### ECE 536 – Integrated Optics and Optoelectronics Lecture 4 – January 27, 2022

### Spring 2022

Tu-Th 11:00am-12:20pm Prof. Umberto Ravaioli ECE Department, University of Illinois

# Lecture 4 Outline

- More on Generation-Recombination
  - Surface recmbination
  - Auger processes
  - Impact ionization

• Brief review of Quantum Mechanical concepts

Semiconductor surfaces may be responsible for substantial non-radiative recombination.

Surfaces are interruptions of the periodic crystal so the band structure is modified locally, including electronic states inside the gap.

Because surface atoms lack some neighbors, there are partially filled electron orbitals or **dangling bonds** which may be acceptor or donor like.

*Surface reconstruction* may also occur with structure different from the bulk. Theoretical prediction is difficult.

Consider a p-type semiconductor illuminated to cause uniform steady-state generation rate G. The continuity equation electrons is 1D is



The current density is caused by electrons flowing to the surface. In the bulk, there is no space dependence so the continuity equation is simply G = R at steady-state. The excess carrier in the bulk is simply  $\delta n_{\infty} = G\tau_n$ .

Assuming a diffusion current for the electrons

$$J_n = eD_n \frac{\partial}{\partial x} \delta n(x,t)$$

we have the continuity equation

$$\frac{\partial}{\partial t}\delta n(x,t) = G - \frac{\delta n(x,t)}{\tau_n} + D_n \frac{\partial^2}{\partial x^2} \delta n(x,t)$$

At the semiconductor surface, carriers recombine rapidly due to surface states



At the semiconductor surface, carriers recombine rapidly due to the surface states. The current boundary condition at the surface is

$$eD_n \frac{\partial}{\partial x} \delta n(x,t) \Big|_{x=0} = eS_n \delta n(x,t) \Big|_{x=0}$$

where *S* is the surface recombination velocity. The steady-state solution for the carrier density is

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



Surface recombination leads to reduced luminescence efficiency and also to heating of the surface, which are unwanted effects for electroluminescent devices.

Semiconductor	Surface recombination velocity			
GaAs	$S = 10^6 \text{ cm/s}$			
GaN	$S = 5 \times 10^4 \text{ cm/s}$			
InP	$S = 10^3 \text{ cm/s}$			
Si	$S = 10^1 \text{ cm/s}$			

## Auger non-radiative processes

## Auger Processes

Auger processes involve three particles.

For instance, in Auger recombination, the energy which becomes available through electron-hole recombination ( $\approx E_g$ ) is dissipated by the excitation of a free electron high into the conduction band, or by a hole deeply excited into the valence band.

The highly excited carriers lose subsequently the energy by multiple phonon emission until reaching the band edge.







### Auger – Hole Capture (k-space) С С 1, Η 2' Η H L ~ s S S(d) CHHH process (c) CHLH process (b) CHSH process C = Conduction bandH = Heavy-hole bandL = Light-hole bandS = Spin-orbit split-off band



## Auger Processes

During Auger recombination energy and momentum must be conserved. Because of the different band details, the two Auger coefficients are generally different. The highly excited carriers lose subsequently the energy by multiple phonon emission until reaching the band edge.

$$R_n = C_n n^2 p$$

more likely to occur in n-type

$$R_p = C_p n p^2$$

more likely to occur in p-type

In thermal equilibrium Auger G-R processes balance:

$$R_{n} - G_{n} = C_{n} n_{o}^{2} p_{o} - e_{n} n_{o} = 0$$
$$R_{p} - G_{p} = C_{p} n_{o} p_{o}^{2} - e_{p} p_{o} = 0$$

$$e_n = C_n n_o p_o = C_n n_i^2$$
$$e_p = C_p n_o p_o = C_p n_i^2$$

Total net Auger recombination rate

$$R = R_{n} - G_{n} + R_{p} - G_{p} = \left(C_{n}n + C_{p}p\right)\left(np - n_{i}^{2}\right)$$

# High-excitation limit

When density of excited carriers is much higher than at equilibrium, the Auger rate equations reduce to

$$R = \left(C_n n + C_p p\right) \left(np - n_i^2\right) \approx \left(C_n + C_p\right) n^3 = Cn^3$$

Typical values of the Auger coefficient C for III-V semiconductors are in the range  $10^{-29} - 10^{-28}$  cm<sup>6</sup>/s.

- Auger recombination reduces luminescence efficiency at high excitation intensity or at high carrier injection, due to the cubic dependence on concentration.
- At lower carrier concentrations, Auger recombination rate is low and practically negligible.

## The Auger-droop controversy in LED

The mechanism causing nitride LED to lose efficiency at high power (*efficiency droop*) was identified as Auger recombination in 2007 by Lumileds Co. However, this started a controversy since another cause, leakage of carriers out of the quantum well structure, was proposed as the responsible mechanism.

Various experimental ("Direct Measurement of Auger Electrons ...", Phys Rev Lett 110, 177406, 2013) and theoretical ("Ultrafast Hot Carrier Dynamics in GaN and Its Impact on the Efficiency Droop" Nano Letters, 2017, 17, 8, p. 5013) papers have since supported one hypothesis or the other.

IEEE Spectrum has chronicled for years the debate. The initial paper "The LED's Dark Secret" (2009) is still interesting reading.

### Radiative vs. non-radiative recombination

Even though non-radiative recombination can be reduced, it cannot be eliminated completely.

Additionally, all real crystals will always have native defects which may introduce deep levels acting as traps.

From thermodynamics considerations, if the energy to generate a defect is  $E_a$ , the associate probability is given by the Boltzmann factor  $\exp(-E_a/k_BT)$ .

### Estimate of point defect concentration

Assume a crystal with lattice constant  $a_o = 5.6$ Å and eight atoms per cubic cell. If the energy needed to move a lattice atom into interstitial position is 1.0eV, estimate the density of interstitial defects at room temperature.

$$N_{a} = \frac{8}{\left(5.6 \times 10^{-8}\right)^{3}} = 4.5 \times 10^{22} \text{ atoms/cm}^{-3}$$
$$N_{def} = N_{a} \exp\left(\frac{-1.0}{k_{B}T}\right) \approx 4.9 \times 10^{5} \text{ cm}^{-3}$$

### Radiative vs. non-radiative recombination

Chemical purity is always an issue. The purest III-V semiconductors will still have impurity concentrations on the order of  $10^{12}$  cm<sup>-3</sup>.

Nonetheless, the internal luminescence efficiency has grown from a fraction of 1% up to 90%+ today, because of improved crystal quality and reduced defect/impurity concentrations.

### Internal quantum efficiency of a semiconductor with non-radiative recombination centers

when 
$$n \gg (n_o + p_o)$$
:  
 $(n \approx \delta n)$ 

$$R = An + Bn^2 + Cn^3 = \frac{n}{\tau(n)}$$

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#### intrinsic quantum efficiency



### **Deep Levels**

Deep levels can be caused by *native defects* (vacancies, interstitials), unwanted impurities, dislocations, impurity-defect complexes, and combinations of different defects.

Experimental analysis is often complicated by the fact that deep-levels may also be associated with radiative transitions.

For instance, Ga vacancies are common point defects in GaN, which luminesce with peak in the yellow band.



## **Stimulated Emission**

An incoming photon interacts with an electron causing it to drop to a lower energy level. The energy transfers to the EM field, generating a new photon with phase, frequency, polarization, and direction of travel which are the same as those of the incident photon.

In contrast, spontaneous emission occurs randomly without particular correlation with the ambient EM field.



## **Stimulated Emission**

 $R = v_g g(n) S$ 

where:

S is the photon density (units  $cm^{-3}$ )

 $v_g$  is the group velocity (units cm/s):

$$v_g = \frac{c}{n_g}$$

g(n) is the optical gain (units cm<sup>-1</sup>)  $n_g$  is the group index  $v_g g(n)$  is the "rate of growth"

## Impact Ionization

It is essentially the reverse of an Auger recombination process, but the rate depends upon current densities as opposed to carrier concentrations.

Detailed theoretical analysis is quite difficult because of the need for a full band structure and it has been addressed with Monte Carlo simulation in some materials. Physics of threshold remains fuzzy.

Models are typically semi-empirical with calibration from measurements.





## Net Generation-Recombination rate



Empirical form of ionization coefficients. Both measure the number of generated electron-hole pairs per unit distance.

$$\alpha_n(E) = \alpha_n^{\infty} e^{-(E_{nc}/E)^{\gamma}}$$
  

$$\beta_p(E) = \beta_p^{\infty} e^{-(E_{pc}/E)^{\gamma}}$$
  

$$E_{nc} \text{ and } E_{pc} \text{ are critical fields}$$
  

$$1 \le \gamma \le 2$$

# Suggestions for your "library"

# E. Fred Schubert, *Light-Emitting Diodes*, 2<sup>nd</sup> Edition, Cambridge University Press (2006)

Part of the "Cambridge Core" collection. This is a good comprehensive reference on semiconductor LED with a lot of technical information and advanced applications up to about 15 years ago.

- A. Buckley, editor, *Organic light-emitting diodes* (*OLEDs*), Woodhead Publishing (2013).
- Kalyani, Swart, Dhoble, Principles and Applications of Organic Light Emitting Diodes (OLEDs), Woodhead Publishing (2017)

Available for free download from our digital library.

## Brief Review of Quantum Mechanical concepts

# Discovery of the electron

# Thomson's experiments with cathode rays (1897) and "plum-pudding" model of the atom

The atom is still believed to be a uniformly distributed substance, with electrons stuck in a mass of positive charges

# Rutherford's experiments on gold foil (1909) and first planetary model of the atom (1911)

The atom is described as a mostly empty volume, including a core of protons at the center and orbiting electrons.

## Quantization

**Planck's hypothesis (1901)**: Explains black body radiation assuming that the energy of an atomic oscillator vibrating at frequency v is restricted to quantized values

$$E_n = nh\nu = n\hbar\omega, \quad n = 0, 1, 2, 3\dots$$

Planck's constant

$$h = 6.628 \times 10^{-34} \text{ J/s} (\hbar = h/2\pi)$$

**Einstein's model (1905)**: Provides an explanation of the photoelectric effect using Planck's quantization

# Light quanta

**Einstein's "heuristic point of view toward the emission and transformation of light" (1905)**: introduces the concept of elementary light quanta as indivisible packets.

The term **"photon"** was introduced in **1926** by Gilbert Lewis.

## Simple model of the atom

**Bohr's model (1913)**: Electrons in a planetary atom are restricted to well-defined orbits assuming only quantized values of the angular momentum *L* and of the energy *E*. For the hydrogen atom

$$L_n = m_0 v r_n = n\hbar, \quad n = 1, 2, 3...$$
  
 $E_n = -\frac{m_0 q^4}{2(4\pi \varepsilon_0 n\hbar)^2} = \frac{-13.6}{n^2} (eV)$ 

## Wave-Particle Duality

**de Broglie's hypothesis (1925)**: Since electromagnetic radiation (waves) exhibit particle-like (photon) properties, particles should also exhibit wave like properties. The momentum of a particle (or wave) can be written as:

$$p = m_0 v = \hbar k$$

This parallel between electrons and photons is at the basis of optoelectronics, with the distinction that electrons obey the Fermi-Dirac statistics and photons the Bose-Einstein statistics

# Schrödinger equation

Wave mechanics (1927): A complex wave function  $\Psi(r,t)$  describes elementary particles according to the evolution equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\Psi + V(r)\Psi$$

**Volume Normalization** 

$$\int_{v} \Psi^* \Psi dr^3 = 1$$

probability to find particle in volume *dr*<sup>3</sup>

$$\langle \alpha \rangle = \int \Psi \alpha \Psi^* \mathrm{d}r^3$$

# Particles in crystalline solid

The Schrödinger equation is used to solve the electron wave functions and energy states in crystals. If the expectation value of an electron's total energy is a constant *E*, the Schrödinger equation becomes

$$-\frac{i}{\hbar}\frac{\partial\psi}{\partial t} = E\psi$$

Using separation of variables the wave function can be expressed as

$$\phi(r, t) = \phi(r) e^{-iEt/\hbar}$$
  
space-dependent  
wave function time-varying  
phase factor

### For zero potential solution is a plane wave

- $V(\vec{r},t) = 0$  Volume =  $\Omega$
- $\Psi(\vec{r},t) = \frac{1}{\sqrt{\Omega}} e^{i\left(\vec{k}\cdot\vec{r}-\frac{E}{\hbar}t\right)} = \frac{1}{\sqrt{\Omega}} e^{i\left(\vec{k}\cdot\vec{r}-\omega t\right)}$  $E = \hbar \omega = \frac{1}{2}mv^{2} = \frac{p^{2}}{2m} = \frac{\hbar^{2}k^{2}}{2m}$  $\omega = \frac{\hbar k^2}{2m}$  $p = \hbar k$

### **Time-independent Schrödinger equation**



The time-independent equation is the basis to solve one-electron energy band structure and related problems in crystals.

### Momentum Space representation

Fourier transform of potential and wave function

$$\tilde{\psi}(\vec{\mathbf{k}}) = \int \psi(\vec{\mathbf{r}}) e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} d^3 r$$
$$\tilde{V}(\vec{\mathbf{k}}) = \int V(\vec{\mathbf{r}}) e^{-i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}} d^3 r$$

Momentum-space of Schrödinger equation

$$\frac{\hbar^2 k^2}{2m} \tilde{\psi}\left(\vec{\mathbf{k}}\right) + \int \frac{d^3 k'}{\left(2\pi\right)^3} \tilde{V}\left(\vec{\mathbf{k}} - \vec{\mathbf{k}'}\right) \tilde{\psi}\left(\vec{\mathbf{k}'}\right) = E \tilde{\psi}\left(\vec{\mathbf{k}}\right)$$

### Quantum wells are very important in optoelectronics



Infinite quantum well – The solution in each region has the form of two counter-propagating plane waves

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}$$
, where  $k = \sqrt{\frac{2m^*}{\hbar^2}(E-V)}$ 

The constants A and B are determined by applications of boundary conditions. In Region 1 and 3, *k* is purely imaginary (evanescent wave) and there is only a forward wave in region 3 and a backward wave in region 1. However, because the potential is infinite, there is no wave penetration and the wave function must be zero at the boundaries of the well.

Solution:

$$k = \frac{n\pi}{L} \qquad E_n = \frac{n^2 \pi^2 \hbar^2}{2L^2 m^*}$$

Combination of the two waves give a cosine standing wave for odd integer and a sine standing wave for even integer

$$\Psi(x) = C \cos\left(\frac{\pi}{L}x\right) \qquad \qquad \int_{-\frac{L}{2}}^{\frac{L}{2}} C^2 \cos^2\left(\frac{\pi}{L}x\right) dx = 1, \quad C = \sqrt{\frac{2}{L}}$$

$$\Psi(x) = \begin{cases} \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi}{L}x\right), & n = 1, 3, 5, \dots \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), & n = 2, 4, 6, \dots \end{cases}$$

#### Example

L = 10 nm

 $m = 0.066 m_o$ 



Finite square well



#### **Boundary conditions**

(i) continuity of the wavefunction across the boundary.

(ii) continuity of the electric current across the boundary.

Current carried by one electron

$$I = -qv = -q\frac{m^*v}{m^*} = -q\frac{\hbar k}{m^*} = iq\frac{\hbar}{m^*}\frac{d}{dx}\Psi(x)$$

Boundary condition conserving electric current

$$\frac{1}{m_W^*}\frac{d}{dx}\Psi_{regionII}(x)_{x=\frac{L}{2}} = \frac{1}{m_B^*}\frac{d}{dx}\Psi_{regionIII}(x)_{x=\frac{L}{2}}$$

 $x = \frac{L}{2}$ 

Application of Boundary conditions

$$Ce^{ik\frac{L}{2}} + De^{-ik\frac{L}{2}} = Fe^{-\kappa\frac{L}{2}} \qquad \frac{ik}{m_W^*} \left( Ce^{ik\frac{L}{2}} - De^{-ik\frac{L}{2}} \right) = -\frac{\kappa}{m_B^*} Fe^{-\kappa\frac{L}{2}}$$
$$\frac{ik}{m_W^*} \left( Ce^{ikL} - D \right) = -\frac{\kappa}{m_B^*} \left( Ce^{ikL} + D \right)$$
$$Ce^{ikL} \left( \kappa m_W^* + ikm_B^* \right) + D \left( \kappa m_W^* - ikm_B^* \right) = 0$$

 $x = -\frac{L}{2}$ 

Using the same procedure

$$Ce^{-ikL}(\kappa m_W^* - ikm_B^*) + D(\kappa m_W^* + ikm_B^*) = 0$$

$$Ce^{ikL}(\kappa m_W^* + ikm_B^*) + D(\kappa m_W^* - ikm_B^*) = 0$$
$$Ce^{-ikL}(\kappa m_W^* - ikm_B^*) + D(\kappa m_W^* + ikm_B^*) = 0$$

Solution exists if the determinant of coefficients is zero

The equation gives the energy of the quantized states in the well. It can be solved by numerical iteration to a desired accuracy. It can also be solved graphically.



### Comparison between wells

L = 10 nm

	V <sub>0</sub>	m* <sub>B</sub>	$m^*_W$	E <sub>1</sub> (eV)	E <sub>2</sub> (eV)	E <sub>3</sub> (eV)
Infinite well	$\infty$	_	0.066	0.056	0.223	0.502
Finite well	0.25 eV	0.092	0.066	0.03	0.121	0.245

In many practical situations relevant for optoelectronics, quantum wells have only several energy levels.

In realistic conditions, there is a field across quantum well, due to applied potentials, differences in electron affinity between the heterostructure materials which define the well, and to the charge distribution associated with the wave functions and with ionized impurities, as well.

The time-independent Schrödinger equation should be solved simultaneously with the Poisson equation for a self-consistent solution.

In addition, there may be onset of quantum Stark effect which tends to separate energy levels in confined spaces when an electric field is applied. The energy shift can be calculated by perturbation theory. Example: Voltage drop of 0.1 V across the 10 nm well examined earlier, cause an electric field of 10<sup>5</sup> V cm<sup>-1</sup>.

The estimate for shift in energy caused by Stark effect is about 2 meV.





Transmission coefficient – analytical result for rectangular well

$$T = \frac{1}{\cosh^2(\kappa L) + \left(\frac{1}{4}\right) \left(\frac{\kappa m_1^*}{km_2^*} - \frac{km_2^*}{\kappa m_1^*}\right)^2 \sinh^2(\kappa L)}$$



### Tunneling



the barrier width is 10 nm and the barrier height is 0.25 eV



## Tunneling





## Tunneling





## Tunneling in reverse biased p-n junctions



### Simple model for tunneling current (GaAs)

tunneling current  $J_{Tunn} = nqv_{sat}$  $n = N_V T$  $v_{sat} = 1.2 \times 10^7 \ {
m cm s}^{-1}$ 

 $N_V = 4$  valence electrons/atom × 8 atoms/unit-cell/unit-cell volume =  $1.7 \times 10^{23}$  cm<sup>-3</sup>

transmission coefficient

$$T = \frac{1}{\cosh^2(\kappa L) + \left(\frac{1}{4}\right) \left(\frac{\kappa m_1^*}{km_2^*} - \frac{km_2^*}{\kappa m_1^*}\right)^2 \sinh^2(\kappa L)}$$

(Approximation: this is for a rectangular well. Well is actually triangular)

### Simple model (GaAs)

electrons at the valence band edge have thermal energy

$$E = \frac{3}{2}k_B\overline{T} = \frac{\hbar^2 k^2}{2m^*}$$

where  $\overline{T}$  is the temperature

barrier height  $V_0 = E_g = 1.43 \text{ eV}$ 

approximate average wave vector in the forbidden gap

$$\kappa = \frac{1}{\hbar} \sqrt{2m^* \left( E_g - k_B \overline{T} \right)} \quad \text{and} \quad |\kappa| = 1.4 \times 10^9 \text{ m}^{-1} \gg |k|$$

width of the barrier

$$\mathcal{E} = \frac{E_g/q}{L} = \sqrt{\frac{2qN_DV}{\epsilon\epsilon_0}}, \text{ where } V = V_{Applied} + \phi_{built-int}$$

(Assume one sided junction with  $N_D = 10^{16} \text{ cm}^{-3}$  and reverse bias V=-1 V)

$$L = \frac{E_G}{\sqrt{\frac{2qN_DV}{\varepsilon\varepsilon_0}}} = 2.7 \times 10^{-7} \,\mathrm{m} \qquad \text{Note: } \kappa L \gg 1$$

Simple model (GaAs)

set effective masses  $m_1^*=m_2^*=m^*$ 

approximate transmission coefficient since  $\kappa L \gg 1$ 

$$T = \frac{1}{\cosh^2(\kappa L) + \left(\frac{1}{4}\right) \left(\frac{\kappa m_1^*}{km_2^*} - \frac{km_2^*}{\kappa m_1^*}\right)^2 \sinh^2(\kappa L)} \cong 16e^{-2\kappa L} \left(\frac{k\kappa}{k^2 + \kappa^2}\right)^2 \cong 16\left[\frac{k}{\kappa}\right]^2 e^{-2\kappa L}$$

also

$$\kappa L = \frac{E_G}{\hbar} \sqrt{\frac{2m^* E_G \varepsilon \varepsilon_0}{2qN_D V}} = C_0 V^{-\frac{1}{2}} \qquad \left(\frac{k}{\kappa}\right)^2 \cong \frac{3k_B \overline{T}}{2E_g}, \text{ where } \overline{T} \text{ is the temperature}$$

finally

$$T \cong 16 \left(\frac{3k_B\overline{T}}{2E_g}\right) e^{-2C_0 V^{-\frac{1}{2}}}$$

$$J_{tunneling} \cong 16N_V q v_{sat} \left(\frac{3k_B \overline{T}}{2E_g}\right) e^{-2C_0 V^{-\frac{1}{2}}} \operatorname{amps-cm}^{-2}$$

## Result from a simple tunneling model



### **Density of States**

$$g(E) \propto (E - E_0)^{d/2 - 1}$$
  
 $d = 1, 2, \text{ or } 3$ 





### 1D Density of States



$$k = \frac{\sqrt{2m^*E}}{\hbar} \qquad dk = \frac{\sqrt{2m^*}}{\hbar} \frac{dE}{2\sqrt{E}}$$



(length of increments dk)



(# allowed k-states per unit length)

$$g(k)dk = \frac{2dk}{2\pi} = \frac{dk}{\pi}$$
$$\frac{2dk}{2\pi} = \frac{1}{\pi} \frac{\sqrt{2m^*}}{\hbar} \frac{dE}{2\sqrt{E}} = g(E)dE$$

$$\implies g(E) = \underbrace{2}_{\text{spin}} \cdot \frac{1}{\pi} \frac{\sqrt{2m^*}}{\hbar} \frac{1}{2\sqrt{E}} = \frac{\sqrt{2m^*}}{\pi \hbar} \frac{1}{\sqrt{E}}$$

## **Reading Assignments**

Chapter 3 of the book by Chuang.