

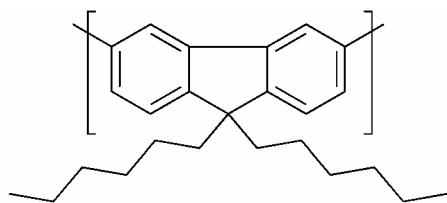
Formation of a Polymer Based Light Emitting Diode

INTRODUCTION:

Light Emitting Diodes (LEDs) are one of the fastest growing areas for display and lighting applications. In a typical incandescent light, current is converted to photons by heating a filament to the point that it produces black body visible radiation. This is a very inefficient process as much of the energy is wasted as heat (infra red and near infra red radiation). In addition, to make color displays, this white light must be filtered to produce red, green, and blue pixels, again wasting energy. In a diode, by contrast, current is directly converted to light with a narrow energy span. The color of the light generally corresponds to the band gap of the material used in the LED.

Currently, inorganic LEDs based on a wide variety of semiconductors are making dramatic inroads into everyday products. For example, all the new bright green traffic signals are green LEDs, and red LEDs are used commonly in toys. The only problem with inorganic LEDs is that they are fairly expensive to produce. In almost all cases, the inorganic semiconductor must be processed in vacuum, and for the bluer wavelengths, extreme care must be taken in preparing the materials.

An alternative to inorganic LEDs is to use organic semiconductors as the active layers. These organic semiconductors can be either small molecules or polymers, but they usually involve aromatic, π conjugated species. The organic systems and the polymeric materials in particular, have the distinctive advantage that they are easy to process. Good quality films of polymers can be generated at ambient pressure by spin coating, dipcoating, rolling, or a host of other methods. Such processability could dramatically reduce the cost of LEDs for both lighting and display applications (imagine a wall sized panel that glowed!). The problem today with the organic systems, however, is that they are not as robust as the inorganic materials. Organic semiconductors tend to oxidize easily, and LEDs made from these organic materials tend to have shorter lifetimes. Despite this fact, polymer LEDs are starting to find applications; a cell phone that uses an array of polymer based LEDs for a full color display was recently released. Prototypes for roll-up TV screens are also being developed and may be released soon.

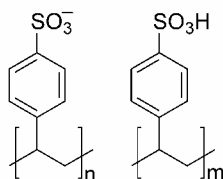
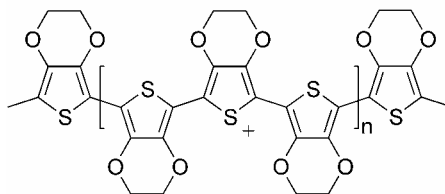


poly(9,9-di-*n*-hexylfluorene) (PDHF)

backbone has long range aromaticity. The polymer is soluble in common organic solvents, and the octyl chains in ADS 129BE are even better at this.

In the actual experiment, you will first make a film of a second conducting polymer, PEDOT/PSS (pictured at right). This is a doped semiconducting polymer which can act as a metal. The polymer is able to conduct holes, but is a poor conductor of electrons. As a result, it keeps the device from shorting, and helps

In this lab, you will make an LED from a blue emitting semiconducting polymer poly(9,9-di-*n*-octylfluorene) [American Dye Source (ADS) #129BE]. The chemical structure of a related polymer with hexyl side-chains is shown at left. Note that you could draw a resonance structure for the polymer that puts the double bonds between the benzene rings, indicating that the polymer backbone has long range aromaticity. The hexyl side chains are present to make the polymer



poly(3,4-ethylenedioxythiophene) (PEDOT)

poly(styrenesulfonate) (PSS)

holes get into the active ADS 129BE layer. While the PEDOT/PSS layer does not itself emit any light, such hole transport layers have been found to dramatically improve the efficiency of polymer based LEDs. Once the PEDOT/PSS layer is produced, the ADS 129BE is put on top of it. As a counter electrode, you will use indium metal. The indium can be melted at a moderate temperature to produce a good contact with the polymer film. In commercial polymer LEDs, higher work function metals such as Ca are used to make more efficient devices. After making the device, you will measure its current-voltage-light output characteristics. You will also determine the chromaticity (red-green-blue make-up) of the light, to assess its suitability for color display applications.

PROCEDURE:

- Overview -- Day 1, Build the device
- Day 2, Measure electrical properties of the polymer LED and of commercial inorganic LEDs
- Day 3, Measure optical properties of polymer films and solutions, determine CIE coordinates of your device.

Build the device:

The first step is to prepare the ITO substrate by cleaning it. Los Angeles has air full of hydrocarbons, and these will form a thin insulating film on the surface of the ITO and affect the adhesion of the polymer layers as well as the charge injection.

Get four (4) 1"x1" ITO on glass wafers. Do not touch them with your fingers at any time, even by the edges. Handle them only with tweezers. Not only will the fingerprints be difficult to clean off, the acids in the oils can actually etch the ITO and leave permanent marks on the surface. Also get one glass cover slip.

Your first goal is to figure out which surface of the wafer has the ITO on it. Wearing powder free gloves (latex or nitrile), take a multimeter and touch both leads to one surface of the ITO. If the ohm-meter reads overflow, that is the glass side; if it reads a finite resistance, that is the ITO. Put a small scratch in the corner of the slide to mark the ITO side. Now fold a single piece of lens paper in half lengthwise, then again. Fold it three times in the short direction, and then pinch it off with locking forceps near the final folded edge. Place 4-5 drops of clean acetone and gently wipe the ITO surface and the cover glass to remove any dust or bits of glass left over from the cutting process. Use each side of the fold only once to avoid re-depositing dirt onto the slide. Use more than one tissue if necessary.

Place the wafers and the glass slide onto the bottom of a crystallizing dish with about 1/2" deionized water (DI) and about 1 teaspoon of Alconox detergent. Cover the dish with a watch glass and place it in the sonicator and agitate for 10 minutes. In the meantime, turn on the vacuum oven and set the temperature to 120 °C.

Drain the soapy water and rinse well with DI and then refill dish with plain DI, cover with watch glass, and sonicate for 5 minutes.

Rinse again with DI and put in 1/2" acetone. Sonicate for 5 minutes.

Rinse with DI, put in 1/2" alcohol (ethanol or isopropanol). Sonicate for 5 minutes.

Drain the alcohol and put the wafers and the glass slide into the preheated vacuum oven, turn on the vacuum, and dry the wafers for 10 minutes.

The next step is to add the hole transport layer. Using a 1 cc syringe, suck up 1/2 ml of the PEDOT/PSS aqueous solution and attach a 0.20 μm syringe filter to the end (it's ok to use a 0.45 μm filter instead of a 0.2 filter if the 0.2 μm filter clogs- you should not have to **force** the PEDOT:PSS through the filter). Put a wafer on the spin coater chuck (make sure it's the medium sized chuck) and center it. On the box next to the spin coater, turn on the nitrogen and push

start. This starts a 15 minute timer so that the nitrogen tank doesn't bleed dry due to negligence. Once the N₂ is on, the spin coater will turn on. Set the spin speed to 1000 RPM and the spin time to 300 seconds. Make sure the start time and stop time are both set to 0 seconds.

Carefully push the PEDOT/PSS solution through the filter and onto the center of the wafer. The blue solution should cover at least the area inside the o-ring. Close the lid and press start on the spin coater. The solution will spread out and the water will evaporate. Before repeating for the next wafers, turn the air box off then on again. The previous settings will be preserved, but the timer will be reset to give another 15 minutes. When finished with all ITO wafers, remember to turn off the nitrogen controller. Place all wafers back into the vacuum oven, turn on the vacuum, and set the temperature to 100 C or above. Let them bake for 20 minutes or more.

Next add the active layer. There may be a pre-dissolved solution of polymer in toluene at a concentration of 10mg/mL. If this solution is not already made, make ~1.5 ml of it. When making a solution, heat while stirring on a hotplate on "low" for an hour and then let cool before spinning. Place the wafer back into the spin coater and turn on as before. Turn the spin speed up to 2000 RPM, but leave all other settings the same. Using an autopipet, put 300 μL onto the center of the substrate, close the lid, and turn on the spinner. Repeat as before for the other ITO wafers. Do the glass cover-slip last and don't worry if you don't have a full 300 μL of solution left; the thickness of this sample is not very important as you are just using the for luminescence measurements. Don't forget to turn off the nitrogen when you're done.

Put the wafers and the slide into the vacuum oven and turn on the vacuum to remove any last traces of toluene that might remain. Leave in for 10 minutes. At this point, you are done with processing the glass slide; do the remaining steps on the ITO wafers only.

With a cotton swab and some chloroform, rub the polymer off of a small corner of each of the wafers to expose the ITO. Be careful not to spread the chloroform too far as it will damage the film.

Next we need cathodes. Cut 7-10 small (~3mm x 3mm) pieces of indium foil per wafer with a pair of sharp scissors (orange handle). Carefully arrange the foil pieces onto one of the slides. Be sure one gets placed on the corner where the polymer was rubbed off. Put 6 - 9 pieces onto the rest of the device, spacing them far enough apart to make it easy to attach wires later. **VERY IMPORTANT** – The polymer films is *extremely* fragile so do not slide the indium around on the film or you will short your devices. Also, try not to put the indium down "point-first". Try to set it flat on the films and don't move it at all!

Next you need to melt the indium so that it makes good contact with the polymer. If you heat the device too much, however, the polymer will exceed its glass transition point and the device can short. The optimum temperature is 150 °C, and there is a small aluminum plate with a thermocouple that can be controlled to exactly this temperature. Set the temperature controller to 150 °C, and then place your device on the aluminum plate. Heat just until the indium melts. (Keep an eye on it!)

If you would like, you can also try using the liquid Ga:In eutectic for the cathode for your LED. The work function of Ga:In is similar to In metal and it does not require heating the metal. It has the disadvantage that it stays liquid, however, so things can get a bit messy.

Finally, wire up the cathodes. If there isn't enough time left in the period, this is a good place to stop. If there is time, cut several 2" pieces of red wire and one piece of green wire and strip each end. Stir the silver paint well with a wooden applicator (or the wooden end of a cotton swab). Remove the top shelf of the vacuum oven and put the wafers on it. Carefully arrange the wires with one end on each of the pads, using the green wires for the anodes and the red wires for the cathodes. Using the wooden applicator, put a very small blob of silver paint onto each pad to glue the wire to the pad (avoid getting ANY paint onto the polymer or again, you will

short your device). When you're done, put it into the vacuum oven and bake at 80 °C for at least one hour to cure the paint. The paint is not very strong, so be careful not to move the wafer and the wires once they're attached.

Get some 5 minute epoxy and squeeze out two dime sized blobs into a plastic petri dish. Mix well with a wooden applicator until the goo turns clear (about 1 minute), trying to introduce as few bubbles as possible. Put a blob of epoxy onto the wafer over the pads and carefully spread around. Using tweezers, put a microscope cover slip on top of the epoxy. Let the epoxy cure for 10 minutes. This will make the wire contacts very robust and help exclude oxygen from the devices. Do not put epoxy onto the slide with no contacts. Put the finished OLED into the OLED drawer until the next lab period.

Device Characterization:

Electrical measurements to be made are:

1. Current vs. Applied Voltage (IV)
2. Light Output vs. Current
3. Electroluminescence Spectrum
4. Electroluminescence CIE Coordinates

Spectroscopic measurements to be made are:

1. Photoluminescence of the film
2. Photoluminescence of the original polymer solution
3. Absorbance of the film
4. Absorbance of the original polymer solution

Note – you can do either the device work or the spectroscopic characterization first; they are completely separate measurements.

Electroluminescence:

Attach the red lead from the Keithley 2400 sourcemeter to the anode and the black lead to one of the cathodes. Set the Keithley to measure resistance and check the leads. Good devices should have a resistance in the high k Ω to low M Ω range. Set the Keithley to source voltage and read current, with a current limit of 100 mA. Slowly ramp up the voltage to 5 V or so, keeping an eye on the current. If the current reaches the limit at low voltage, your device is shorted out. By 8 V (no more than 12 V), you should be able to see bluish white light coming from the OLED. Use the Ocean Optics fiber wand to capture the electroluminescence spectrum and save it (do this fast as your device probably won't last long!). Calculate CIE coordinates from your emission spectra using the Lab View program CIEfit. Save your data as a tab-delimited text file for use with the LabView program and remember to tell the program you are looking at emission, rather than absorption.

If possible, use the colorimetry viewer to measure the CIE coordinates of the same diode. If possible, get emission spectra and coordinates at several different voltages.

Repeat the above experiments with one of the inorganic LEDs. How does it compare with the OLED?

LIV Curves:

For any devices that showed good electroluminescence, collect *LIV* curves. Hook up a device to the sourcemeter. Put the emitting side of the OLED against the detector head of the light meter and run the *LIV* program. Set the minimum voltage around -2 V and the maximum around 10 V.

Repeat the above experiments with some of the inorganic LEDs.

Photoluminescence:

From the original polymer solution, prepare 5 mL of a 20:1 diluted solution in toluene. In a plastic cuvette, measure the absorbance spectrum from the UV through the visible. Do the same for the polymer film on the glass slide. For the solution spectrum, be sure to use a cuvette with toluene as a blank, and for the film, use a blank glass slide.

Collect photoluminescence on solutions and films. For photoluminescence, use the UV LED as an excitation source and collect the luminescence. Use the Lab View program CIEfit to calculate the CIE coordinates.

QUESTIONS TO THINK ABOUT:

1. Why do the devices form a diode?
2. How does the PEDOT/PSS layer improve device efficiency? What are some ways the processing could be improved to make the device even more efficient?
3. Does the OLED work better or worse than the inorganic LED? What advantages does the OLED have over conventional inorganic LED? Disadvantages?
4. One of the supplemental papers discusses failure modes for OLEDs using this particular polymer. How could the processing procedure outlined above be changed to improve device lifetime?
5. Why do you see current before the device starts to give off light?
6. What controls the voltage at which current starts to flow?
7. Based on the CIE coordinates, would this OLED be suitable for RGB display applications?