Luminescence basics

• Types of luminescence
  – Cathodoluminescence: Luminescence due to recombination of EHPs created by energetic electrons. Example: CL mapping system
  – Photoluminescence: Luminescence due to recombination of EHPs created by energetic photons. Example: PL mapping system
  – Electroluminescence: Luminescence due to recombination of EHPs created by injected electrons and holes. Example: LEDs, Lasers
  – Chemiluminescence: Luminescence due to light energy obtained from chemical energy. Example: Luminescence in deep sea-water fishes, Mg burning in air

• Emission wavelength is $\frac{hc}{(E_1 - E_2)}$, where $E_1$ and $E_2$ are the initial (higher energy) and final (lower energy) states

• Visible range: 0.4 – 0.7 µm corresponding to energy of 3.1 – 1.77 eV

We are lucky that common semiconductors have bandgaps which cover entire visible range, so solid state light emitting devices are very useful
Photo-Luminescence measurement system

- An UV laser is used as the excitation source (for III-Nitrides)
- The chopper is used for averaging to reduce noise
- The cryostat helps to go to a lower temperature
- The monochromator helps to select wavelength of the luminescent light
- The detector converts light signal into electrical signal with a large gain
- The power meter is used to measure the electrical signal for each wavelength and give an output of intensity vs. wavelength
Hydrogenic model of doping impurities

- For acceptors the effective mass is higher than donors so the acceptor energies are higher.
- When the concentration of impurity increases so that the average distance between atoms is twice the orbital radius of an excited state then they produce banding.
- Donor and acceptor energies usually increase for higher bandgap as effective mass increases. This explains why activation energy for p-GaN is lower than in p-AlGaN.

\[
E_C - E_D = E_A
\]

Radius: \( r = 0.529n^2 (\varepsilon m_0 / m^*) \)

For GaN, \( r = 22.85 \, \text{Å} \)

Energy:

\[
\Delta E_{D,n} = E_C - E_{D,n} = \frac{13.6}{n^2} \frac{m^*}{\varepsilon^2 m_0}
\]

For GaN \( E_D = 33.15 \, \text{meV} \)

(Similar calculation for \( E_a \))

Values calculated for effective mass of 0.22 \( m_e \) and \( n = 1 \)
Hydrogenic model for excitons

Exciton definition: An electron in the conduction band and a hole in the valence band coming together in real space and revolving around their common center of mass is called an excitonic pair or simply exciton.

- Excitonic transitions are only observed for very pure material and at low temperature. At higher temperature the excitonic pair breaks down due to thermal energy. At higher impurity level the ionized impurity screens the electric field and formation of excitons becomes difficult.
- Excitons do not contribute to the carrier conduction as it does not have a net charge.
- Excitons can be either free, or bound to neutral or charged donors and acceptors.

Bound exciton

\[ E_{\text{ex}}^{\text{bind}} = -\frac{13.6}{n^2} \frac{m_{\text{red}}^*}{m_0} \frac{1}{\varepsilon^2} \]

\[ r = 0.529n^2(\varepsilon m_0 / m_{\text{red}}^*) \]

where \[ \frac{1}{m_{\text{red}}^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \]
Radiative transitions in semiconductors

- Process 1: Intraband transition
- Process 2: Band-to-band transition
- Process 3: Excitonic transition
- Process 4: Valence band to donor transition
- Process 5: Conduction band to acceptor transition
- Process 6: Shallow donor to shallow acceptor transition

Others: Donor to conduction band, acceptor to valence band
Intraband and interband transitions

Process 1: Intraband transitions

Hot electrons relax their energy mainly by emitting phonons, but sometimes under phonon’s or/and other electron’s assistance can also emit photons. This mechanism is truly rare, as many particles are involved.

Process 2: Band-to-band transitions

Peak of the emission spectrum $\lambda \approx \frac{hc}{E_g}$

Direct bandgap: $\alpha(E) = A_0 (E - E_g)^{1/2}$

Indirect bandgap: $\alpha(E) = \frac{A(E - E_g \pm E_p)^2}{\exp\left(\frac{\mp E_p}{KT}\right) - 1}$

$\alpha$ = absorption coefficient,
$E_p$ is the phonon energy. Intensity proportional to $\alpha$.
+ve and –ve signs are for absorption and emission.
Other radiative transitions

Process 3: Excitonic transitions

For free excitons: \( h\nu = E_g - E_{\text{ex}}^{\text{bind}} \)

For bound excitons: \( h\nu = E_g - E_{\text{ex}}^{\text{bind}} - E_b \)

\( E_b \) is the energy binding the exciton to the donor or acceptor

Process 4 and 5: Free-bound transitions

For \( D^0h \): \( h\nu = E_g - E_D \)

For \( A^0e \): \( h\nu = E_g - E_A \)

Process 6: Donor-acceptor pair transitions

\[ h\nu(r) = E_g - (E_A + E_D) + \frac{e^2}{4\pi\varepsilon r} \]

where \( r \) is the distance between the donor and acceptor
Variation of PL with temperature and doping

• With increase in temperature:
  – Lattice spacing increases so bandgap reduces, peak shift to higher wavelength

\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \]

  – Full width at half maximum increases due to increased lattice vibrations
  – Peak intensity usually reduces

• As doping increases
  – PL peak blueshifts due to band filling
  – FWHM can increase due to thicker band of states from which transition can be made
  – Intensity will also increase by enhancing the probability of radiative recombination
**Variation due to other factors**

- **Strain**: Bandgap varies with strain as the lattice spacing changes.
- **Electric field**: Reduction in effective bandgap due to enhanced probability of tunneling.
- **Excitation intensity**: Variation of the luminescence peak energy, same effect as increasing doping.

---

Fig. 10. Exciton spectra of Al$_{0.24}$Ga$_{0.76}$As recorded at various excitation densities ($P$). The relative gain used to record each spectrum is given on the left. The linewidth of the separate ($D^0, X$) peak (FWHM) of each spectrum is given on the right.
**GaN PL spectrum**

Typical room temperature PL of GaN

![GaN PL spectrum](image)

- $I_2$ is the neutral donor bound recombination. A and B are free exciton lines associated with the A and B hole bands.
- $D^0A^0$ is donor-acceptor (residual, background) pair recombination.
- The “LO” refers to phonon replicas of the particular transitions, at multiples of ~90 meV lower energies (could be zone center phonons).

**PL variation with temperature**

![PL variation with temperature](image)

$E(T)(eV) = E(0) - 8.87 \times 10^{-4}T^2/(T + 874)$

FIG. 1. Typical temperature dependence of the luminescence spectra of high quality undoped GaN. The spectra have been shifted vertically for clarity. The sample is grown by MOVPE.
Variation with Al alloy composition in AlGaN

For bulk AlGaN the bandgap variation is accurately reflected in the PL spectrum, however it is not true for AlGaN/GaN heterostructures where due to stark effect there is a red shift. So Al composition calculated from PL peak position is NOT totally accurate.

77K PL spectra of Al$_x$Ga$_{1-x}$N ($x=0.11$-$0.60$) films grown on the 6H-SiC substrates.
PL spectrum for non-polar QW

- With increasing well width
  - The intensity increases due to increased confinement
  - The peak position shifts to lower energy due to reduction in quantum size effect (QSE) i.e. splitting of energy levels in a QW
  - The full width at half maximum (FWHM) $\sigma$ also decreases

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2m_e(m_h)L^3}, \quad \delta E_n = -\frac{\hbar^2 \pi^2 n^2 \delta L}{2m_e(m_h)L^3}, \quad \sigma = \frac{\hbar^2 \pi^2}{\mu L^3 \Delta L},$$

Fig. 3. PL spectra (77 K) from GaAs/AlAs QWs grown on (411)A under V/III:Al pressure ratio of 7, 12, 17.
Nitride QW PL spectrum

Electron and hole wave-functions for non-polar material

Electron and hole wave-functions for polar material due to built-in electric field

- With increase in well thickness
  - Intensity decreases due to reduced overlap due to quantum confined stark effect (QCSE)
  - Energy decreases due to quantum size effect (QSE), and by lowering of energy gap between the energy states
**PL as indicator of material quality**

- Better quality of epilayers means higher intensity and narrower FWHM
- Also true for quantum wells where the interface fluctuations control the FWHM of PL peaks
- AlGaN epilayers grown on superlattice (SL) buffered GaN layers produces the best quality