frac{d\Delta n(t)}{dt}}$$

: definition of carrier lifetime

High-level excitation

$$\tau(t) = -\frac{\Delta n(t)}{\frac{d\Delta n(t)}{dt}} = t + (B\,\Delta n_0)^{-1}$$

time-dependent carrier lifetime

## Luminescence Decay

- The carrier decay in semiconductors can be measured by the decay of the luminescence after a short optical excitation pulse.
- luminescence intensity $\propto$ recombination rate ( R )

$$R = -\frac{dn(t)}{dt} = \frac{\Delta n_0}{\tau} e^{-t/\tau} \qquad \text{for low excitation}$$

$$R = -\frac{dn(t)}{dt} = -\frac{B}{\left(Bt + \Delta n_0^{-1}\right)^2} \qquad \text{for high excitation}$$

- All non-exponential decay functions can be expressed by an exponential function with a time-dependent time constant.

$$\Delta n(t) = \Delta n_0\, e^{-t/\tau(t)} = \Delta n_0\, e^{-\frac{t}{t+(B\Delta n_0)^{-1}}}$$

➔ stretched exponential function



## Radiative Recombination for High-level Excitation

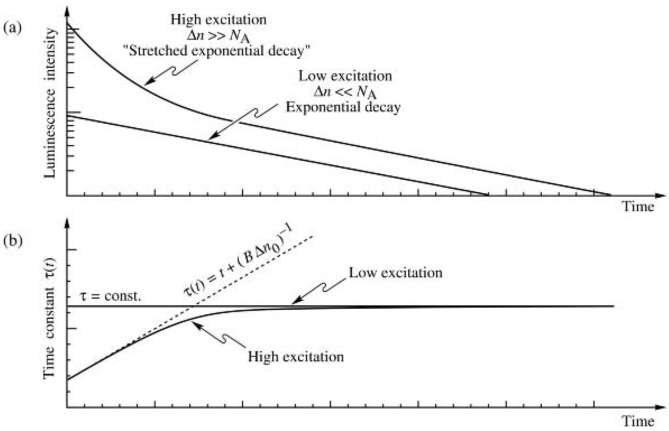



Fig. 2.4. (a) Luminescence decay for low and high excitation density. (b) Time constants for low and high excitation density.

- For sufficient long times, low-level excitation conditions will be reached and $\tau$ will approach the low-level value.

## Non-radiative Recombination in the Bulk

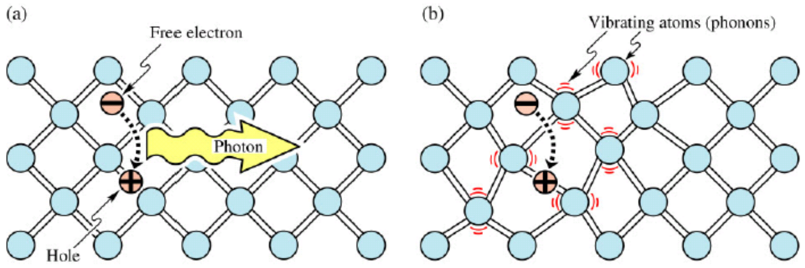



Fig. 2.5. (a) Radiative recombination of an electron-hole pair accompanied by the emission of a photon with energy $h\nu \approx E_g$. (b) In non-radiative recombination events, the energy released during the electron-hole recombination is converted to phonons (adopted from Shockley, 1950).

**Two basic recombination mechanisms in semiconductors**

***Radiative recombination***

**: One photon with energy equal to the bandgap energy is emitted.**

***Non-radiative recombination***

**: The electron energy is converted to vibrational energy of lattice atoms (phonon). ➔ Heat generation**



## Cause for Non-radiative Recombination Events

- **The most common cause for non-radiative recombination events**

**: Defects in the crystal structure**

**foreign atoms – interstitial, substitutional**
**native defects – vacancies, antisite defects, interstitials**
**dislocations**
**complexes of defects**

- **All such defects have energy level structures that are different from substitutional semiconductor atoms.**

**➔ One or several energy levels within the forbidden gap of the semiconductor**

## Electron and Hole Concentrations

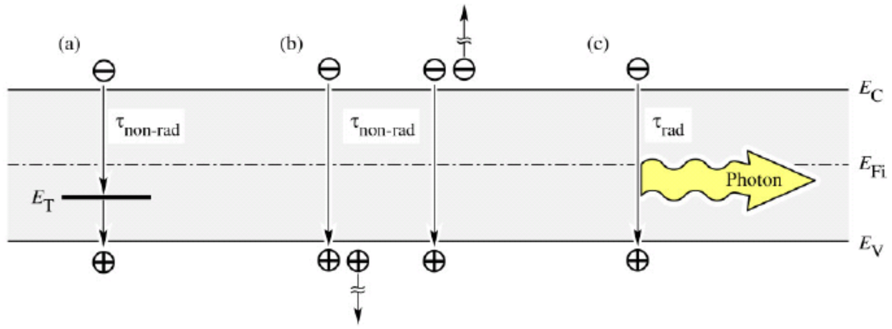



Fig. 2.6. Band diagram illustrating nonradiative recombination (a) via a deep level, (b) via an Auger process and (c) radiative recombination.

(a) Recombination via deep levels

(b) Auger recombination

(c) Radiative recombination



## Electron and Hole Concentrations

| | |
|---|---|
| $E_F$ | energy of Fermi level |
| $E_c$ | energy of lowest conduction band level |
| $E_v$ | energy of highest valence band level |
| $N_c$ | effective density of levels for conduction band |
| $N_v$ | effective density of levels for valence band |
| $n_i$ | density of electrons in an intrinsic semiconductor |
| $n_0$ | density of electrons at equilibrium condition |
| $p_0$ | density of holes at equilibrium condition |

$$n_0 = N_c \exp\left(\frac{E_F - E_c}{kT}\right) \qquad p_0 = N_v \exp\left(\frac{E_v - E_F}{kT}\right)$$

$$n_0 p_0 = N_c N_v \exp\left(\frac{E_v - E_c}{kT}\right) = n_i^2$$

## Electron and Hole Concentrations ( $E_F = E_T$ )

$E_T$ energy of the trap level in the bandgap

$n_1$ density of electrons in the conduction band for $E_F = E_T$
$p_1$ density of holes in the valence band for $E_F = E_T$

$$n_1 = N_c \exp\left(\frac{E_T - E_c}{kT}\right) \qquad p_1 = N_v \exp\left(\frac{E_v - E_T}{kT}\right)$$

$$n_1 p_1 = N_c N_v \exp\left(\frac{E_v - E_c}{kT}\right) = n_i^2 = n_0 p_0$$



## Shockley-Read Recombination

$C_p = N_t v_p \sigma_p$ probability per unit time that a hole in the valence band will be captured at the traps filled with electrons

$C_n = N_t v_n \sigma_n$ probability per unit time that an electron in the conduction band will be captured at the empty traps

$N_t$ : the concentration of the traps
$v_n$ and $v_p$ : the electron and hole thermal velocities
$\sigma_n$ and $\sigma_p$ : the capture cross sections of the traps

The net capture rate of electrons in conduction band

$$R_{cn} = C_n(1 - f_t)n - C_n f_t n_1$$

The net capture rate of holes in valence band

$$R_{cp} = C_p f_t p - C_p(1 - f_t)p_1$$

*Ref) W. Shockley and W. T. Read Physical Review 87, 835 (1952)*

$f_t$ : fraction of traps occupied by electrons

## Shockley-Read Recombination

For steady-state conditions, $R_{cn} = R_{cp} = R_{SR}$

$$f_t = \frac{C_n n + C_p p_1}{C_n(n+n_1)+C_p(p+p_1)} \qquad 1-f_t = \frac{C_n n_1 + C_p p}{C_n(n+n_1)+C_p(p+p_1)}$$

Non-radiative recombination rate by Shockley-Read Recombination

$$R_{SR} = \frac{C_n C_p (pn - p_1 n_1)}{C_n(n+n_1)+C_p(p+p_1)} = \frac{C_n C_p[(p_0+\Delta p)(n_0+\Delta n) - p_1 n_1]}{C_n(n_0+n_1+\Delta n)+C_p(p_0+p_1+\Delta p)}$$

$n_1 p_1 = n_0 p_0 = n_i^2$ ➡

$$R_{SR} = \frac{n_0 \Delta p + p_0 \Delta n + \Delta p \Delta n}{C_n^{-1}(n_0+n_1+\Delta n)+C_p^{-1}(p_0+p_1+\Delta p)}$$



## Non-radiative Lifetime by Shockley-Read

The non-radiative lifetime of excess electrons can be deduced from the equation $R_{SR} = \Delta n / \tau$ (constant recombination rate) and $\Delta n = \Delta p$.

$$\frac{1}{\tau} = \frac{p_0 + n_0 + \Delta n}{C_p^{-1}(n_0+n_1+\Delta n)+C_n^{-1}(p_0+p_1+\Delta p)}$$

When small deviation from equilibrium is assumed,

p-type semiconductor $\Rightarrow$ $p_0 >> n_0$ , $p_1$ and $\Delta n << p_0$

$$\frac{1}{\tau} = \frac{1}{\tau_{n_0}} = C_n = N_t v_n \sigma_n$$

n-type semiconductor $\Rightarrow$ $n_0 >> p_0$ , $n_1$ and $\Delta n << n_0$

$$\frac{1}{\tau} = \frac{1}{\tau_{p_0}} = C_p = N_t v_p \sigma_p$$

## Non-radiative Lifetime of Intrinsic Materials

When we assume $C_n = C_p$ and very small $\Delta n$ and $\Delta p$

$$\frac{1}{\tau} = (N_t v_n \sigma_n) \frac{p_0 + n_0 + \Delta n}{(n_0 + n_1 + \Delta n) + (p_0 + p_1 + \Delta p)}$$

$$= \frac{1}{\tau_{n_0}} \frac{p_0 + n_0}{(n_0 + n_1) + (p_0 + p_1)} \quad \Rightarrow \quad \tau = \tau_{n_0}\left(1 + \frac{p_1 + n_1}{p_0 + n_0}\right)$$

For the special case of intrinsic materials, $\Rightarrow \; n_0 = p_0 = n_i$

$$\tau_i = \tau_{n_0}\left(1 + \frac{p_1 + n_1}{2n_i}\right)$$

$$= \tau_{n_0}\left[1 + \frac{n_i \exp((E_T - E_{Fi})/kT) + n_i \exp((E_{Fi} - E_T)/kT)}{2n_i}\right]$$

$$= \tau_{n_0}\left[1 + \frac{\exp((E_T - E_{Fi})/kT) + \exp(-(E_T - E_{Fi})/kT)}{2}\right]$$

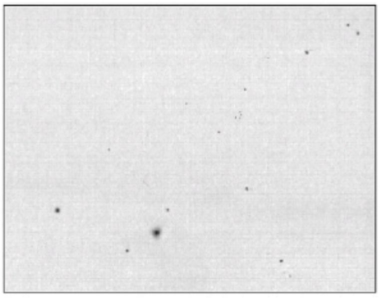


## Non-radiative Lifetime of Intrinsic Materials

$$\tau_i = \tau_{n_0}\left[1 + \cosh\left(\frac{E_T - E_{Fi}}{kT}\right)\right]$$

- When the trap level is at or close to the mid-gap energy ( $E_T - E_{Fi} = 0$ ), the non-radiative lifetime is minimized ( $\tau = 2\tau_{n0}$ ).
  - ➔ Mid-gap levels are effective non-radiative recombination centers.
- As T increases, the non-radiative recombination lifetime decreases.
  - ➔ The radiative band-to-band recombination efficiency decreases at high temperatures.
- Some devices are based on radiative recombination through a deep state. ex) N-doped GaP
  - ➔ The deep-level recombination rate increases with increasing temperature.

# Visualization of Defects



GaAs
$T$ = 300 K
10 μm

Fig. 2.7. Cathodoluminescence micrograph of a GaAs epitaxial layer. The dark spots are due to large clusters of non-radiative recombination centers (after Schubert, 1995).

- **Clusters of defects or extended defects (dislocations)**
  **➔ Luminescence-killing nature**

- **Luminescence in the vicinity of the defects is reduced due to the non-radiative recombination channels.**



# Luminescence from Deep-level Transition

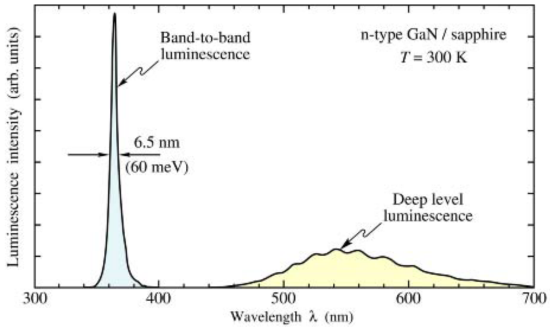



Fig. 2.8. Photoluminescence spectrum of GaN with a band-to-band transition at 365 nm and a second transition at 550 nm which was identified as an optically active deep-level transition (after Grieshaber *et al*. 1996).

- **While most deep-level transitions are non-radiative, some deep-level transitions are radiative.**

- **n-type GaN / sapphire**
  **365 nm : band-to-band transition**
  **~ 550 nm : deep-level transition (related to $V_{Ga}$ )**

## Auger Recombination

- The electron-hole recombination energy ( ~ $E_g$ )

  ➔ Excitation of a free electron high into the conduction band or a hole deeply excited into the valence band

- The highly excited carriers will subsequently lose energy by multiple phonon emission until they are close to the band edge.

$$R_{Auger} = C_p n p^2 \quad \text{p-type semiconductor ( 2 holes + 1 electron )}$$

$$R_{Auger} = C_n n^2 p \quad \text{n-type semiconductor ( 1 holes + 2 electron )}$$

$C_p$ Auger coefficient in valence band
$C_n$ Auger coefficient in conduction band

➔ Owing to the differences in conduction and valence band structure in semiconductors, $C_p$ and $C_n$ are generally different.



## Auger Recombination

- In the high-excitation limit, the non-equilibrium carriers have a much higher concentration than equilibrium carriers.

  $\Rightarrow n \approx p$

$$R_{Auger} = (C_p + C_n) n^3 = C\, n^3$$

$C$ : Auger coefficient
$10^{-28} \sim 10^{-29}$ $cm^6/s$ for III-V semiconductors

$$R_{Auger} \propto n^3$$

➔ Auger recombination reduces the luminescence efficiency at very high excitation intensity.

➔ At low carrier concentrations, the Auger recombination rate is very small and negligible for practical purposes.

## Non-radiative Recombination at Surfaces

### *Band diagram model*

- This model is based on the strict periodicity of a crystal lattice.
- Surfaces are strong perturbation of the periodicity of a crystal lattice.

➔ The modified band diagram at a semiconductor surface. (the addition of electronic states within the forbidden gap)

### *Chemical point of view*

- Atoms at the surface cannot have the same bonding structure as bulk atoms due to the lack of neighboring atoms.
- Some of the valence orbitals do not form a chemical bond. ➔ dangling bonds
- These partially filled electron orbitals are electronic states that can be located in the forbidden gap.



## Non-radiative Recombination at Surfaces

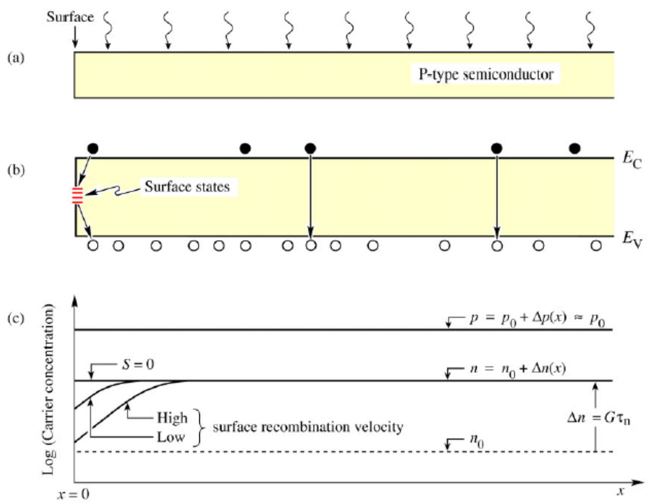



Fig. 2.9. (a) Illuminated p-type semiconductor, (b) band diagram, and (c) minority and majority carrier concentration near the surface assuming unifom carrier generation due to illumination. The excess carrier concentrations are $\Delta n$ and $\Delta p$.

## Surface Recombination

**Assuming**

**p-type semiconductor**

**uniform steady-state generation rate   ex) illumination**

$$n(x) = n_0 + \Delta n(x) = n_0 + \Delta n_\infty \left[ 1 - \frac{\tau_n S \exp(-x / L_n)}{L_n + \tau_n S} \right]$$

**S** surface recombination velocity

***x*** distance from semiconductor surface

$L_n$ carrier diffusion length

| | S |
|---|---|
| GaAs | $10^6$ cm/s |
| InP | $10^3$ cm/s |
| Si | $10^1$ cm/s |

For $S \to 0$ , $n(0) \to n_0 + \Delta n_\infty$

For $S \to \infty$ , $n(0) \to n_0$

**Non-radiative recombination at the surface**

**→ reduced luminescence efficiency & heating of the surface**



## Demonstration of Surface Recombination

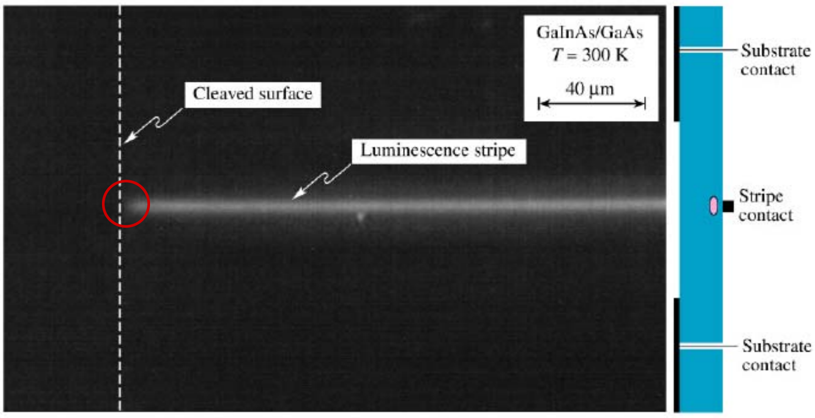



Fig. 2.10. Micrograph of a GaInAs/GaAs structure with a stripe-shaped contact on the top side and a contact widow at the substrate side of the device under current injection conditions. The luminescence emanating from the active region located below the stripe contact clearly decreases in the vicinity of the surface due to surface recombination.

- **The luminescence decreases in the near surface region.**

## Concentration of Native Defects

- Any semiconductor crystal will have some native defects.
  ➔ Even though the concentration of these native defects can be low, it is never zero.

- $E_a$ : energy to create a specific point defect in a crystal lattice

  Probability that such a defect indeed forms at a specific lattice site
  $= exp\,(-E_a / kT)$

- Concentration of specific point defects

$$N_{defect} = N \exp(-E_a / kT)$$

N : concentration of lattice sites



## Internal Luminescence Efficiency

- In the 1960's,
  ~ 1 % of the internal luminescence efficiencies (RT)

- At the present time,
  > 90 % of the internal luminescence efficiency (RT)

  ➔ improved crystal quality
  reduced defect and impurity concentration
  quantum well structures

$$\tau^{-1} = \tau_{rad}^{-1} + \tau_{non-rad}^{-1}$$

- $\tau$ carrier lifetime
- $\tau_{rad}$ radiative carrier lifetime
- $\tau_{non\text{-}rad}$ non-radiative carrier lifetime
- $\eta_{int}$ internal quantum efficiency

Internal quantum efficiency

$$\Rightarrow \eta_{\text{int}} = \frac{\tau_{rad}^{-1}}{\tau_{rad}^{-1} + \tau_{non-rad}^{-1}}$$

*relative probability of radiative recombination*