Design and Construction of a Polymer Light-Emitting Diode Based on PEDOT/PSS

Submitted in partial fulfillment of the requirements for the degree of Bachelor of Arts with a concentration in Physics

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¹ See Appendix D, Figure 25.
Introduction

History

Organic semiconductors were largely unnoticed and underutilized throughout the 50’s, 60’s, 70’s, and 80’s as large strides were made in inorganic semiconductor technology. The invention of the transistor at Bell Labs by Bardeen, Brattain, and Shockley\(^2\) in 1947 and the subsequent rise of inorganic semiconductor-based technologies in the following decades revolutionized technology by increasing the efficiency of many processes by many orders of magnitude. Examples include increases in the number of calculations that are able to be performed by a computer and the astonishing decreases in the size of the transistor. As a result of their many technological applications, inorganic semiconductors have been widely studied and characterized.

Organic semiconductors were widely overlooked for the first \(\frac{3}{4}\) of the 20\(^{th}\) century. There discovery early in the century did not immediately bring about any profound technological gains, but recent developments have shown that devices made from organic semiconductors hold great promise for increased performance and decreased energy consumption.

Molecular solids were both the first organic semiconductors that were investigated and the first that were made into devices. William Bragg studied the crystal structure of naphthalene\(^3\) and

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\(^3\) See Bragg (1921).
anthracene\(^4\) (figure 1) as early as 1921, and the importance of delocalized pi-orbitals\(^5\) to the semiconducting properties of these organic molecules has been suspected and studied since the late 1950's\(^5\). C.W. Tang and S.A. Van Slyke demonstrated the first organic light-emitting diode (OLED) in 1987\(^7\) using diamine and Alq\(_3\)\(^8\). In this case, Alq\(_3\) is the emissive (electroluminescent) layer, and diamine is a hole-transporting layer\(^9\) used to block electron transport. The specific and generalized structure of their OLED is shown in figure 2. This structure is the general, simplified model for the majority of organic and polymer light-emitting diodes made since then.

According to Dr. David Braun\(^10\), semiconductivity was discovered in polymers in 1977 for doped polyacetylene\(^11\) (figure 3); electroluminescence in poly(\(p\)-phenylene vinylene) was demonstrated 12 years later\(^12\). In 1989 a group at Cambridge University led by Professor Richard Friend discovered by accident that polymers could emit light while attempting to make a different, but somewhat similar device. In Professor Friends

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\(^4\) See Bragg (1922).
\(^5\) Orbitals where the electronic wave functions are generally spread out over an area much greater than just two bound atoms. I will discuss this phenomenon shortly.
\(^6\) See Kao.
\(^7\) See Tang.
\(^8\) 8-hydroxyquinoline aluminum, a fluorescent metal chelate complex
\(^9\) “Hole transport” layers do not facilitate the transport of holes per se, rather they are relatively effective at inhibiting the conduction of electrons. Therefore, they are also referred to as “electron-blocking” layers. The analogous case of “electron-transport” and “hole-blocking” layers exists as well.
\(^11\) See Chiang.
\(^12\) Discovery of the first polymer light-emitting diode. See Burroughes.
words, “We wanted to sandwich (the polymer) between two electrodes and use it as an insulator in these field-effect transistors. We were seeing how much voltage we could put across it and we saw a light emerging through this structure, actually through one of the electrodes, which was thin enough to be partially transparent. That was in February 1989, and that was the beginning of the polymer light-emitting diode.”

Research into polymer light-emitting diodes (PLEDs) flourished after the findings of the resulting work were published. Since 1989, the efficiency of polymer LEDs has increased dramatically. Figure 4, adapted from a Physics World article\textsuperscript{14}, shows the efficiency in lumens per watt of different kinds of light-emitting diodes as a function of time. Included are inorganic (III-V), nitride, molecular solid (OLED), and PLEDs. On the far right side of the graph, we can see the path of PLED development, whose efficiency has now caught up to that of the unfiltered incandescent bulb familiar to us all. The first PLED made with poly $p$-phenylene vinylene had poor efficiency due to (relatively) crude processing methods, simple sandwich design, and not-quite-perfect cathode and anode materials. In the 13 years after the first viable demonstration, researchers have used and analyzed other materials, developed more complex, efficient heterostructures\textsuperscript{15}, and refined materials choices. The biggest obstacle facing PLEDs now is device lifetime; although OLEDs and PLEDs now rival many other technologies in

\textsuperscript{14} See Friend.

\textsuperscript{15} Heterostructures, in this sense, refers to using multiple materials for one device component. For example, the OLED in figure 2 is a heterostructure because it used both ITO and diamine as hole-injection layers.
efficiency and

Figure 4: A short history of the development of semiconductor-based solid state lighting devices. The plot shows efficiency vs. time.

brightness, they generally have much shorter lifetimes, especially in the blue light regime. Fortunately, the low production costs and high tenability of the energy bandgaps (see Figure 24) of PLEDs make them extremely attractive as replacements for
LEDs and liquid-crystal displays (LCDs) and the area is well funded for research for this reason. Also, because PLED films have good resilience and do not require high manufacturing temperatures, they have the potential to be used on flexible substrates. Commercial products that use OLED displays are already available\textsuperscript{16}, and tens of companies have licensed patents from Kodak for OLEDs and Cambridge Display Technologies for PLEDs\textsuperscript{17}. Therefore, it is very likely that we will be seeing applications of OLED and PLED technology all around us in the next few decades.

**Project Goals**

While I hope that I have made it apparent that polymer light-emitting diodes have scientific and technological importance, the case for attempting the construction of a PLED at Pomona College is also strong. The construction of a PLED involves many aspects of physics and chemistry that would make it a good project for a lab-based Materials Science course. It is my hope that a process for making a PLED can be devised such that the timeline for its construction would be reasonably short, e.g. can be accomplished in three afternoons or less. While this may seem like a fairly large reduction in time scales from my project into a lab, I suspect that with all the kinks worked out of the process, a working device could be constructed with good reproducibility on this time scale. Therefore, my goals for this project were threefold: to gather, operate, and characterize all the equipment necessary to make a PLED, to make devices based on a simple sandwich design, and demonstrate a working PLED.

In this paper I will first discuss the theory relevant to semiconductor technology and apply it to what is known about polymer light-emitting diodes. I will then discuss my basic design for a PLED. I will then spend time taking the reader through the steps that I

\textsuperscript{16} \url{http://www.pioneerelectronics.com} (26 April 2002)
\textsuperscript{17} Companies that have licenses from Kodak include: Pioneer, TDK, eMagin, Sanyo, Nippon Seiki, RITDisplay, Lite Array, and Opsys. Companies that have licenses from Cambridge Display Technologies include: Uniax/DuPong/RITDisplay, Dow, Delta Electronics, Phillips, and Sumintomo. Source: \url{http://www.sidchapters.org/pacificnorthwest/meetings/dec5_01_presentation.pdf}
took in order to understand and successfully use the resources available to me. Finally I will discuss the results of my work and the outlook for the future.

Theory

Probably the best way to go about thinking about how and why a polymer light-emitting diode works is to first consider how a P-N junction works, then build from there. However, it is important to realize that the actual mechanism behind the PLED is a contested model that is currently hotly debated. The $p-n$ junction is very well characterized, which is why we will start there. Next, I will attempt to draw a clear picture behind the workings of inorganic LEDs. I will then introduce semiconducting polymers and discuss transport mechanisms and some of their unique electronic features. Finally, I will attempt to expand what is known about LEDs to give a general understanding of the models presented for PLEDs. Finally, I will discuss some possible applications of PLED technology, including simple display models and polymer photovoltaics.

Semiconductors

Solid semiconductors are materials that have band gaps of approximately 0 - 3.5 eV between their filled valence band and their empty conduction band. This gap means that under standard conditions, i.e. room temperature, atmospheric pressure, and no strong electromagnetic fields present), the populations of the energy states in the conduction band are relatively small. Recall that fermions, in this case electrons, attempt to occupy the lowest energy states first, only occupying higher energy states when excited by thermal energy ("standard conditions"). Their distribution function is given by the Fermi-Dirac distribution

$$f_{FD}(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \quad (1)$$

\footnote{See Krane.}
However, for $E - E_F >> kT$, which is true for all of the semiconductors that we are interested in at room temperature, the Fermi-Dirac distribution is approximately equal to

$$f(E) \approx e^{-(E_E - E)/kT}$$

(2)

Thus, the number of electrons and holes at a particular energy level is given respectively by

$$n = n_0 e^{(E_F-E)/kT}$$

(3)

$$p = n_0 e^{(E-E_F)/kT}$$

(4)

where $n_0$ is the number of electrons initially in that particular energy level.

Assume for a moment that we are at room temperature, 298K, and that we are interested in silicon with $E_F$, the Fermi energy, in the middle of silicon’s 1.1 eV band gap. Given Equation 2 we can calculate that an electron will occupy an energy level at the bottom of the conduction band one part in $4 \times 10^9$ of the time. It is important to note here for future reference that an electron excited into the conduction band leaves behind a hole in the valence band, which possesses positive charge that the electron is electrostatically attracted to, and properties similar to the electron. Holes do not have the same distinction as electrons as having a physical mass since they are more or less the lack of an electron in a system. However, holes can have an effective mass, as well as mobility, one can measure the hole current and the density of holes, and there is such a thing as materials that are classified as being “hole-carriers” or “hole-injectors”. These two charge carriers, the electron and the hole, are the two primary players in the interactions that characterize an LED. Although the mechanisms of conduction in a PLED involve other charge carrying states besides electrons and holes, the concepts of carrier distribution and state populations/vacancies are still very much applicable.

**p-n Junction**

What makes a semiconductor really useful technologically is when extra electrons or holes are added to the material in a process called doping to create a diode.
Using germanium as an example, we notice that this semiconductor has four valence electrons. Thus if in place of some of the germanium atoms we substitute arsenide atoms, we then have one more electron per atom. This is known as n-type doping since it results in an excess of negative charge carriers. The resulting electron energy states, known as donor states, lie just below the conduction band with a gap typically of \(~0.01 - 0.05\) eV. Equation 2 now tells us that about 10% - 40% of the doping atoms’ electrons will be in the conduction band at a given time. Conversely, if we substitute in gallium atoms we have one less electron per atom and we get acceptor states just above the valence band. Acceptor states are states that an electron can be excited into, to leave a hole in the valence band. This is known as p-type doping, for its positive charge contribution. In n type materials most of the charge carriers are electrons and are thus termed “majority carriers”. However, there can be holes that act as charge carriers in n-type material, and these are called “minority carriers”. Similarly, holes are “majority carriers” and electrons are “minority carriers” in p-type material.

Now we take a material that is p type and a material that is n type and place them together. The excess, nonbonding electrons of the n type material diffuse across the interface into the p type region leaving behind regions of positive charge, while the holes of the p type material diffuse into the n type region leaving behind negative charge. The process of electron, n, and hole, p, diffusion in a solid in one dimension is described by the heat equation

\[
D_Z \frac{\partial^2 Z}{\partial x^2} = \frac{\partial Z}{\partial t}
\]  

where \(D_Z\) is the diffusion coefficient for a charge carrier Z (either p or n). The diffusion coefficient of a charge carrier is related to its mobility, \(\mu\), by the Einstein relation

\[
D_Z = \left(\frac{kT}{e}\right)\mu
\]  

Charge carriers diffuse until equilibrium reached between diffusion and the force on the charge carriers due to the electric field resulting from the residual charges. The region
near the interface where there are both excess electrons and holes, which effectively cancel each other’s charge out, is known as the depletion layer due to a lack of charge carriers.

**Light-Emitting Diodes**

The short explanation of LEDs is that they diodes that emit photons when a forward bias is applied to them. The forward voltage effectively injects minority carriers into either side of the diode. Electrons from the

**Semiconducting Polymers**
Most polymer backbones are comprised of carbon-carbon sigma-bonds (C-C) that tightly hold the polymer together. These bonds have a large gap between the valence and the conduction bands that renders them electrically insulating and optically transparent. However, these sigma-bonds are important to give the molecules structural stability.

However, some polymers have backbones that consist of alternating C-C bonds and C=C double bonds that comprise what is known as a pi-conjugated system. Such a system of alternating pi-bonds is a necessary, but not sufficient, requirement for conjugation. The two molecules in figure 3 are examples of such a system. The C=C bonds have one sigma-bond and one pi-bond, the pi-bond being the higher energy bond.

In these systems, there is a significantly smaller gap between the valence and conduction bands, often leading to semiconducting properties. It is important to note that in the pi-conjugated system, the electrons are actually delocalized across an area greater than just the two bound atoms. The wavefunctions of such electrons often overlap with other electrons over the space of about 15 atoms or so\(^{19}\). Figure 5 shows the resonant structure of such systems, where the bonds can be in either of two orientations\(^{20}\). Conduction by the polymers can be explained based on this theory in the

\(^{19}\) See Salaneck.

\(^{20}\) Resonance theory is really just chemistry's way of dealing with what is really a quantum mechanical phenomenon with a standard bonding model. However, resonance theory is fairly intuitive and easy to grasp, so I will use it for the sake of clarity in this discussion.
quasi-one-dimensional case, where the molecules are highly ordered into straight, rod-like structures.

Unlike metals or inorganic semiconductors, there are strong interactions between the charge carriers (electrons and holes) and the molecular lattice, giving rise to the existence of unusual charge carrying species such as solitons and polarons. Imagine that instead of all of the bonds switching orientations as in figure 5, only some do, leaving non-bonded electrons in the molecule. This results in the creation of solitons\textsuperscript{21}, a species that must be formed in pairs; one can intuitively see this in figure 6. In reality, solitons are not so much a created “thing”, but are a method of transport through a conjugated system, much the same way a tidal wave is not a “thing”, but has energy and some properties of a position. However, solitons and polarons possess quantum numbers such as spin and charge.

If only an electron or a hole is injected into the polymer molecule, an electron or hole polaron will be created\textsuperscript{22}. Polarons can be thought of as these higher energy charge carriers or as a soliton-antisoliton pair (one charged and one neutral). Polarons

![Diagram of solitons and polarons](http://www.ma.hw.ac.uk/~chris/scott_russell.html)

Figure 7: (top left) neutral solitons with unpaired spin, (top right) spinless positively charged solitons, (bottom left) spinless negatively charged soliton, (bottom right) bipolaron state in PPV; the energy states are equally above and below the middle of the energy gap

\textsuperscript{21} Solitons in this sense are named after the mathematics that describe them. Solitons are commonly thought of as self-propagating, one-peak waves, first observed in water in a canal by John Scott Russell in 1834, and given the name “solitons” in the 1960’s. [http://www.ma.hw.ac.uk/~chris/scott_russell.html](http://www.ma.hw.ac.uk/~chris/scott_russell.html) (23 April 2002)

\textsuperscript{22} See Heeger p. 20
readily combine within the polymer, decaying into the lower energy state of the soliton. Different soliton and polaron states are drawn schematically in figure 7, and their contributions to states in the band gap are shown. An isolated soliton has an energy state that lies in the middle of the gap. These states are the lowest energy eigenstates of the electron (hole)-lattice system\textsuperscript{23}, and are the main contributors to the unique properties of semiconducting polymers.

**Polymer Light-Emitting Diodes**

Polymer light-emitting diodes (PLED) operate on principles analogous to those of the LED. Instead of a filled valence band as in inorganic semiconductors, polymers have what is known as a highest occupied molecular orbital (HOMO). HOMOs are like the valence band in that they are the highest filled energy states of the molecule. In a pi-conjugated system, the HOMO is the energy state of the highest energy pi-bond. The energy state that is analogous to the conduction band in polymers is the lowest unoccupied molecular orbital (LUMO). The LUMO in a pi-conjugated system is the higher energy pi\textsuperscript{*}-bond, which is antibonding, i.e. it weakens the molecular bond when

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\textsuperscript{23} See Salaneck, p. 53
sigma-bonds. The simplest model of a PLED says that electrons are injected into the polymer’s LUMO from the cathode and holes are injected into the polymer’s HOMO from the anode where they recombine to form a high-energy exciton. This exciton is a bound excited state that can decay by emitting a photon. The energy of this photon is on the order of the energy of the polymer’s band gap. This process is known as electroluminescence since the emission of light is caused by the electric field that is generated between the cathode and anode. Figure 8 shows the process of electroluminescence schematically.

The efficiency of a PLED is limited both by the materials that are utilized and by spin statistics. When electrons and holes capture each other to form an exciton, the exciton can either form a singlet or a triplet state. Singlet states have an overall spin of zero, where the spin ½-electron and ½-hole have oppositely oriented spins. Triplet states have an overall spin of one, where the ½-electron and ½-hole have their spins oriented in the same direction (this situation is illustrated in figure 9 for the simple harmonic oscillator model). However, transitions from the triplet exciton state are forbidden, so no light can be emitted in that case. Also, the triplet states are lower in energy than the singlet states, so the likelihood of a triplet undergoing a spin-flip up to the singlet state before decaying is very small. Statistically, there are three triplet states formed for every one singlet state, so a PLED has an upper limit on its quantum efficiency of 25%. The internal quantum efficiency $\eta_{\text{int}}$ of a device is the ratio of the number of electrons flowing into a device to the number of exciton formation events and is given by

\[ \eta_{\text{int}} = \frac{\text{number of electrons}}{\text{number of exciton formation events}} \]
\[ \eta_{\text{int}} = r_{st}q\gamma \]  
(7)

Here \( r_{st} \) is the fraction of excitons that are formed as singlets, \( q \) is the efficiency of the radiative decay of the singlets (this depends on the photonic structure of the device), and \( \gamma \) is the ratio of the number of exciton formation events per electron. This model is somewhat lacking however, as PLEDs have been made with quantum efficiencies upwards of 10\%, which cannot be explained by saying that nearly half of the electrons and holes capture each other perfectly\(^{25}\).

A PLED’s efficiency is limited intrinsically by quantum statistics, but choosing different materials for the cathodes, anodes, and polymers has the greatest effect on device efficiency. The design of a highly efficient PLED would consist of a polymer with a band-gap corresponding to the wavelength of light that one desired, an anode with a work function equal to the energy of the HOMO, and a cathode with a work function equal to the energy of the LUMO. With the work functions thus matched, there would be no energy barriers to electron and hole injection, so the there would be no loss in efficiency due to the material interfaces.

In reality, it is quite difficult to match the work functions as precisely as we would like. However, certain materials are much closer than others. Indium-tin oxide (ITO) is a transparent conducting oxide (TCO) with a high work function (\( \Phi_{\text{ITO}} = 5.0 \pm 0.2 \text{ eV} \))\(^{26}\) that is well-suited as an anode. The commercially available ITO that was used in this project boasted a resistivity of 5 – 15 \( \Omega/\text{üb} \) and a nominal transmission of >85% at a thickness of 2,000 Å\(^{27}\). It is a notoriously variable material, whose optical and electrical properties are sensitively coupled to the exact composition of the material. The fact that it is mostly transparent makes it perfect for the side of the PLED that we want to look at. Other materials that can work as a TCO include indium oxide\(^{28,29}\), molybdenum doped indium

\(^{25}\) Friend, p. 37  
\(^{26}\) Friend, p. 36  
\(^{27}\) http://www.delta-technologies.com (24 April 2002)  
\(^{28}\) See Pan.  
\(^{29}\) See Adurodija.
oxide\textsuperscript{30}, zinc oxide, tin doped zinc oxide, tin oxide, and fluorine doped tin oxide\textsuperscript{31}, but ITO is almost universally regarded as the best TCO. Calcium makes a good cathode because it is such a low work-function ($\Phi_{Ca} = 2.87$ eV)$\textsuperscript{32}$ metal, thus it is efficient at injecting electrons into the polymer. Other cathodes that have been used in PLEDs include aluminum ($\Phi = 4.16 \pm 0.1$ eV) and magnesium/silver alloy ($\Phi_{Mg} = 3.66$ eV and $\Phi_{Ag} = 4.63 \pm 0.11$ eV)$\textsuperscript{33}$

\textsuperscript{30} See Meng.  
\textsuperscript{31} See Manifacier.  
\textsuperscript{32} See Lide.  
\textsuperscript{33} See Lide.
Equipment and Supplies
(see Appendix C for equipment pictures)

- Hi-Vacuum Thermal Evaporation System (<5X10^{-6} torr)
- High vacuum pump: CTI Cryogenics Cryo-torr 8 (“cryo-pump”)
- Roughing pump: Duo Seal Vacuum Pump
- Pressure gauge: Varian BA2 Sentorr
  - Ion Gauge
  - 2 Thermocouple Gauges
- Crystal Monitor: Sycon Instruments STM-100/MF thickness/rate monitor
  - Gold crystal, ~5.95MHz
- Power supply (~220A max, fuse limited)
- Variac
- AC voltage gauge
- Tungsten deposition boats (4x½x0.010 in): RD Mathis Company, S9A-.010W
- Al_{2}O_{3} (.005in) coated tungsten deposition boats (4x½x0.010 in): RD Mathis Company, S9A-AO-W
- Al_{2}O_{3} (.005in) coated tungsten deposition boats (4x½x0.010 in): RD Mathis Company, S9A-AO-W
- Dry box
- Spinner
- LSE Stokes Ellipsometer: Gaertner Scientific Corporation 7109-C-351-RE1
- Curve tracer
- Voltage supply
- Electronic probes
- Ultrasound bath: Branson 2200
- Oven: Sybron Thermolyne 10500 Furnace
- Diamond scribe: Lenzer Omin Scribe
- UV light source: UVP 90-0012-08 Pen Ray mercury lamp
- Silicon (100) wafer, 4” diameter
- PEDT/PSS (Baytron® P): Bayer Corporation
- Glass slides: Trident Pre-cleaned microscope slides
- Aluminosilicate slides: ITO coated, RS = 5-15 ohms, Delta Technologies, Ltd
- Scotch® tape
- Aluminum metal: purity unknown
- Indium/Tin shot (90%/10%): 99.999% pure, Electronic Space Products Inc.
- Calcium shot: 99.5% pure, Alfa Aesar
- Isopropanol: Spectrum Chemicals and Laboratory Supplies
- Acetone
• Reverse osmosis water
• Lab Set-up and Preparation
  The very first thing that I did to start my project was to familiarize myself with the lab areas and establish a lab bench in Millikan B21 (MB21). MB21 is the location of the high-vacuum deposition system, as well as a fume hood, a flammable materials storage cabinet, and other workspaces. Down the hall is Andrew B57 (AB57), Dr. Tanenbaum's materials lab, where the atomic force microscope is located. The dry box is located in the basement of Seaver North (SN) and belongs to the chemistry department, while the spinner is in Professor Wayne Steinmetz’s lab in SN and is on loan to Peter Chiarelli ('03) from Los Alamos National Laboratories. The ellipsometer is owned by Harvey Mudd College and is located in Professor Shenda Baker’s lab in Jacobs (HMC).

  The first task I undertook was to acquire the PEDT/PSS (poly(3,4-ethylenedioxythiophene)/poly(styrene sulphonic acid)) that would be used for my polymer emissive layer. PEDOT\textsuperscript{34} was originally developed and patented by the German chemical company Bayer for use as a conductive film for glass windows. Due to its popularity as a hole-transport layer in PLEDs and OLEDs, PEDOT/PSS has since become available in a special electronics grade. Through a contact in the Bayer Corporation Electronic Chemicals division\textsuperscript{35}, I was able to acquire a free 1.0 kg sample of PEDOT/PSS in a spin-ready aqueous solution. Because of its sensitivity to light, it is necessary to store PEDOT/PSS in a dark location, thus I kept the solution in a dark cabinet. All other materials, chemicals, and solvents are available from multiple vendors. Those that I utilized are listed above.

  The vacuum deposition system is the most physically complex piece of equipment. I made a couple of modifications to the system after I began using it, including adding the pneumatic valve closest to the roughing pump. This was to aid in attempts to deposit thin films of In\textsubscript{2}O\textsubscript{3}/SnO\textsubscript{2}, known as indium-tin oxide (ITO). For this

\textsuperscript{34} “PEDT”, the name given to poly(3,4-ethylenedioxythiophene) by Bayer, is commonly referred to as “PEDOT” in the literature. This is a widely used convention that I will also follow in this paper.

same purpose I created a gas injector with which a desired gas could be leaked into the bell jar for depositions with small partial pressures of different gases, namely oxygen. It consisted of an expandable bladder that was secured to a needle valve, which opened up to a tube that could be easily attached and detached from the system’s vent valve. Thus, the manifold could be evacuated from the roughing pump as far as the needle valve, leaving only the gas in the bladder to be released into the manifold (with the pneumatic valve closed to prevent oil contamination from the rough pump), and subsequently into the bell jar for deposition.

It was necessary to turn on the cryosorption pump for the thermal evaporation system since it had not been in use for the previous couple of months before I started my project. Cryo-pumps work by maintaining a very large surface area at very low temperatures using liquid Helium. The liquid Helium is kept at around 190 psi by a compressor, so it is not below 4.2 K, but it is very cold none the less.

As with any high-vacuum pump, the cryo-pump does not have an effective pressure range that includes atmospheric pressure. Cryo-pumps can only effectively sustain a vacuum in about the $10^{-10} - 10^{-4}$ torr range, but can evacuate a volume that starts at approximately $1 \times 10^{-1}$ torr if pushed. As with any pump where adsorption is utilized to maintain a vacuum (this includes sputter-ion pumps), the less material that is adsorbed the longer the vacuum can be used. Thus, I pumped the cryo-pump down into the high $10^{-3}$ torr range with the roughing pump (maximum effective range: $\sim 5 \times 10^{-3}$ – 760 torr) through the manifold and bell jar. I then sealed the cryo-pump off from the rest of the system with the gate valve in preparation for its activation. After turning on the compressor and cold head, the cryo-pump took about 2 hours to cool down to 16 K at a pressure in the cold head of 4 psi. There was a sudden, noticeable drop in temperature and pressure after 1¼ hours that is characteristic of these kinds of pumps and should be looked for to indicate proper operation.

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36 Smith, p. 37
37 Smith, p. 37
It was necessary to assemble parts of the glove box since it was in many pieces when I first found it in the physical chemistry lab in the basement of SN. I put everything back together and acquired the necessary components to run the system, including a nitrogen source from MB21, then purged air from the system with nitrogen by repeatedly evacuating the transfer chamber then venting it with air from the main chamber. When the pressure in the main chamber dropped, an automatic valve would open to allow in nitrogen gas into the main chamber. In this way I could continually increase the partial pressure of nitrogen in the main chamber. Assume briefly that the transfer chamber is $\frac{1}{4}$ the total volume of the glove box, that we can completely evacuate the transfer chamber\(^{38}\), that nitrogen composes 70% of ambient air ($P_n=0.70$), and that our source is pure nitrogen gas. Then, the percent of nitrogen in the glove box is given by the recursive relationship

$$
P_n = \frac{3}{4} P_{n-1} + \frac{1}{4}
$$

(8)

where $P_n$ is the percent of nitrogen in the atmosphere after $n$ cycles of evacuation and venting. I ran the process 12 times to reach a theoretical percentage of 99.05% $N_2$.

After the initial purging, the glove box maintains a pressure just above atmosphere with air valves coupled to a pressure gauge. If the pressure drops to atmosphere, the valve opens to put in more nitrogen. Since the main purpose in using the glove box was to protect my elemental calcium, which oxidizes rapidly in the presence of oxygen or water, I also kept the calcium sealed in a container within this atmosphere, so that the calcium would be limited to reacting with the small amount of oxygen and water vapor that was trapped in the container. Despite all these precautions however, some oxidation was visible after a couple weeks of storage. The couple of pieces that I left out of the container in only the glove box showed significant oxidation, worrying me a little that 99% was not sufficient considering the reactivity of the calcium. A liquid hydrocarbon

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\(^{38}\) The roughing pump can reach approximately $5\times10^{-3}$ torr and atmosphere is $\sim760$ torr, so we have essentially 150,000 times less air, which is close enough to being entirely evacuated for our purposes here.
such as kerosene or toluene can also be used as the storage medium to prevent oxidation\textsuperscript{39}. Coupled with a nitrogen environment, this would probably be the most ideal method, although I did not choose to employ it during the duration of my project because I did not know the effects of these liquids on the high-vacuum environment and did not wish to upset the system.

Besides making modifications to some of the major pieces of equipment, I needed to acquire glassware, solvents, and substrates. The Chemistry Department stockroom was a valuable resource because of their large selection of common glassware and solvents, and their willingness to sell or give small quantities of common items to a (ex-chemist) physicist with an account number and a friendly smile. From the stockroom I acquired four wash bottles, acetone, isopropanol, concentrated soap solution, two beakers, an Erlenmeyer flask, two watch glasses, two sealable vials, two funnels, several pieces of filter paper, and kimwipes\textsuperscript{40}.

**Substrate Preparation**

Most of the films that I initially deposited were on glass substrates. These were pre-cleaned microscope slides and could be cut to my specific requirements. I found early on that it was easier to achieve good polymer film coverage and uniformity if I used smaller substrates. Therefore I needed to make my glass slides and silicon wafers into smaller pieces. I used a diamond scribe and a straight-edged piece of steel to scratch a small groove in the surface. The scratching disrupts the stability of the glass, temporarily introducing local weaknesses in the solid that one can exploit to make a smooth break. Using the edge of the same piece of steel as a fulcrum, I quickly snapped the glass along the scratch. Of course, not all the breaks were quite perfect, but the good consistency of the procedure is somewhat surprising. The same technique can be performed for crystalline silicon, although one should note that unlike glass, silicon has preferred lines of breakage. Silicon (100) has square symmetry when viewed

\textsuperscript{39} Sax pp. 72-73
\textsuperscript{40} The Chemistry Department stockroom also has a large selection of chemical catalogs (e.g. Sigma-Aldrich, Alfa Aesar, etc) and general lab supplies (e.g. Fisher Scientific)
perpendicular to its face. The orientation is indicated in commercial silicon wafers by shaving off part of the edge perpendicular to one direction of orientation. The other direction of orientation is perpendicular to this flat edge in the plane of the wafer. Thus, if one desires straight and predictable breaks, one should only break off square pieces with breaks in the directions of orientation of the crystal. Also, since the crystal is more fragile than glass, it should be handled gently.

Most of the slides were by no means brand new and needed to be “pre-cleaned” again. Wearing gloves, I washed the slides with a clean paper towel in a strong, generic soap solution that is common for cleaning laboratory glassware. I subsequently rinsed the slide in tap water, quickly followed by a thorough rinse with distilled water to remove any ionic or polar species. I then dabbed the bottom edge of the slide on a kimwipe to remove excess water and blew desiccated, compressed air gently over the slide to facilitate evaporation. I then rinsed the slides with acetone to remove organic species and again dried it with desiccated, compressed air. I then subjected the slide to an ultrasound cleaning for 5 minutes is an isopropanol bath.

I used the above process initially for my glass substrates, but noticed that acetone appeared to adversely affect my films. Acetone usually leaves behind some organic residue, but it should be easily removable in the isopropanol bath. The general idea is that acetone will remove compounds that isopropanol will not, but that it leaves behind some residual compounds of its own. However, these compounds should be easily removable in a standard isopropanol bath, which leaves very little residue. I eliminated the acetone wash from my procedure and found that the aluminum films’ quality improved considerably in appearance, i.e. they were much more highly uniform.

For the ITO-coated aluminosilicate slides, I performed the same procedure as described above, sans acetone bath, but also subjected the slides to an ultra-violet treatment for 15 minutes as recommended by Braun\textsuperscript{41}. I placed the slides close to a mercury bulb that emits light in the UV range\textsuperscript{42}. Diatomic oxygen gas, $O_2$, absorbs

\textsuperscript{41} See Braun.
\textsuperscript{42} See Staudt.
wavelengths of light at 184.9 nm, reacting with other oxygen gas to form ozone, $O_3^{2−}$.

Ozone, which is a relatively weak cleaning agent, can then absorb light at 253.7 nm breaking it up once again to produce $O_2$. The chemical processes are summarized here for clarity.

\[
\begin{align*}
3O_2 & \xrightarrow{\lambda=184.9\text{ nm}} 2O_2^{2−} + 2O_2 \\
2O_3^{2−} & \xrightarrow{\lambda=253.7\text{ nm}} 2O_2^{2−} + 2O_2 \rightarrow 3O_2
\end{align*}
\]  

Intermediate in both reactions is atomic oxygen, $O^{2−}$, which is “a very strong oxidizing agent”\textsuperscript{43}. Atomic oxygen is thus well suited to break up organic compounds that are often highly reduced, cleaning the substrate surface of organic contaminants.

The silicon wafers were cleaned by blowing off dust with compressed air, then washing them with distilled water followed by drying with desiccated air. They were then subjected to an isopropanol wash followed by drying with desiccated air. As they were not to be used in any electronic devices, only for ellipsometry, and were generally very clean to begin with cleaning them may have had little or no effect, but was done anyway as a precautionary measure.

**Aluminum Evaporation**

Before making any attempts at actually constructing a PLED, I wanted to make sure that I was confident depositing each of the component layers. Since I had previous experience depositing aluminum thin-films with this system in a previous course, I chose to evaporate an aluminum films first.

\textsuperscript{43} See Vig.
Generally, aluminum films are fairly easy to evaporate. Aluminum has a melting point of 660°C\textsuperscript{44} and has a vapor pressure as shown in Figure 10\textsuperscript{45}. This chart shows two important properties: vapor pressures increases with temperature and the rate of change of temperature as a function of vapor pressure is about the same for all materials, i.e. the curves all look about the same. Of course, our independent variable is temperature, not pressure, but it is nice to know that once we reach a given vapor pressure, if we increase the temperature by a certain amount, the vapor pressure should respond in about an equivalent manner for that vapor pressure, regardless of material.

Also, one should notice that aluminum has a curve that is in a relatively low temperature range compared with the other elements\textsuperscript{46}, indicating that thermal evaporation is at least

\textsuperscript{44} Thin Film Evaporation Source Reference, The R.D. Mathis Company

\textsuperscript{45} This figure is taken directly from p588 of Smith.

\textsuperscript{46} Approximately $\frac{1}{3}$ of the elements are shown in Figure ######, but the plots for the other $\frac{2}{3}$ have similar distributions. See Smith pp. 589-590.
relatively conceivable. Aluminum films generally have good adhesion, as aluminum oxidizes very rapidly and adhesive strength is loosely correlated with the free energy of formation for a metal’s oxides\textsuperscript{47}. This correlation makes more sense intuitively if one considers that a few monolayers of water, CO\textsubscript{2}, and various organic vapors are almost always physisorbed\textsuperscript{48} on the substrate surface, regardless of cleaning precautions. These contaminants can make surface adhesion poor by preventing chemisorption\textsuperscript{49} of the incoming flux of atoms with the substrate surface. If the evaporated atoms bind only to themselves or only weakly with the contaminants and not at all with the surface, there will be few covalent bonds with the surface and adhesion will be poor. However, if the metals react with the contaminants to form oxides that bind both the newly formed film and the substrate, adhesion will improve.

For the aluminum evaporations I used Al\textsubscript{2}O\textsubscript{3} (aluminum (III) oxide) coated tungsten deposition boats. Aluminum wets and alloys tungsten\textsuperscript{50}, and Al:W has a significantly lower melting temperature than tungsten alone. Thus if the alloy is allowed to form on an unprotected boat, the boat will melt away at that point, increasing the temperature locally due to the increased resistance of the boat. This causes increased alloying until the electrical circuit is entirely broken as the boat severs in two. I discovered that this can happen very quickly and generates a bright flash of light.

For each of the aluminum evaporations I cleaned the substrate as previously described and placed a strip of Scotch® Tape across the film. Scotch® Tape has a very straight edge and leaves very little residue on the glass. Thus it makes a good edge for imaging with AFM. If there is poor adhesion to the substrate, there can be some peeling of the film upon removing the tape however. I pumped the system down to below 1×10\textsuperscript{-6} torr before depositions when possible, which generally took about 45 minutes. I increased the current flowing through the boat slowly to the deposition current over about 6

\textsuperscript{47} Smith, pp. 198-199
\textsuperscript{48} Physisorbed refers to atomic or molecular species that interact with the surface via Van der Walls interactions, but do not form ionic or covalent bonds.
\textsuperscript{49} Chemisorbed refers to atomic or molecular species that form covalent bonds with a surface, although these need not be particularly strong bonds.
\textsuperscript{50} Thin Film Evaporation Source Reference, The R.D. Mathis Company
minutes in order to allow the boat time to warm up. Since the resistance of tungsten, and most metals, decreases as a function of temperature, it is important to allow the current to stabilize to ensure a stable deposition temperature. I found that the aluminum would consistently melt at 145±3 amps, which I assume is just about 660ºC based on figure 10 and other reliable sources\textsuperscript{51}, although I have no direct way of measuring the temperature at this time. Also, I waited until I could see that the aluminum was fully melted to begin deposition as this would ensure the most consistent flux of atoms from the aluminum surface. I opened the shutter to allow a flux of atoms to strike the substrate surface at the top of the chimney, and closed the shutter when a desirable thickness had been reached. I also varied the current and observed the rate of evaporation. This data is attached in Appendix D. The current was slowly decreased over about 2 minutes so as not to crack the boat. The vacuum chamber was then allowed to cool for at least an hour, usually longer, to prevent air molecules from condensing on the surface as it cools. The manifold was vented through a desiccant, followed by the chamber through the manifold and desiccant, before removing the sample. Boats were replaced if they appeared to have an unreasonable quantity of deposited material on them before the next deposition.

\textsuperscript{51} Weast p. B-7
I successfully evaporated four aluminum films onto glass slide substrates, both to practice using the system and to calibrate the crystal monitor. The thicknesses of the first three films could be determined by using the AFM. The image analysis software for the AFM has a function that can determine step-height. It allows you to select two different square areas whose heights it averages to give a good estimation of the step-height in most cases. I utilized this feature to give the step-heights as reported here to calibrate the crystal monitor. I could not determine the step-height from one of the films because of poor edge qualities. However, since my project did not have rigid constraints for the thickness of the aluminum films, three data points were sufficient for a rough calibration of the crystal monitor (see figure 11).

**Indium-Tin Oxide**

As discussed the theory section, indium-tin oxide (ITO) is one of the best and widely used transparent conducting oxides and is a great match for the requirements of my project here. Initially, I thought that it would be a good idea to try to make ITO films for my devices. Knowing from literature and previous experience with the material that films could be deposited by evaporative methods, I purchased some ITO in hopes of...
evaporating it here. I followed procedures as described previously for evaporating metals, but could see no effects even as I reached 220 amps for the evaporating current. This is the limiting current on the power source fuse and it blew as I tried to increase the current just a little more. Needless to say, ITO, like almost every other oxide, has a very high melting temperature, approximately 1900°C, that is not readily obtainable by standard means.

My mistake regarding ITO lie in thinking that the film composition would be the same as the evaporating source composition. ITO is generally only used in its oxide form for electron beam and sputter depositions. Although some references report using ITO prepared by evaporative means, they are most certainly not talking about evaporating ITO to make an ITO film. They are probably talking about a much easier method, which involves co-evaporating indium and tin, usually as an alloy. If one performs the evaporation in an oxygen atmosphere, then the indium and tin react with the oxygen on their path towards the substrate, to form their oxides: In₂O₃ and SnO₂. This form of reactive evaporation is the method that I really should have been attempting.

**Indium/Tin Alloy Evaporations**

Indium/Tin (90%/10%) alloy has a low melting point of 244°C somewhere between indium and tin, 157°C and 232°C respectively. Films of this material can be deposited much like any other metal. By varying the partial pressure of the oxygen atmosphere, one can vary the amount of oxygen that gets incorporated into the film. Since the conductive properties of ITO are based on free electrons in an oxygen deficient crystal lattice, tuning the oxygen partial pressure is the key to achieving optimal film properties. Through a contact at the National Renewable Energy Lab who has experience making ITO via an evaporative method, I learned that approximately 2.4 x 10⁻² torr was an especially good pressure to attempt a reactive thermal evaporation for

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52 http://www.cerac.com/pubs/proddata/ito.htm
53 Value given by the Materials Safety Data Sheet for In:Sn as provided by Electronic Space Products Inc. for #Knc6069
54 Thin Film Evaporation Source Reference, The R.D. Mathis Company
ITO\textsuperscript{55}. This particular method was used to deposit ITO on amorphous silicon substrates and yielded films with a sheet resistance of approximately 60 $\Omega/\square$ at a thickness of 800Å.

I first made a film of In:Sn without oxygen present at $4.5 \times 10^{-7}$ torr to find the melting current of the alloy and generally feel out how it would respond during evaporation. I found that In:Sn melted at ~145 amps and that the deposition rate depended on the current in this pressure regime as shown in figure 12.

I next attempted to perform an evaporation such that the partial pressure of oxygen in the chamber would be around $2.4 \times 10^{-2}$ torr. Atmospheric air is 21% $O_2$, so if one uses $1.0 \times 10^{-1}$ torr of air as the gas present during evaporation, one has a partial pressure of oxygen of $2.1 \times 10^{-2}$ torr. I was not able to deposit any In:Sn at this pressure. I feel that this is most likely due to rapid cooling of the In:Sn by the working gas and the highly decreased path length for the evaporated molecules. Evidence for this lies in the fact that the source material did not melt until the current was at nearly 200 amps, which indicates that there was considerable cooling via gaseous molecules.

Although I constructed a device to store and inject oxygen gas into the system, I did not end up using it. I decided that although I was fairly confident I could eventually get ITO films that were of sufficiently high quality to use as part of an PLED, that the process of fine-tuning the ITO films would be much too time consuming a process to tackle within the scope of my thesis. ITO coated glass is a fairly common, inexpensive commercial product, so I decided to buy it instead of try further to make it and consider the ITO ordeal part of the learning process.

\textsuperscript{55} Of course, process pressures are system dependent due to different geometries.
Calcium Evaporations

Calcium is a very reactive metal, oxidizing easily in air to form a non-protective Ca(OH)$_2$ layer, releasing hydrogen gas.

$$Ca_{(s)} + 2H_2O_{(g)} \rightarrow Ca(OH)_{2(s)} + H_2_{(g)}$$  \hspace{1cm} (10)

Calcium is fairly soft and ductile and has a melting point of 839°C$^{56}$. Knowing that calcium would be highly reactive in air, I took steps to prevent too much exposure time for the calcium by using the glove box. Before an evaporation of calcium, I vented the chamber and prepared all the substrates so that the last thing to do would be to actually load the calcium. This minimized the time during which the calcium would be both out of the nitrogen filled glove box and the sealed vials that I used as transport vessels.

Evaporations of calcium were characterized by deposition at a small rate for some amount of time, followed by a very brief deposition time in which a lot of material was deposited, often at a rate greater than 10 Å/s. From observing this process happen in vivo, my hypothesis is that the calcium hydroxide layers act as a structural support until the vapor pressure due to the heated calcium actually ruptures the outer shell, depositing a large amount of calcium very quickly. Calcium has a melting point of 839°C and calcium hydroxide has a melting point of 580°C, but the vapor pressure of calcium is higher. For arguments sake, let’s say we maintain the temperature at 460°C. At this temperature, calcium has a vapor pressure of 1x10$^{-4}$ torr, but it is trapped inside the thin calcium hydroxide shell that is not evaporating very quickly at this temperature. Once just enough calcium hydroxide has evaporated, the shell bursts and the calcium can escape, quickly depositing on the substrate in this temperature regime. There are two ways to avoid this scenario: maintain an entirely water free environment by doing each step of the evaporation in a glove box or minimize exposure as much as possible and wait for the right time to begin deposition. I opted for the latter because to facilities constraints.

$^{56}$ See Othmer.
### Spinning PEDOT/PSS Films

Spin coating a polymer is a quite straightforward process relative to other thin-film deposition techniques. One coats one’s substrate in a solution containing the polymer to be deposited then spins the substrate at a high angular velocity until the film is uniform. The thickness of the film is dependant on the angular velocity of the substrate during deposition in a roughly inverse relationship. Data for films of PEDOT/PSS that I spun onto crystalline silicon substrates is shown in figure 15.

The film thicknesses were determined primarily by ellipsometry in Professor Baker’s lab at Harvey Mudd College and confirmed with AFM at Pomona College. Film thicknesses reported below for devices are based on this calibration unless otherwise stated. Using the ellipsometer, I took cross-sectional data for two of the films, passing

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57 See Appendix A for more information regarding ellipsometry.
through the center of the film from corner to corner. This data is shown in figures 13 and 14. As you can see, the films are not as ideally uniform as one would like. However, the uniformity seems to improve with increasing spin speed (good for thin-films devices). Also, these films were deposited by dropping the solution on the substrates while spinning at full speed for 60 seconds. I have since increased the duration of the spin to 90 seconds and began coating the substrates with solution before spinning. Both techniques appeared to make a noticeable difference in film uniformity based on greater uniformity of the film colors. Recall that for films with thicknesses roughly on the order of the wavelengths of visible light, certain wavelengths are absorbed more strongly than others, such that different film thicknesses appear different colors for a given material.

**ITO/PEDOT/Ca/Al Device Preparation**

Combining the steps that I had done separately, I undertook to make full devices of the design shown in figure 2 on the right. I used calcium as the cathode (with a layer on aluminum on top of that to prevent oxidation of the calcium film), PEDOT/PSS as the polymer, and ITO as the anode (as commercially available). The substrate preparation for the ITO coated slides was the same as for plain glass sides except that I did not wash the slides with soap or attempt to touch the slide surface in any way. The deposition steps were the same as previously described. Thin-film devices are highly sensitive to the elements, so I took steps to minimize the exposure of the films to harsh elements. I undertook to complete all the steps necessary to make a full device with as little time between steps as possible so as to minimize the chance of contamination from airborne sediments and vapors. I found early on that metal tweezers visibly scratched the sample surfaces and that even Teflon-coated tweezers could do damage to the thin polymer films. Since any scratch or pinhole in the polymer layer would lead to a short when I deposited the calcium cathode, the utmost care needed to be taken with the samples after spinning on the polymer. As it was necessary to touch the samples, it was done with sterile, gloved hands and only on the

58 I apologize that the figure numbers are out of order; it is a result of Word formatting problems.
edges of the slides. I minimized the risk of an entirely bad sample by statistics: I made more than one device per substrate. Using an aluminum mask, I was able to deposit several small circles of calcium (and aluminum on top of that as a protective layer against oxidation) on each polymer/ITO/glass substrate. The circular patterns of calcium/aluminum are pronounced in device pictures (see figure 16). AFM imaging showed that although the masked edges were not as sharp and pronounced as those made using scotch tape (previously described), they were not prone to peeling off the substrate surface and gave reliable film thicknesses for that reason.

I have made 18 devices total as of April 26, 2002. I made 9 devices on two substrates with a polymer layer thickness of 600 ±50Å at 6500 rpm spin speed (based on calibration curve: figure 15). I also made another 9 devices on two different substrates with a polymer layer thickness of 900 ±100Å at 2500 rpm spin speed (based on calibration curve: figure 15).
ITO/PEDOT/Ca/Al Device Testing and Results

I tested three things regarding the devices that I had made: if they were shorted, if they would emit visible under an applied voltage, and whether they the electrical characteristics of a diode. To make good electrical contact and not risk penetrating the films with the probes, I applied a thick solution of colloidal silver to the aluminum cathode and the ITO where I had rubbed off some polymer. I immediately found out that several of the device that I had made were shorted. In just using a variable power supply and a digital multimeter, one could see that several of the devices responded ohmically, the resistance being much to low to be a diode. This was to be expected as a peer of mine had warned me that for every three OLEDs he’s ever made, about 2 have been shorted.

To check if the devices emitted light, I simply applied a forward voltage, increasing the voltage incrementally. I generally stopped at about 15 volts, reasoning that this was sufficiently high to insure that I had reached the turn-on voltage\textsuperscript{59}. For several devices there started to be a very faint blue glow emanating from the device.

\textsuperscript{59} The “turn-on voltage” is loosely defined as the voltage at which light emitted from a device is visible to the human eye.
after applying this voltage (see figure 16), I doubt that this effect was due to an electroluminescent phenomena within the polymer. It could be that the light was being emitted as the PEDOT/PSS, which is acidic, reacted with the oxides of the ITO layer. However, this is just speculation; further investigation would be required to determine the source of this light, as most materials will emit light when supplied with sufficient energy.

Finally, I used a curve trace to plot the current through the device as a function of voltage. Two typical curves are shown in figures 17 and 18 for the forward and reverse voltages respectively. While it is clear that the devices are non-ohmic, it is equally clear that they are not diodes. Recall that the typical curve for a diode would consist of very little current as a function of the reverse voltage (negative voltages) until some characteristic “break-down” voltage, after which the current increases very quickly. In the forward direction the current increases exponentially as a function of voltage. Thus, it is not clear how to characterize these devices other than to say they currently do not function as polymer light-emitting diodes.

I have two theories as to why my particular PLED design has not worked. The first is simply that the design cannot work. While I have yet to find in literature that this particular design does not work, I have yet to find evidence that anyone else has gotten it to work either. I suspect however that others have tried and also been unsuccessful.

Conclusions and Outlook

While I was not successful at constructing a working polymer light-emitting diode, I did manage to accomplish my other goals. I managed to set up a system for construction of PLED devices, utilizing various resources within the five college community. I characterized some important elements in the process, such as calibrating the crystal monitor and calibrating the spinner so that construction of PLEDs will be easier and faster in the future. I have also established contacts at the various companies and organizations so that acquiring the different parts and chemicals necessary for this project can be accomplished easily. Necessarily, I have also tested
the limits of the current equipment, setting some upper limits on what can be done, hopefully so that others do not do the same.

This project is not yet fully complete, nor will my involvement end here. As of this week, I have made arrangements to try another device structure, one that I am much more confident will work. ITO/PPV/Al\textsuperscript{60}, ITO/PPV/Ca\textsuperscript{61}, and ITO/PEDOT/PPV/Ca\textsuperscript{62} devices have all been demonstrated with good results. I have made arrangements to synthesize poly (p-phenylene vinylene) from its molecular precursors, so I am hopeful that I will have more results in the next couple of weeks. If a successful device can be made, then I will try to formulate a feasible lab for Dr. Tanenbaum’s Material’s Science course.

\textsuperscript{60} See Burroughes
\textsuperscript{61} See Greenham
\textsuperscript{62} See Friend
References


Bruan, David. *EE 422 – Polymer LED Fabrication Laboratory Manual*. Electrical Engineering Department, California Polytechnic State University, San Luis Obispo, CA.


Appendix A: Ellipsometry\textsuperscript{63}

Ellipsometry is a non-destructive surface analysis technique that, in the case of the ellipsometer used in this project (figure ######), can quickly measure the thickness and index of refraction for thin-films. The area resolution of ellipsometry is determined primarily by the focus of the incident laser beam. The ellipsometer consists primarily of an arrangement that linearly polarizes laser light (in our case from a HeNe laser at $\lambda = 632.8$ nm) and measures the change in polarity of the light after it has been reflected off a sample.

The reflectance coefficients are related to the indices of refraction, $n_1$, and $n_2$, for the two interfaces by

$$ R = \frac{I_R}{I_0} = \left( \frac{n_2 - n_1}{n_2 + n_1} \right)^2 $$

(11)

where $I_0$ is the intensity of the incident light and $I_R$ is the intensity of the reflected light. After reflection on a sample surface, a linearly polarized light beam is generally elliptically polarized. The reflected light has phase changes that are different for electric field components polarized parallel (p) and perpendicular (s) to the plane of incidence. Ellipsometry measures this state of polarization, or more precisely the complex ratio, $\rho$, of the perpendicular and parallel Fresnel coefficients of reflection given by

$$ \rho = \frac{R_p}{R_s} = \tan \Psi \times e^{i\Delta} $$

(12)

where $\Psi$ and $\Delta$ are the amplitude ratio and phase shift, respectively, of the p and s components. These are known as the ellipsometric parameters when they are given by $\tan \Psi$ and $\cos \Delta$. The reflectance coefficients are directly related to the optical

\textsuperscript{63} Portions of this discussion closely follow the explanation of ellipsometry given by Nicolae Sfetcu. http://alfaie.virtualave.net/elch/ellips/ (26 April 2002)
constants of the surface, assuming the ambient is air (n=1), by the Fresnel relations and are given by

$$R_p = \frac{n \cos \phi_i - \cos \phi_t}{n \cos \phi_i + \cos \phi_t}$$

$$R_s = \frac{\cos \phi_i - n \cos \phi_t}{\cos \phi_i + n \cos \phi_t}$$

where $n$ is the complex refractive index ($n = N - iK$) of the surface, $\phi_i$ is the incident angle, and $\phi_t$ is the angle of transmission.

The angle of refraction may be obtained by using Snell-Descartes's Law:

$$\sin \phi_i = n \sin \phi_t$$

If the sample can be modeled as an ideal solid and we know the incident angle, then the real and imaginary parts of the complex refractive index may be calculated from the measured $\tan \Psi$ and $\cos \Delta$ parameters. The thickness, $t$, of a transparent layer on known substrate can also be deduced from

$$I_t = I_0 (1 - R)^2 e^{-t/\beta}$$

where $\beta$ is the absorption coefficient.

The thin-films may be a single film on a substrate of known index of refraction, or multiple thin-films on a substrate. In the latter case, the indices of refraction and thicknesses of the films should be determined by building up the structure one film at a time, always having only one unknown film. The computational technique involved actually relies on function fitting where a computer minimizes the mean square deviation between calculated and measured ellipsometric parameters $\tan \Psi$ and $\cos \Delta$.

The reader is encouraged to consult the literature for a more thorough and comprehensible treatment of ellipsometry.

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64 For a complete derivation and further information regarding the Fresnel equations see pp. 111-113 of Hecht.
65 Callister, p. 15
66 Tompkins is a good source of information. See also Riedling.
Appendix B: Quartz Crystal Monitors

One of the more important pieces of equipment used in thin-film work is the quartz crystal monitor. The crystalline quartz crystal vibrates at some natural resonant frequency (~5.95 MHz), which two electrodes pick up and amplify to drive it. The crystal monitor can detect reductions in the resonant frequency due to mass accumulation. If we model the crystal as a simple harmonic oscillator, with its period and frequency given by

$$T_v = \frac{1}{v_r} = 2\pi \sqrt{\frac{m}{k}}$$  \hspace{1cm} (17)

where we define our variables such that $T_v$ is the vibrational period of the crystal, $T_{v0}$ is the vibrational period of the crystal prior to any new deposition, $v_r$ is its resonant frequency, $k$ is the spring constant for the crystal, $m_d$ is the mass deposited, and $m_c$ is the mass of the crystal. The change in the period of oscillation due to mass accumulation then is given by

$$\Delta T_v = T_v - T_{v0}$$

$$\Delta T_v = 2\pi \sqrt{k} \frac{m_c + m_d}{m_c} = 2\pi \sqrt{km_c} \left(1 + \frac{m_d}{m_c}\right)^{\frac{1}{2}}$$ \hspace{1cm} (18)

$$\Delta T_v = 2\pi \sqrt{km_c} \left(1 + \frac{1}{2} \frac{m_d}{m_c}\right) = \left(\frac{\pi \sqrt{km_c}}{2m_c}\right) m_d + \pi \sqrt{km_c}$$

$$\Delta T_v = \left(\frac{\pi \sqrt{km_c}}{2m_c}\right) m_d + \pi \sqrt{km_c} - T_{v0}$$ \hspace{1cm} (19)

In short, the change in the period of oscillation is simply proportional to the mass deposited on the crystal. I have used Newton’s binomial formula between the second and third lines of equation #####, so our equation only holds true when $m_d << m_c$, the mass deposited is much less than the mass of the crystal. This inequality sets

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67 Smith, p. 102
boundaries on the lifetime of the crystal with an approximate practical limit\textsuperscript{68} of
\[ m_d / m_c < 0.1. \] Since we are interested primarily in the thickness, \( t_d \), of our film, not its
mass, we use
\[ t_d = m_d / \rho_d \]
where \( \rho_d \) is the bulk density of the material, to get
\[ t_d \propto \Delta T_v \]
There are three variables that the crystal monitor needs to properly measure the
thickness of a deposited film: the material’s density, the z-factor\textsuperscript{69}, and the “tooling”, a
scaling factor that depends on the location of the crystal monitor relative to the substrate.
The first two variables are published, well known constants for most materials, but the
last needs to be determined uniquely for each system.

\textsuperscript{68} Smith, p. 102
\textsuperscript{69} The z-factor has to do with the elastic modulus of the material and extends the effective lifetime
of the crystal by taking into account how \( k \) changes with mass accumulation. This is beyond the
scope and relevance of my discussion here: see Smith for more information.
Appendix C: Equipment Pictures

Figure 19: Atomic Force Microscope.
Figure 20: Ellipsometer (HMC)

Figure 21: Fume hood with ultrasonic bath, substrates, and solvents.
Figure 22: A glowing evaporation boat during deposition.
Appendix D: Various Figures

Figure 23: Various substitutions of polythiophenes, tuned to emit particular wavelengths of light. These are in the same family as PEDOT. (Figure taken from...

Figure 24: Karl and Sara are little red monsters or motivation.