Lecture 16: Light emitting diodes

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1 Introduction

Optoelectronic devices are generally divided into two main categories. Those that convert electrical current to electromagnetic radiation (light) and those that convert light into electrical current. Light emitting diodes (LEDs) belong to the first category of devices. Only a small portion of the electromagnetic radiation is traditionally accessible by electronic devices. This lies in the near-IR, visible, and UV region of the spectrum, shown in figure 1.

Figure 1: Portion of the EM spectrum from IR to UV, including the visible region. The various colors in the visible region along with the sensitivity of the human eye to those colors are plotted. Most LEDs operate in the visible region, while the ones in IR and UV are used for optical communication.
LEDs belong to the general class of luminescent devices. Luminescence is defined as the optical radiation due to electronic excitation. When the excited system goes back to the ground state energy is emitted in the form of EM radiation. There are different types of luminescence, depending on how the electronic excitation is originally created:

1. Photoluminescence - electronic excitation is created by incident light
2. Cathodoluminescence - electronic excitation is created by an electron beam
3. Radioluminescence - electronic excitation is created by ionizing radiation (β-rays)
4. Electroluminescence - electronic excitation is created by an electrical field.

LEDs usually work by electroluminescence. Electric current, i.e. electron and holes, are passed to the device by an applied bias. These electrons and holes recombine to emit light.
2 Radiative transitions

In LEDs, electroluminescence (EL) is created by injected carriers, e.g. in a \( pn \) junction. These recombine to give photons. EL occurs in both direct and indirect band gap semiconductor, though the efficiency of radiative transition is higher in a direct band gap semiconductor. EL was first discovered in 1907, but significant advances in practical device development were made after the discovery of \( pn \) junctions in 1949. Optical efficiency improved after GaAs was used in 1962. LEDs depend on recombination of electrons and holes. There are 3 main mechanisms of this recombination

1. Interband transitions
2. Defect transitions
3. Intraband transitions

These are summarized in figure 2. Not all these transitions are radiative. In LEDs the radiative transition must be maximized relative to the non-radiative transition. This can be accomplished by choosing the right materials and the right external bias.
Figure 2: Various mechanisms of electron-hole recombination in semiconductors. (a) Interband transitions (b) Band to localized defect states transitions (defect transitions) (c) Intraband transitions. Not all of these recombination mechanisms can produce light.
3 \textit{pn} junction LEDs

The basic structure of the LED is the \textit{pn} junction. A \textit{pn} junction under equilibrium and forward bias is shown in figure 3. In this figure, the \textit{n} region is heavily doped so that the depletion width lies mostly in the \textit{p} side. At equilibrium the Fermi levels line up and there is a built in potential. When a forward bias is applied, electrons and holes are injected into the depletion region. These recombine, and radiation is emitted whose wavelength depends on the band gap of the \textit{p} type material. This is called \textit{injection EL}. Recombination is a \textit{statistical spontaneous process} and emission takes place in all directions.

![Figure 3: pn junction LED at (a) equilibrium and (b) forward bias.](image)

In equilibrium there is a depletion region and a built in potential. In forward bias, this potential is reduced and electrons and holes are injected into the depletion region. These can recombine to produce light, an example of interband transitions.
When the $pn$ junction is made of the same material then it is called a homo junction. If we can confine the electrons and holes to a small region (like a potential well) then it is possible to increase radiative recombination efficiency. This can be achieved by using a heterojunction. The difference in band alignment between a GaAs based homo junction and GaAs-AlGaAs heterojunction LED is shown in figure 4.

Figure 4: GaAs based (a) homo junction and (b) heterojunction. The heterojunction has a higher quantum efficiency since the carriers are localized in GaAs. Thus, recombination occurs only in the i-GaAs region. For both LEDs, the emitted wavelength is the same because it is related to GaAs energy gap.
3.1 Double heterostructure LED

Heterostructure LEDs are used to increase the efficiency by confining the carriers (electrons and holes) in a small spatial region. Consider a LED formed by using AlGaAs and GaAs. The structure of this device is shown in figure 5. AlAs is an indirect semiconductor with a band gap of 2.16 eV and GaAs a direct band semiconductor with a gap of 1.42 eV. Al$_x$Ga$_{1-x}$As, formed by substitutional doping of Ga with Al, is a direct band gap for $x < 0.4$ and its band gap depends on $x$, given by $1.43 + 1.247x$. For $x > 0.4$, this becomes an indirect band gap semiconductor. For the heterostructure junction shown in figure 5 the band gap of AlGaAs is 2.0 eV, which corresponds to $x = 0.45$. Two heterostructure junctions are formed in this device. At equilibrium the Fermi levels line up and the depletion region lies mostly in the GaAs region, which is lightly doped.

When a forward bias is applied, electrons and holes are injected into the depletion region (GaAs) where they recombine radiatively, with energy equal to the band gap of GaAs. The wide band gap AlGaAs acts as confining layers for the carriers. The double heterostructure device is usually fabricated in such a way that emission takes place from one surface. This is shown in figure 6. This is usually accomplished by suitable deposition of the electrical contacts. Another example of a double heterostructure system is GaAs$_{1-x}$P$_x$ with GaAs.
Figure 5: Double heterostructure based LED. (a) Device structure, with a single pn heterojunctions and a p-p isojunction (b) Equilibrium band diagram, with the built-in potential at the pn junction (c) In forward bias electrons and holes are injected in the GaAs (d) Light emission, with wavelength depending on the band gap of GaAs.
Figure 6: Double heterostructure device structure with (a) surface or (b) edge emission. For surface emission, the top layers are made thin and have low absorption for the emitted radiation. For side emission optical cladding layers are used to confine the light to the emitting layer. A similar principle is also used in solid state lasers.
4 LED line width

Light emission in the LED is from band to band transitions i.e. from conduction to valence band. These band transitions also involve thermal fluctuations which cause a slight deviation in the energy of the carriers and are responsible for the finite width of the LED emission. Consider light emission in a LED. The energy of the radiation is given by

\[ h\nu = (E_c + \frac{\hbar^2 k^2}{2m_e^*}) - (E_v - \frac{\hbar^2 k^2}{2m_h^*}) \]

This is called a \textit{joint dispersion relation} and \( m_r^* \) is called the \textit{reduced effective mass} given by

\[ \frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \]

It is also possible to define a \textit{joint density of states function} using the approximation of a particle in a three dimensional box. This gives the density of available states, in the conduction band, as

\[ g(E) = \frac{4\pi (2m_r^*)^2}{\hbar^3} \sqrt{E - E_g} \]
For electrons and holes at the band edges, these are located far away from the Fermi level and it is possible to approximate the Fermi function by the Boltzmann distribution. This is given by

\[ p(E) = \exp\left(-\frac{E}{k_B T}\right) \]  

(4)

The spontaneous emission rate is then given by the product of the density of available states, given by equation 3, with the occupation probability, given by equation 4. This can be written as

\[ I (E = h\nu) \propto \sqrt{E - E_g} \exp\left(-\frac{E}{k_B T}\right) \]  

(5)

This is represented graphically in figure 7. The peak of the spectrum is located at \( E_g + \frac{k_B T}{2} \) and the line width (full width at half maximum) is given by

\[ \Delta \lambda = \frac{1.8k_B T \lambda^2}{hc} \]  

(6)

\( \lambda \) is Wavelength related to \( E_g \)

The line width for emission in the center of the visible spectrum (\( \lambda \) is 400 nm) at room temperature is approximately 6 nm. This broadening is due to thermal effects. With decrease in temperature, the line width decreases, since \( T \) is in the numerator in equation 6. GaAs emission width as a function of temperature is shown in figure 8.
Figure 7: Theoretical line width in a LED. The line width is determined by two opposing functions, the density of available states, which increases as the square root of the energy and the occupation probability that decreases exponentially with energy. As temperature increases line width increases, since the occupation probability increases while density of states is unchanged.

Figure 8: (a) PL spectrum from a GaAs LED, at two different temperatures. The spectrum shows a narrowing at lower temperature. (b) Plot of the photon energy vs. temperature showing the peak shift to higher wavelengths (lower energy) with increase in temperature. Due to lattice expansion there is a reduction in band gap with temperature.
5 LED materials

The commonly used LED materials are shown in figure 9. LEDs are made of direct band gap semiconductors and since the visible region lies above energy of 1.8 $eV$, materials with band gap above this value are chosen. Most the commonly used LEDs are based on the GaAS system. GaAs is a direct band gap semiconductor, but its band gap lies in the IR region (1.42 $eV$).

Figure 9: A graphical representation of some commonly used LED materials and the their band gap ranges. This is superimposed on top of the visible region of the EM spectrum. Adapted from Physics of semiconductor devices.
So higher band gap materials like AlGaAs, GaAsP, GaP (indirect band gap semiconductor) are used with suitable substitutional doping to ‘tune’ the band gap to the required value. Typical materials that operate in different regions of the EM spectrum are enumerated below.

1. **AlGaAs** - While AlAs is an indirect band gap semiconductor, AlGaAs for Al < 0.45 is a direct band gap semiconductor. This is typically used in the infra red and red regions of the spectrum. AlGaAs can be directly grown on GaAs substrates.

2. **InAlGaP** - this covers a wider region in the visible spectrum, from red to green. This is due to the higher band gap of the base GaP system i.e. 2.3 eV. But GaP is an indirect band gap semiconductor so there is only a limited composition region. This also limits the maximum energy of this system. GaP based devices can also be grown on GaAs substrates, due to the low lattice mismatch.

3. **InGaN** - this is a higher band gap LED that covers the green, blue, and violet region of the spectrum. Due to lattice mismatch this cannot be grown on GaAs but usually sapphire, SiC, or GaN is used as a substrate. The substrate cost increases the overall cost of the device.
4. GaAsP - this covers the middle of the visible region to the IR region of the spectrum. It is similar to the AlGaAs system and can be grown.

Most of the LED materials are grown by a vapor deposition process as thin films on suitable substrates. Typically, chemical vapor deposition (CVD) is used for the film growth. Variations of CVD, like plasma enhanced CVD (PECVD) or low pressure CVD (LCVD) are also employed. Achieving the right growth conditions to get the exact stoichiometry and microstructure is challenging. This is one of the reason that LED materials are chosen so that growth can be performed on GaAs, since it is one of the few compound semiconductors with extensive background literature along with lower substrate cost. For growing very thin layers, especially on lattice mismatched substrates, atomic layer deposition (ALD) is used. ALD is a variation of the CVD process where the precursors are introduced one at a time to form an atomically thin layer on the substrate. ALD can be used for precise control of the process but it is very slow since growth happens layer-by-layer.

Physical vapor deposition techniques like sputtering and e-beam evaporation are also used for growing LEDs. Pulsed laser deposition (PLD) is used for systems with complex stoichiometry and where preserving this is essential to get the right emission wavelength. The disadvantage of physical vapor deposition is that it produces polycrystalline films and there are usually a lot of defects in the film. These defects can reduce device efficiency by causing non-radiative recombination and some post deposition annealing is usually needed to eliminate them. Each of the growth techniques have their own advantages and disadvantage and the cost and overall ease dictates the choice. Safety is a paramount issue since many of the gases used in CVD (especially the As based ones) are poisonous.
7 Organic LEDs

Organic LEDs or OLEDs, as they are more commonly known, are a new class of materials where the emissive layer is an organic compound sandwiched between two electrodes. The structure of an OLED device is shown in figure 10.

Organic or polymer materials are used in OLEDs and they work on a similar principle to solid state LEDs. Carriers are injected into the active emissive layer, where they recombine and emit light. For organic molecules, instead of valence and conduction bands, there are discrete electron energy states called **HOMO** (highest occupied molecular orbital) and **LUMO** (lowest unoccupied molecular orbital) and recombination occurs across these levels. The color of the radiation depends on the energy gap between these two levels. Usually, the anode is a transparent material like Indium Tin oxide (ITO) so
that the light emitted can be extracted out of the device. The cathode is usually a reflective material, like a metal film, and is deposited on the substrate.

Commonly used organic materials in OLEDs are organometallic chelates and fluorescent dyes. An example is Alq$_3$ which stands for Tris (8-hydroxyquinolinato) aluminum and has the chemical formula Al($C_9H_6NO$)$_3$. The formula is shown in figure 11. The organic material is thermally vapor deposited on substrates of choice. The advantages of OLEDs are that they can be used to form flexible displays by depositing on suitable substrates. The devices are light weight, have wider viewing angles, and a faster response time. However, OLEDs are costly, and have a short lifespan due to degradation of the organic layer. The color balance, especially in the blue region, is not good and they are susceptible to water damage and consume more power than solid state LEDs.

Figure 11: Crystal structure for Alq$_3$ that is commonly used in OLEDs as the emissive layer.