Lab 3: Light Emitting Diodes

Laboratory Goals
In this week’s lab you will:
- fabricate a circuit containing a light emitting diode (LED)
- investigate the effect of chemical composition and temperature on the emission properties of LEDs.

Introduction
Light-emitting diodes (LEDs) are used in a wide range of applications as compact and efficient light sources. Unlike incandescent sources, which emit a broad range of visible and infrared frequencies according to the spectrum of a blackbody at the high temperature of the glowing filament, LEDs emit light only over a narrow spectrum corresponding to the band gap of the semiconductor material that is used as the active component. Accordingly, LEDs emit useful visible light much more efficiently than is possible for ordinary light bulbs.

In this laboratory, you will construct a circuit that can be used to drive a set of LEDs with different semiconductor compositions. The effects of the composition and temperature on the emission spectrum of the LEDs will be observed and recorded visually and using the Ocean Optics spectrograph/CCD detector system. The wavelength of light emitted is related to the band gap. Changes in the band gap, due to changes in orbital overlap from composition and structure, will then result in changes in the emitted light.

Background Reading
There is a good section on the band theory for materials in Kotz, Treichel and Weaver, supplemental section on materials (pages 643-655), which may be helpful to read prior to coming to the laboratory. Section 3 in Chapter 1 of What Science Is and How It Works by Derry describes the efforts to understand the motion of electrons in solids using quantum mechanical models that ultimately led to the discovery of band structure in solids. Below is a partial summary of the process.

Theory
As shown in some of the earlier laboratory exercises in this course, molecules and atoms emit light at wavelengths corresponding to the transition energies between a pair of energy levels. These energy levels arise from the molecular or atomic orbitals that are resident on single molecules or atoms. In crystals, however, the energy levels arise from a vast number of interacting atoms, which are arranged in repeating sequences according to the structure of the crystal. In a real sense, a single crystal of NaCl can be considered as an enormous single molecule. The overlapping atomic orbitals in a crystal lead to delocalized orbitals that extend over the entire crystal. These delocalized molecular orbitals tend to congregate around certain energies and in practice merge into bands. Whereas the energy levels of an atom or molecule are sharp, being at discrete energies,
the bands of a crystal are a continuum of energies (see Figure 1). These bands are the origin of the high electrical conductivity of metals. The electrons in a metal are only weakly associated with the nuclei; in a way, bonding in metals can be described as a sea of delocalized and mobile valence electrons that serve to hold the positively charged metal nuclei together. The delocalized orbitals permit electrons to move from one part of the crystal to another, so that an electrical impulse is transmitted across the material.

Not all materials conduct electricity as well as metals. Insulators have very low electrical conductivity compared to metals, and semiconductors conduct electricity well only in the presence of an electric field. The conductivity ($\sigma$) is the current density in $\text{A/m}^3$ established in a solid when an electric field of 1 $\text{V/m}$ is applied. The quantity that is typically measured is resistance ($R$), not conductivity or its reciprocal, resistivity ($\rho$). The resistance of a wire is related to the conductivity or resistivity by the equation $R = L / (\sigma A) = \rho L A$, where $L$ represents the length of the wire and $A$ is the cross-sectional area. Over the range of materials that is known, the conductivity varies over thirty orders of magnitude (see figure 1).

The high conductivity of metals arises from the partial occupancy of the upper or conduction band by the valence electrons. Figure 2 shows in a schematic way how insulators and semiconductors differ from metals. In an insulator, the conduction band is essentially empty. The band gap, the energy gap between the valence and conduction bands, is large enough that very few electrons can be promoted thermally from the valence band to the conduction band. A semiconductor, on the other hand, has a small enough band gap that thermal promotion of electrons to the conduction band is possible. Lastly, the band gap for metals is small enough that the valence band overlaps somewhat with the conduction band, allowing electrons in the valence band to occupy the
The conduction band directly.

One can distinguish between metals and semiconductors by characterizing the temperature dependence of the electrical conductivity. Metals exhibit a conductivity decrease with increasing temperature; conversely, the electrical conductivity of semiconductors increases. On an atomic level, electrical resistance in all conducting materials arises from free electrons being scattered by the vibrating nuclei. As the temperature increases, nuclei vibrate with both higher frequency and greater amplitude, which in turn increases the incidence of electron scattering, thus decreasing the conductivity. In both metals and semiconductors, the number of conduction electrons also increases with temperature. However, the increase in conduction electrons in metals with temperature is relatively small and is overshadowed by the increased scattering of electrons by the vibrating nuclei. In semiconductors, the increase in the number of charge carriers (electron-hole pairs) with temperature has a greater effect leading to increased conductivity.

**What affects band gap?**

The magnitude of the band gap depends mostly upon the degree of overlap between orbitals on adjacent atoms. As the internuclear separation increases, the orbital overlap decreases, and thus the splitting between the bonding (valence) and antibonding (conduction) bands decreases. (How would this affect the energy of the light emitted?) The internuclear separation in a crystal is controlled by the size of the unit cell, the repeating structure that forms the crystal. As one goes down the periodic table, the unit cell size increases owing to expansion of the atomic radius. As an example, the unit cell’s lattice constant (the spacing between adjacent repeating units) for crystals formed from Si is 5.43 Å; and 5.66 Å for crystals formed from Ge, (the element below Si in the periodic table…ack! Periodic trends coming back to haunt you.) Accordingly, the band gap corresponds to an 1100-nm photon (or 1.1 eV of energy) for Si and a less energetic 1900-nm photon (0.66 eV) for Ge.

It turns out that it is possible to form solid solutions of materials that have
comparable crystalline structure and atoms of comparable size. An especially important type of solid solution is the mixture of the so-called zinc blende semiconductors GaAs and GaP. These solutions exhibit tunable band gaps that depend on the relative composition of the components. The zinc blende structure is one resembling that of ZnS, in which the anion S$^{2-}$ forms a face-centered cubic arrangement and the cation Zn$^{2+}$ occupies half of the tetrahedrally shaped holes (see figure 3). A large number of compounds isoelectronic to pure Si or pure Ge with the stoichiometry called AZ form this type of structure; for instance, the series BN, AlP, GaAs, CdSe, and AgI illustrate the sequence of isoelectronic pairs of elements that are centered on the group IV elements C, Si, Ge, and Sn in the periodic table. Because As has a larger atomic radius than P, the lattice constant is 5.65 Å for GaAs compared to 5.45 Å for GaP. By mixing GaP and GaAs in different relative compositions to form solid solutions, one obtains a material in which the lattice constant can be linearly tuned from 5.65 Å to 5.45 Å, with a resulting scan of the band gap from 1.4 eV (a 890-nm photon) for pure GaAs to 2.3 eV (a 540-nm photon) for pure GaP.

In semiconductors like GaAs or GaP, it is possible to determine the band gap energy by observing the emission of light that arises as electrons promoted to the conduction band by an electric field (from a battery or other source of electrical potential energy) drop into holes created in the valence band. The recombination of a conduction electron with a hole in the valence band usually results in the emission of a photon of the energy. (Keep in mind that this energy can also be released as an increase in vibrational, or heat, energy.). The emission spectrum of an LED constructed from GaAs, GaP, or a mixture of the two is typically narrow (though not nearly as narrow as an atomic emission line). Even though electrons can be created well above the bottom edge of the conduction band and holes can be created well below the top edge of the valence band, the electrons and holes rapidly come to the band edge by dissipating the excess energy as vibrational energy, which effectively raise the temperature of the crystal. So the electron-hole recombination emission occurs at a photon energy that is nearly equal to the band gap. Some LEDs emit multiple emission peaks; these LEDs have been doped with impurities in order to optimize the efficiency of the conversion of electrical energy into light.

**Construction of an LED Circuit**
In this laboratory you will construct a simple electronic circuit that is capable of driving an LED. Figure 4 illustrates the circuit to be constructed. The LED will be run by a 9-V battery. A 1 kΩ resistor will be placed in series with the battery and LED to limit the current dissipated.

1. First, connect one of the leads of the battery snap to a 1 kΩ resistor by winding the stripped end of the lead around one end of the resistor. Use solder and the soldering iron to make the connection permanent. To do this, heat the junction between the
resistor and the battery snap (where the stripped lead is wrapped) with the soldering iron until the solder melts and flows. (Do not try to heat the solder directly.) CAUTION: the soldering iron’s tip is really hot, and molten solder may cause burns of the skin. Keep your safety glasses on and work carefully with the soldering iron. Be patient; it takes a little practice to learn how to solder properly. A good junction is typically shiny looking and relatively smooth; a bad, nonconducting junction looks rough or crystalline. You may want to reheat your solder junction if you suspect the junction is bad; the solder will reflow around the parts, leading to a good electrical connection when it cools down.

2. Solder the other lead of the resistor to one of the two terminals on the LED socket. You may want to use a pair of forceps or tong to hold the plastic part of the resistor LED socket while making contact between the LED socket and resistor leads. Another pair of forceps could be used to hold the resistor itself (but not on the lead, since the metal forceps would conduct heat away from the connection). Again, use the soldering iron to heat the resistor lead at the connection point until solder flows around the resistor lead and the socket terminal. Be careful to hold the LED socket still until the molten solder solidifies (a few seconds).

3. Connect the other lead of the battery snap directly to the open terminal on the LED socket. Solder the two together using the techniques described above. Be sure to unplug the soldering iron when not using it, or else it will overheat and burn out (plus it is safer not to have hot items randomly sitting on the bench.)

**Emission of LEDs at Room Temperature**

Using the 1-kΩ circuit constructed following the instructions given above, obtain a series of emission spectra and voltage-drop readings with a range of GaP/GaAs LEDs of different compositions.

1. Snap a 9-V transistor radio battery into the battery snap of the 1-kΩ circuit.
2. Insert an LED into the socket. This completes the circuit across the LED from one battery terminal to another. The LED should light up. Does it matter which way the
LED is inserted? Why would this be expected? (To answer this optional question, the student will have to read up on how LEDs are constructed from \( p-n \) junctions in your textbook.) What is the apparent color of the emission from the LED?

3. With the LED lit up in the circuit, look at the LED emission using the Ocean Optics spectrograph/CCD system. Determine the range and extent in wavelength of the spectrum that is observed. Where is the emission maximum? (You may need to adjust the setting on the Ocean Optics, or just hold the detector off to the side of the LED.

4. Repeat steps 2–3 with the other LEDs that are available, noting the composition each time. There are two examples (from different manufacturers) for some of the LED compositions; do you observe any differences in the spectra obtained for a given quoted composition?

5. Place an LED into the socket. Then, measure the voltage drop across the LED by holding the probes of the multimeter on the two LED-socket terminals (or the solder junction on the terminals). Note the magnitude of the voltage drop (the sign will depend on the order of the two multimeter probes; note that reversing them causes the sign to reverse). This is a direct measurement of the band gap of the LED material. Note: if the measured voltage drop is greater than 3 V, then no current is flowing across the LED because it is inserted backwards into the LED socket. If this is the case, remove and invert the LED in the socket, and then repeat the measurement.

6. Repeat step 6 with the other LEDs that are available, noting the composition each time.

7. To analyze your results, plot the band gap obtained from the two types of measurements (in eV) as a function of the lattice constant for the unit cell. You can determine the lattice constant from the information given above in the theory section; assume that there is a linear relationship between the lattice constants for the GaP and GaAs unit cells. Compare the band-gap estimates for the LEDs, as obtained by the emission and voltage-drop methods. (Note that the voltage-drop measurement also obtains a contribution from thermally excited electrons flowing in the LED, but the shift as a function of lattice cell constant will exhibit the correct trend.) Determine the change in band-gap per 0.001 angstrom expansion in unit lattice constant, as determined using the two methods (note your answer should be in units of eV/A).

Emission of LEDs at 77 K

In this part of the experiment, you will compare the LED emission spectrum that you observed at room temperature to the spectrum observed at or near the temperature of boiling liquid nitrogen (77 K). Owing to thermal contraction of the LED’s semiconductor crystal, one would predict that the band gap for the semiconductor will increase with a corresponding blue shift (higher energy) of the emission spectrum as the temperature is lowered. As an example, a decrease in the temperature from room temperature (300 K) to 77 K results in a decrease of the lattice constant for GaP from 5.451 Å to 5.447 Å. (As mentioned in the theory section, as the atoms get closer together, the band gap should increase)

1. Obtain a styrofoam coffee cup full of liquid nitrogen from the TA. CAUTION:
Liquid nitrogen is extremely cold. Do not play around with the liquid nitrogen. Wear your safety goggles at all times when working with liquid nitrogen. Do not allow your eyes, skin or clothes to come into contact with spilled liquid nitrogen. The skin is easily frozen by liquid nitrogen. If you spill liquid nitrogen on your clothing, pull the nitrogen soaked clothing away from your body so that the absorbed or trapped liquid nitrogen will boil away before freezing your skin.

2. Using the 1-kΩ circuit, light up an LED by inserting it into the socket. Carefully dip the LED only, if possible, just into the surface of the liquid nitrogen in the cup. Does the color of the emission change in a noticeable way?

3. Record the emission spectrum from the LED using the Ocean Optics spectrograph/CCD setup. Be careful: DO NOT insert the fiber optic cable into the liquid nitrogen. Hold the tip of the fiber optic cable just above the LED.

4. Remove the LED from the liquid nitrogen, and allow it to warm back up to room temperature. Are the temperature-induced changes in the emission spectrum reversible?

5. Repeat steps 2–4 for each of the LEDs. Analyze the results as suggested above. Can you determine from your results the apparent contraction of the unit cell that occurs as a result of the lowering of the temperature to 77 K?

**Composition of the Four Colored LEDs**

The LEDs that you will use in this laboratory have the following approximate compositions:

<table>
<thead>
<tr>
<th>Color</th>
<th>Composition</th>
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<tbody>
<tr>
<td>Red</td>
<td>GaP₀.₄As₀.₆₀</td>
</tr>
<tr>
<td>Orange</td>
<td>GaP₀.₆₅As₀.₃₅</td>
</tr>
<tr>
<td>Yellow</td>
<td>GaP₀.₈₅As₀.₁₅</td>
</tr>
<tr>
<td>Green</td>
<td>GaP₁.₀As₀.₀</td>
</tr>
</tbody>
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**Lab Write-up**

In pairs, answer the assorted questions posed in the previous portions of the lab. You are encouraged to answer in paragraph form addressing the individual groupings of questions together.

**Acknowledgment**

This laboratory procedure, introductory materials, and figures are adapted from materials provided by the Institute of Chemical Education at the University of Wisconsin, Madison. Source materials for this laboratory can be found in the following: