

PLED Enhancement and Re-use

A Thesis

Presented to the Faculty of

California Polytechnic State University

San Luis Obispo

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science in Electrical Engineering

By

Carlos Antonio Ayala

May 2010

Carlos Antonio Ayala
©2010
ALL RIGHTS RESERVED

COMMITTEE MEMBERSHIP

TITLE: PLED Enhancement and Re-use

AUTHOR: Carlos Antonio Ayala

DATE SUBMITTED: May 21st 2010

COMMITTEE CHAIR: David Braun, Professor
Electrical Engineering

COMMITTEE MEMBER: Robert Echols, Associate Professor
Physics

COMMITTEE MEMBER: Helen Yu, Associate Professor
Electrical Engineering

ABSTRACT

PLED Enhancement and Re-use

Carlos Antonio Ayala

Polymer light emitting diodes (PLEDs) represent new technology for display applications. However, these polymer based devices could benefit from increased efficiency and material longevity.

This thesis examines how preprocessing PLED indium tin oxide (ITO) anodes and reprocessing previously used substrates can create brighter, more efficient PLEDs. The project accomplishes this by simple changes to fabrication techniques, such as additional cleaning, etching, or thermal annealing, to improve pristine device luminance and efficiency. The project also examines substrate re-use techniques to repair ITO substrate damage, and effects of polymer aging on PLED luminance and efficiency.

PLEDs fabricated with polymer aged to varying degrees exhibit increased efficiency and luminance. Etching previously used substrates allows PLED re-use; substrates etched in hydrochloric acid also demonstrate increased efficiency and luminance.

Preprocessing improves device performance, while etching results in reusable substrates.

ACKNOWLEDGEMENTS

Ineffable gratitude belongs to my advisor, Dr. David Braun, who guided me through the days and years with ostensibly superhuman patience. No portion of intellectual contribution from this thesis would exist without his deft commitment to curiosity, and empyreal belief that the temporal effort would endeavor to matter. It does and it will.

I also wish to thank Allen, whose friendship and example helped me surpass the most arduous times during the project. Gramercy to Donna, whose love continually strengthened me and kept the cavalcade moving onward. These years are etched with your names.

Thank you to my parents and family for their unequivocal support. Kathryn and Moses, it was all worth it.

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	viii
CHAPTER 1 OLED INTRODUCTION	1
CHAPTER 2 TIMING AND TEMPERATURE EXPERIMENTS	14
2.1 Experiment #1 Varying delay between UV ozone reactor treatment and PEDOT application	16
2.2 Experiment #2 Temperature Modification	23
2.3 Experiment #3 Silicon Wafer Modification	32
CHAPTER 3 CLEANING AGENT EXPERIMENTS	45
3.1 Experiment #4 Substrate Reuse: Initial Cleaning Agents	47
3.2 Experiment #5 Substrate Reuse: Secondary Cleaning Agents	58
3.3 Experiment # 6 Substrate Reuse: Simple Cleaning Agents	65
CHAPTER 4 AGING AND ETCHING EXPERIMENTS	72
4.1 Experiment #7 Substrate Reuse: Aged Polymer Performance	73
4.2 Experiment #8 Substrate Reuse: Etching ITO	85
CHAPTER 5 CONCLUDING REMARKS	100
REFERENCES	104

LIST OF TABLES

Table 1. Summary of experiment # 3 luminance and efficiency averages with T-test results.	41
Table 2. P values for large pixels.	81
Table 3. Variance and standard deviation for large pixels.	82
Table 4. P values for small pixels.	82
Table 5. Standard deviation and variance for small pixels.	83
Table 6. P values for large pixels, with check IV data at 10 mA.	95
Table 7. Standard deviation and variance of large pixel data.	95
Table 8. P values for small pixels, with check IV data at 0.9 mA.	96
Table 9. Standard deviation and variance of small pixels.	97

LIST OF FIGURES

Figure 1. Structures of PPV, MEH-PPV, and OC1C10.	14
Figure 2. Energy band diagrams of a PLED made with an ITO anode and calcium cathode	16
Figure 3. Depiction of electron orbitals in saturated and conjugated polymer semiconductors.	16
Figure 4. PLED diagram with various cathodes.	18
Figure 5. Standard PLED fabrication process flow.	21
Figure 6. Check IV Luminance vs. time for large pixels at 10 mA.	29
Figure 7. Check IV Small pixel luminance vs. time at 0.9mA.	30
Figure 8. Check IV Efficiency vs. time for large pixels at 10 mA.	31
Figure 9. Check IV Small pixel Efficiency vs. Time at 0.9 mA.	31
Figure 10. Check IV Small pixel Efficiency vs. Time at 5 V.	32
Figure 11. Experimental process depicting substrates heated before UV Ozone reactor treatment	35
Figure 12. Check IV at 5V, Large Pixels, efficiency vs. temperature Substrate.	36
Figure 13. Check IV at 5V, Large Pixels, Luminance vs. Substrate Temperature.	37
Figure 14. Check IV at 5V, Small Pixels, Luminance vs. Substrate Temperature.	38
Figure 15. Check IV at 5V, Small Pixels, Efficiency vs. Substrate Temperature	39
Figure 16. Check IV at 10mA, Large Pixels, Efficiency vs. Substrate Temperature.	40
Figure 17. Check IV at 10mA, Large Pixels, Luminance vs. Substrate Temperature.	40
Figure 18. Check IV at 0.9 mA, Small Pixels, Efficiency vs. Substrate Temperature.	41
Figure 19. Check IV at 0.9 mA, Small Pixels, Luminance vs. Substrate Temperature.	41
Figure 20. Experimental process depicting substrates atop a silicon wafer during UV ozone reactor treatment.	44
Figure 21. Check IV data for large Pixel Luminance vs. Temperature at 5V.	46
Figure 22. Check IV data for large pixel efficiency vs. temperature at 5V.	47
Figure 23. Check IV data for small pixel luminance vs. Temperature at 5V.	48

Figure 24. Small pixel efficiency vs. temperature at 5V.	48
Figure 25. Check IV data at 0.9 mA for small pixel luminance vs. temperature.	49
Figure 26. Check IV data at 0.9 mA for small pixel efficiency vs. temperature.	50
Figure 27. Check IV data for large pixel efficiency vs. temperature at 10mA.	51
Figure 28. Check IV data for large pixel luminance vs. temperature at 10 mA.	51
Figure 29. Experimental process for experiment #4.	59
Figure 30. All pixel A (Large Pixel) Luminance vs. Voltage curves.	61
Figure 31. All pixel D (Large Pixel) Luminance vs. Voltage curves.	61
Figure 32. All pixel b (small pixel) luminance vs. voltage curves.	62
Figure 33. All pixel c (Small pixel) luminance vs. voltage curves.	63
Figure 34. Luminance Check IV points for all large pixels at 10mA.	64
Figure 35. Luminance Check IV points for all small pixels at 10mA.	64
Figure 36. Efficiency Check IV points for large pixels at 10mA.	65
Figure 37. Efficiency Check IV points for small pixels at 10mA.	67
Figure 38. Experimental process of experiment #5.	70
Figure 39. Luminance of large pixels at 10mA.	71
Figure 40. Efficiency of large pixels at 10mA.	72
Figure 41. Luminance for small pixels at 0.9mA.	73
Figure 42. Efficiency for small pixels at 0.9mA.	73
Figure 43. Luminance of Large Pixels at 10mA.	77
Figure 44. Efficiency of Large Pixels at 10mA.	79
Figure 45. Luminance of small pixels at 0.9mA.	80
Figure 46. Efficiency for small pixels at 0.9mA.	81
Figure 47. Experimental process utilizing aged OC1C10.	85
Figure 48. Luminance plot of large pixels at 10mA.	87
Figure 49. Luminance plot of small pixels at 0.9mA.	87
Figure 50. Luminance vs. Voltage curves for large pixels.	88
Figure 51. Luminance vs. Voltage curves for small pixels.	88

Figure 52. Efficiency of large pixels at 10mA.	89
Figure 53. Efficiency of small pixels at 0.9mA.	90
Figure 54. Efficiency vs. Voltage curves for large pixels.	91
Figure 55. Efficiency vs. Voltage curves for small pixels.	91
Figure 56. Experimental process including initial etch of previously used substrates.	97
Figure 57. Luminance of large pixels at 10mA.	99
Figure 58. Luminance of small pixels at 0.9mA.	99
Figure 59. Efficiency of large pixels at 10mA.	101
Figure 60. Efficiency of small pixels at 0.9mA.	101
Figure 61. Full luminance curves for large pixels.	102
Figure 62. Full efficiency Vs. voltage curves for large pixels.	103
Figure 63. Luminance vs. Voltage.	104
Figure 64. Full efficiency curves for small pixels.	105

Chapter 1 OLED Introduction

The world grows increasingly attuned to visual stimuli. High definition television, ubiquitous computers, and the internet all place high value on vision, resolution, and accessibility of this visual stimuli. In addition, studies indicate that not only is visual stimulation the dominant form of information processing and learning for the 6.8 billion human beings on earth, but that the words we read, often associated with both speech and sound, are actually processed as a series of individual pictures, with the inherent speech sounds of words playing the role of afterthought or largely unimportant data. This leads to a direct link between our abilities to optimize visual representations and accessibility of information, and our collective, cumulative worldwide knowledge base.

With the potential of images more clearly understood, research improving visual devices acquires another dimension of importance. Organic light emitting diodes (OLEDs) provide a great vehicle to revolutionize when and where people have access to a video screen. Flexible OLED screens could appear wrapped around a telephone pole, a human arm or leg, on the corner of a building, or as part of a physically transforming display. The known potential and importance of OLEDs drives this thesis project to discover methods which improve the efficiency or output luminance of OLEDs.

Economic and empirical data suggest tuning other device layers and fabrication more cogently maximizes device efficiency and luminance than adjusting the polymer light emitting diode (PLED) bulk. A designed and formed electroluminescent polymer layer leaves little room for adjustment during full device fabrication. However, changes

to type, thickness, temperature, and fabrication equipment of the device can still occur during the fabrication process. Also, locally manufacturing electroluminescent polymers is expensive and difficult, leading to the option to research other methods of PLED enhancement. Discovering if PLEDs have sustainable potential commensurate with their economic potential led to exploration of PLED reusability.

This thesis examines how preprocessing PLED indium tin oxide (ITO) anodes and reprocessing previously used substrates can create brighter, more efficient PLEDs. The project accomplishes this by simple changes to manufacturing techniques, such as additional cleaning, etching, or thermal annealing, to improve pristine device luminance and efficiency; the project also examines substrate re-use techniques to repair ITO substrate damage, and effects of polymer aging on PLED luminance and efficiency.

Selected Historical Highlights Of Organic LEDs

Electroluminescence was first discovered in a piece of carborundrum, SiC crystal, by H.J. Round in 1907¹; Bernanose discovered electroluminescence in organic acridine orange and quinacrine by applying a high voltage alternating current field². Over fifty years later, Nick Holonyak Jr. fabricated the first inorganic light emitting diode (LED) in 1962³. Pope et al discovered single crystal anthracene electroluminescent devices by constructing LEDs with III-V compound semiconductors⁴. In 1975, the first organic electroluminescent device was made using the polymer polyvinyl carbazole (PVK), which would later produce highly efficient organic LEDs⁵. Next, in 1987, the now famous C.W. Tang group from Kodak Chemical built the first efficient multilayered

organic LED ⁶. This device provided significant device improvement over previous iterations.

In 1977 Heeger, MacDiarmid, and Shirakawa made another famous discovery: the use of conjugated polymers as a semiconductor ⁷. Conjugated polymers possessed unique chemical and physical properties while heavily doped; scientists carefully examined the polymers' nonlinear optical performance under photoexcitation, and polymer metal interface behavior.

At first, Schottky polyacetylene film diodes used metal-semiconductor-polymer layers. The diodes produced high photosensitivity, but low electroluminescence, due to polyacetylene's weak electronic configuration ⁸. Following this, the 1980's produced much conjugated polymer research, both in material research and solution fabrication. This led to the polythiophene derivative poly(3-alkylthiophene)(P3AT) . Shortly thereafter, the University of Californian Santa Barbara showed the solution fabrication of metal/P3AT/metal thin-film devices ⁹. This unleashed the grand behemoth. Cambridge's J.H. Burroughes and R.H. Friend unveiled a light emitting device made with unsubstituted poly(p-phenylenevinylene) (PPV), shown in the top left of figure 1 ¹⁰. This begat a highly efficient polymer light emitting diode constructed of solution processed polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene](MEH-PPV) , shown in the top right of figure 1, fabricated by Braun and Heeger in Santa Barbara, California ¹¹. The polymer shown in the bottom left of figure 1, OC1C10, used in all

experiments described in this thesis, is an alkoxy-substituted poly para-phenylene vinylene (PPV) derivative.

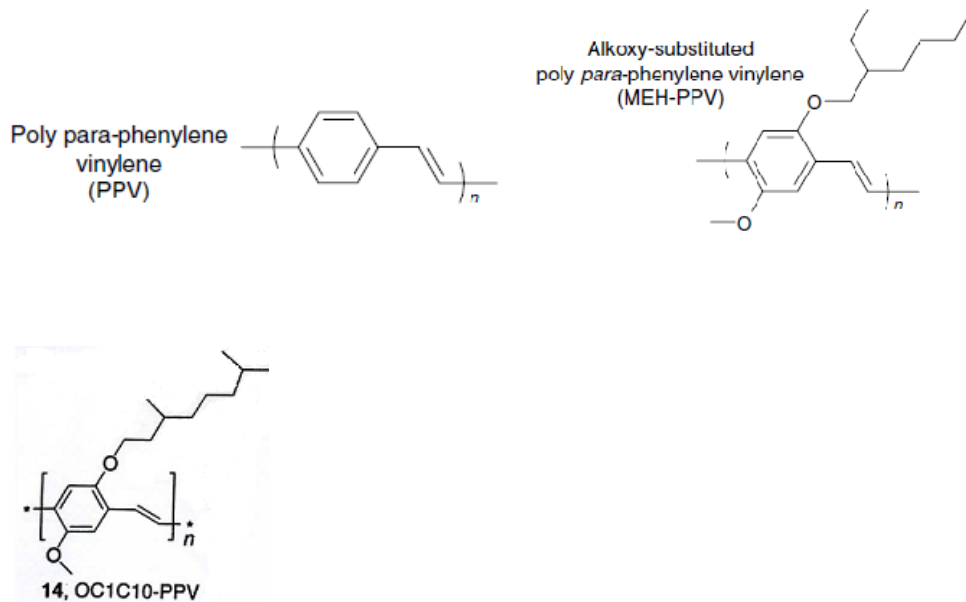


Figure 1. Structures of PPV, MEH-PPV, and OC1C10. Li, Zhigang et al. *Organic Light-emitting Materials and Devices*. CRC Press, Boca Raton, 2007.

Derivatives of PPV have high molecular weights and are soluble in common organic solvents, such as toluene or xylene. These polymers also possess low intrinsic impurities, below $10^{14} / \text{cm}^3$, and high photoluminescence efficiency, typically in the range of 20-60%. Combining these characteristics produces a material yielding long lasting, highly efficient, low turn-on voltage PLEDs.

Conjugated Polymers

Before researching conjugated polymers, polymers were of the saturated variety. Saturated polymers have all four electrons paired with a carbon atom; all electronic orbitals are fully saturated. The lack of free electrons in saturated polymers yields large band gaps, and insulating properties. Conversely, conjugated polymers have an

electronic structure with sp^2p_z carbon orbitals, allowing one unpaired electron, also known as the pi electron. This pi electron corresponds to the highest occupied molecular orbital (HOMO), while the π^* electron corresponds to the lowest unoccupied molecular orbital (LUMO). The carbon atoms covalently bond to other atoms, leaving the p_z orbitals free to form delocalized pi bands. The delocalized pi bands overlap across the backbone of the polymer, giving the polymer semiconducting or metallic properties. The polymer exhibits metallic properties with partially filled pi bands; the polymer exhibits semiconducting properties with the pi band completely filled with the HOMO at the top of the pi band. The number of atoms in the repeat unit determines the number of pi sub-bands. Each sub-band can only hold two electrons. Half the sub-bands correspond to pi sub-bands, and half the sub-bands correspond to π^* sub-bands. The polymer PPV, of which OC1C10 is a derivative, has four filled pi sub-bands with the lowest energy, and four empty π^* sub-bands with the highest energy. The difference in energy between the pi sub-band and the π^* sub-band is the pi- π^* energy gap E_g . This is analogous to the band gap energy in traditional semiconductors¹².

Figure 2 shows the pi band positions in a PLED with a calcium cathode and ITO anode. The arrows in the rightmost figure indicate charge injection from the cathode (top) and anode (bottom). Figure 3 depicts the difference between conjugated and saturated, unconjugated, electron orbitals. Figure 3(b) clearly demonstrates the oft mentioned “backbone” of a conjugated polymer.

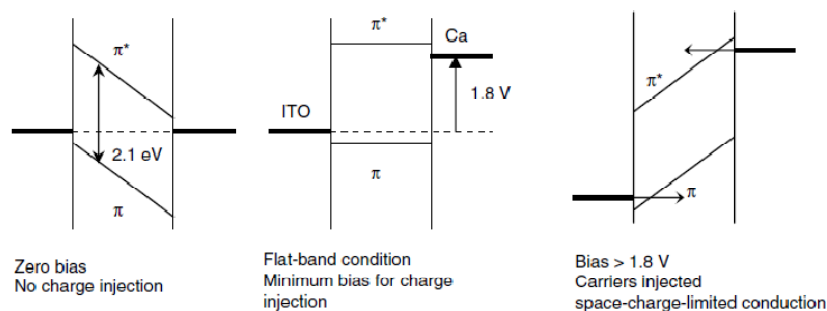


Figure 2. Energy band diagrams of a PLED made with an ITO anode and calcium cathode, with pi and pi* sub-bands shown. Scherf, Ulrich et al. *Organic Light-Emitting Devices*. Wiley, New York, 2006.

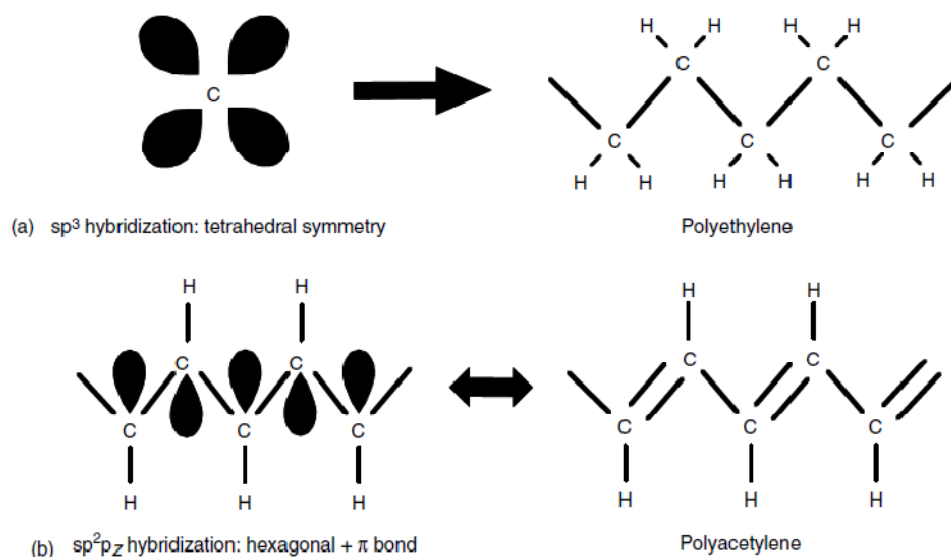


Figure 3. Depiction of electron orbitals in saturated and conjugated polymer semiconductors. Li, Zhigang et al. *Organic Light-emitting Materials and Devices*. CRC Press, Boca Raton, 2007.

The polymer OC1C10 is an alkoxy-substituted MEH-PPV derivative. Unsubstituted PPV's conjugated form makes it insoluble in organic solvents (Toluene or Xylene) and provides the primary reason for placing alkyl groups in the 2 and 5 positions, forming alkyl-substituted PPV. Alkyl-substituted PPV has a 2.4 eV band gap, and similar luminescence spectrum to PPV. Additionally, alkyl-substituted PPV is soluble in THF in conjugated form. Attaching alkoxy groups, instead of alkyl groups, in the 2 and 5 positions in alkyl-substituted PPV converts the polymer into MEH-PPV or OC1C10 like

polymers, with a 2.1eV bandgap and similar luminescence spectra. All presented experiments used toluene as a solvent and the polymer OC1C10.

PLED Structure

All presented PLEDs contain the following structure: ITO/PEDOT/OC1C10/Ca. After deposition, device layers build upwards from a glass substrate. PLEDs differ in device fabrication from small molecule organic LEDs (SMOLEDs) by using solution processing rather than vacuum deposition. PLED solution processing should cost less than conventional LED processing.

The ITO functions as the device anode, with the ability to conduct holes at a thickness of 100nm, while maintaining high transparency in the visible wavelength region. ITO fabricated using a hydrogen-argon mixture with hydrogen partial pressure at 7.9×10^{-6} Torr has an average transmittance of 89%¹³. A particular advantage of ITO is the partial pressure that yields high transparency also provides high conduction. ITO has a high work function, which helps hole injection by better matching the HOMO of the next deposited layer. This is important because holes are the majority charge carriers in PLEDs. However, ITO has free electrons from tin dopants and ionized oxygen vacancy donors, which function as charge carriers; it is a degenerate N type oxide semiconductor.

ITO performance is normally improved by exposure in a UV ozone reactor. This is standard practice in PLED fabrication where oxygen plasma treatment is not used. UV ozone treatment improves emission efficiency of PLEDs and increases device lifetime¹³.

Poly(ethylenedioxythiophene) (PEDOT) is the layer adjacent to the ITO and helps planarize the ITO surface, helps improve hole injection, keeps indium or other contaminants from diffusing into the OC1C10 electroluminescent (EL) layer, and increases the PLED lifetime. Planarization strongly affects device performance due to the thin film nature of PLEDs and the relatively large film thickness variations caused by surface roughness. These variations can reach several nanometers. PEDOT has a work function of 5.2 eV, which nearly matches the 4.7 eV work function of ITO. Figure 4 shows a PLED with an ITO anode, and a 4.7 eV work function, along with the corresponding work functions of various cathodes. Calcium cathodes, used in all presented PLEDs, possess a 2.9 eV work function.

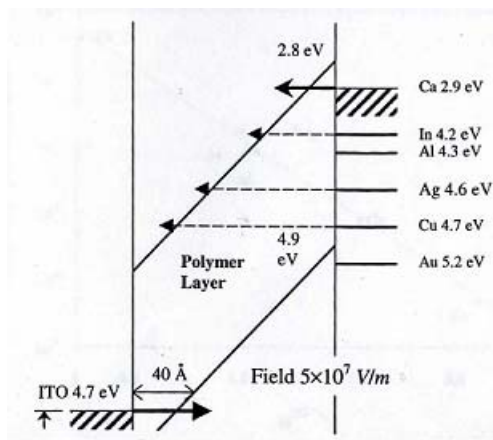


Figure 4. PLED diagram with various cathodes. Note Ca has a work function of 2.9 eV. Scherf, Ulrich et al. *Organic Light-Emitting Devices*. Wiley, New York, 2006.

OC1C10-PPV has similar emission profiles to MEH-PPV, but has 3,7-dimethyloctyl group substitutions, which improves its solubility and film forming ability [12]. In the OC1C10 layer holes and electrons radiatively recombine and emit light. The polarons move slowly in OC1C10, which increases total recombination. If the charge carriers move too quickly in the electric field, recombination rate decreases, causing charge

carriers to traverse the entire length of the device. Visible light spectrum radiative recombination in OC1C10 only occurs with singlets. OC1C10 does not emit light in the visible spectrum when triplets recombine, though small molecule organic LEDs can exhibit phosphorescence.

Calcium functions as the cathode for all the presented PLEDs. Calcium's low work function, 2.9 eV, matches the π^* sub-band, or conduction band, well, allowing efficient electron injection. Due to high reactivity, real world devices using a calcium cathode must be hermetically sealed or device lifetime will suffer. The difference in work functions between the anode and cathode creates a field which sweeps out all charge carriers. The operating depletion depth is larger than the OC1C10 film thickness, which produces no little to no band bending. The depletion depth is normally in the micron range, while film thicknesses are in the hundred nanometer range.

PLED Currents And Efficiencies

With matched electrodes, doping occurs at the polymer-metal interface; this creates an inverting layer and associated p-type or n-type polarons in the corresponding regions. Despite the best attempts to match electrodes, differences between the anode and HOMO energy level, or between the cathode and LUMO energy level, will create barriers for hole and electron injection. The charges carriers tunnel through these barriers according to Fowler-Nordheim tunneling theory when barrier heights are greater than 100 meV; otherwise, thermal-assisted carrier tunneling, and trap-assisted tunneling more accurately describe charge carrier tunneling behavior ¹⁴. Aside from tunneling behavior,

hole currents are space charge limited, while electron currents are trap limited. Space charge collecting near the anode, due to hole population and mobility, blocks the electric field and limits the hole current. Polymer disorder and impurities cause defective energy levels below the conduction band, limiting the electron current.

Polymer thickness does not affect device turn on voltage, but does alter current density; external quantum efficiency (QE_{ext}(EL)) is also a function of polymer thickness. OC1C10 shows a definite loss of efficiency at thicknesses greater than 3000 angstroms.

Quantum efficiency limits PLED performance. In OC1C10 only singlets can radiatively recombine, while triplets cannot. Electron-hole pairs form either singlet states 25% of the time or triplet states 75% of the time. However, there may be two ways to increase the quantum efficiency. Increasing the proportion of singlets to triplets would increase the efficiency. Also, if separated triplets could convert into singlets, via spin-orbit interaction, that would increase the quantum efficiency. The separated triplet would have to avoid recombination until changing its spin for this to occur¹⁴.

The preceding historical highlights place OC1C10 use in perspective; other polymers came before and after it. OC1C10 PLEDs presented in this project represent a stable, relatively well known, polymer and configuration. As such, this project examined effects in PLED luminance and efficiency, by varying well known device fabrication routines. Figure 5 outlines our standard PLED process.

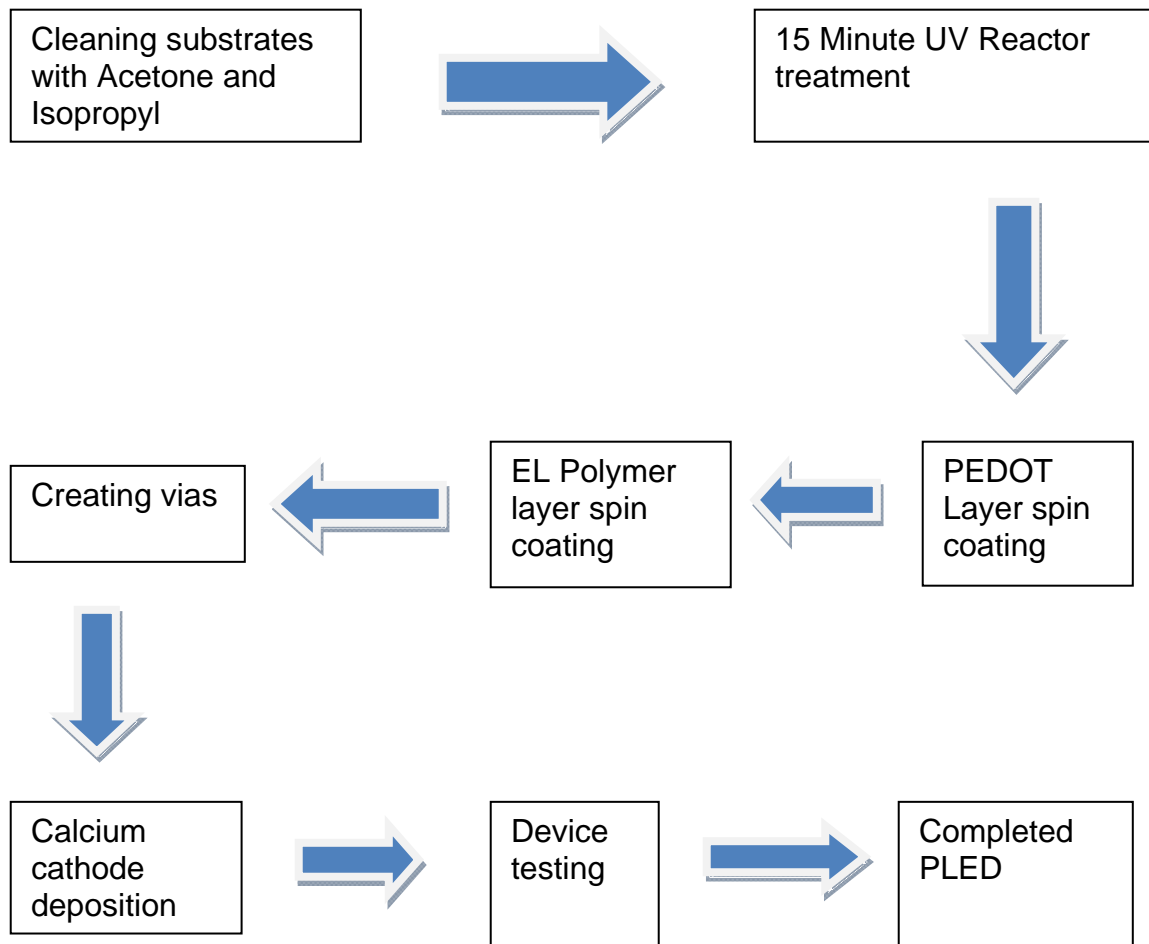


Figure 5. Standard PLED fabrication process flow.

Device fabrication consists of: cleaning the substrates in acetone and isopropyl sonic baths, UV ozone reactor treatment, PEDOT application, a 15 minute anneal, polymer application, via creation, cathode (calcium) deposition, then testing.

Believing the given procedures lack optimization, most ideas for fabrication variations stem from a desire to verify optimal procedure results. The UV reactor treatment seems underpowered, thus a way to increase either the amount or efficacy of the UV light radiated appears likely to yield increased device performance. A similar line of reasoning leads to the many cleaning agents used in substrate reuse experiments.

Acetone and isopropyl do not appear able to thoroughly remove all device layers down to the ITO anode, thus using different detergents and cleaning agents seems promising.

Many fabrication variations are possible. Annealing experiments provided simple variations with high precision since temperatures varied only 1-2 degrees Celsius. Making changes to OC1C10 presented desirable variations, but also lowered precision and increased fabrication complexity. Designing a new polymer provides the most exciting possibilities; however, the time, effort, and low success rate drives the research into less complicated experimentation. Other unperformed experiments include increasing indium content in a previously used substrate, etching substrates with hydrofluoric acid, and charge carrier path/device contact alteration. The following chapters reflect the remaining experimental ideas.

Chapter 2 discusses timing and temperature experiments. The first experiment examines if any time dependency exists on PLED luminance or efficiency between when a device completes UV ozone reactor treatment, and PEDOT application. Fortunately, the data show little correlation between delayed PEDOT application post UV ozone reactor treatment and device performance. Other experiments investigate heating substrates prior to UV ozone reactor insertion, and placing heated substrates on specific materials to increase the efficacy of the reactor process.

Chapter 3 examines the effects of cleaning agents on previously used device performance. The first set of cleaning agents depicts the effects of commonly available household cleaners on device luminance and efficiency. Many cleaning agents further degrade PLED performance; surprisingly, some substrates respond positively to this line of experimentation. Another round of cleaning agents finds stronger cleaning agents can

visibly harm substrates and their luminance and efficiency, while some cleaners may restore previously used substrates to performance levels on par with control substrates. With a known substance to “restore” PLEDs, the next experiment examines individual components of a cleaner, seeking one ingredient that provides a majority of the device improvement.

Finally, chapter 4 discusses aging and etching experiments. While the performance of PLEDs degrades over time, constructing PLEDs from aged OC1C10 provides greater insight into device failure mechanisms. The first experiment in chapter 4 fabricated PLEDs from polymer aged 7 years to 1 week. Experimental results generate surprising data, nearly contrary to expected outcomes. The concluding experiment explores the effects of etching previously used substrates. Etching substrates with HCL and KOH, in differing orientations and durations, aims to remove any impurities formed in PLED fabrication and operation. This experiment succeeds in finding evidence for substrate reuse.

Figure Credits

Figs 1, 3. Z Li, et al. *Organic Light-emitting Materials and Devices*. CRC Press, Boca Raton, 2007.

Figs 2, 4. U Scherf, et al. *Organic Light-Emitting Devices*. Wiley, New York, 2006.

Chapter 2 Timing and Temperature Experiments

This first set of experiments seeks precision and simplicity in experimentation. Heating substrates to various temperatures before insertion into the UV ozone reactor and varying intervals between UV ozone reactor treatment and PEDOT application meet the criteria. Annealing experiments examine device performance after increased heat at various manufacturing stages. Higher kinetic energy in the UV ozone reactor could potentially remove more contaminants than the normal procedure and encourage more oxygen diffusion into the ITO. Hence, placing heated substrates in the UV ozone reactor, instead of room temperature substrates, could yield brighter or more efficient PLEDs. In addition to increased temperature, silicon wafers placed underneath the substrates may absorb the UV light, heat up, and engender more heat conduction to the LED. Section 2.3 describes device variations when a heated substrate atop a silicon wafer experiences UV ozone reactor treatment. UV light excites ozone and removes contaminants from the ITO surface, before any other layers cover the anode. Absorbing UV light with a silicon wafer underneath the substrate may enable a new way to possibly increase UV reactor efficiency without expending additional energy. The UV light that passed through the substrate would theoretically generate additional heat to help the decontamination process. Normally, the substrates simply sit on the metal tray inside the UV reactor, but this metal tray reflects the UV light to encourage ozone formation as well as the silicon wafer underneath the device.

This UV light creates and destroys ozone and also creates atomic oxygen which forms volatile molecules with contaminants that desorb from the sample surface. The UV ozone treatment can create almost atomically clean samples. The presence of silicon wafers aimed to increase the likelihood and efficacy of the contaminant reactions with atomic oxygen. Additionally, the added heat in the form of kinetic energy could potentially increase the “volatility” of the molecules which desorb from the sample surface.

2.1 Experiment #1 Varying delay between UV ozone reactor treatment and PEDOT application

Introduction

The first experiment tests the hypothesis that the time interval the substrates spend between the UV reactor and PEDOT application and spinning does not influence PLED efficiency or brightness. The hypothesis proves true, as the data show.

Procedural Notes

The lab manual¹⁵ describes the fabrication of polymer OLEDs. Six substrates left the UV ozone reactor in pairs at intervals from 30 seconds to 31 minutes. The first pair of substrates immediately received PEDOT application in the spinner. The first pair of substrates went from the UV ozone reactor to the spinner with as little delay as possible, less than two minutes, before PEDOT application. Substrates 1 and 2 represent control substrates. The next pair, substrates 3 and 4, followed roughly 15 minutes behind the 2nd pair. Thus substrates 5 and 6, the last pair, underwent PEDOT application 30 minutes after the first.

Data and Analysis

Figures 6 through 10 show little change in the efficiencies or brightness for the substrates across the 30 minute post-UV reactor interval.

Current information from the Check IV function in the laboratory test suite supplies the data points used in making the graphs. Check IV data implies data points measured at 5 Volts, or either 10 mA for large pixels or 0.9 mA for small pixels. In figure 6 the Check IV data pertains to data at 10 mA for large pixels. In addition to measuring pixel voltage or current at those specific points, other measurements sweep pixel output from the turn on voltage, around 2.2 Volts, to 8-10 Volts. The voltage sweeps produce voltage curves containing roughly 20-30 data points which more clearly depict pixel luminance and efficiency characteristics as the voltage increases incrementally. The presented curves do not include “burn in” curves often seen in PLED testing. These curves often yield a maximum PLED luminance or efficiency far below a “typical” value. Pixels with curves that increase normally then suddenly fall to nearly zero, only to produce a virtually monotonically increasing curve the very next sweep, commonly occurred. “Burn in” often explains this behavior, though setting the maximum voltage sweep value too high, roughly 8-9 volts or higher, could damage pixels causing any secondary voltage sweeps to yield luminances or efficiencies measuring zero or marginally above zero.

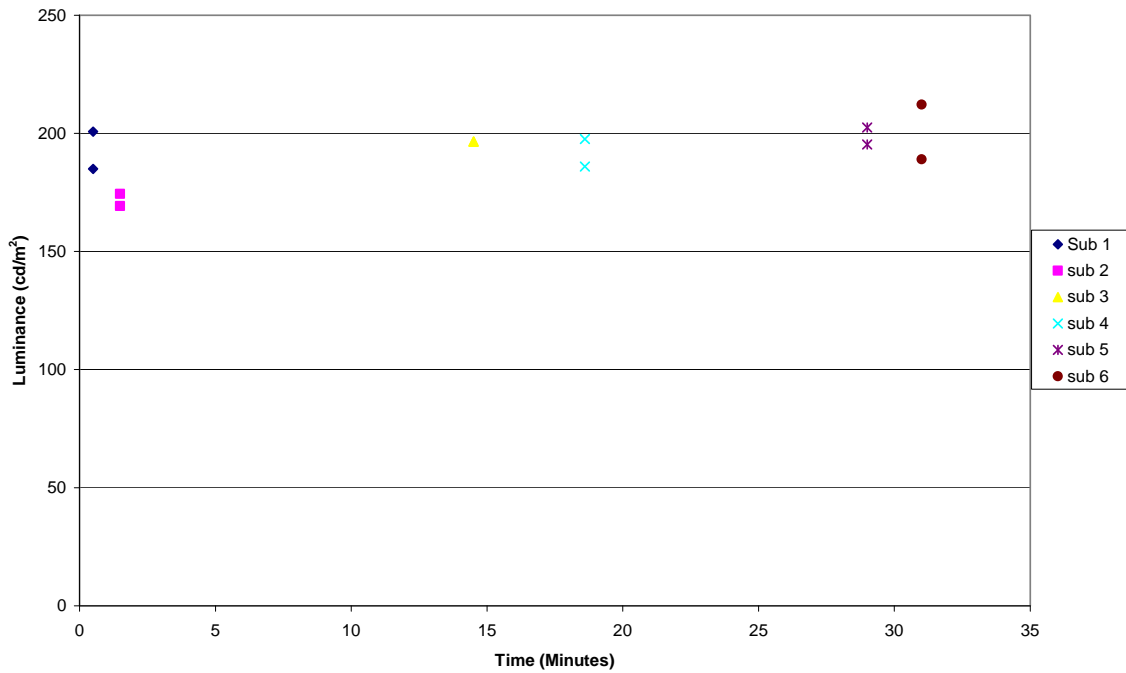


Figure 6. Check IV Luminance vs. time for large pixels at 10 mA. The total variance in luminance is roughly 40 cd/m².

Figure 6 shows no significant difference in brightness between the substrates quickly applied with PEDOT, and those which waited 15 or 30 minutes. Figure 7, luminance for small pixels, shows the same behavior.

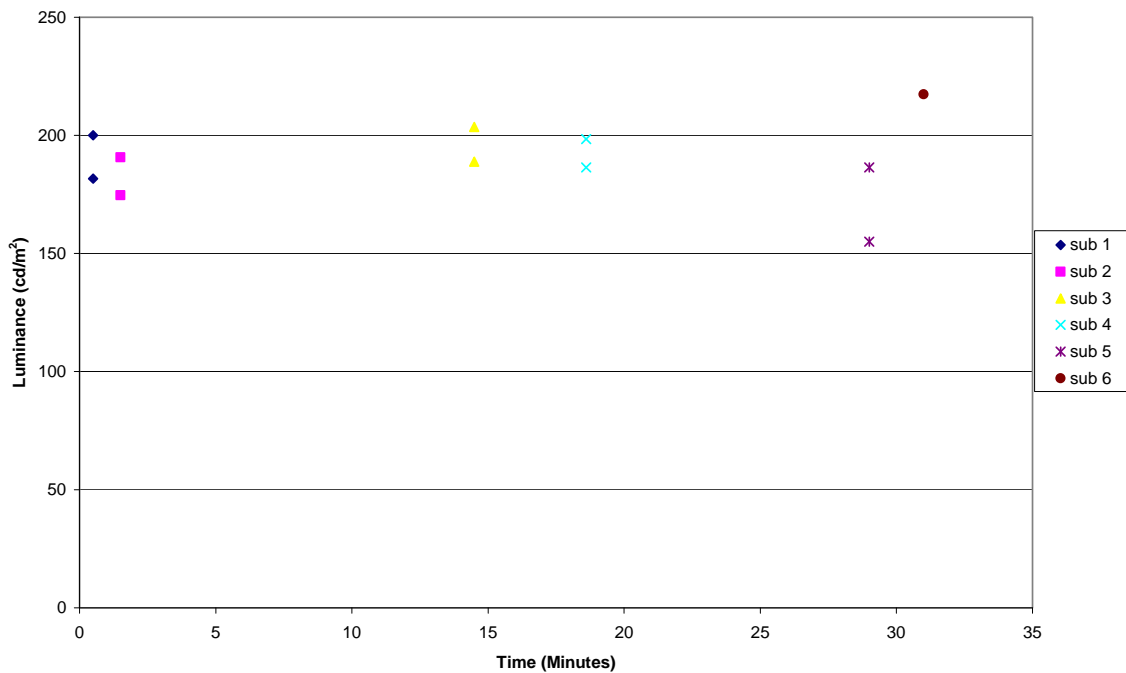


Figure 7. Check IV Small pixel luminance vs. time at 0.9mA. UV reactor interval plays no role in small pixel luminance.

Figures 8 and 9 show the effects of delays PEDOT application on efficiency. The large pixels display no significant change, but the smaller pixels show a marked drop in efficiency for the 30 minute delays. Dropping substrate #5 during fabrication may explain the lower efficiency, however, no such anomaly exists with substrate #6. We could not devise an explanation with the presented data to account for the lower efficiency of small pixels in substrate #6. No clear reason explains the drop in efficiency for substrate #6, possibly showing an overly extended period between the UV reactor and PEDOT application may affect efficiencies in small pixels.

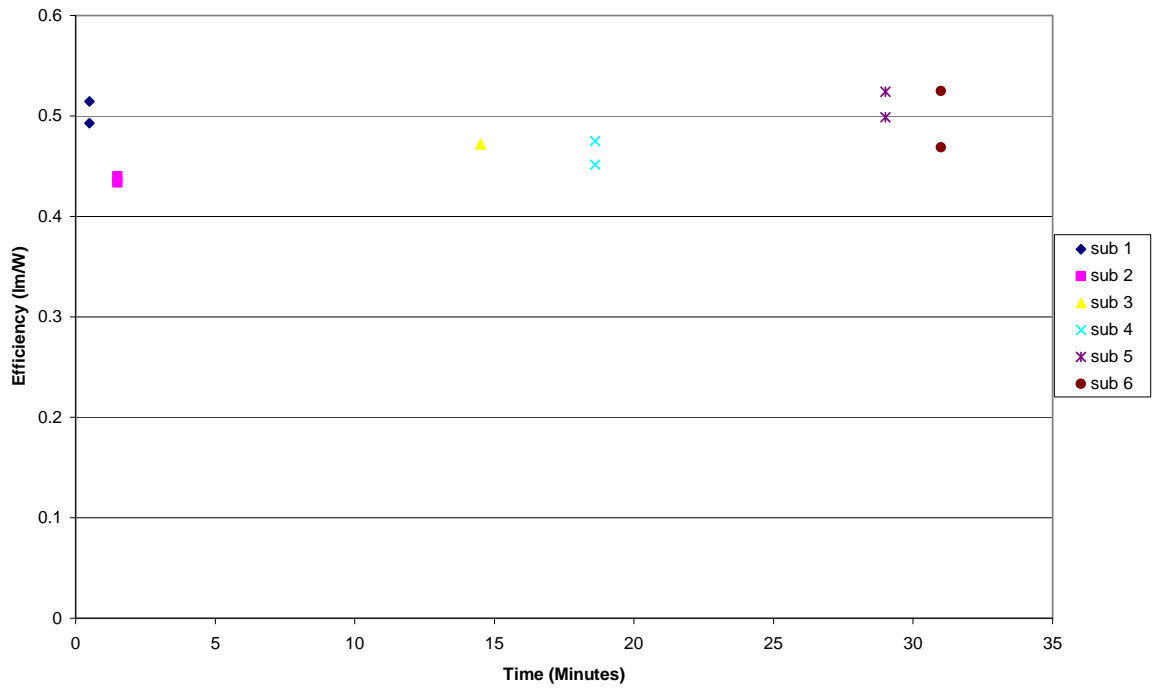


Figure 8. Check IV Efficiency vs. time for large pixels at 10 mA.

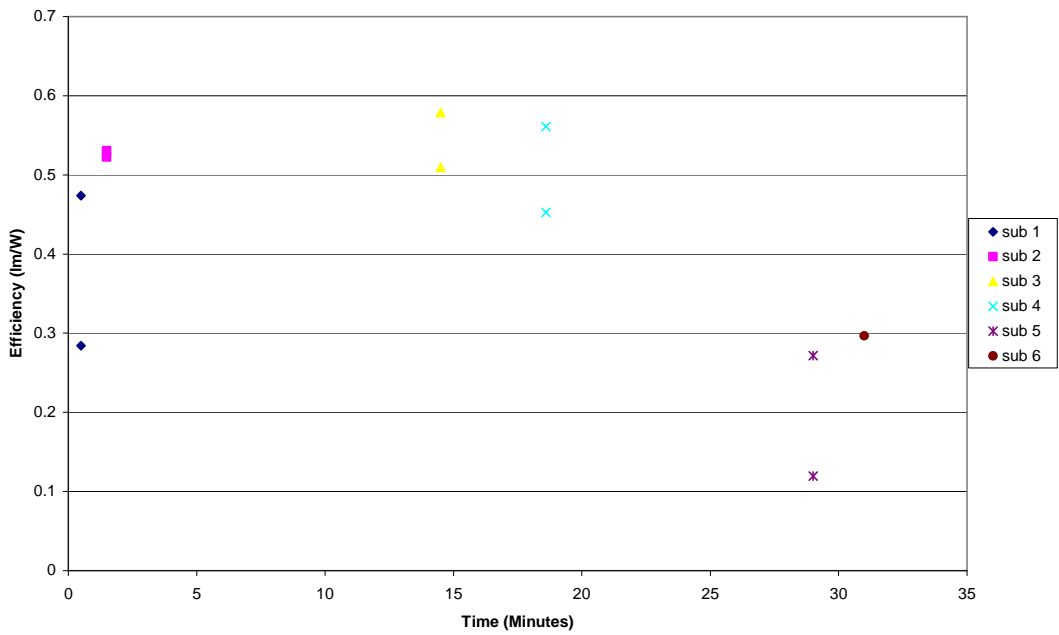


Figure 9. Check IV Small pixel Efficiency vs. Time at 0.9 mA. Note the marked decrease in efficiency for 30 minute experimental substrates 5 and 6.

Figure 9 shows a large drop in small pixel efficiency, and the voltage check IV data in figure 10 show a similar decline, though not as pronounced.

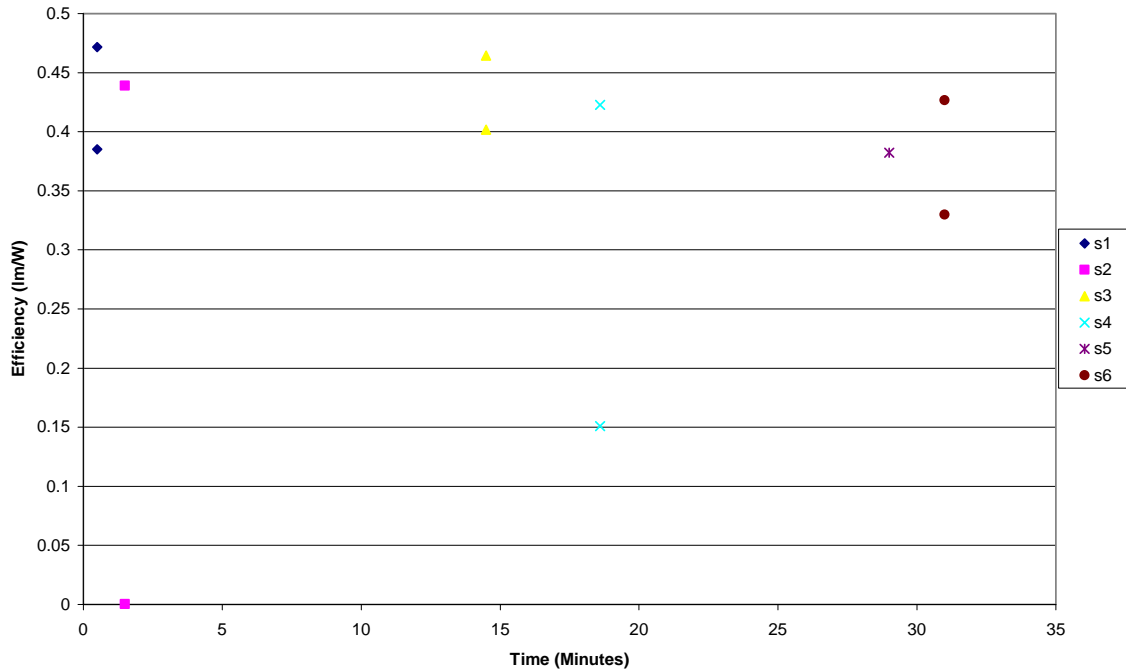


Figure 10. Check IV Small pixel Efficiency vs. Time at 5 V.

Conclusion

In conclusion, the experiment depicts no significant relationship between the length of the interval between the UV reactor and PEDOT application. For the time delays tested, the time that samples wait in the UV ozone reactor for PEDOT application does not appear to influence pixel brightness. An efficiency decrease in small pixels that have waited approximately 30 minutes may result, but that is not conclusive from the data. This result matches the expected results, and is a favorable outcome. Had the interval between the UV reactor and PEDOT application altered PLED performance, fabrication would incur additional constraints to optimized PLED construction.

Though many different intervals in the fabrication process exist, changing the substrates themselves appears the next logical step in experimentation. Moving forward from the PEDOT application interval, the project examines changing substrate temperatures while inside the UV ozone reactor.

2.2 Experiment # 2 Temperature Modification

Introduction

The second experiment tests the effect of higher substrate temperature prior to placement in the UV ozone reactor on efficiency and luminance of polymer LEDs. Heating the substrates before placing them in the UV ozone reactor could possibly increase the available kinetic energy used to clean the substrate while in the reactor, producing cleaner substrates, and thus more efficient, and brighter LEDs.

Procedural Notes

Fabrication proceeded as described in the lab manual with only one difference: heating the experimental substrates to 125 degrees Celsius before placing them in the UV reactor ¹⁵. Data from Cecchi reported decreased PLED performance when heated above 125 C ¹⁶. A hot plate heated the substrates to the specified temperature. Figure 11 outlines the experimental process.

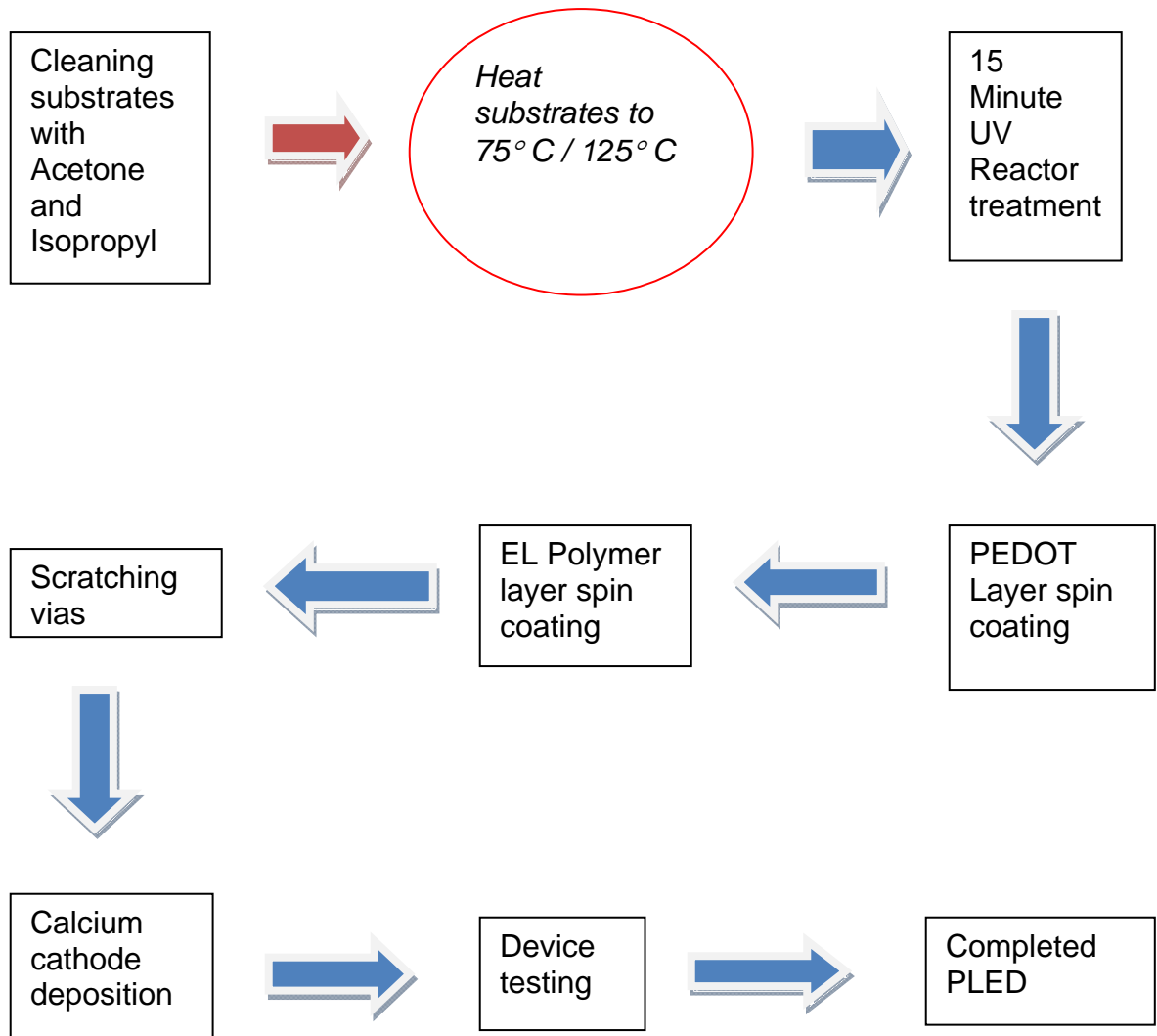


Figure 11. Experimental process depicting substrates heated to 75 °C and 125 °C before UV Ozone reactor treatment.

Figure 12 shows the control substrates with a higher efficiency than the two substrates that were heated prior to placement in the UV reactor. The control substrates outperformed the heated substrates in virtually every comparison.

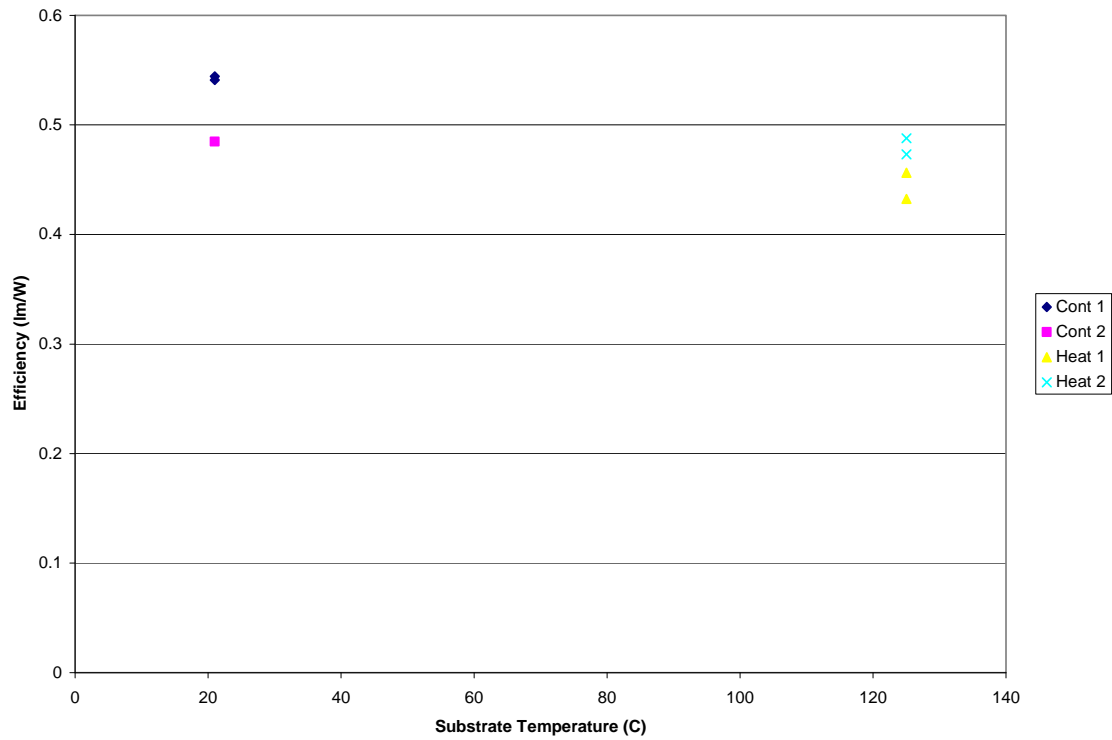


Figure 12. Check IV at 5V, Large Pixels, efficiency vs. temperature Substrate. Note the higher control substrate efficiency.

Figure 13 shows a heated substrate with far more luminance than those fabricated in the conventional manner. However, the second experimental substrate did not show the same brightness, and was actually lower than the conventionally fabricated polymer OLEDs.

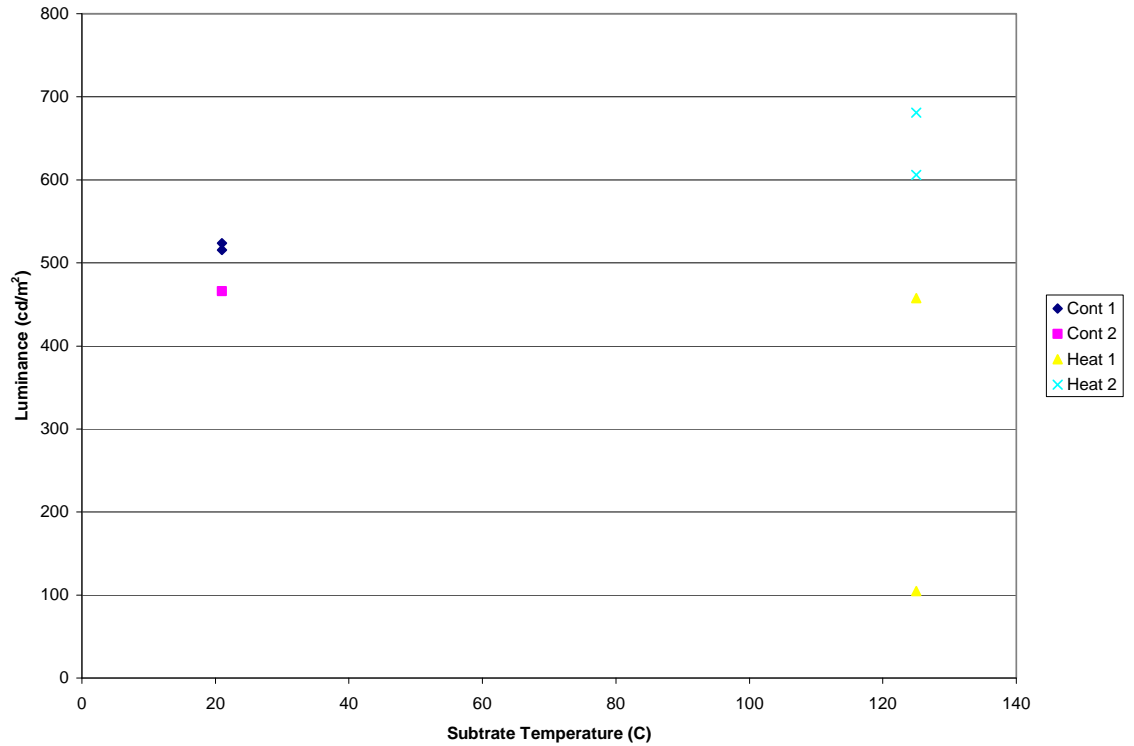


Figure 13. Check IV at 5V, Large Pixels, Luminance vs. Substrate Temperature. Note heated substrate #2 displays luminance from 700-600 cd/m², much higher than the control substrates.

Figure 14 again shows the experimental polymer OLEDs with greater luminance, but only with half of the data points. The conventional polymer OLEDs consistently provided better efficiency and luminance. Figures 12-15 depict data taken with respect to 5 volts; they also display erratic experimental device behavior. Conversely, data taken with respect to current show more consistent and clear results.

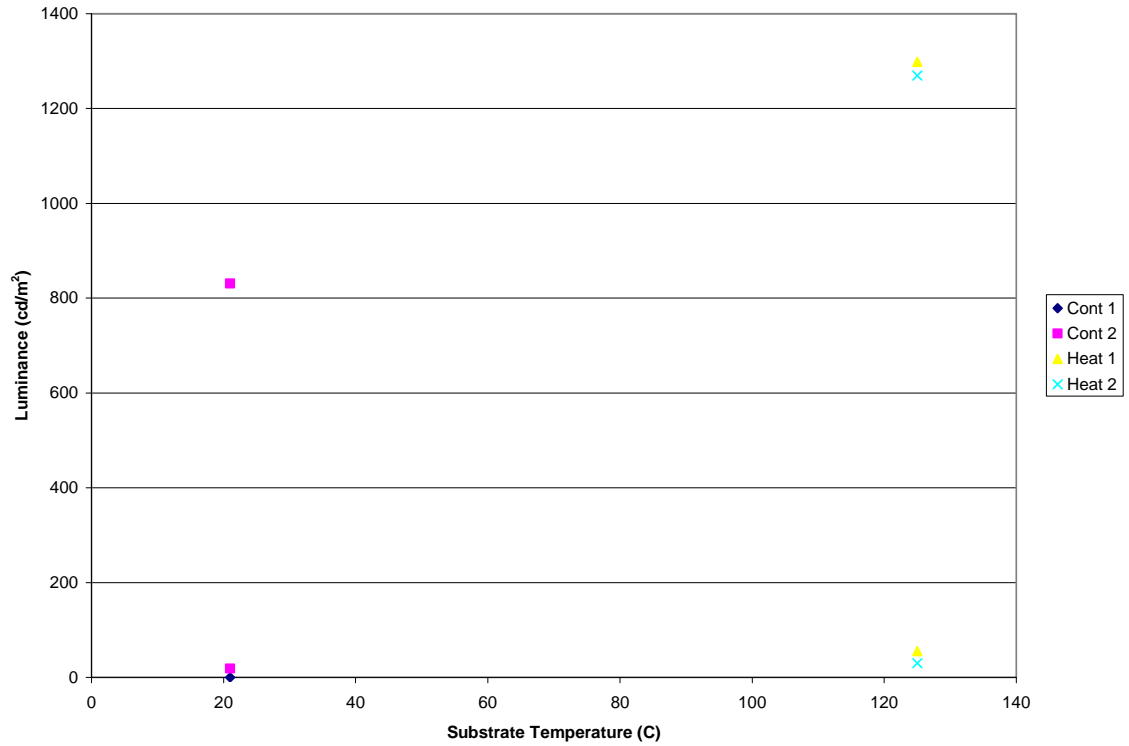


Figure 14. Check IV at 5V, Small Pixels, Luminance vs. Substrate Temperature. Low emitting data points included for completeness.

Figure 15 shows the conventional PLEDs outperforming the experimental PLEDs. The low-luminance data points should be disregarded, since they represent known non-functioning pixels, but are included for completeness. The experimental PLEDs are representatively grouped between 0.5-0.6 lm/W below the highest conventional data point. This may indicate that heating the substrate prior to UV reactor insertion may impair performance.

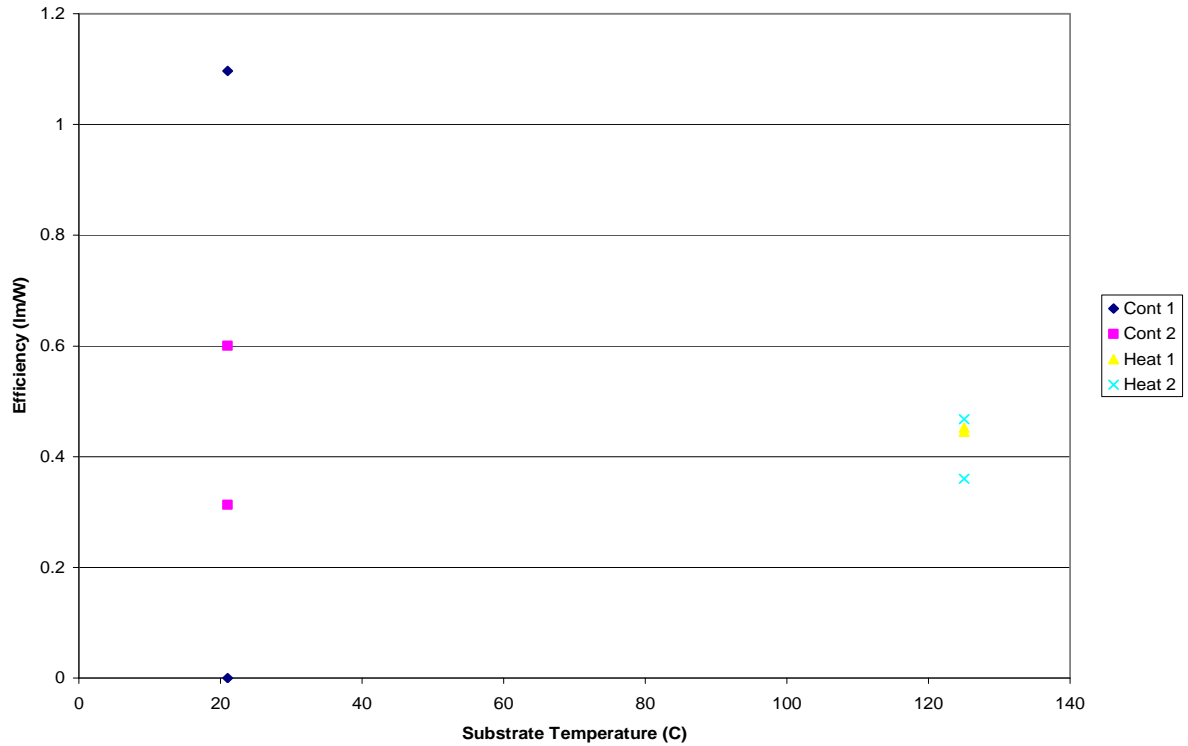


Figure 15. Check IV at 5V, Small Pixels, Efficiency vs. Substrate Temperature

The check IV data based on constant current shows the experimental polymer OLEDs underperforming in luminance and efficiency in every graph. Figures 16 and 17 represent current based check IV data for large pixels, and figures 18 and 19 represent data for small pixels. According to the current based check IV data, the experimental PLEDs barely met the same performance levels as conventionally fabricated polymer OLEDs; this too suggests heating the substrates before insertion into the UV reactor impairs performance.

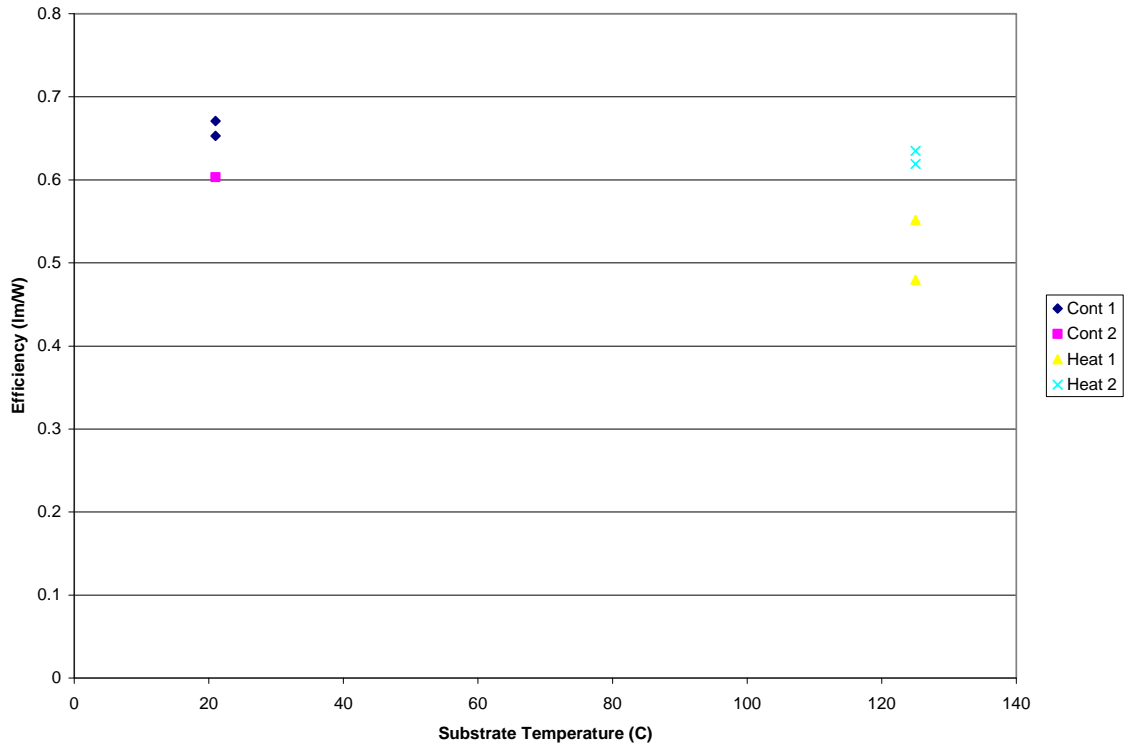


Figure 16. Check IV at 10mA, Large Pixels, Efficiency vs. Substrate Temperature.

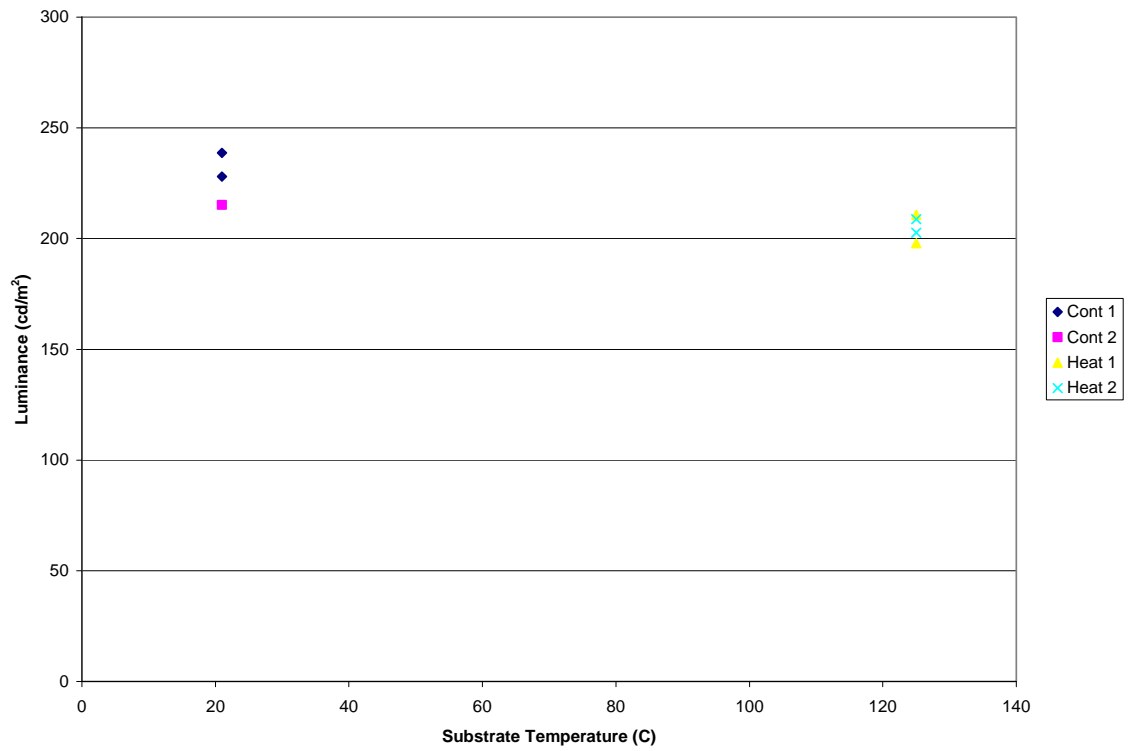


Figure 17. Check IV at 10mA, Large Pixels, Luminance vs. Substrate Temperature.

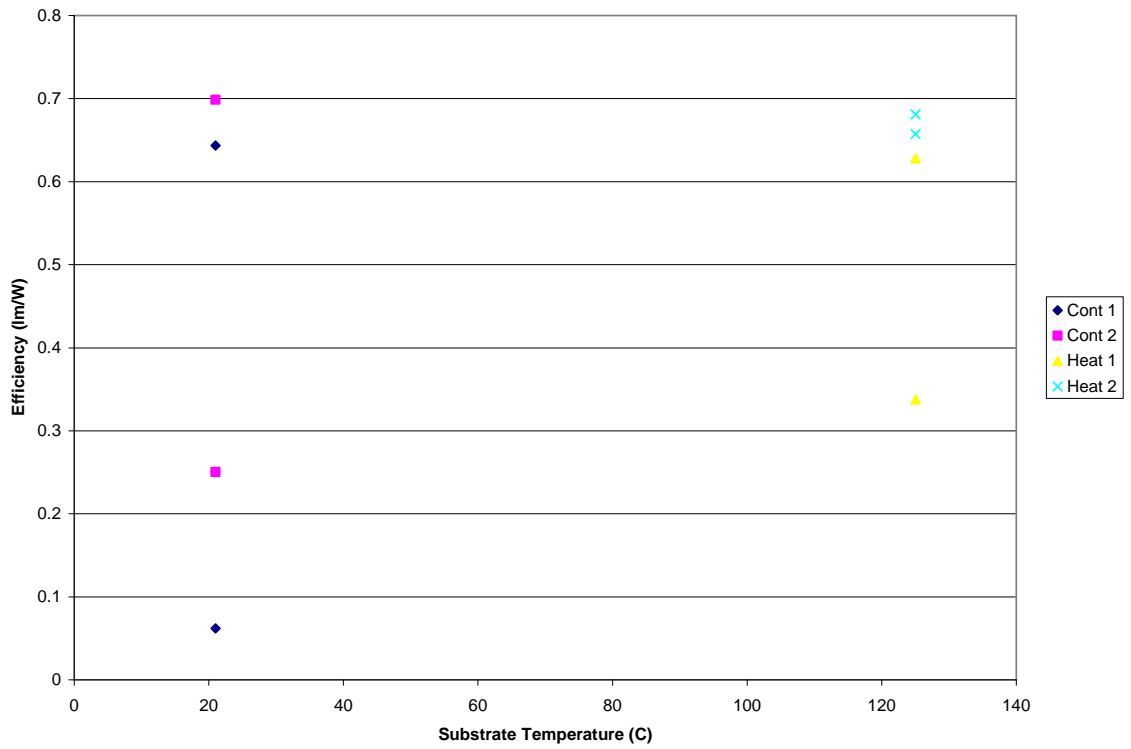


Figure 18. Check IV at 0.9 mA, Small Pixels, Efficiency vs. Substrate Temperature.

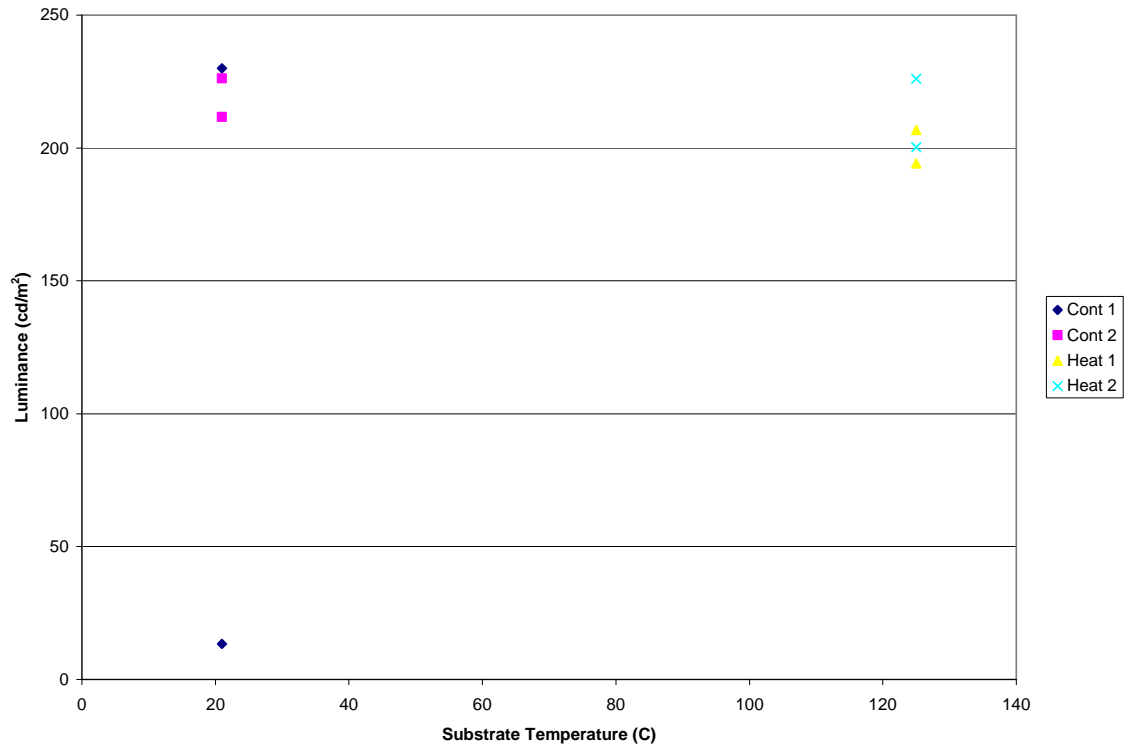


Figure 19. Check IV at 0.9 mA, Small Pixels, Luminance vs. Substrate Temperature.

Conclusion

In conclusion, the measured results contradicted the expected increase in performance. With the exception of the 150-50 cd/m^2 increase in luminance depicted in figure 13, and the almost 500 cd/m^2 increase shown in figure 14, the experimental polymer OLEDs are not better than the conventional versions. Figure 14 does show a large increase, but only 2 data points achieve a brightness of 1300 cd/m^2 . More data points with similar brightness would justify increasing substrate temperature prior to UV reactor insertion. However, data points measured by current would more firmly convince substrate temperature could improve device luminance or efficiency. It is not clear why the experimental PLEDs have difficulty surpassing, or even meeting conventional PLED performance. The data points from this experiment depicting increased brightness or efficiency largely come from voltage measurements rather than current measurements. Figures 16 through 19, based on current, show less erratic, stable data demonstrating no difference in PLED performance with increased temperature while in the UV ozone reactor.

Enhancing the potency of the UV reactor treatment seems an idea with reasonable potential for increasing device performance. Since heating substrates shows none of the expected increases, another method of altering the UV reactor treatment warrants examination.

2.3 Experiment #3 Silicon Wafer Modification

Introduction

This experiment measures the effect of placing a silicon wafer underneath a substrate, heated to 75 and 125 degrees Celsius, prior to UV reactor treatment, on PLED brightness and efficiency. Again, data from Cecchi dictates the 125 °C maximum hotplate temperature¹⁶. The UV reactor treatment being one of the most effective of all cleaning procedures provided great impetus to improve UV reactor treatment efficacy¹⁷. Possible mechanisms for improvement from a silicon wafer beneath a substrate prior to UV ozone reactor treatment are: increased ITO surface activation prior to PEDOT deposition, increased oxygen diffused into the ITO, or increased contaminant removal. Increasing the amount of oxygen diffused into the ITO benefits the pixel by increasing the ITO work function; while extra heat generated from the silicon wafer beneath the PLED substrate during the UV ozone reactor treatment would theoretically remove more contaminants.

This experiment attempts to increase the UV exposure of the glass substrate and ITO anode, in the UV reactor fabrication step, by placing the substrate on top of a piece of bare silicon. The silicon wafer absorbs more of the UV rays emitted by the reactor than the transparent substrate; this experiment examines if the increased exposure improves device illumination and efficiency. Figure 20 describes the experimental process.

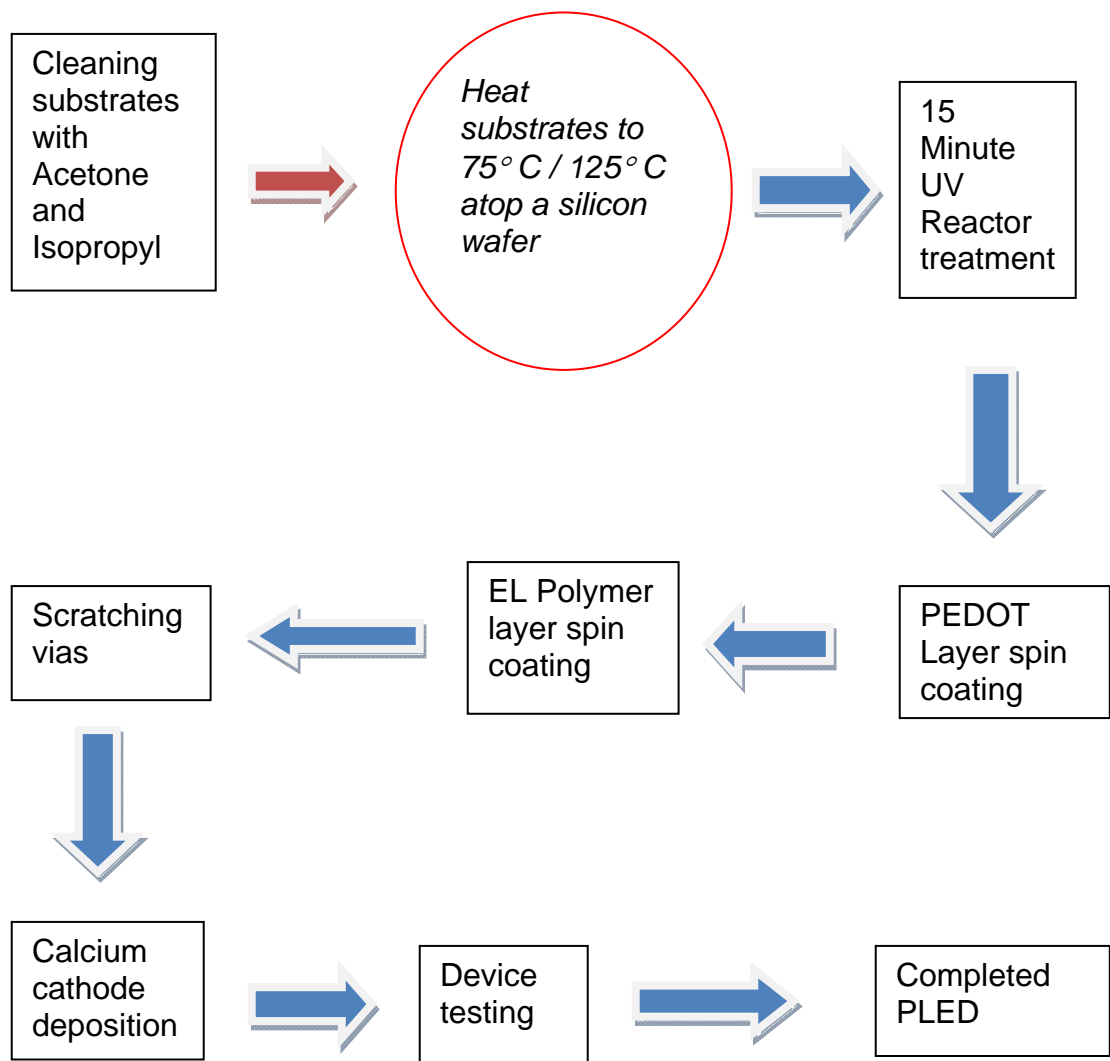


Figure 20. Experimental process depicting substrates atop a silicon wafer during UV ozone reactor treatment.

Procedural Notes

The PLED fabrication follows the manner described in the EE 422 course manual¹⁵, with the only difference being substrates are heated while atop a silicon wafer on a hot plate prior to UV reactor insertion. Two substrates provide control data, except with a silicon wafer underneath the substrate during UV Ozone cleaning. Four more substrates are fabricated; two reach 75 degrees Celsius on a hot plate, and two reach 125 degrees Celsius. All substrates rest atop a silicon wafer and receive exposure to UV light in the reactor for fifteen minutes while they are still heated. Device construction proceeds in the same manner for all subsequent stages of fabrication.

Data and Analysis

The data show both a measurable increase and decrease in both illumination and efficiency between the room temperature substrate, 75 °C substrates, and 125 °C substrates. The data shown in figure 21 did present increased efficiencies, however, T tests run on those same comparisons yielded p values of .2-.7, which signify some results have a high likelihood of lacking statistical significance.

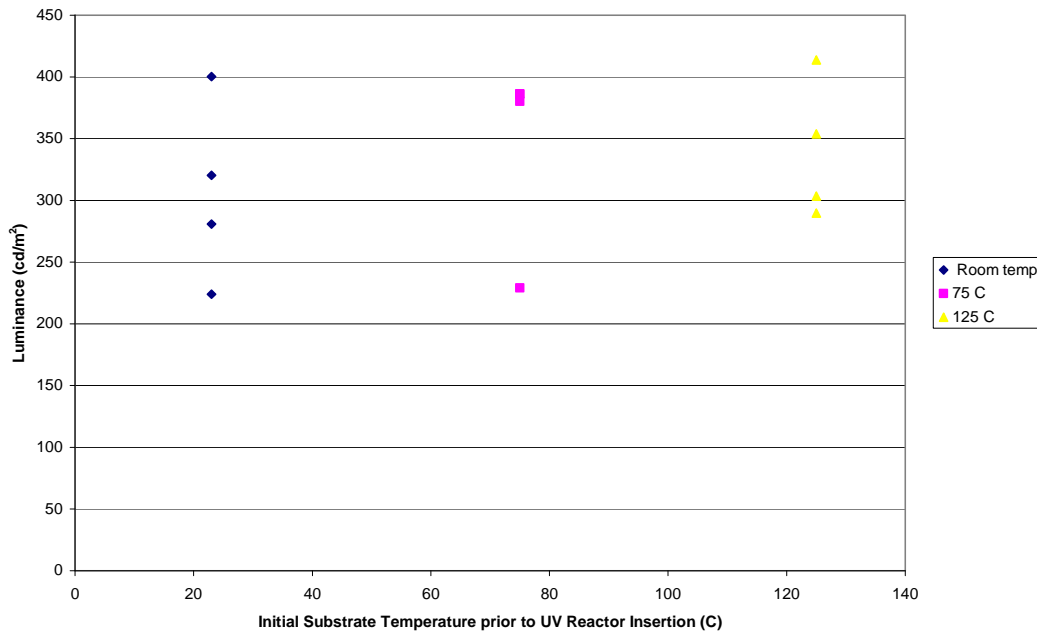


Figure 21. Check IV data for large Pixel Luminance vs. Temperature at 5V.

Figure 21 shows no large increase between large pixels fabricated at higher temperatures with their substrates heated on silicon wafers. However, figure 22 shows a consistent increase in both sets of large pixels made with substrates heated to 75 °C and 125 °C. The best performing pixel only had an efficiency of 0.18 lm/W; this is far below a typical efficiency of 0.6-0.7 lm/W for a PLED of this architecture. The silicon wafer appears to drastically lower efficiency, while leaving luminance relatively unaffected.

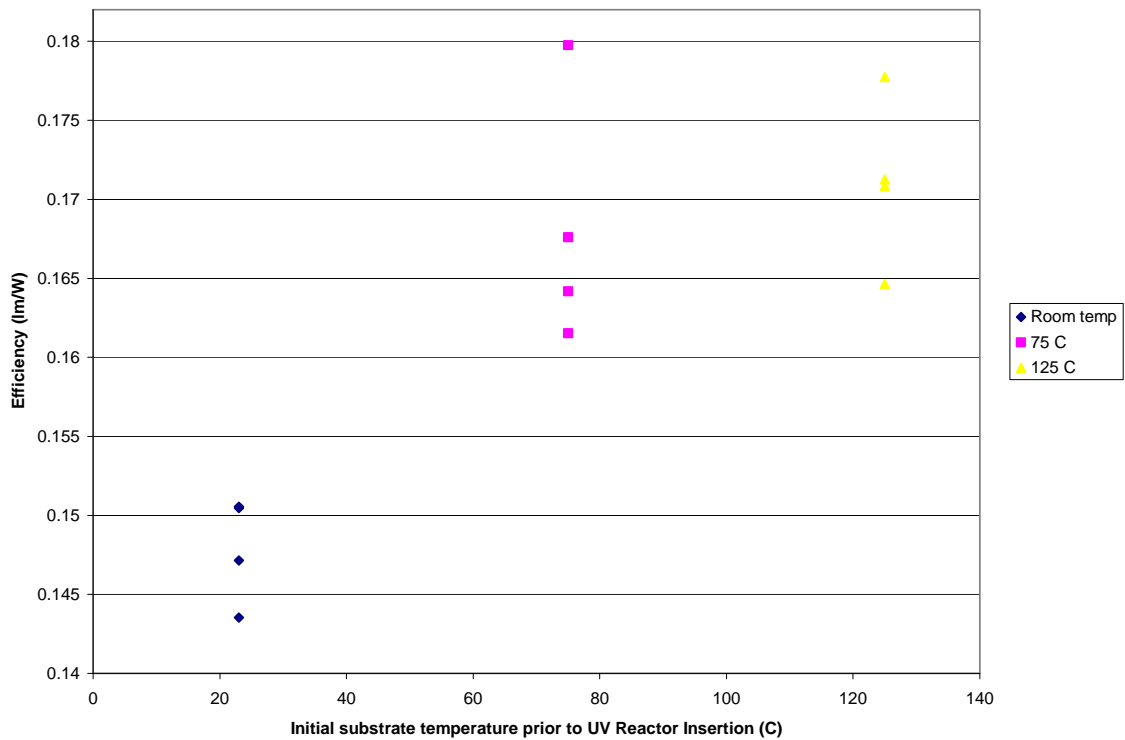


Figure 22. Check IV data for large pixel efficiency vs. temperature at 5V. Note the increased efficiency of substrates heated to 75 and 125 °C.

Both figures 23 and 24 show a decrease in luminance and efficiency with small pixels that were fabricated with substrates heated on silicon wafers. This trend also continues with data taken at currents of 0.9 mA and 10 mA. Again in figure 24, there is a drastic reduction of efficiency to levels below 0.18 lm/W. This suggests the heated silicon wafer may degrade PLED performance rather than enhance it; however, the control pixels also had low efficiencies. Barring any hidden benefits, the small change between experimental and control pixels does not warrant the extra fabrication step.

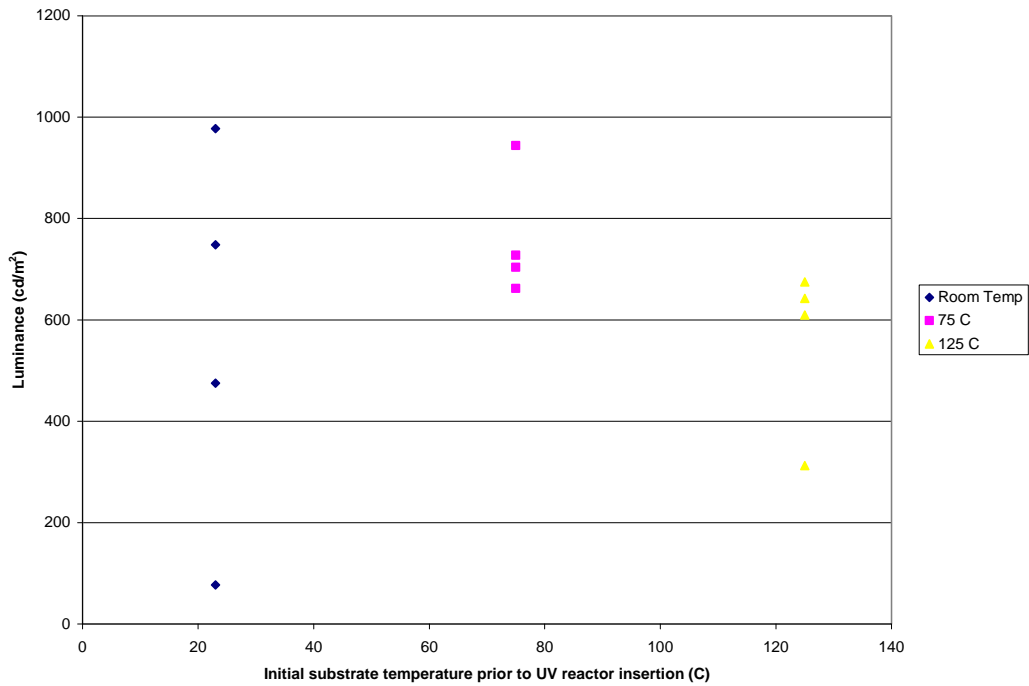


Figure 23. Check IV data for small pixel luminance vs. Temperature at 5V.

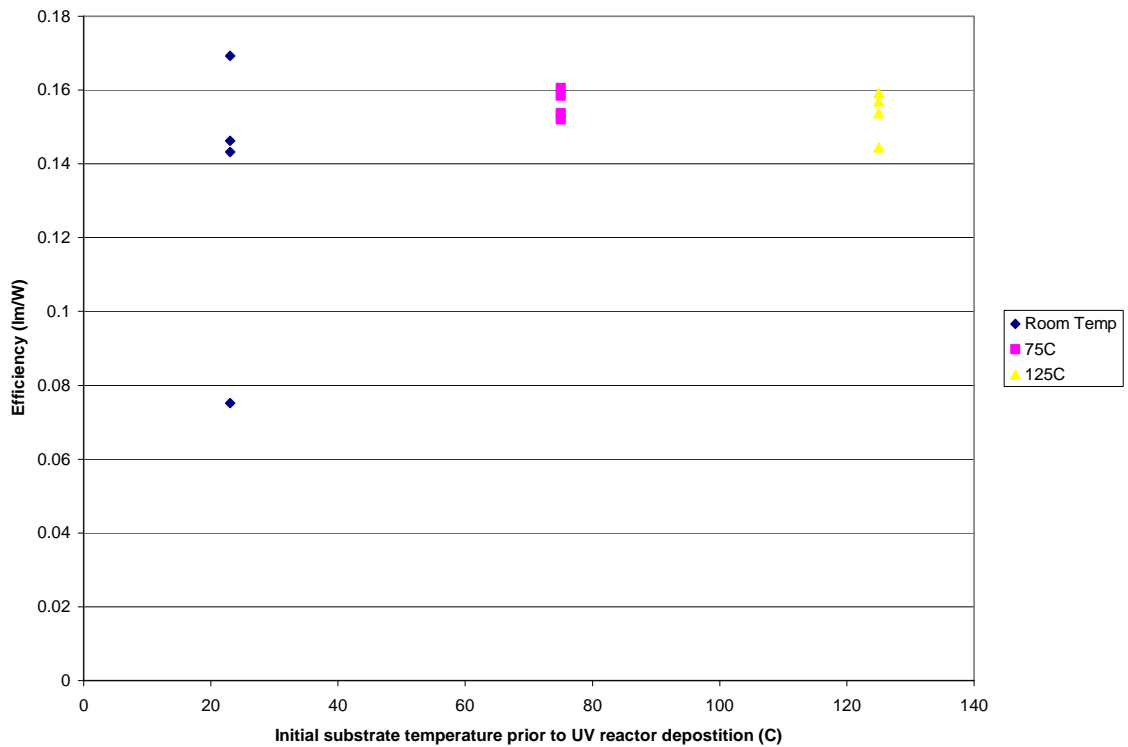


Figure 24. Small pixel efficiency vs. temperature at 5V. Note efficiencies of 0.18 lm/W, far below the typical 0.6-0.7 lm/W.

Figures 25 through 28 depict data obtained through current based measurements. The data show greatly diminished luminance, while matching the low efficiency seen in voltage based measurements.

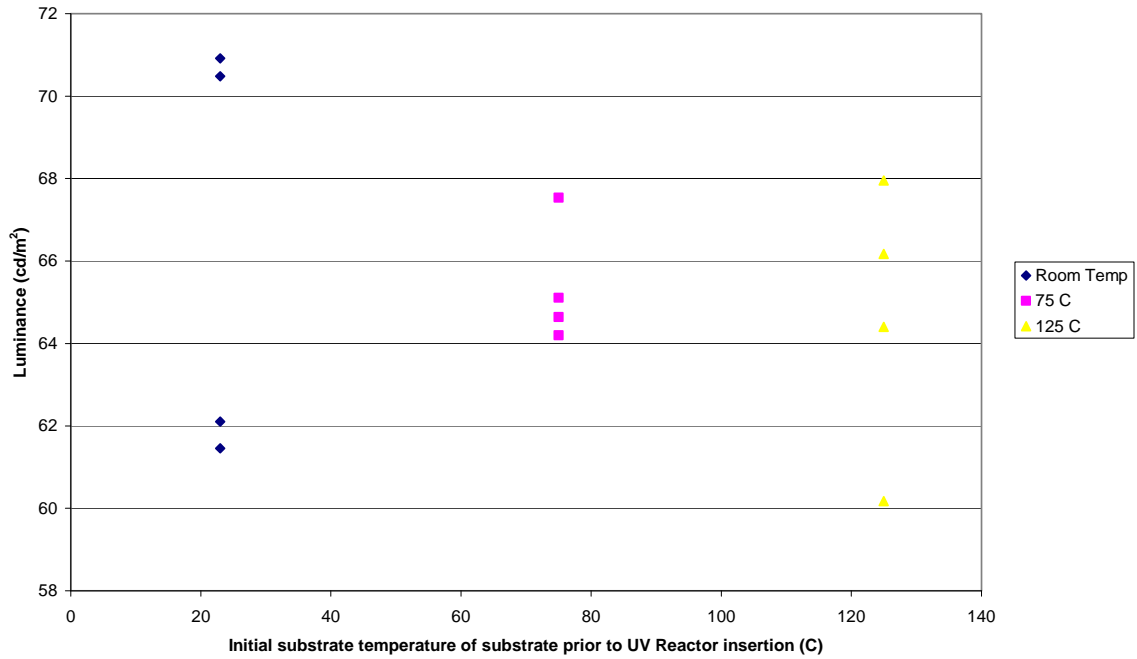


Figure 25. Check IV data at 0.9 mA for small pixel luminance vs. temperature. All substrates in this figure show much lower luminance than data taken from voltage based check IV points in figures 21- 24.

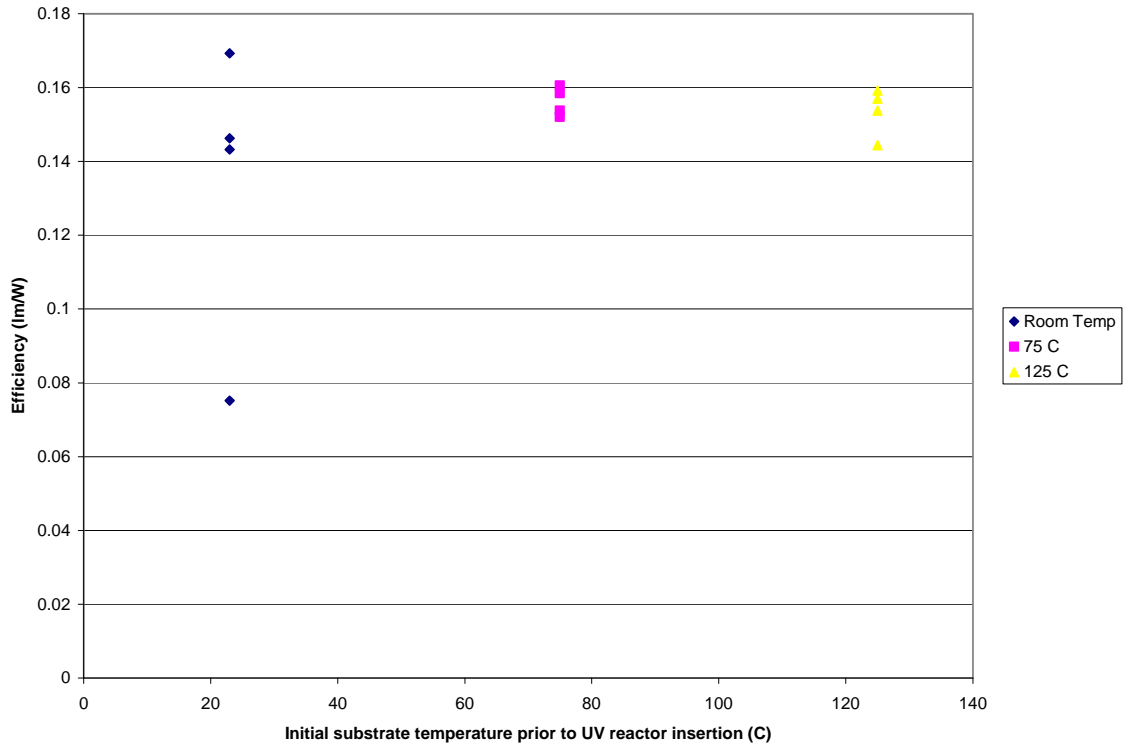


Figure 26. Check IV data at 0.9 mA for small pixel efficiency vs. temperature. This figure also shows low efficiencies below 0.2 lm/W, corroborating findings with voltage based check IV data in figure 24.

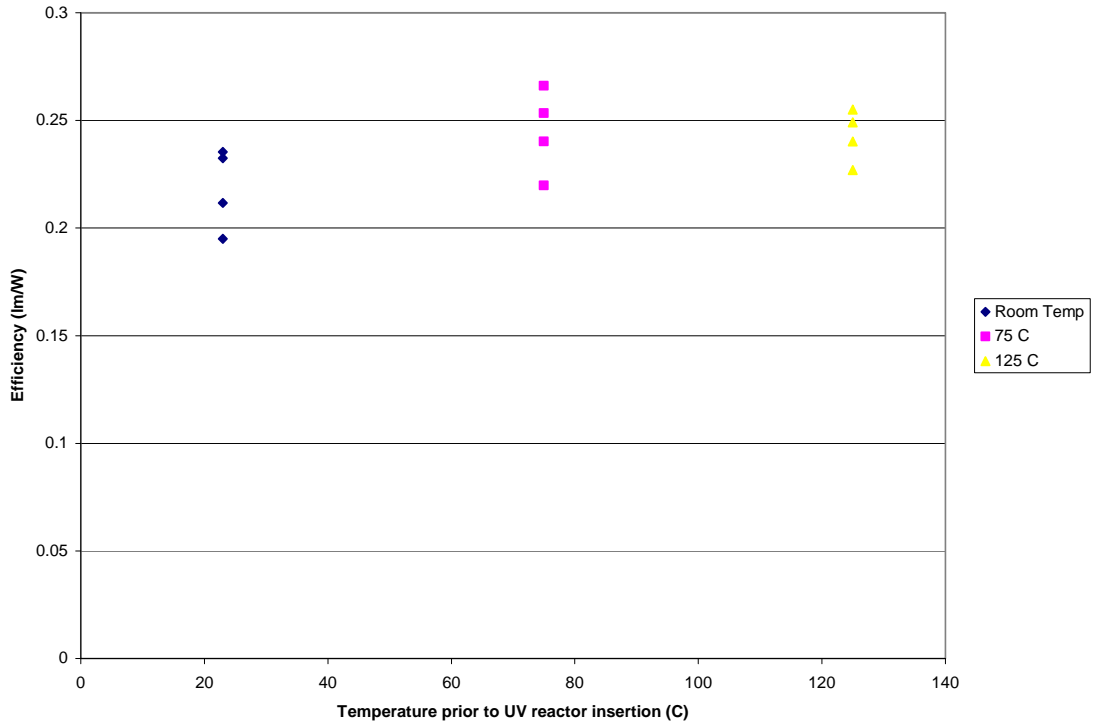


Figure 27. Check IV data for large pixel efficiency vs. temperature at 10mA. Efficiencies for large pixels are still lowered than the expected 0.6-0.7 lm/W, but slightly higher than the 0.18 lm/W exhibited by the small pixels in the preceding figure 26.

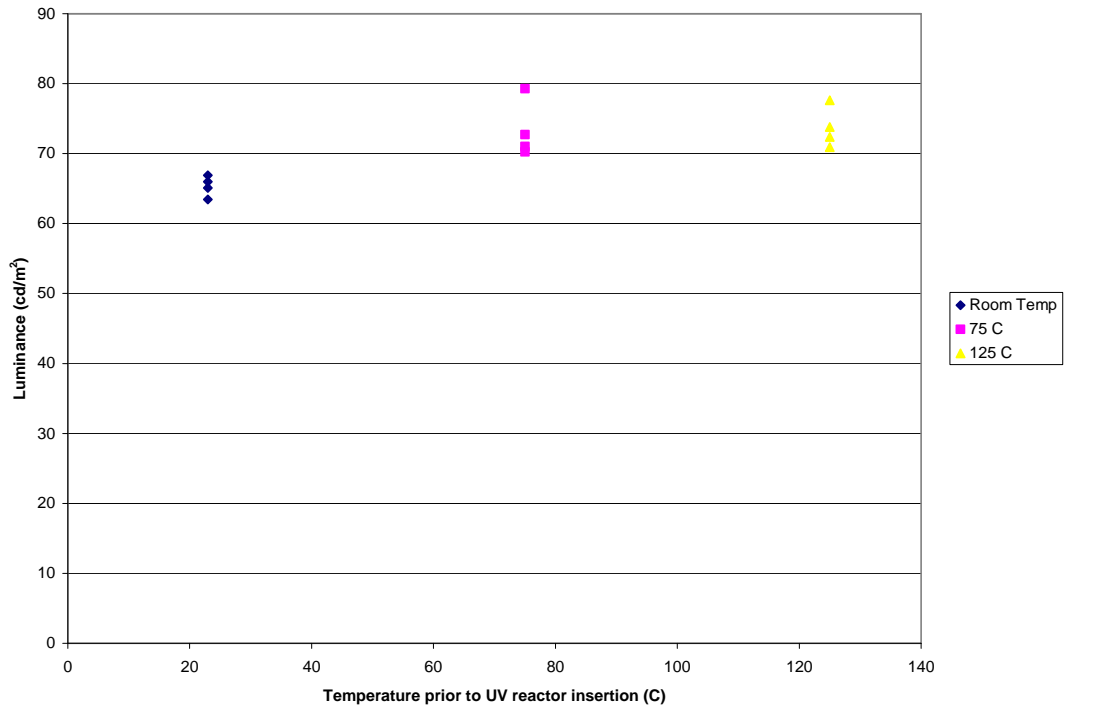


Figure 28. Check IV data for large pixel luminance vs. temperature at 10 mA. This figure shows much lower luminance for all large pixels than the 200 – 400 cd/m² in figure 21.

Table 1. Summary of experiment # 3 luminance and efficiency averages with T-test results.

	Large Pixels at 10mA	Large Pixels at 5V	Small Pixels at 0.9mA	Small Pixels at 5V
Average luminance for Room Temperature Substrates	65.3	306.3	66.2	569.5
Average luminance for 75C Substrates	73.3	345.3	65.3	759.0
Average luminance for 125C Substrates	73.6	340.2	64.6	559.7
Average Efficiency for Room Temperature Substrates	0.21	0.14	0.21	0.13
Average Efficiency for 75C Substrates	0.24	0.16	0.22	0.15
Average Efficiency for 125C Substrates	0.24	0.17	0.21	0.15
T-test results comparing room temperature and 75C luminance values	0.02	0.49	0.76	0.40
T-test results comparing room temperature and 125C luminance values	0.004	0.49	0.63	0.9
T-test results comparing room temperature and 75C Efficiency values	0.1	0.009	0.23	0.34
T-test results comparing room temperature and 125C Efficiency values	0.082	0.0007	0.29	0.39

Table 1 displays the averages of the substrate luminance and efficiencies by temperature, along with corresponding T-tests. The luminance averages show the large pixels at 5 V gained 12% and 11% with UV ozone reactor substrate temperatures of 75

°C and 125 °C; at 10 mA the large pixels gained 11% and 12% respectively. The luminance averages show the small pixels at 5V gained 33% and lost 1% with UV reactor substrate temperatures of 75 °C and 125 °C; at 0.9 mA the small pixels lost 1% and 2%. The small pixels, on average, lost luminance due to 1 single “faulty” pixel, which only produced half the normal luminance and efficiency. Ignoring the faulty small pixel would have yielded increases with both substrate temperatures of 75 °C and 125 °C, as opposed to only the 75 °C substrates shown in the table.

On average, the large pixels at 5V gained efficiencies of 13% and 15% with temperatures of 75 °C and 125 °C respectively; at 10 mA the large pixels gained 14% for both 75 °C and 125 °C. The small pixels at 5V gained efficiencies of 17% and 15% with temperatures of 75 °C and 125 °C ; at 0.9 mA the small pixels gained 4% and lost 4% at 75 °C and 125 °C. Again, the increase in small pixel efficiency at 5 V would have been higher, on average, if a “faulty” pixel had been omitted from the average.

Table 1 also shows many of the T-test results yield p values far above the customary 0.05 cutoff point for statistical significance. However, despite the very high p-values, data suggest possible increased performance for both large and small pixels, in both efficiency and luminance.

Conclusion

In conclusion, placing heated substrates on a silicon wafer before exposure in the UV reactor does not always increase the substrate luminance and efficiency higher than

simply placing the substrate directly in the UV reactor at room temperature. Large pixels exhibit slightly higher luminance and efficiency, but small pixels show lower performance. No dominant mechanism for producing the observed lowered performance stands out from the data

The previous experiment with substrates heated to 125 C did not exhibit lower efficiencies, especially not in the sub 0.2 lm/W range. This provides strong evidence that the mechanism behind the low efficiencies in this experiment is not the increased temperatures. Isolating the source of the lower device performance would require many more experiments, if isolation of the unknown mechanism is even possible. The melting point of silicon is 1410 degrees Celsius, which precludes lowered efficiencies due to silicon melting onto the device glass substrate and obstructing light emission. But, one of many possible mechanisms for the lowered efficiency may be the heated silicon wafer transferred surface contaminants onto the device substrate, despite cleaning the silicon wafer beforehand, causing lowered efficiencies. With such a high melting point, assuming negligible silicon to device contamination seems plausible.

Though data taken at the standard constant test current showed large pixels with much lower luminance and efficiency; control pixels still perform worse than large experimental pixels. The performance percentage increase of the large pixels probably cannot be taken at face value; however, since large pixels were more efficient and brighter, both in the 5 V and 10 mA measurements, ample evidence suggests the silicon wafer technique does indeed offer slight device improvement.

More experiments exploring the mechanism responsible for the lower performance in the current-based data points, and the mechanism responsible for the over-all increased performance are needed. It is unclear whether the silicon wafer caused lower device luminance of 60-70 cd/m² or if some aspect of fabrication affected each substrate. Additionally, experiments with other materials underneath heated substrates could provide insight as to which material properties grant the brightest and most efficient devices. A more direct, but less convenient, experiment would use a heater in the UV ozone reactor.

Changing the timing of process steps, and substrate temperature, produces few positive results; but these largely passive efforts emphasize the potential of more active efforts to change the experimental substrates. Investigation of previously used substrates prepared with various cleaning agents emerges as a feasible method to alter substrates and increase PLED luminance or efficiency.

Chapter 3 Cleaning Agent Experiments

The next phase of experimentation focuses on reusing previously used PLED substrates. All substrates presented in the following experiments underwent physical removal of the calcium anode, OC1C10 layer, and PEDOT layer under warm water. Scrubbing each previously used substrate by hand under warm water, in open air, removed as much of the aforementioned layers as physically possible.

Availability and curiosity recommended the initial cleaning agents. All were readily available and relatively inexpensive. Common household cleaners possess “hidden” ingredients not listed on their bottles. Any positive or negative results may have come from these unknown ingredients, yielding results limited to a specific cleaner, not a specific ingredient.

Common household cleaners offer inexpensive solutions that may increase PLED luminance and efficiency, and thus a high benefit to cost ratio; this presents the strongest reason for their inclusion. Scrubbing previously used PLED substrates with rubber gloves under warm water leaves too many contaminants invisible to the naked eye, but far larger than standard isopropyl/acetone/UV ozone cleaning encounters in pristine substrates. This precluded experimentation with substrates cleaned only with warm water from experimentation.

Substrates came covered in previously deposited layers of OC1C10, cathodes, and possibly human oils; surfactants, basic cleaners, and ammonium cleaners aimed to remove all if not most of the substrate contaminants. These cleaning agents promoted bonding to oils, dirt, and prior device layers, then encouraged contaminant separation

from the substrate in water. Ammonium based cleaners, such as Windex® facilitated substrate contaminant removal with little rinsing. In contrast to basic cleaners, an acidic cleaning agent attempted to “etch” some of the prior device layers away before the reused substrate underwent standard acetone and isopropyl sonic bath cleaning. In the experiments, two categories of cleaners existed: brand name agents, and homemade agents. Examples of brand name agents are Dawn®, Tide®, or Windex®, while examples of homemade agents are lime juice, cream of tartar with water, or homemade Windex®.

3.1 Experiment # 4 Substrate Reuse: Initial Cleaning Agents

Introduction

This experiment investigated the effects of using various soaps to clean a previously used PLED substrate. The experiment used two different kinds of soap: the first was Dawn® dish soap, while the second soap was Tide® detergent. This experiment aims to have both cleaning products increase the luminance or efficiency of the PLEDs by one of the following mechanisms: possibly remove more debris from the ITO and glass substrates, increases the contact between the ITO and PEDOT layer, or increase charge transport from the anode¹⁵. Figure 29 depicts the experimental process for experiment #4.

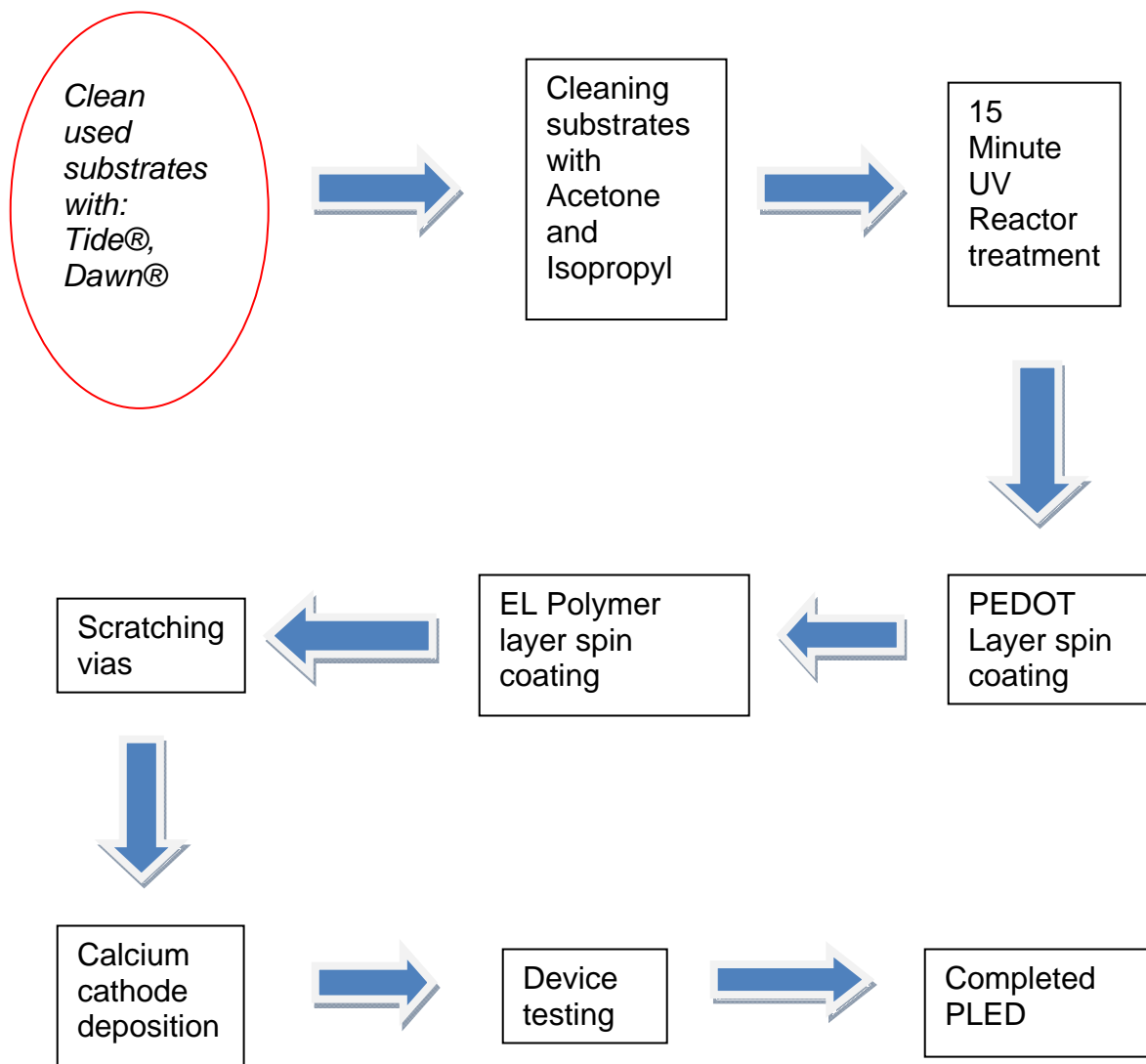


Figure 29. Experimental process for experiment #4.

Procedural Notes

The control LED fabrication followed the manner described in the lab manual¹⁵. The experimental substrates had the previous cathode, OC1C10 layer, and PEDOT layer removed by scrubbing with rubber gloves under tap water. After removing the previous

layers, two substrates underwent soaking and scrubbing, with rubber gloves, in Dawn® hand soap while Tide® detergent cleaned another two substrates. Running tap water rinsed the experimental substrates for an additional ten minutes to remove any residue soap before drying. The experimental substrates then underwent the standard acetone and isopropyl baths, followed by a fifteen minute UV ozone reactor treatment.

Data and Analysis

Each substrate contains two large pixels labeled A and D, and also two small pixels labeled c and d. Figures 30- 33 depict full luminance curves measured with respect to voltage. A substrate labeled “Dawn®1PA” refers to pixel A of substrate 1 (out of 2) treated with Dawn®, and so forth. In figures 34-37, the horizontal axis merely separates data points, and thus has no units.

One of the most important features of full luminance curves is the simultaneous display of the turn on voltages for multiple substrate curves; Figures 30- 33 show all pixels have approximately the same turn on voltage, regardless of treatment. Figures 30 and 31 show luminance versus voltage curves for all large pixels. Note, in both figures, the control substrates, made from regular unused substrates, exhibit the highest luminance.

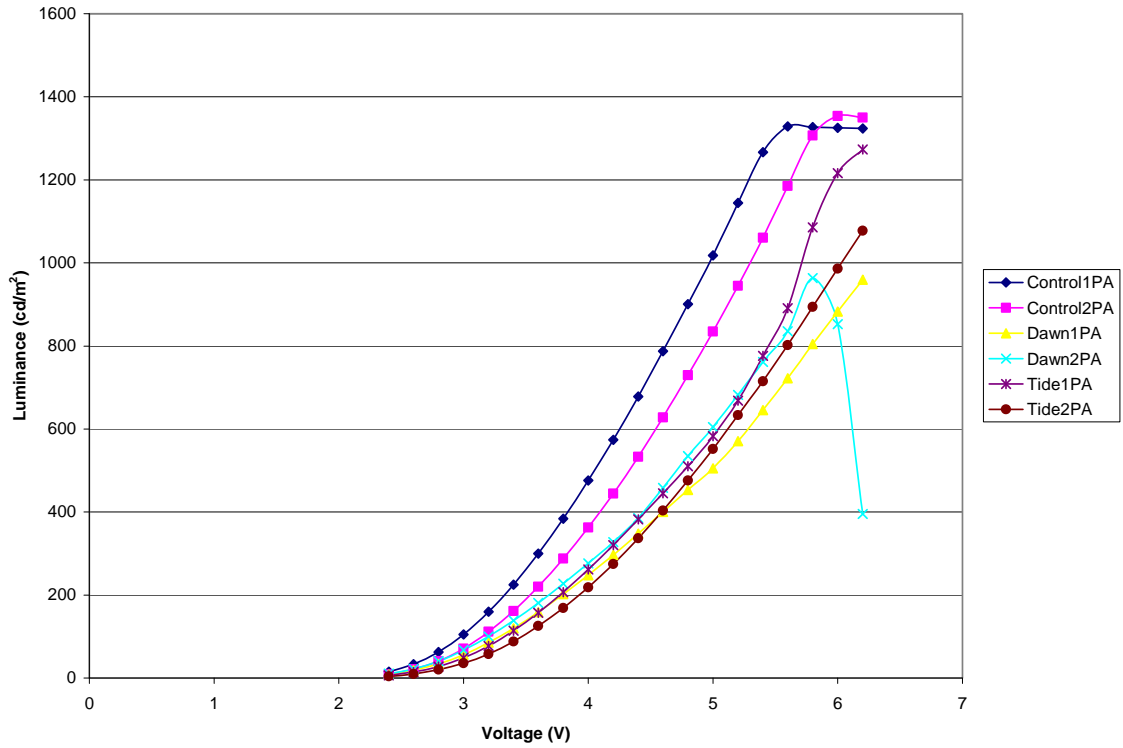


Figure 30. All pixel A (Large Pixel) Luminance vs. Voltage curves.

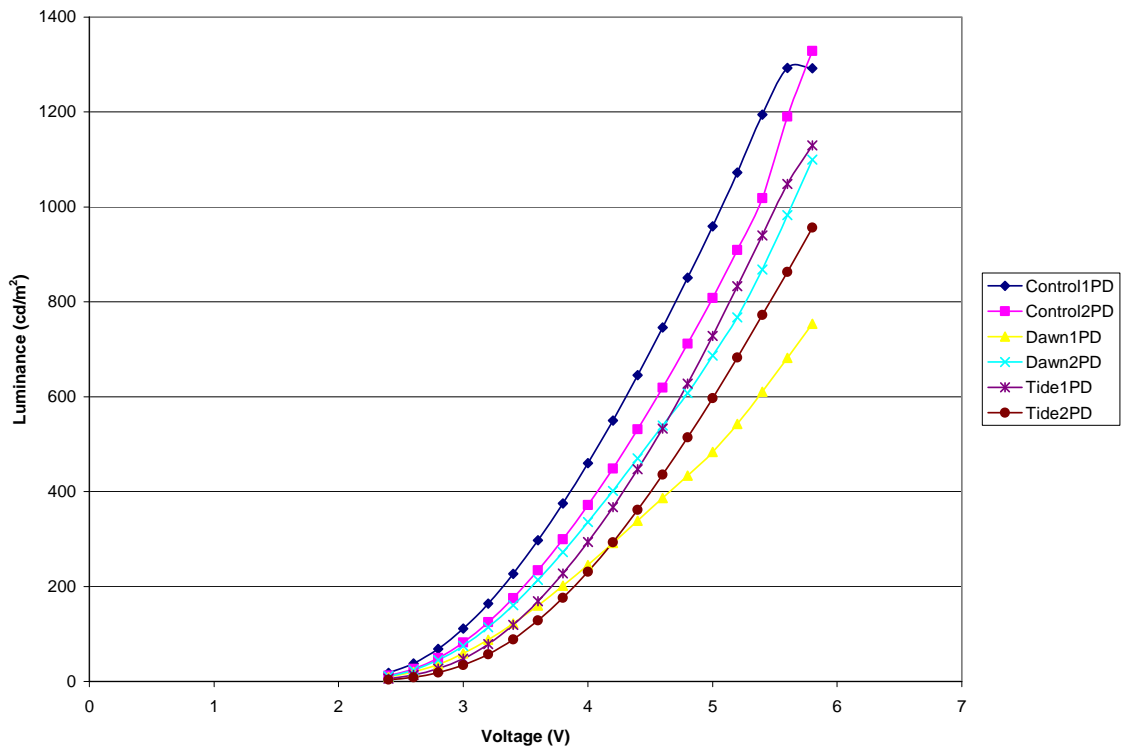


Figure 31. All pixel D (Large Pixel) Luminance vs. Voltage curves.

For the small pixels, the control substrates did not definitively best the experimental substrates. In figures 30 and 31, the control substrates, control1 and control2 for both pixels A and D, did produce the most luminance, but not all pixels on the control substrates outperformed the experimental substrates. The underperforming control substrate in figures 32 and 33, control 2P, did not ever reach regular operating luminance during testing and is included only for completeness.

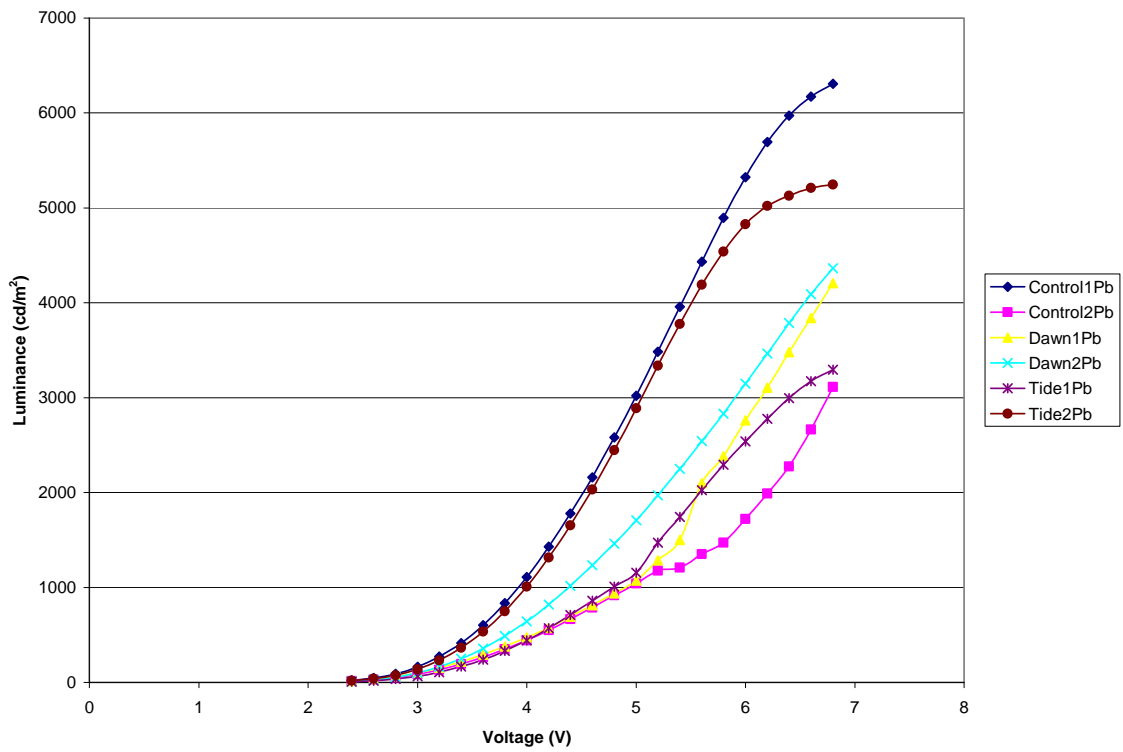


Figure 32. All pixel b (small pixel) luminance vs. voltage curves.

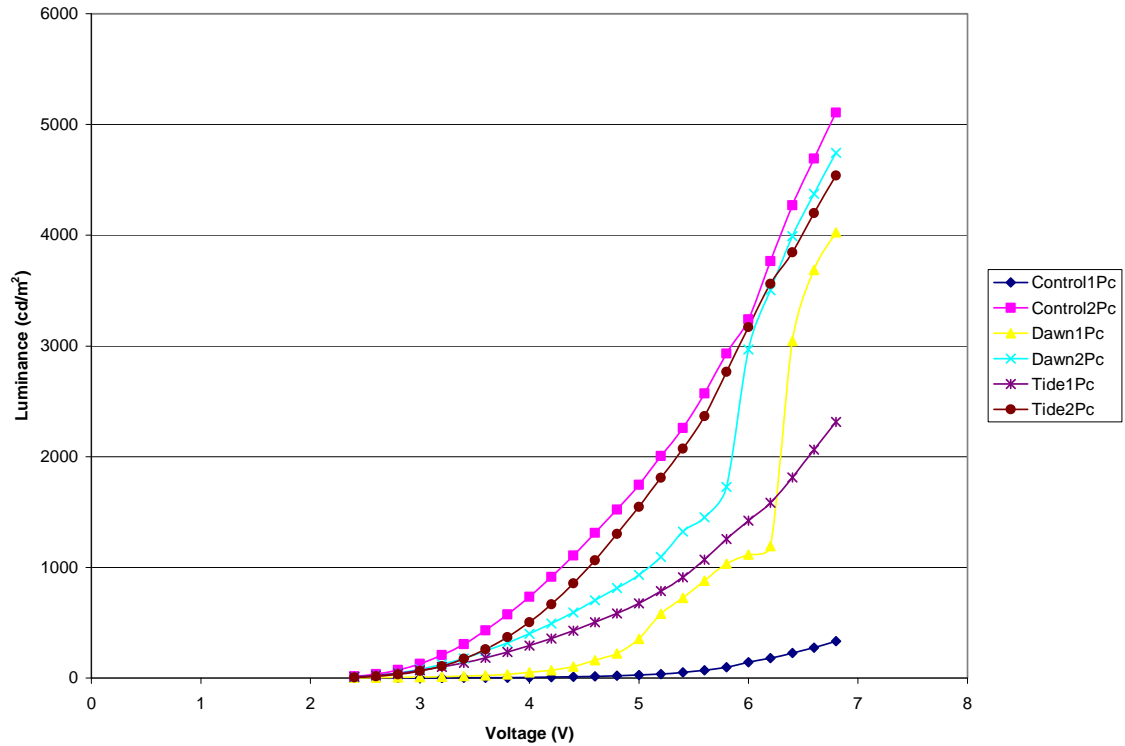


Figure 33. All pixel c (Small pixel) luminance vs. voltage curves.

Since both small pixels, b and c, had one control substrate underperform, it was unclear if the small control pixels did indeed dominate the experimental substrates as shown in the large pixel luminance versus voltage curves.

Comparing all the pixels with the check IV points found during the experiment shows one dominant type of substrate. The horizontal axes in figures 34-37 display arbitrary units that simply space data apart. The figures 34 and 35 exhibit luminance check IV points at 10 mA for large and 0.9 mA small pixels.

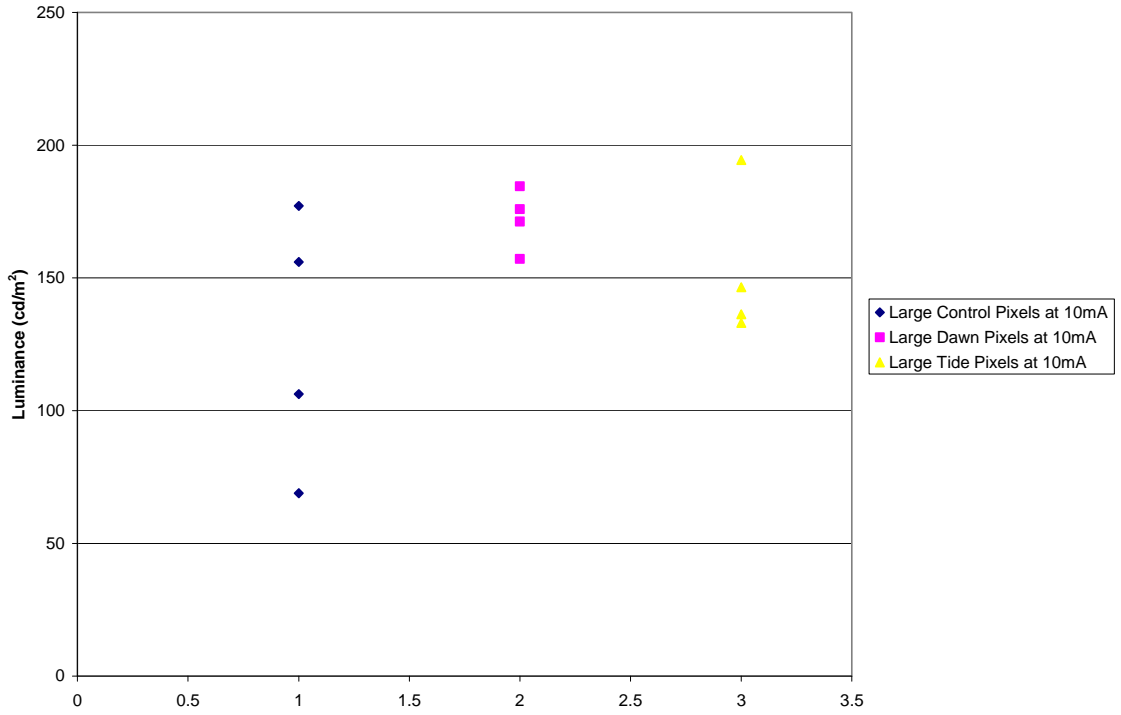


Figure 34. Luminance Check IV points for all large pixels at 10 mA.

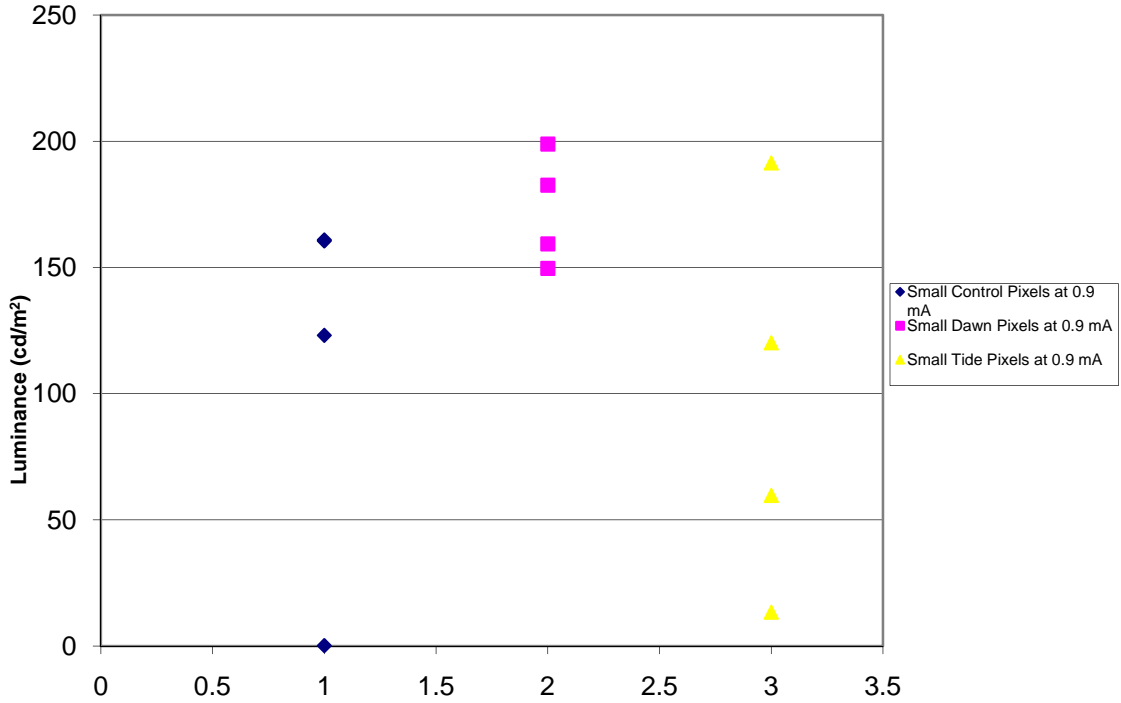


Figure 35. Luminance Check IV points for all small pixels at 0.9 mA. Dawn® pixels are almost 40 Cd/m² brighter than the control pixels.

From the luminance curves, the control substrates appear to radiate more luminance, but from the check IV points, the substrates cleaned with Dawn® show more consistent, and occasionally higher, luminance. This is especially true in the case of the small pixels in figure 35. Also note in figure 35 that Tide® displayed a large range of values for small pixels at 0.9 mA; these values were mostly lower than the other pixels.

The data for efficiency show some similar patterns found in the luminance graphs. In figure 36 the graph shows Dawn®, nearly eclipsing the control substrates in efficiency, while Tide® again has one pixel performing very well, at 0.59 lm/W, while the remaining three pixels are lower than the Dawn® pixels.

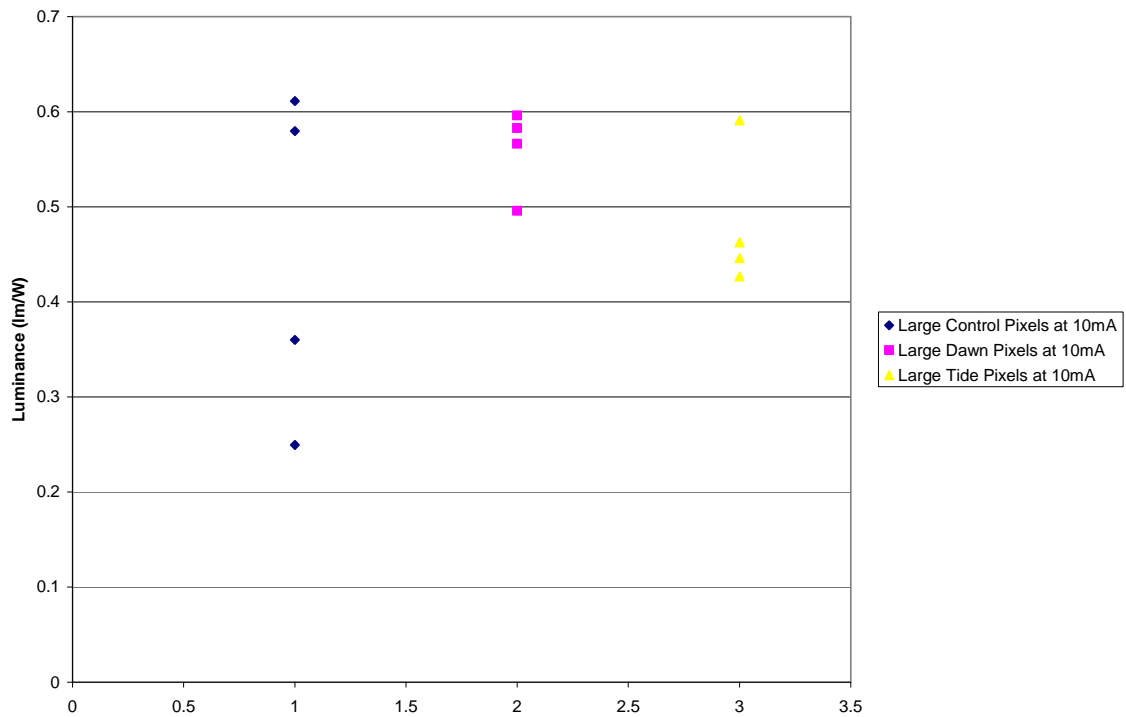


Figure 36. Efficiency Check IV points for large pixels at 10mA.

Figure 37, again, shows Tide® with a wide range of values for small pixels, while Dawn® is far more consistent. Unlike the luminance graphs, however, only one Dawn® pixel is more efficient than the control substrates.

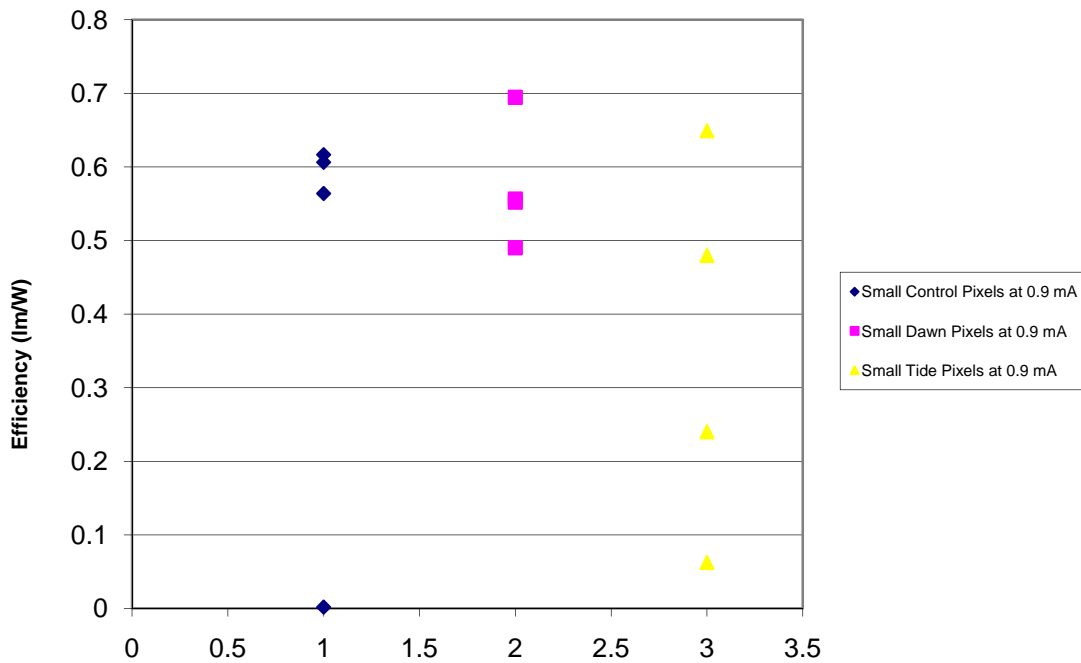


Figure 37. Efficiency Check IV points for small pixels at 0.9 mA.

T-Tests verified statistical significance of all check IV points, and the only p-values less than 0.05 were those comparing large pixels at 5V, where the control substrates clearly produced more luminance than every experimental substrate. Figure 26 agrees with the T-test result of 0.0067 between the control substrate and Dawn®, and with 0.0087 between the control substrate and Tide®, meaning statistical significance supports observed increased luminance of large pixels. All other T-tests comparing

substrate luminance or efficiency values fall in the range of 0.3 to 0.9 suggesting low statistical significance.

Conclusion

The preceding graphs make clear that reused substrates prepared with Dawn® and Tide® cleaning agents failed to produce greater efficiency or luminance than the control substrates. However, considering the experimental substrates left the clean room environment, and underwent cleaning with tap water and soap, that the Dawn® substrates performed well compared to control substrates evinces surprise. Tide® reduced the consistency of the substrates too much to use in practice

Another component not addressed in this experiment is how well the experimental substrates would have performed if the used substrate's previous use extended for a much larger period of time, perhaps 500 hours before cleaning and reusing the substrates. Experimental effects may differ based on how close to "end of life" the PLED experiences cleaning agent pre-treatment. Lastly, both the ingredients in Tide® and Dawn® are only partially revealed on their respective labels. Proprietary ingredients may account for the diminished performance in the Tide® substrates or the comparably strong performance in the Dawn® substrates.

Since previously used substrates cleaned with Dawn® performed comparatively well, increased device performance appears feasible given the correct cleaning agent and technique. The project next examines other cleaning agents in search of steady and measured increases in luminance or efficiency.

3.2 Experiment #5 Substrate Reuse: Secondary Cleaning Agents

Introduction

This experiment tested previously used PLED substrates after being cleaned with the following agents: Clorox® bleach, Oxyclean®, and Windex®. Stronger cleaning agents provided a step toward removing “damaged” or stressed material at the ITO/PEDOT interface studied by Nguyen, et al¹⁸. The previous experiment yielded pixels that performed close to a control pixel; this experiment sought performance exceeding a control pixel’s performance. With this aim, stronger, inexpensive, household cleaners cleaned the previously used substrates. Though more potent, the cleaners used still retained the high cost to benefit ratio desired in the previous experiment. The experiment searched for signs of improvement in brightness or efficiency after cleaning and fabrication of a new PLED on the previously used substrate. Evidence of performance equal to the control substrates was critically important in the event no experimental substrate exceeded the control substrate’s performance.

Procedural Notes

The control LEDs were fabricated as described in the lab manual¹⁵. The experimental substrates had the previous cathode, OC1C10 layer, and PEDOT layer removed by scrubbing under warm tap water. After cleaning, the experiment compares two used substrates soaked in Clorox®, two in Windex®, and two soaked in Oxyclean®. All experimental substrates were then rinsed under warm tap water for 5 minutes and dried. Again, the substrates received the standard acetone and isopropyl sonic baths,

followed by a UV ozone reactor treatment for fifteen minutes. Figure 38 describes the experimental process.

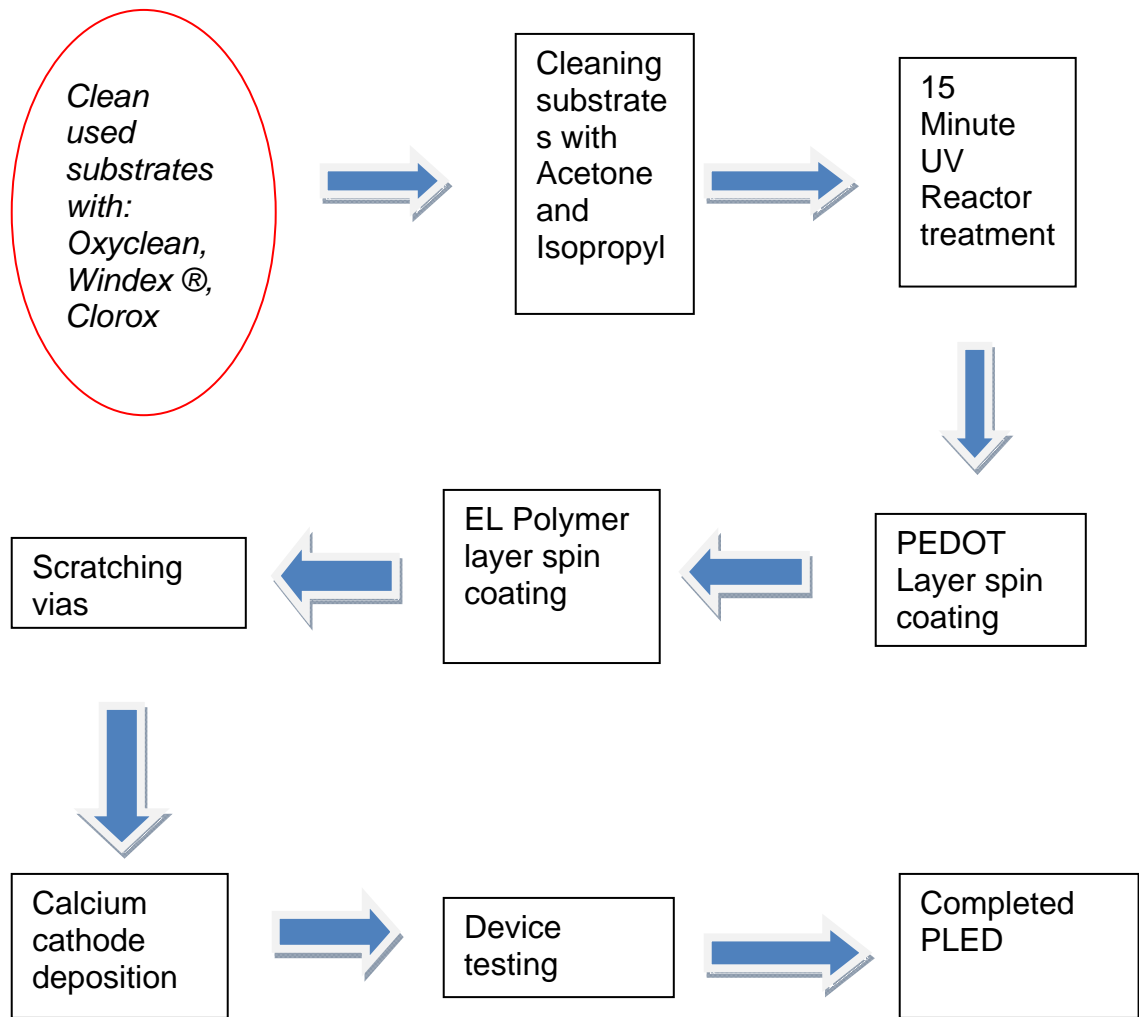


Figure 38. Experimental process of experiment #5.

Data and Analysis

Harsh cleaning agents applied to the used substrates in this experiment often compromised the PLED's ability to shine brightly or efficiently. Clorox® bleach polarized both the PLED's brightness and efficiency, driving substrates cleaned with Clorox® to very low and very high performance.

Figure 39 shows large pixel luminance at 10mA. Clorox® shone less bright than the controls, while the substrates cleaned with Oxyclean® produced nearly half the light or less, when compared to the controls.

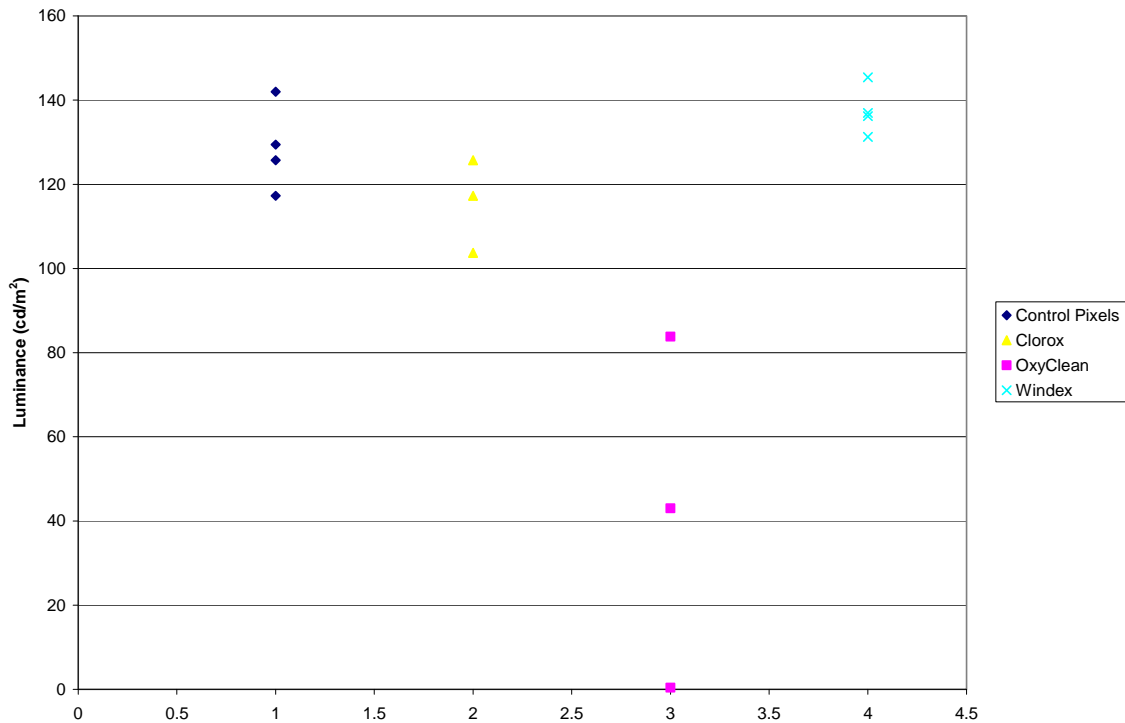


Figure 39. Luminance of large pixels at 10mA. Note Windex® substrates perform as well as control substrates.

The efficiencies of the large pixels reflect the luminances. Figure 40 shows the control substrates performing better than substrates cleaned with Clorox® and Oxyclean®, while Windex®, again, almost performs better than the controls. Clorox® and Oxyclean® both had non-functioning pixels, though the trend is low performance for both. The large pixels for Windex® in these two figures do not have as large a variation as other substrates.

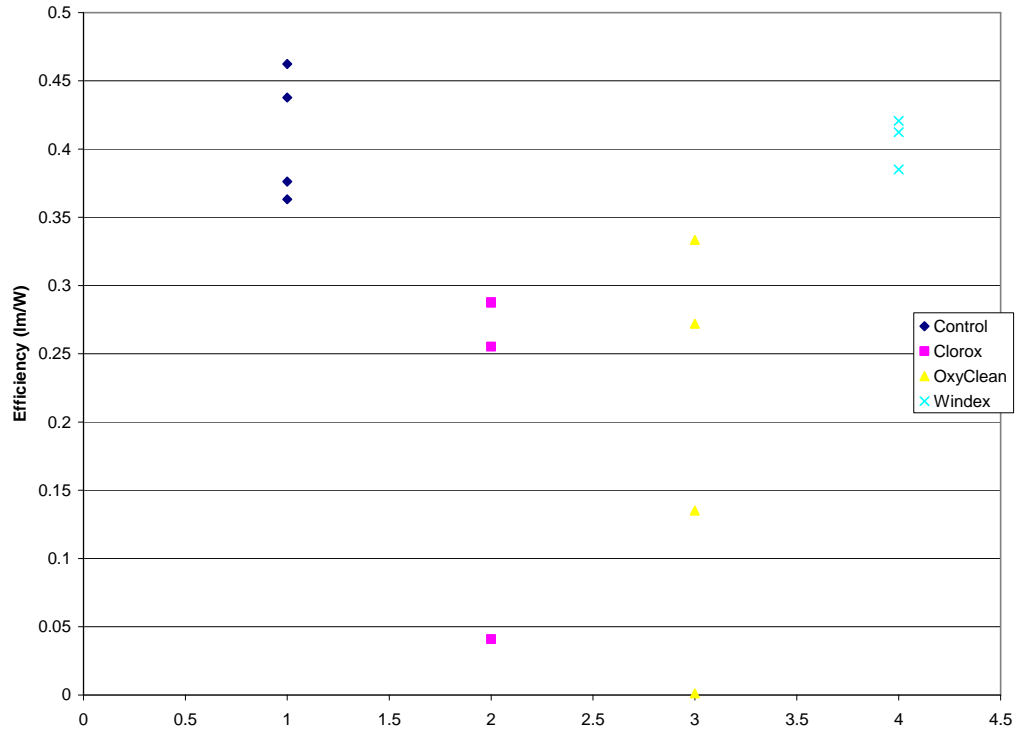


Figure 40. Efficiency of large pixels at 10mA. Note again Windex® performs almost as well as the controls, while Clorox and Oxyclean are visibly less efficient.

The figures depicting performance of the small pixels follow. In both figures, Windex ® again outperforms Oxyclean® and Clorox®, though the margin is not as great as in the large pixels. However, in terms of luminance, some of the Windex® pixels did shine 15 cd/m² brighter than the best control pixels. The control pixels were dropped during fabrication, but it is unlikely that is the explanation.

Though subtle, it is important to note that Windex® did not perform as well with small pixels in terms of efficiency. Windex® did dominate in every other graph except figure 42. There is no clear reason for this, but retrying the experiment to check small pixel efficiency in used substrates cleaned with Windex® could help explain the phenomenon.

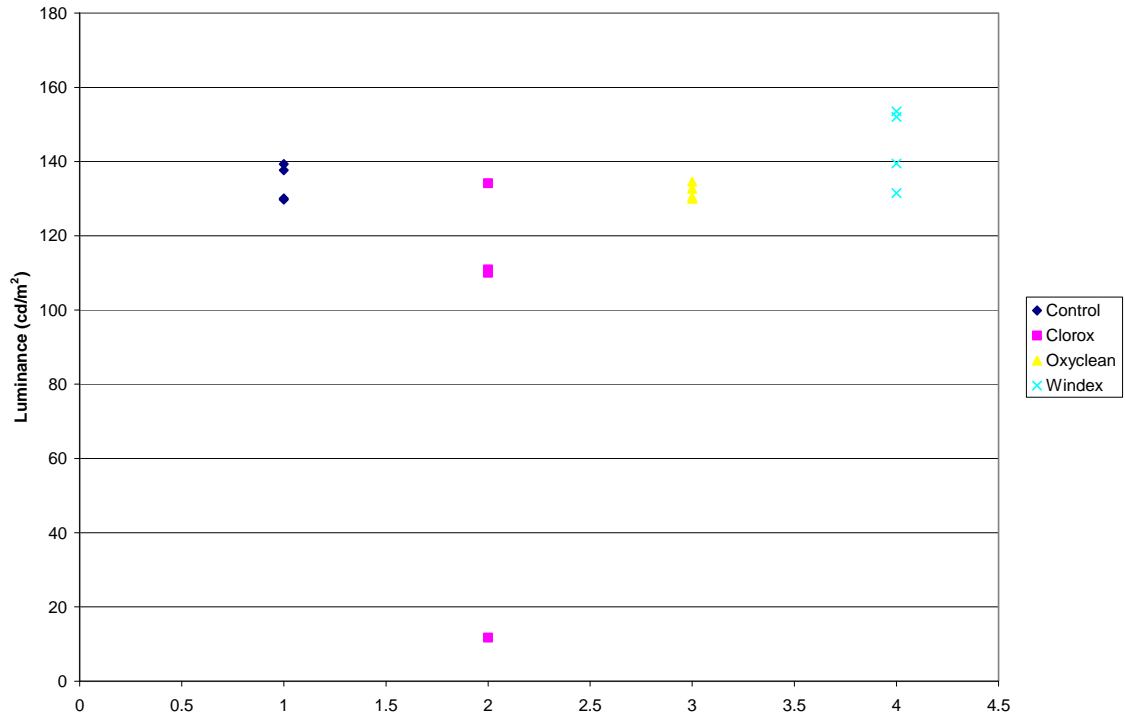


Figure 41. Luminance for small pixels at 0.9mA. Note Windex® almost outperforms every other substrate.

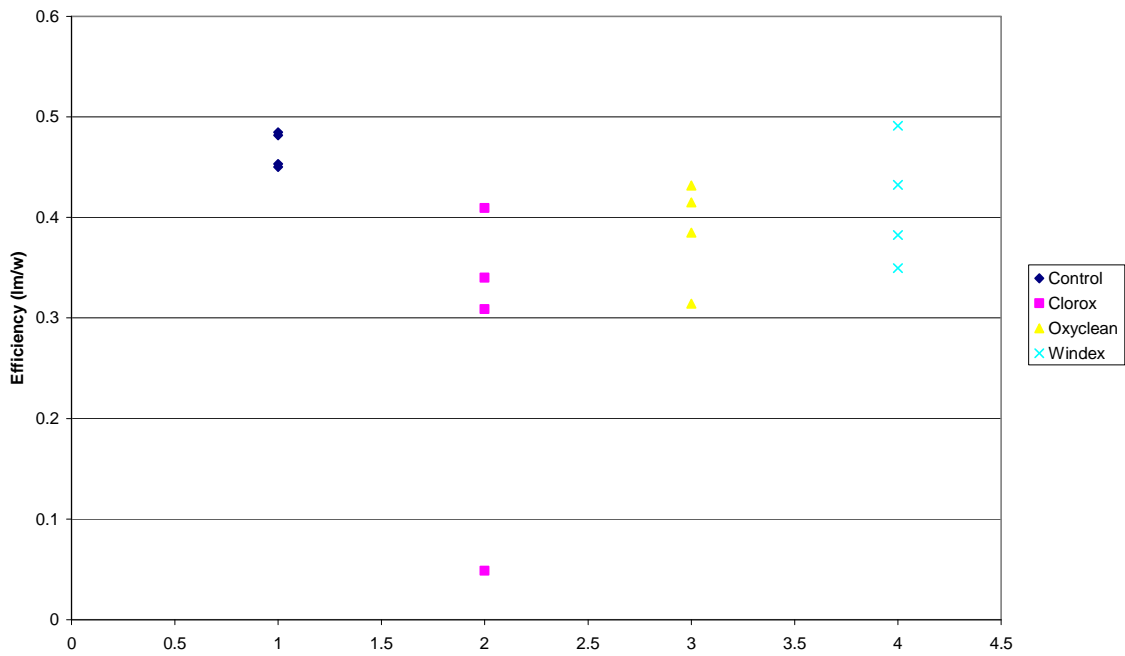


Figure 42. Efficiency for small pixels at 0.9mA.

The P-values comparing the large control pixels versus Clorox®, Oxyclean®, and Windex® in terms of luminance were, 0.083, 0.0799, and 0.197. These first two values state a reasonable level of statistical significance, while 0.197 shows less statistical significance. The P-values comparing the large control pixels versus Clorox®, Oxyclean®, and Windex® in terms of efficiency were, 0.040, 0.050, and 0.708. The 0.708 P-value of Windex® is particular because, from the preceding graphs, Windex® mirrored the efficiency of the control substrates well. Additionally, the high 0.708 P-value shows a low level of statistically significant difference between the control and Windex® samples.

Conclusion

A hypothesis as to why Windex® fared much better than bleach or Oxyclean® is that Windex® did not alter or harm the used substrate. Substrates cleaned with Clorox® had a streaky reddish film after PEDOT application that appeared to interfere with luminescence through the glass. Substrates cleaned with Oxyclean® were not as transparent as the Windex® or control substrates, and this too is reflected in the data. Additionally, Windex® on the emitting, non-active side of the device could preserve and enhance device luminance. This theory seems plausible since Windex® is indeed a window cleaner, with the bottom side of the device operating as a small window. Windex® could also clean the ITO side, as well.

When put in context of the experiment's goals, neither Oxyclean®, nor Clorox® produced disappointing results. Also, in this context, Windex® produced the desired results. The LEDs sprayed with Windex® could replace control substrates if the data were unlabeled. Another important characteristic of the Windex® substrates was the

small variance exhibited in the large pixels. The harshness of the cleaning agents can explain the large variations in Clorox® and Oxyclean®, but Windex® did not suffer the same problem.

Now that Windex® substrates proved they may help make substrates renewable, a future experiment could be to track the degradation process of these two Windex® substrates. The Windex® results were so close to control substrate performance, perhaps fabricating another pair of used substrates cleaned with Windex® is in order.

Data from this experiment leads to immediate curiosity concerning the existence of an isolated ingredient in window cleaner that provides device performance tantamount to substrate renewal.

3.3 Experiment # 6 Substrate Reuse: Simple Cleaning Agents

Introduction

Windex®, based on experiment # 5, allows a reused substrate to perform almost like a brand new substrate. The luminance and efficiency of a used Windex® substrate is very close to the luminance and efficiency of a brand new substrate. This experiment tests single components in Windex®, as well as a homemade version of Windex®, to see if any performed as well. The possible etching effects of tartaric acid on residual device layers promote its inclusion; these same etching effects also account for the inclusion of lime juice. The main ingredient in Windex® is ammonia, though a much stronger concentration than household ammonia.

Procedural Notes

The single components tested were cream of tartar, lime juice, and household ammonia. The homemade Windex® was 1 cup rubbing alcohol, 1 cup water, with 1 tablespoon of vinegar. All the reused substrates soaked in their respective cleaning agents for 30 minutes, except for the lemon juice, which soaked for 1 hour and 30 minutes. The cream of tartar mixed with one-third a cup of water and then scrubbed the substrate for 10 minutes, then soaked for an additional 20 minutes.

Data and Analysis

That horizontal axes in figures 43-46 display arbitrary units that simply space data apart. Figure 43 below shows the luminance plot for large pixels at 10mA. The dominance of the control pixels is obvious, but the similarity of all the experimental pixels was not expected. The control pixels shine almost 100 cd/m^2 brighter than the experimental pixels. Also, the substrates treated with lime juice did seem damaged from the streaks seen on the substrates themselves; this damage is not reflected in the luminance plot for large pixels. The homemade Windex® and the cream of tartar and water solution had the smallest variance in luminance.

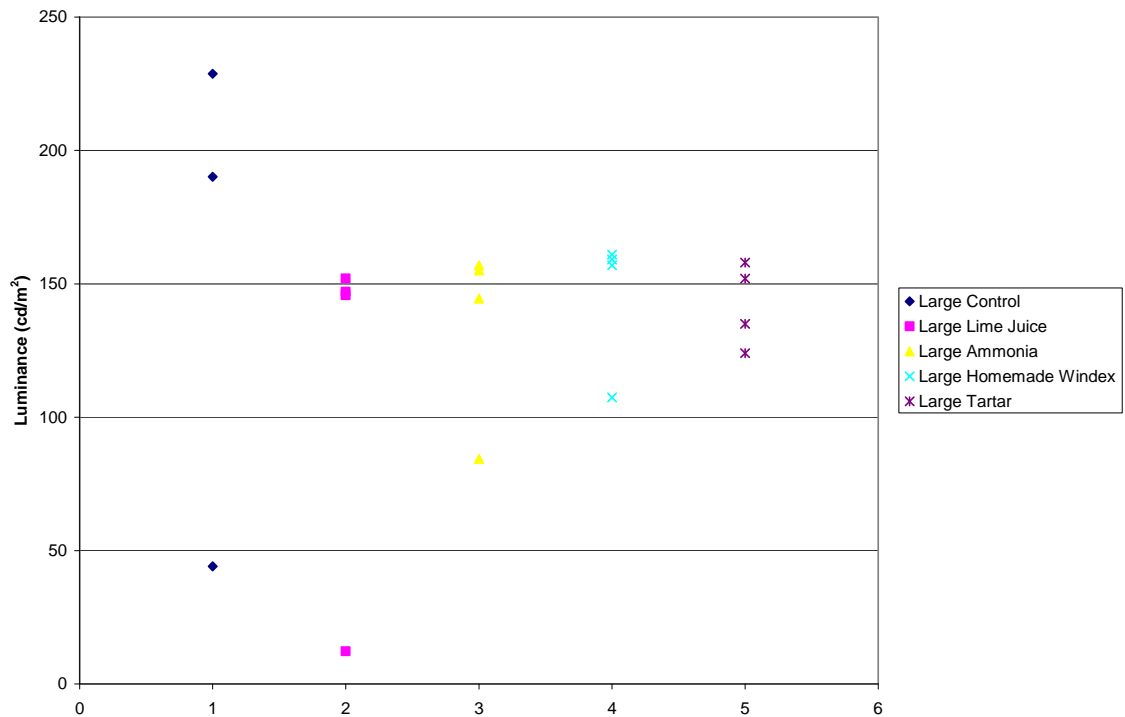


Figure 43. Luminance of Large Pixels at 10mA.

Figure 44 below shows the efficiency of the large pixels at 10mA. The figure depicts the control substrates as having almost twice as the efficiency as the experimental

substrates at the 10mA test current. One large control substrate had a maximum efficiency of 0.87 lm/W, while the experimental substrates had a maximum efficiency of 0.503 lm/W. The efficiency plot mirrors the luminance plot for large substrates. Again, the Windex® and tartar had the smallest variance in efficiency. One possible reason for the low performance of the large experimental pixels was that the separate cleaning ingredients needed to be used in conjunction with one another to be effective. Also, maybe the lack of dedicated surfactants in each experimental solution contributed to the low performance. The data do support this theory, as the homemade Windex® did result in highest luminance and second highest efficiency among the experimental pixels. This presents an idea for another experiment with cleaning agents mixed together sequentially, for example, soap and water, then vinegar, then alcohol. Perhaps the sequence of different cleaning agents, and different sequential cleaning mechanisms, may provide greater decontamination effectiveness, and yield improved overall device performance.

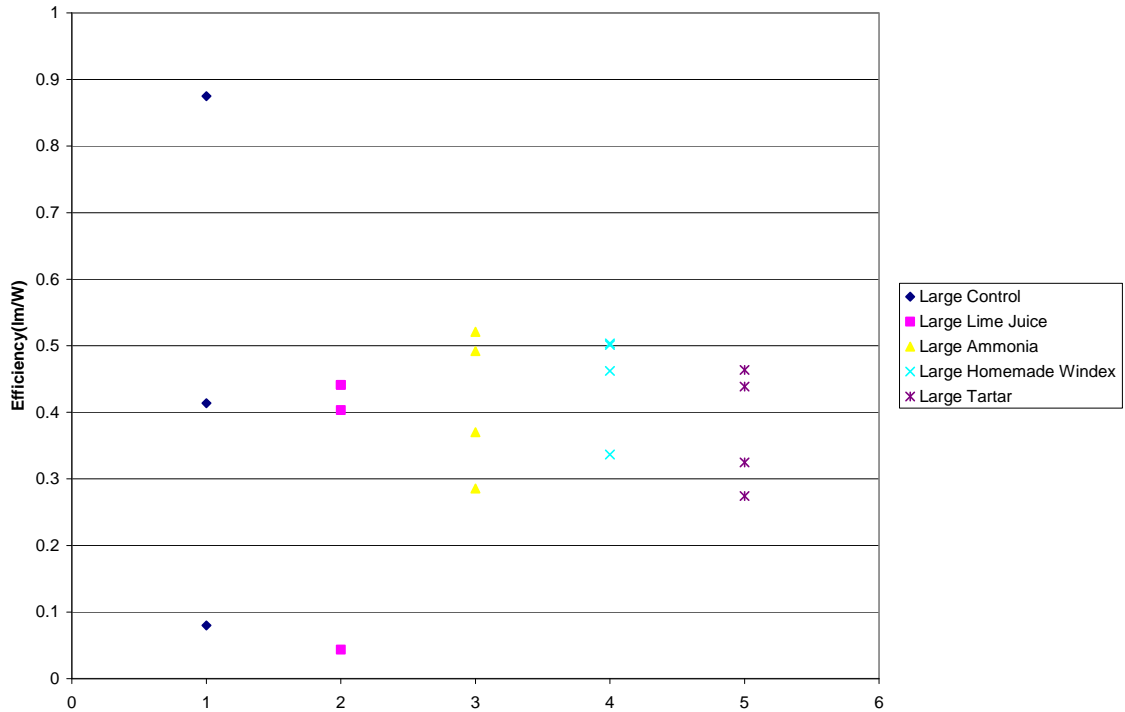


Figure 44. Efficiency of Large Pixels at 10mA.

The data for smaller pixels was expected to match that of the large pixels. Figure 45 below depicts the luminance of the small pixels at 0.9mA. The small pixels performed much better than the large pixels, reaching 159 cd/m² compared to the control value of 196 cd/m². This represents only a 20% reduction in performance from a brand new PLED. However, this performance was reached by lime juice, which had a large variance in both small and large pixels. The homemade Windex® was 6 cd/m² less bright than the lime juice, but had one of the smallest variances in each data set. In terms of reusability, the homemade Windex® was more reliable.

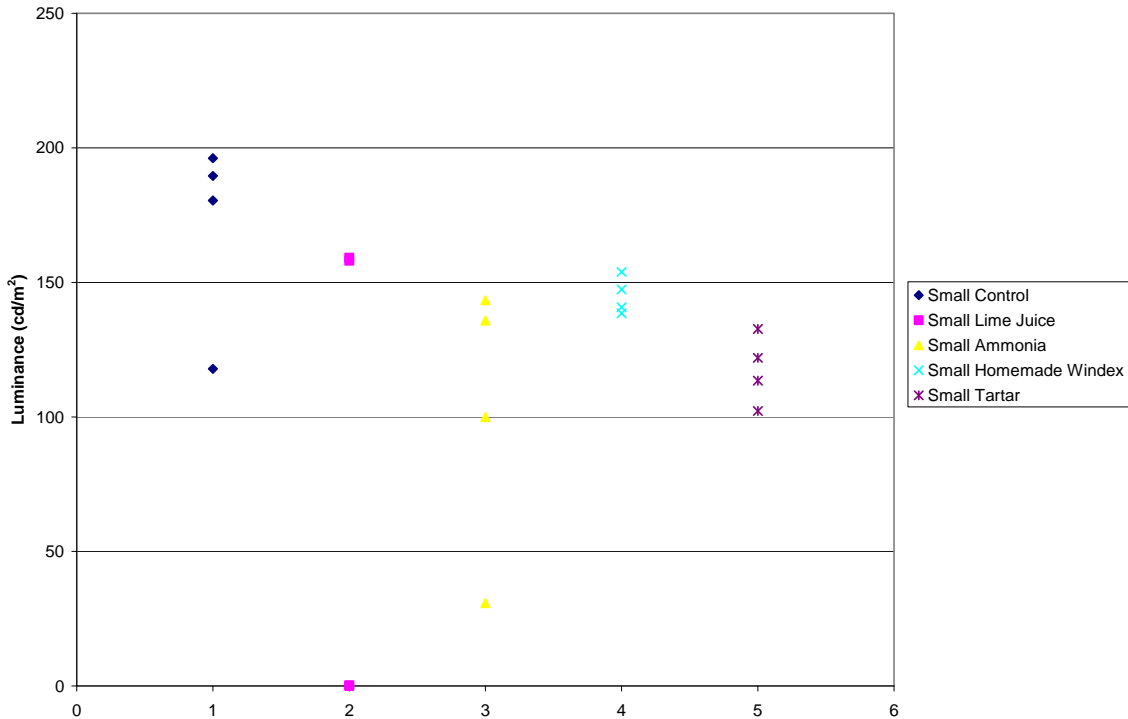


Figure 45. Luminance of small pixels at 0.9mA.

Figure 46 depicts the efficiency of the small pixels at 0.9mA. Again, the efficiency of the experimental substrates is almost half that of brand new control substrates. Also, as in the large substrates, the efficiency plot mirrors the luminance plot with lime juice and homemade Windex® having the highest efficiencies at 0.56 lm/W and 0.52 lm/W. However, all experimental pixels exhibit much lower efficiencies than the control substrate. Again, the experimental pixels are almost half as efficient, since the control pixels had an efficiency of 0.79 lm/W.

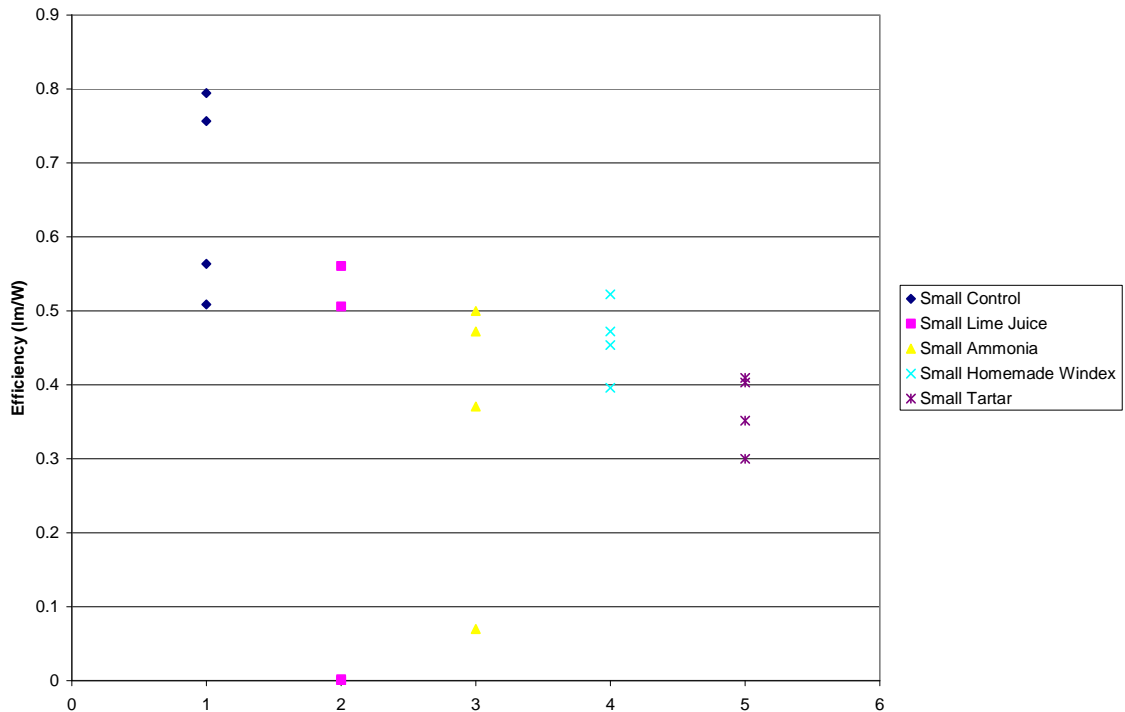


Figure 46. Efficiency for small pixels at 0.9mA.

Conclusion

None of the experimental pixels provided high enough performance to justify use in reusing a PLED. Though figure 45 did seem to suggest that perhaps reuse of small pixels may be possible, the greatly diminished efficiency of the small and large pixels denies that possibility. Only the variance of the tartar and homemade Windex® solution was small enough to be practical in the field, even if the efficiency was not. Also, the large losses in performance from just one reuse with these solutions brings into question how many times these substrates could be reused. Ideally, each reuse would cause less than 10% loss in efficiency and luminance. Since lime juice could possibly be procured relatively cheaply, it maybe could have been economically viable, but the unpredictable results in both luminance and efficiency rendered its high points of little value.

It does seem that a combination of cleaning agents is more stable, with a lower variance, and produces better performance. Perhaps the concentration of household ammonia or tartar was too low, yielding weaker results than are possible with those two agents. Tartar though readily available is more expensive than other cleaning agents; even if it had performed well, that too is an impractical choice.

Scrubbing cream of tartar on the used substrate may have irreparably damaged the ITO surface. Another experiment may test the effect of cream of tartar on a substrate that is only soaked in the solution, not scrubbed.

After experimenting with various cleaners, the project next examines the effects of using old polymer on pristine substrates and etching previously used substrates. The departure from cleaning agents intentionally seeks different mechanisms for improving device performance.

Chapter 4 Aging and Etching Experiments

The next phase of experimentation shifted the focus of reusing PLEDs into two different experiments. Firstly, brand new substrates used polymer of different ages: 7 years old, 4 years old, and 1 week old. Polymer reuse grants many bottles of excess polymer in the polymer lab use, even if from early in the decade; also, it helps characterize polymer degradation in an inert environment over the course of many years. Secondly, previously used substrates scrubbed clean under warm water in open air, as in earlier experiments, underwent etching. The experiments used two etchants, HCL and KOH, in various orientations and durations.

4.1 Experiment #7 Reuse: Aged Polymer Performance

Introduction

This experiment examined the effects of using old polymer on the luminance and efficiency on PLEDs. It is known from past experience that PLED luminance and efficiency degrade without the PLED even being driven. Since PLEDs degrade over time in the nitrogen filled glove box, newer polymers should outperform older polymers. The mechanism for degeneration is not entirely known; though one similar to diffusion does occur, the glove box and PLED temperature is too low to indicate diffusion. Figure 47 shows the experimental fabrication process including aged polymers.

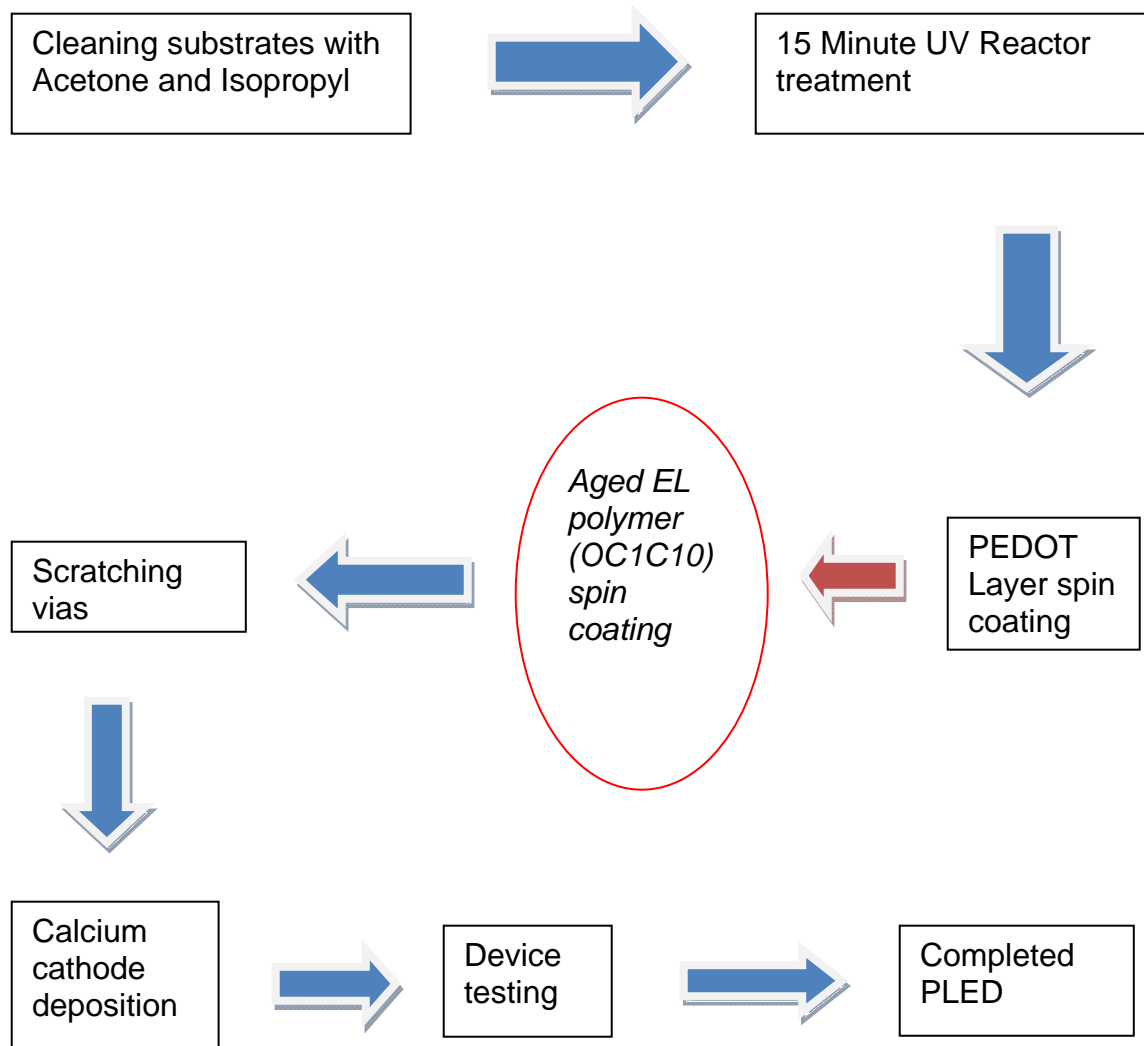


Figure 47. Experimental process utilizing aged OC1C10.

Procedural Notes

Unused polymer resides in the glove box after fabricating all substrates of a given batch. Over many years, polymer batches from a variety of occasions accumulate in the glove box. The polymers used were 7 years old, 4 years old, and 1 week old. A hotplate stirred each polymer overnight, then heated them to 50 C prior to application. None of the polymers required filtering again, nor was any additional solvent used. The 2001 polymer did have some concentrated polymer at the bottom of the bottle, and the

polymers were slightly different shades of orange. Aside from these differences, all polymers experienced usual fabrication.

Data and Analysis

That horizontal axes in figures 48,49,52, and 53 display arbitrary units that simply space data apart. Figures 48 and 49 show the luminance plot for the large pixels at 10mA, and small pixels at 0.9mA. Both plots look similar, and both show dominant performance of the 2001 polymer shining almost 200 cd/m² higher than the controls. The 2001 polymer also shines roughly 50 cd/m² brighter than the 2004 polymer. Of importance are the small variances for all test groups except the 2008 polymer.

Figures 50 and 51 show the full luminance curves with respect to voltage. In those curves, the 2001 polymer is still dominant in the top 4 curves, both in small and large pixels. Among large pixels in figure 50, the 2001 polymer is roughly 500 cd/m² brighter than the 2004 polymer, which matches the earlier single point graphs. In figure 51, three of the top four curves are small 2001 polymer pixels. A 2004 pixel did perform very well, though no other 2004 pixels displayed such brightness.

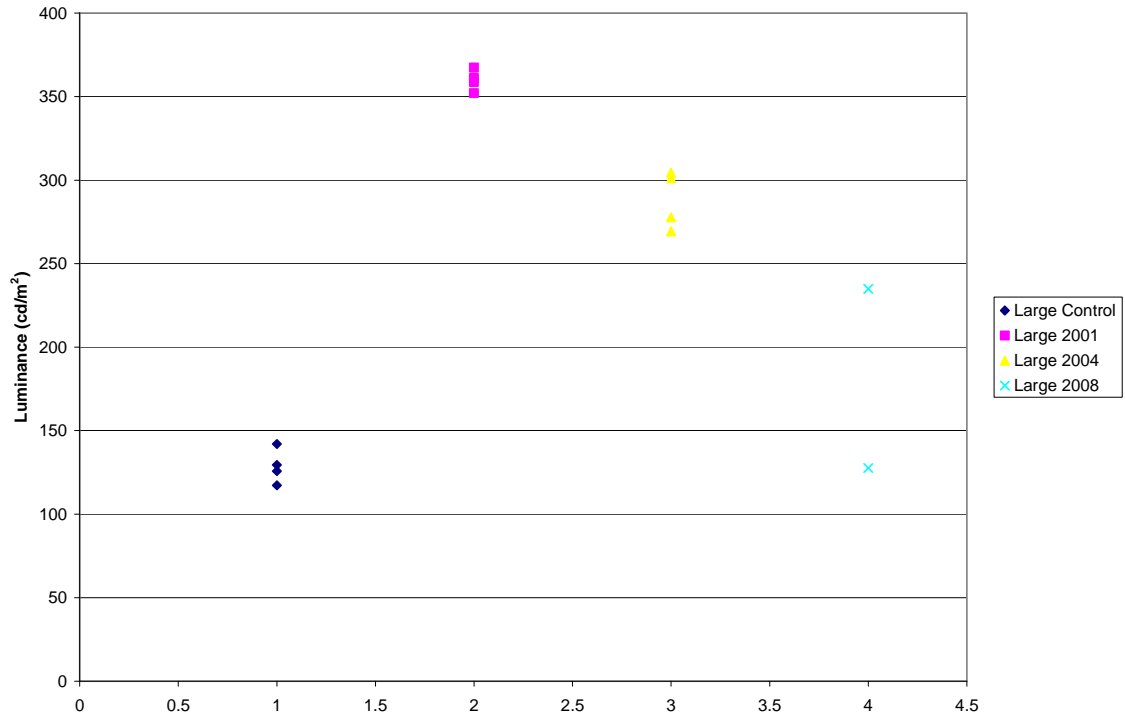


Figure 48. Luminance plot of large pixels at 10mA.

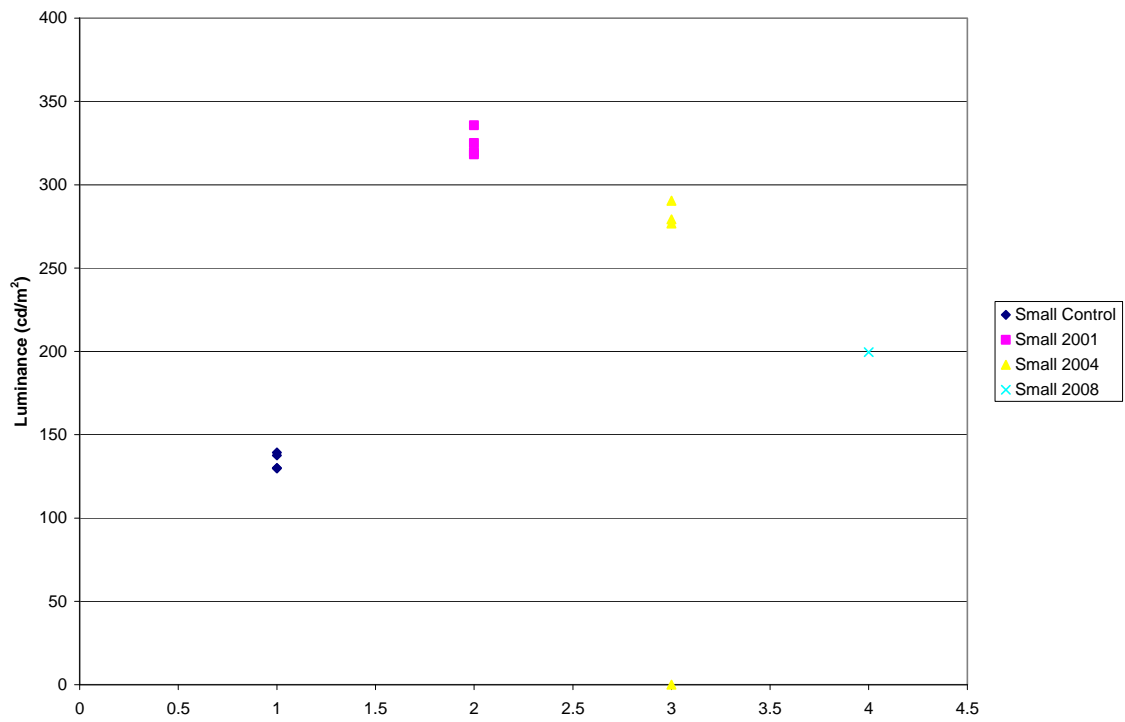


Figure 49. Luminance plot of small pixels at 0.9mA.

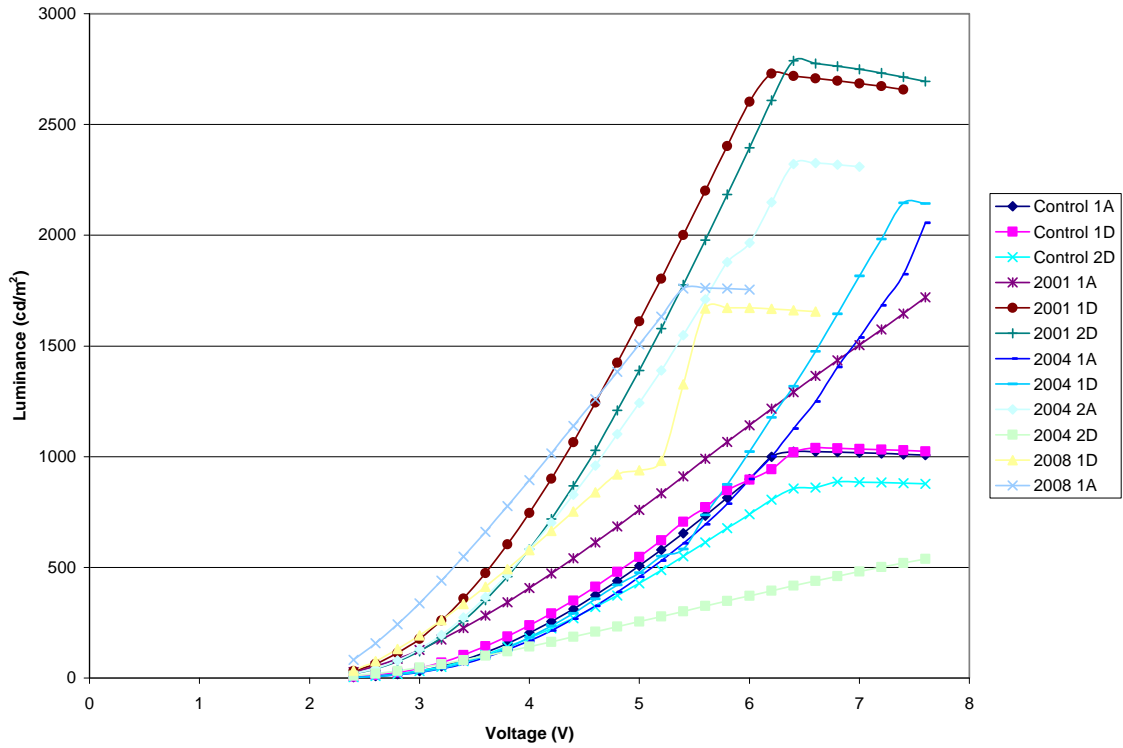


Figure 50. Luminance vs. Voltage curves for large pixels.

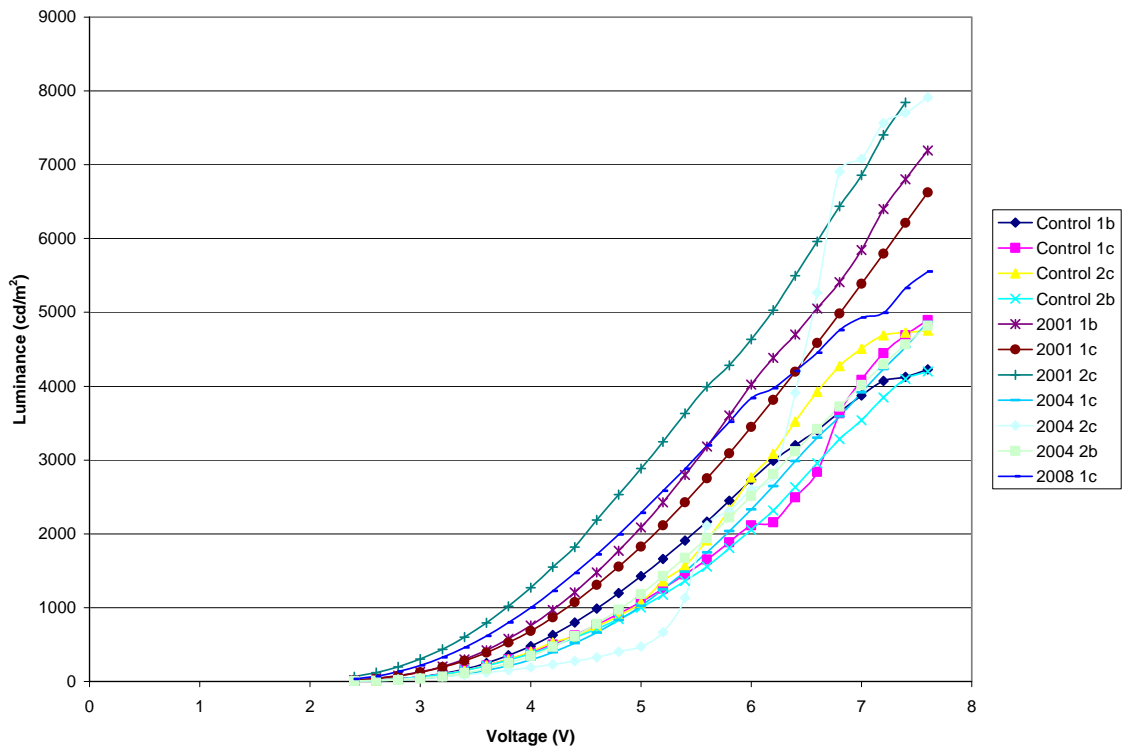


Figure 51. Luminance vs. Voltage curves for small pixels.

Figures 52 and 53 show the efficiency plots for large and small pixels. They both mirror each other similar to the luminance plots in figures 48 and 49, but the variances are greater in both figures 52 and 53. The 2001 polymer still yielded the most efficient pixels, but the 2004 polymer was much closer in performance than in the luminance plots. Both the 2008 and the control pixels were not as efficient in either plot, also similar to the voltage plots.

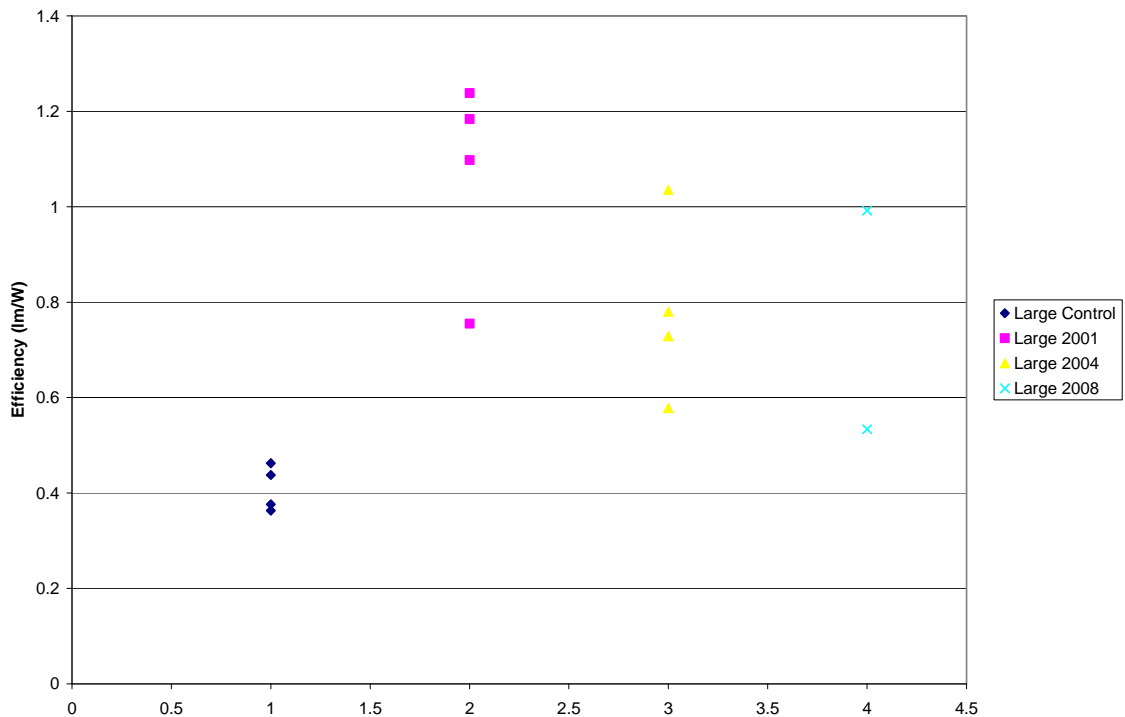


Figure 52. Efficiency of large pixels at 10mA.

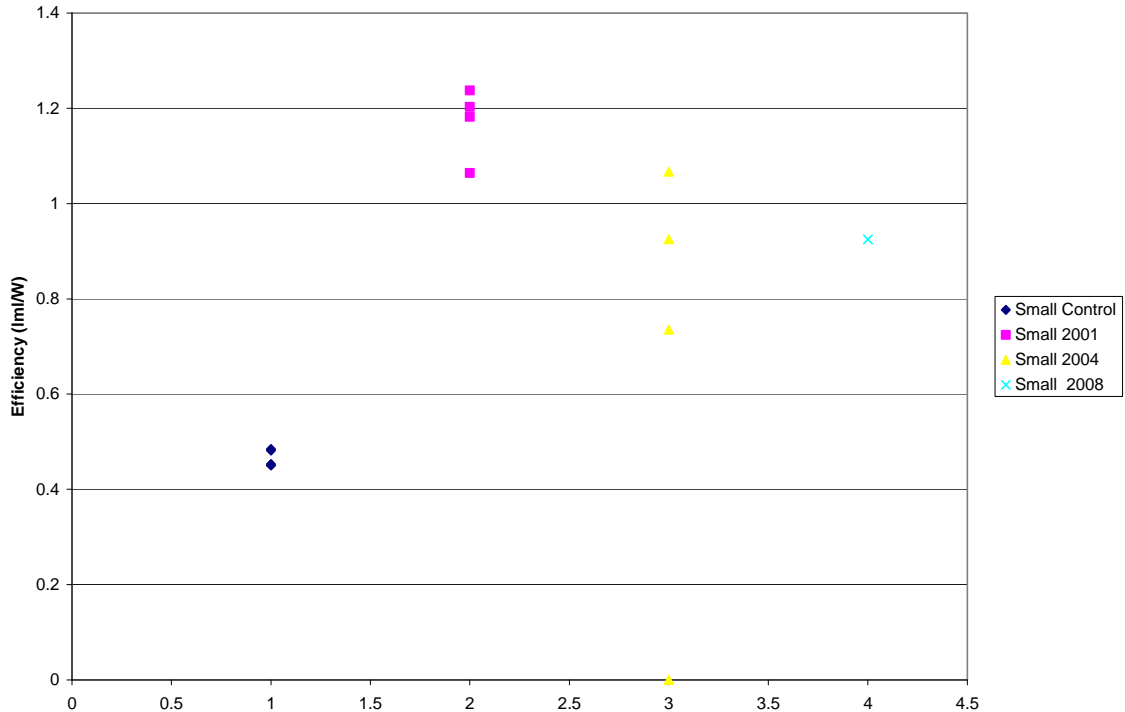


Figure 53. Efficiency of small pixels at 0.9mA.

To again contrast the point plots, figures 54 and 55 depict the full efficiency vs. voltage curves for large and small pixels. For large pixels, the top three efficiency curves are all from the 2001 polymer, and centered about 1.4 lm/W. The next highest curve peaks at 1.2 lm/W. After seeing the previous data curves, that the 2001 polymer performed so well, and so consistently, is no surprise.

In figure 55 every single one of the top 4 curves are from the 2001 polymer. Also, pixel 2001c plainly outperforms every other small pixel in the data set, peaking at 1.1 lm/W. Ignoring pixel c, the next highest efficiency curve peaks at slightly less than 0.6 lm/W, while the 3 other 2001 curves peak about 0.7 lm/W. The difference in the peaks does not seem so great, but the consistent performance is again important to note.

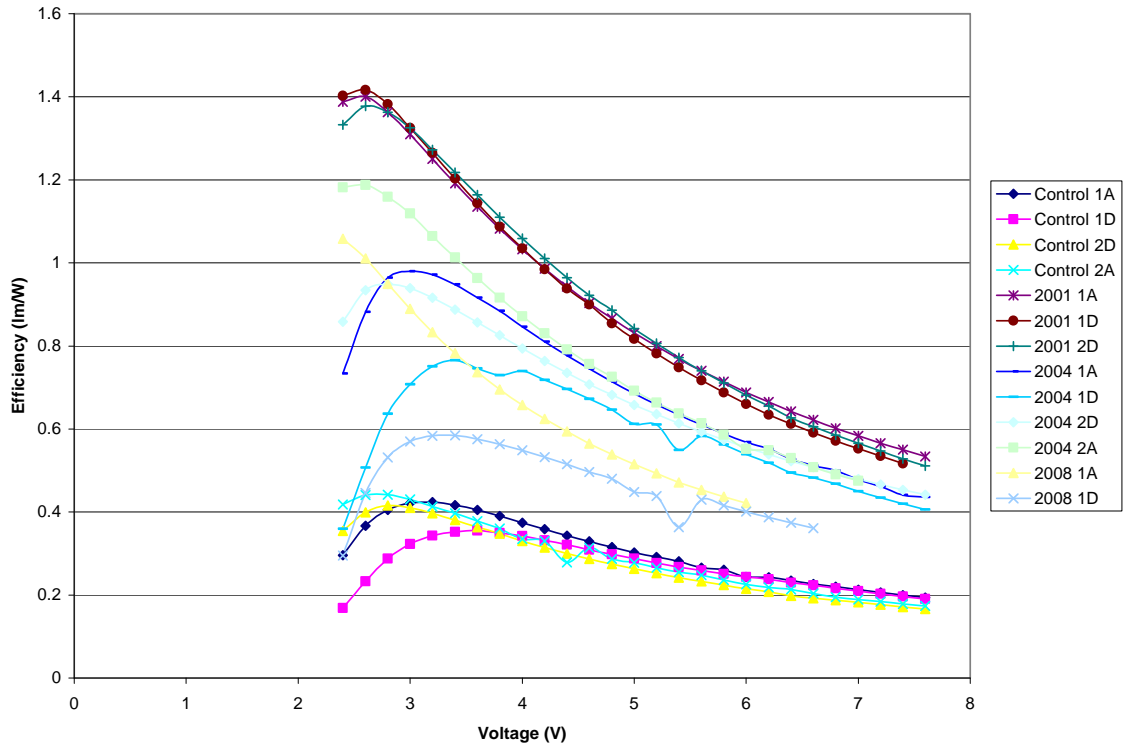


Figure 54. Efficiency vs. Voltage curves for large pixels.

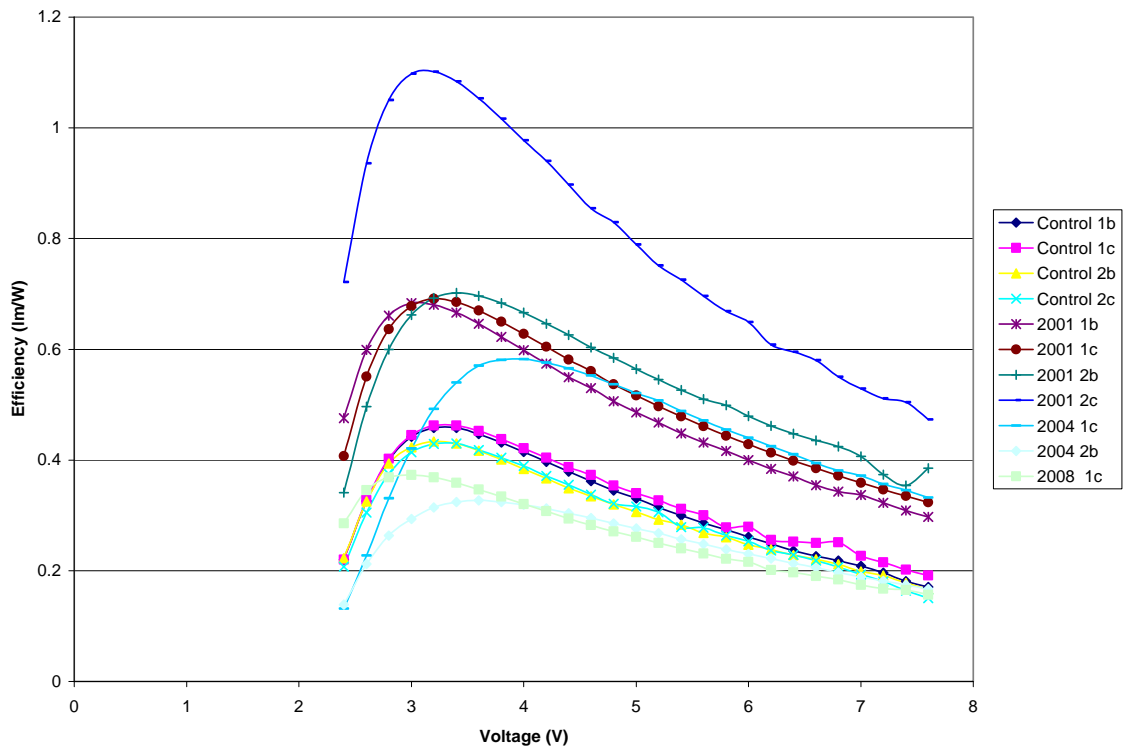


Figure 55. Efficiency vs. Voltage curves for small pixels.

Statistical Data

Table 2 presents p values for large pixels. With the exception of the 2008 large pixel efficiency, every result demonstrates statistical significance. This corroborates the findings in chart 48 and 52. The relatively large p value for the 2008 pixels, 0.36, may result from fewer data points, since only 1 substrate survived the experiment. Table 3 also expresses this effect, with much higher variance for 2008 luminance, 5756 compared to a variance of 298 for 2004 large pixels. In contrast, the standard deviation of the control, 2001 and 2004 pixels exhibits a maximum value of 75, again confirming data and trend validity.

Table 2. P values for large pixels. Note the low p values for all categories, save for 2008 efficiency. This lower value attributed to loss of data during experimentation.

P-Values for Large Pixels for Check IV data at 10 mA		
T-test Luminance Control and 2001	T-test Luminance Control and 2004	T-test Luminance Control and 2008
0.00	0.00	0.5
T-test Efficiency Control and 2001	T-test Efficiency Control and 2004	T-test Efficiency Control and 2008
0.007	0.02	0.36

Table 3. Variance and standard deviation for large pixels. Note the small standard deviation for all pixels except for the 2008 pixels.

Variance and Standard Deviation for Large Pixels at 10 mA				
	Control	2001	2004	2008
Large Pixel Luminance Standard Deviation	10.28	6.29	17.29	75.87
Large Pixel Luminance Variance	105.79	39.68	298.99	5756.67
Large Pixel Efficiency Standard Deviation	0.04	0.21	0.19	0.32
Large Pixel Efficiency Variance	0	0.04	0.03	0.10

Table 4 displays the p values for small pixels. These values represent the most favorable outcome possible considering all potential sources of variation during experimentation. Each pixel type p value is below or near the desired 0.05 threshold and expresses statistical significance, confirming experimental results. Table 5 displays small pixel standard deviation and variance for both luminance and efficiency; all small pixels exhibit low variance and standard deviation, further supporting statistical significance.

Table 4. P values for small pixels. Note the p value for every category expresses statistical significance.

P-Values for Small Pixels for Check IV data at 0.9 mA		
T-test Luminance Control and 2001	T-test Luminance Control and 2004	T-test Luminance Control and 2008
0.00	0.00	0.00
T-test Efficiency Control and 2001	T-test Efficiency Control and 2004	T-test Efficiency Control and 2008
0.00	0.04	0.09

Table 5. Standard deviation and variance for small pixels. Note the low standard deviation in both small pixel luminance and efficiency.

Standard Deviation and Variance for Small Pixels at 0.9 mA				
	Control	2001	2004	2008
Small Pixel Luminance Standard Deviation	4.98	7.93	7.24	2.37
Small Pixel Luminance Variance	24.83	62.92	52.43	5.66
Small Pixel Efficiency Standard Deviation	0.01	0.07	0.16	0.09
Small Pixel Efficiency Variance	0.00	0.00	0.02	0.00

Conclusion

In virtually every graph, the pixels made with 2001 polymer possessed the most luminance with the most efficiency. No explanation emerged for this completely unexpected result. The repeated consistency of the 2001 pixels justifies a measurable, though unknown, reason for this higher performance. Some theories as to the cause of this performance are that possibly the 7 years in the bottle allowed the polymer to condense and increase radiative decay, while allowing shorter, more efficient, paths through which current may flow. Why this might happen is unknown. Also, as noted above, there was a dense mass on the bottom of the 2001 bottle, which may have altered the true concentration of the polymer, which may increase the brightness and efficiency.

Another experiment may be performed utilizing another bottle of aged polymer with a similar dense mass on the bottom of the bottle, if such a polymer can be found in the lab. If the other aged polymer performed equally well, that would help narrow the focus on why an older polymer could produce such superior PLEDs. Additionally, the 2004 polymer also showed increased performance, higher than the 2008 polymer, though lower than the 2001 polymer. According to each of the point graphs, each aged polymer produced brighter, more efficient pixels than the control polymer. This too was unexpected. Aging polymer seems impractical, but demonstrates how much brighter and efficient PLEDs can become compared to conventional devices.

Finding improved performance with aged polymers, the project now aims to replicate the success with experimentation governing etching of previously used substrates prior to standard fabrication.

4.2 Experiment #8 Substrate Reuse: Etching ITO

Introduction

This experiment tests the effects of reusing a previously used substrate after etching a portion of the ITO layer away. This experiment used two etchants: HCL, at 2 different lengths of time, and KOH, at three different lengths of time. The experiment aimed to remove enough of the residual PEDOT, Calcium, polymer layer, and ITO to remove any impurities formed in the PLED fabrication and operation. Previous studies explored etching ITO with HCL and KOH, but not on reused substrates^{19,20}. Figure 56 describes the experimental process starting with the additional etches.

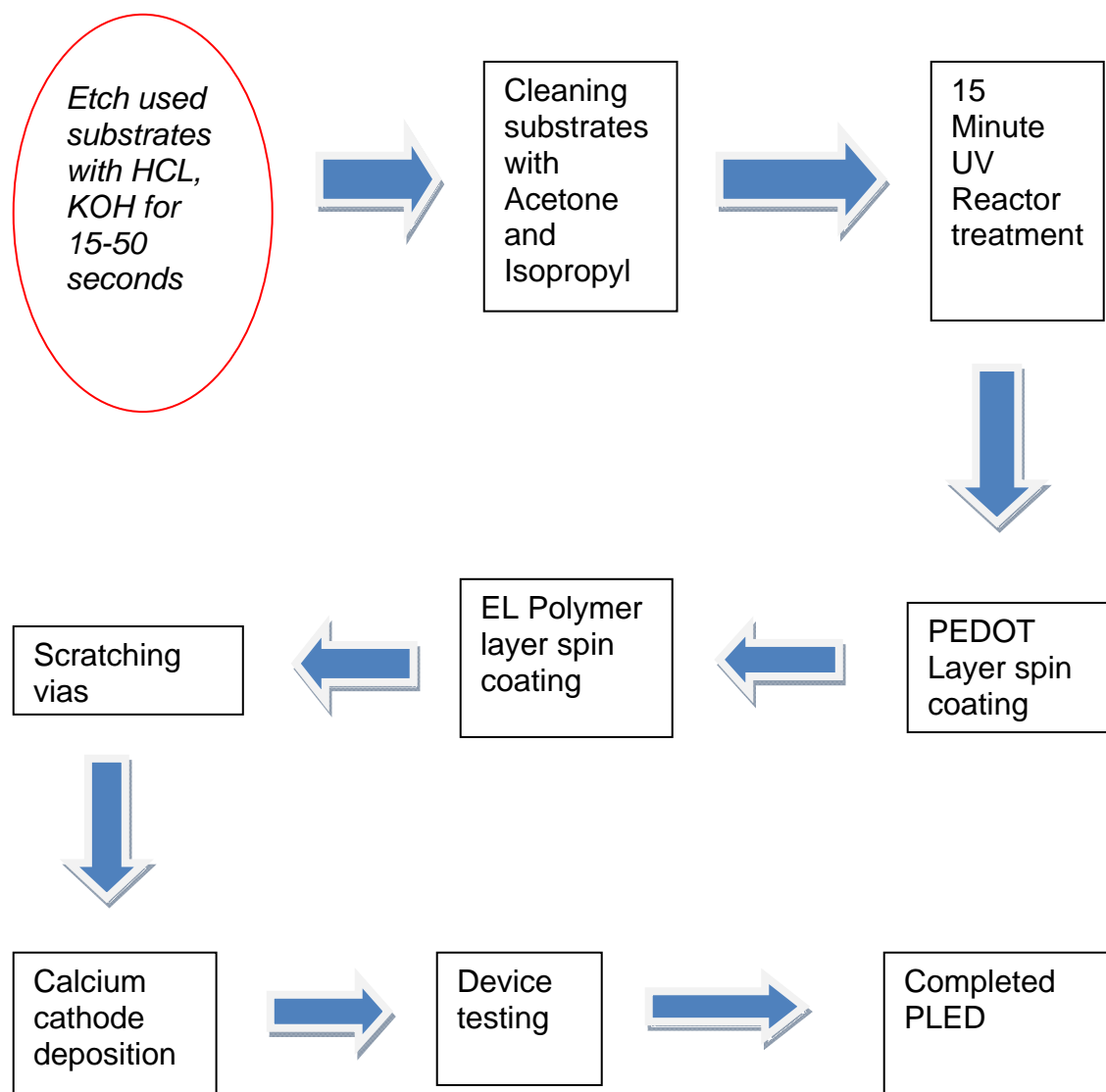


Figure 56. Experimental process including initial etch of previously used substrates.

Procedural Notes

The experimental substrates first received scrubbing in warm water to remove all device top layers down to the ITO anode. Isopropyl cleaned the substrates, followed by a de-ionized water rinse. HCL vertically etched the substrates at room temperature 9M concentration for 100 seconds and 150 seconds. Fifteen percent room temperature KOH

horizontally etched the substrates for 20, 25, and 50 seconds. Then, the experimental substrates and control substrates followed fabrication per the lab manual¹⁵.

Data and Analysis

The experimental data follows. In general, the data measured by current at 10mA and 0.9mA had less variance than data measured at 5 volts. The following graphs show groups of single data points of the experimental substrate groups at 10mA or 0.9mA. In all figures, 100 S or 150 S corresponds to a 100 second etch or 150 second etch. The data sets are presented in the order they were etched, thus KOH 25 s precedes KOH 20 s. The horizontal axes in figures 57-60 display arbitrary units that simply space data apart.

Figure 57 shows the large HCL pixels either 50 cd/m² brighter or 30-40 cd/m² less bright than the brightest large control pixels, which represents a larger than expected gap in performance. The KOH 25 second pixels did produce more luminance than the control pixels, but also too wide a variance in performance. KOH 20 s and KOH 50 s could barely match the luminance of the least bright large control pixels.

Figure 51 below shows the small pixels at a current of 0.9mA. The small HCL 100 S pixels clearly dominated all other types of pixels, reaching a maximum luminance of 221 cd/m². The HCL 150 second etch produced pixels that provided luminance almost identical to that of the control pixels. Again the KOH 25 second etch produced 2 pixels with high luminance and 2 pixels with lower luminance, resulting in a high variance. The KOH 20 and 50 S pixels again provided the lowest performance of all the pixels, barely peaking at 150 cd/m².

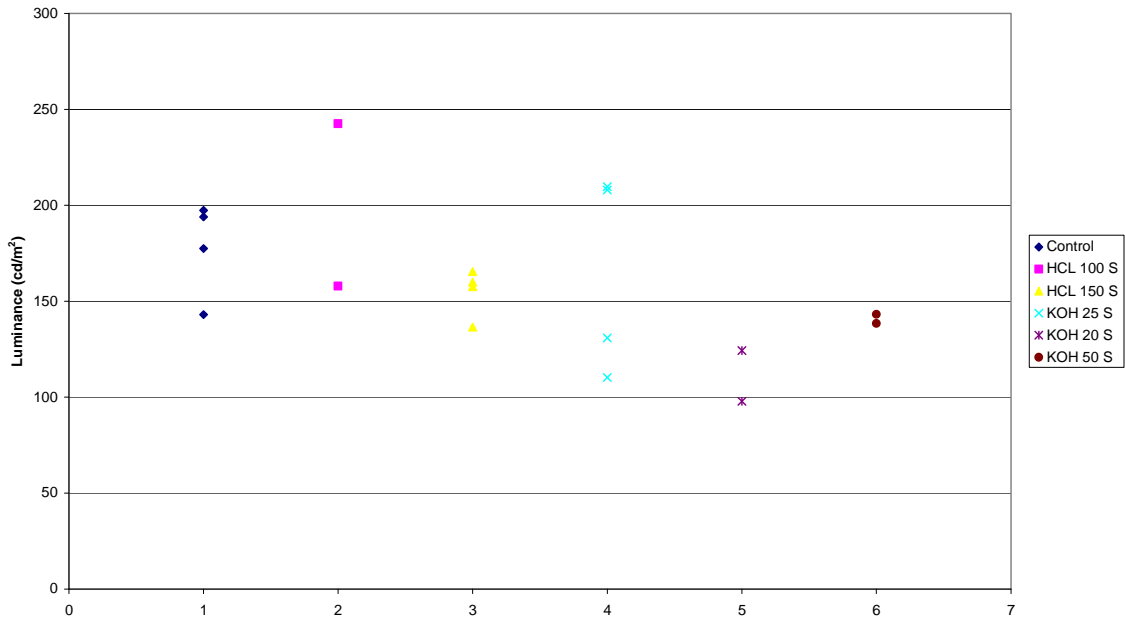


Figure 57. Luminance of large pixels at 10mA. Note the large variance of KOH25, and the high performance of HCL 100 S. Two HCL 100 S data points are missing, since those pixels did not emit any light during testing.

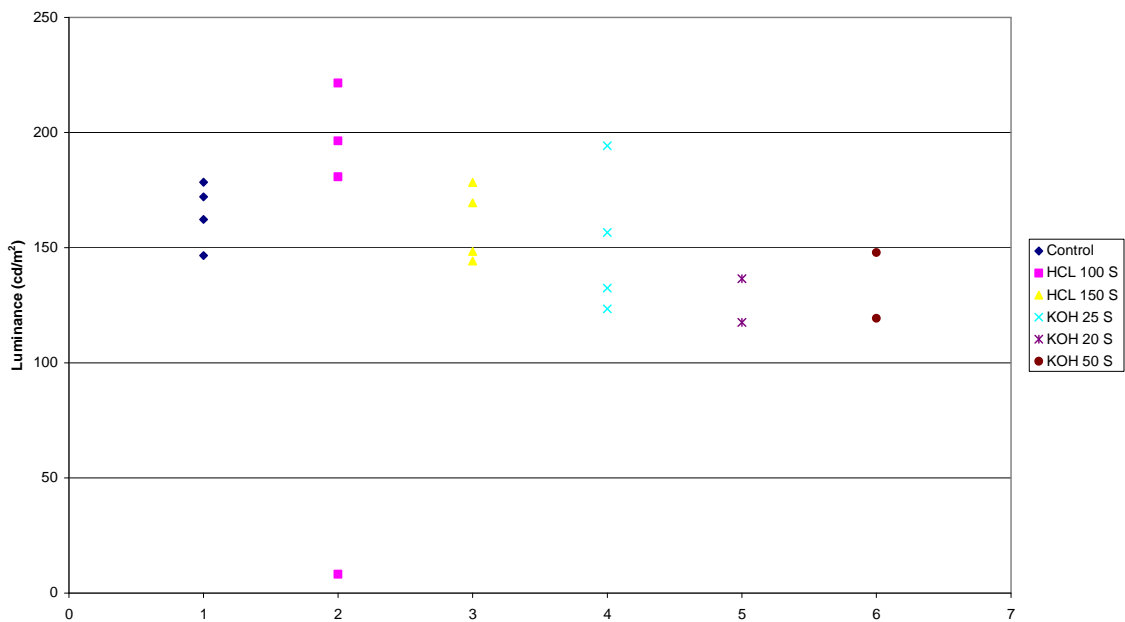


Figure 58. Luminance of small pixels at 0.9mA. Note the higher brightness of HCL 100 S pixels.

Figure 59 shows the efficiencies of the large pixels at 10mA. No large experimental pixels consistently performed as well as the large control pixels. The large pixel KOH 25 second etch did produce 2 pixels almost equaling control pixels' efficiency, but the same KOH 25 second etch produced 2 pixels less efficient than the least efficient control pixels. The KOH 20 and 50 second etches both produced pixels less efficient than the control pixels, yielding poor performance similar to the luminance characteristics. Also similar to the luminance plot of the large pixels, the HCL 100 second etch produced only two pixels; one pixel barely more efficient than the worse control pixel, the other pixel more efficient than all other pixels.

Figure 60 depicts the efficiency of small pixels at 0.9mA. Notice three control pixels produce efficiencies above 0.5 lm/W, and one pixel below 0.4 lm/W. Also of importance is the large variance of both the HCL 100 S and HCL 150 S pixels. Figure 60 shows both HCL etches capable of producing pixels with efficiencies on par with control pixels. The KOH 20 S and 50 S again produced the worst performing pixels, with efficiencies topping out at 0.39 lm/W and 0.47 lm/W. The KOH 25 second etch again produced 2 pixels with strong efficiency at about .55 lm/W, but still yield one pixel only .35 lm/W efficient.

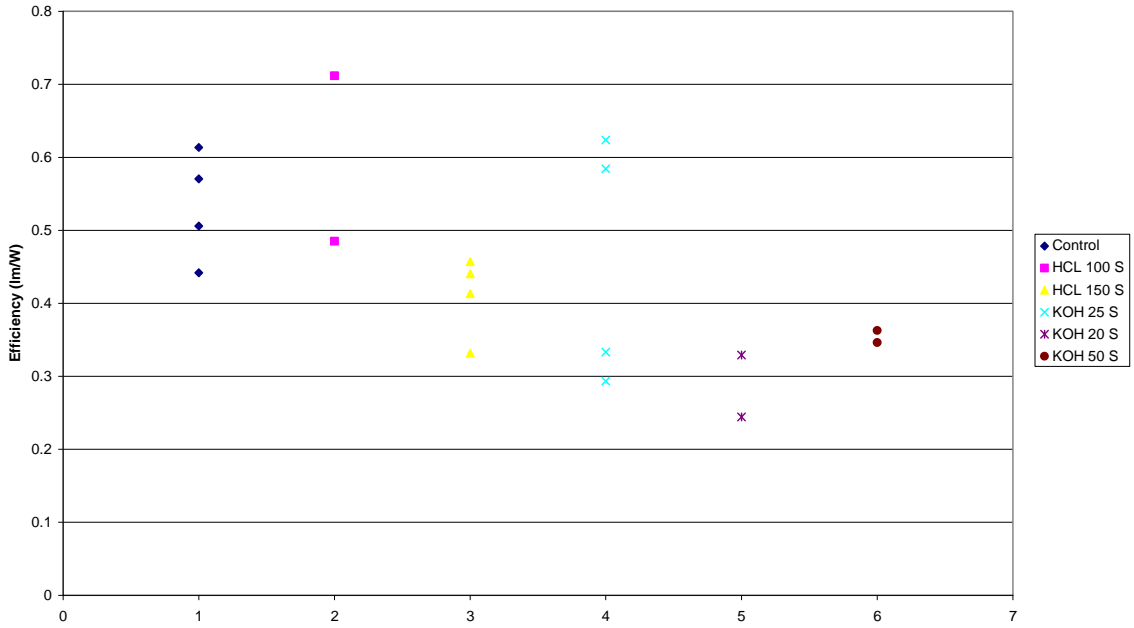


Figure 59. Efficiency of large pixels at 10mA. Note the large variance of KOH 25 S and also the low efficiencies of the KOH 20 S and KOH 50 S groups, also that HCL 100 S produced the most efficient pixel of all.

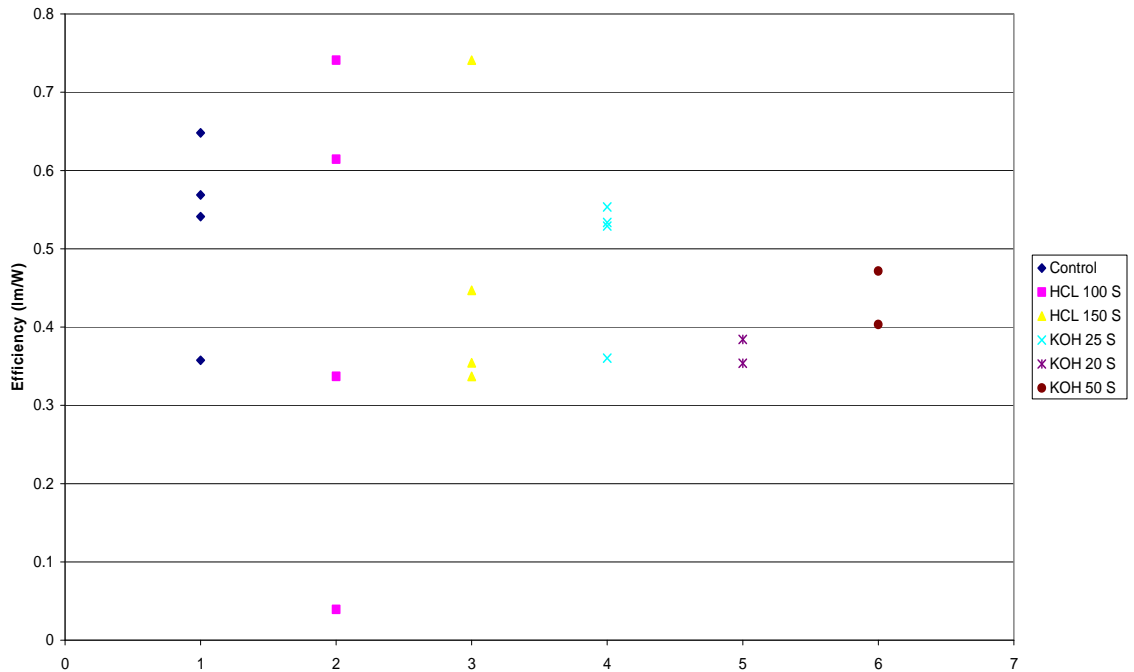


Figure 60. Efficiency of small pixels at 0.9mA. Note the large variances of both HCL 100 S and HCL 150 S, and that both HCL etches produces the most efficient pixels. The KOH 20 S pixels were again the least efficient.

Figure 61 shows the full luminance curves for the large pixels. Here, control pixels emit more light at lower voltages; but that advantage diminishes from about 6

volts, mainly due to current limiting of control pixels during testing. The HCL 100 S and 150 S curves provide the closest approximation to the control pixel luminance curves, but both HCL etches still emit 200-300 cd/m^2 less light than their control counterparts. Data acquisition errors lost the luminance curve data pertaining to the brightest HCL 100 S large pixel. All the KOH curves show these substrates emit too little light for reuse.

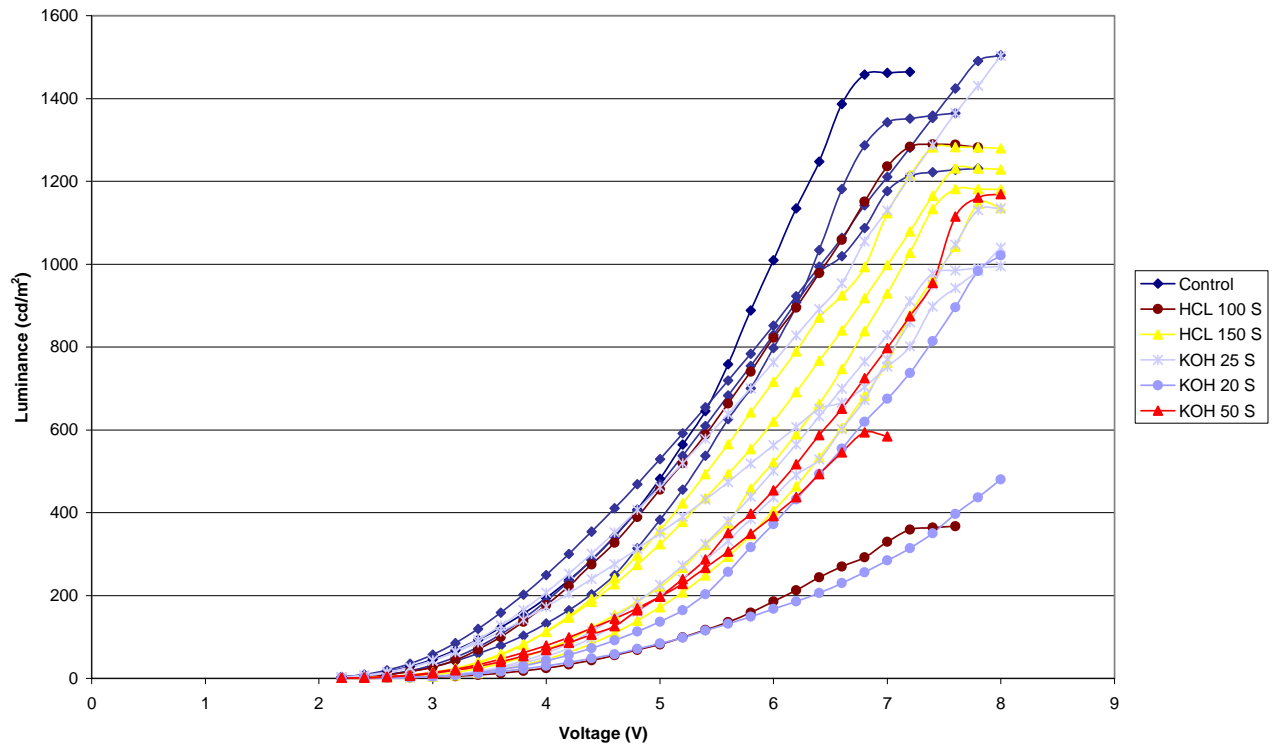


Figure 61. Full luminance curves for large pixels. Note the control pixels are brighter at lower voltages. The HCL 100 S and HCL 150 S most closely resemble the control curves. Note there is only 1 complete HCL 100 S curve shown. An HCL 100 S data curve expected to best all other curves was lost in data acquisition. Only one KOH 20 S curve even reached the least bright control curve, all other KOH etches were far less efficient than the control pixel luminance curves.

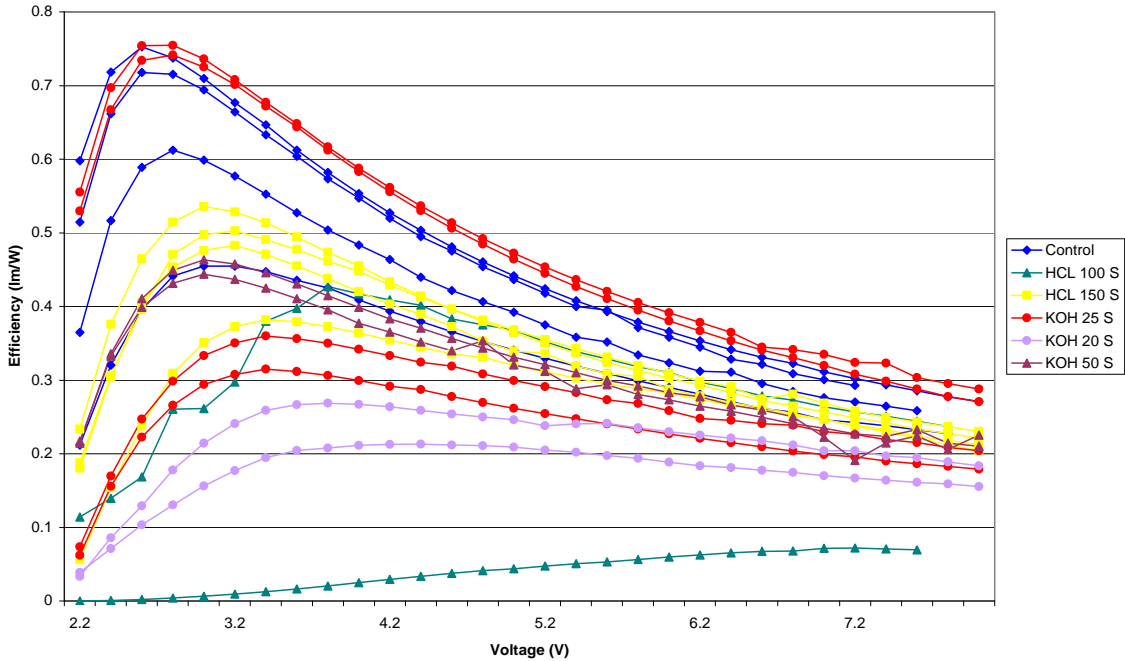


Figure 62. Full efficiency Vs. voltage curves for large pixels. Note the control pixels are more efficient than all pixels except KOH 25 S at lower voltages, and peak at higher maximum efficiencies. This figure does not display the lost data for the HCL 100 S curve.

Figure 62 depicts the full efficiency curves for the large pixels. The control pixels exhibit more efficiency at lower voltages, and peak at higher efficiencies, for all pixels except the two KOH 25 second etch pixels, which also performed well in figures 57 and 59. These two particular KOH 25 pixels, shown in red, provide more efficiency than control substrates for almost the entire gamut of voltages.

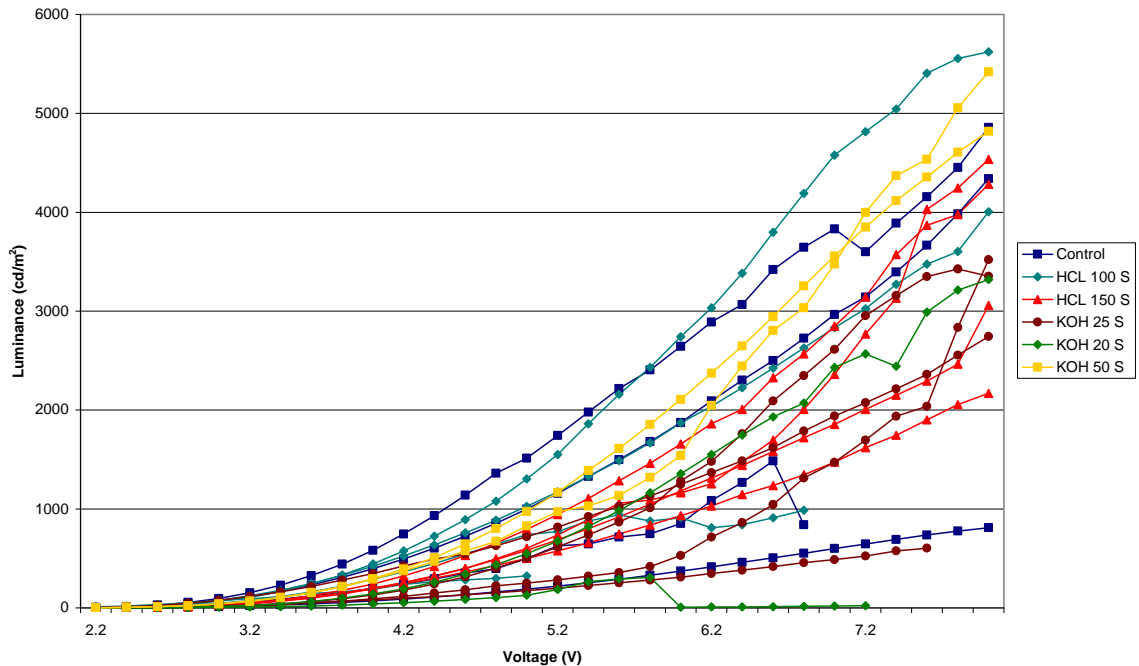


Figure 63. Luminance vs. Voltage. Full luminance curves for small pixels. Note the red HCL 150 S curve does emit more light above 7 volts. The top HCL 100 S curve in green describes the best outcome for that etch.

Figure 63 shows the full luminance curves for small pixels. The small control pixels do not dominate the small experimental pixels like the large control pixels. Surprisingly, the KOH 50 second etch performed very well. The control pixels are brightest up to 5.6 volts, which matches the results of the large pixel curves. The HCL 100 second etch curve that shines so brightly matches the bright pixels seen in figure 51. The red HCL 150 second etch had 2 pixels that shone brightly compared to control pixels, but only at very high voltages of 7 volts and beyond.

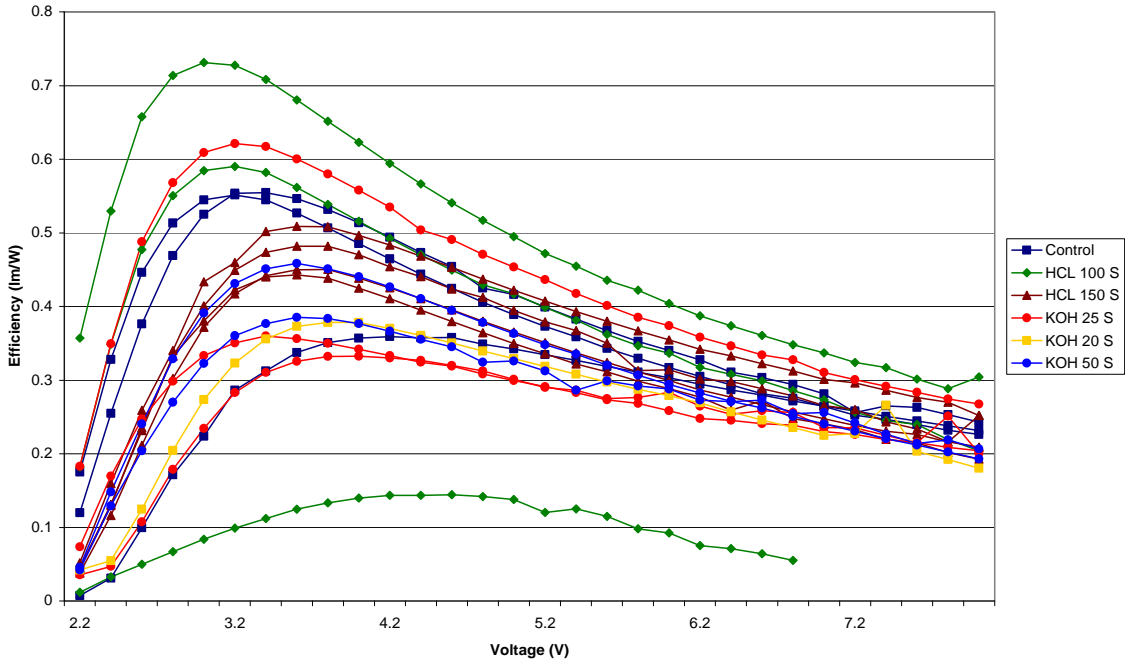


Figure 64. Full efficiency curves for small pixels. Note the high efficiencies of the HCL 100 S and KOH 25 S pixels, and the low efficiencies of the KOH 20 S and 50 S pixels. The bottom HCL 100 S pixel is not fully functional.

Figure 64 depicts the full efficiency curves of the small pixels. The most efficient curve is from the HCL 100 S etch, followed by a pixel from the KOH 25 S etch, then another HCL 100 second pixel. The control pixels appear to reach their peak efficiency at about the same 3.2 Volts, while the HCL 150 second etch pixels reach their peak efficiency at about 3.6 Volts. The comparable efficiency of the HCL pixels is again confirmed by their relative efficiencies in figure 60. The KOH 20 S and KOH 50 S pixels again represented the lowest efficiency.

Statistical Data

Table 6 shows the high p values in both luminance and efficiency for HCL 100 S and KOH 25 S. Though the KOH 25 S data are expected to produce high p values, the HCL 100 S data should have been lower than 0.66 given the strong performance of the

two functioning pixels. The KOH 20 S and 50 S pixels had very low p values, less than 0.05, for both luminance and efficiency. This gives credence to statistical significance of the low luminance and efficiency displayed by those etches.

Table 6. P values for large pixels, with check IV data at 10 mA. Note only HCL 150 S efficiency and KOH 20, 50 have p values near 0.05. With only 2 useable data points, the HCL 100 S etch had very high p values.

Large Pixel P-Values				
T test control and HCL 100 luminance	T test control and HCL 150 luminance	T test control and KOH 25 luminance	T test control and KOH 20 luminance	T test control and KOH 50 luminance
0.69	0.16	0.66	0.03	0.05
T test control and HCL100 efficiency	T test control and HCL 150 efficiency	T test control and KOH 25 efficiency	T test control and KOH 20 efficiency	T test control and KOH 50 efficiency
0.66	0.04	0.46	0.02	0.01

Table 7. Standard deviation and variance of large pixel data.

Large Pixel Standard Deviation of Luminance					
Control	HCL100s	HCL150s	KOH25	KOH20	KOH50
24.86	59.85	12.69	51.66	18.76	3.35
Large Pixel Luminance Variance					
618.29	3582.56	161.05	2669.45	352.21	11.24
Large Pixel Standard Deviation of Efficiency					
Control	HCL100s	HCL150s	KOH25	KOH20	KOH50
0.07	0.16	0.05	0.16	0.06	0.01
Large Pixel Efficiency Variance					
0.005	0.02	0.003	0.02	0.003	0.0001

Table 8 depicts the p values for the small pixels. The high p values for HCL etches predict low statistical significance for HCL luminance and efficiency, except for the HCL 100 S luminance p value of 0.07. This agrees with the small pixel HCL 100 S luminance of figure 58. The KOH 20 S etch had a low p value of 0.07 for luminance, which indicates a strong likelihood of statistical significance. This does not agree with the KOH 20 S small pixel performance in figure 58. There were only two data points for KOH 20 which may lead to inaccurate p values.

Table 8. P values for small pixels, with check IV data at 0.9 mA. Note the p value of 0.07 for the HCL 100 S etch, which confirms the bright pixel performance in figure 58. The p value of 0.67 for HCL 150 S seems unusually high, considering those pixels yielded luminance similar to the HCL 100 S pixels. Also, the KOH 20 S etch produced low p values, but with only two data points, leaving the p value suspect.

Small Pixel P-Values				
T test control and HCL 100 luminance	T test control and HCL 150 luminance	T test control and KOH 25 luminance	T test control and KOH 20 luminance	T test control and KOH 50 luminance
0.07	0.67	0.48	0.07	0.22
T test control and HCL100 efficiency	T test control and HCL 150 efficiency	T test control and KOH 25 efficiency	T test control and KOH 20 efficiency	T test control and KOH 50 efficiency
0.81	0.43	0.18	0.11	0.26

Table 9. Standard deviation and variance of small pixels.

Small Pixel Standard Deviation of Luminance					
Control	HCL100s	HCL150s	KOH25	KOH20	KOH50
13.86	20.54	16.44	31.66	13.47	20.19
Small Pixel Luminance Variance					
192.22	422.09	270.51	1002.98	181.59	407.91
Small Pixels Standard Deviation of Efficiency					
Control	HCL100s	HCL150s	KOH25	KOH20	KOH50
0.12	0.20	0.084	0.094	0.087	0.048
Small Pixel Efficiency Variance					
0.01	0.04	0.007	0.008	0.007	0.002

Conclusion

The large pixels at 10mA were not as bright as desired. With HCL pixels reaching a maximum luminance of 150-170 cd/m^2 , compared to the control pixels' 200 cd/m^2 , the pixels were tolerable, but not remarkable. Also, the fact that the KOH 25 second etch produced some pixels that were brighter than the control pixels was negated by the some of the same pixels underperforming greatly. The small pixels at 0.9mA provided results that the HCL 100 and 150 second etches could realistically produce pixels that can be reused. The HCL 100 second etch fabricated small pixels that hit a maximum brightness 70 cd/m^2 higher than the maximum control pixels' luminance. This represents a 24% luminance increase over the brightest control pixel. The HCL 150 second etch produced pixels that provided luminance equal to that of the control pixels.

In terms of efficiency, none of the large experimental substrates provided an acceptable efficiency. Each substrate measured 0.1-0.4 lm/W less efficient than the most efficient control. Two KOH 25 S highly efficient pixels failed to validate their efficiency with an associated p value of 0.466. Small experimental pixels showed much more promise in terms of efficiency than the large pixels, with the HCL 100 S, HCL 150 S, and KOH 25 S etches producing pixels near the performance of the control pixels. In some cases, the HCL etches produced pixels that were more efficient than the controls, matching the results of the luminance measurement in figure 58.

The full curves for the large pixels showed the control pixels were brighter and more efficient, with the experimental pixels either lagging far behind, or only catching up in performance at 5-7 volts. These high voltages would most likely preclude recycling used substrates for most applications. However, since the presented data lacks some full HCL 100S curves, large pixels may indeed possess the capability to produce more luminance than control pixels. The small substrates lost a smaller fraction of their brightness and efficiency, and, in some cases, exceeded the control pixels' efficiency by 0.15 lm/W. The smaller pixels also matched the control's efficiency at lower voltages, 4-4.4 Volts. Though small pixels reached their maximum efficiency about 0.4 Volts higher than control pixels, the overall efficiency curves overarched the control pixel efficiency curves, particularly the HCL 100 S pixels.

The experiment succeeded with respect to the small pixels. The HCL 100 and 150 second etches produced many pixels that could realistically replace control pixels. The surprisingly consistent failures of the large pixels particularly contrast the performance of the small pixels. Large HCL 100 S luminance showed promise, but the efficiency could limit applications. Why the small pixels met or exceeded the performance of the control pixels, yet the large pixels could not, presented an empirical unknown. Other experiments also displayed this dichotomy between large and small pixel performance.

Chapter 5 Concluding Remarks

The preceding thesis demonstrates solutions to problems keeping PLEDS from reaching their maximum efficiency and brightness. Modulating the delay between UV ozone reactor treatment and PEDOT deposition does not produce any increase in device performance, nor does heating substrates to 75° C or 125° C in the UV ozone reactor, or placing heated substrates on silicon wafers while in the UV ozone reactor. That delay after UV ozone treatment does not negatively affect PLED performance helps keep fabrication variables to a minimum, because had measurable differences between this delay and device performance been detected, keeping the interval precise would present an added challenge to all future experiments. Despite the lack of encouraging data in terms of increased brightness or efficiency, these early experiments set a precedent for future experiments: singular thrusts into experimental modifications, with slight to considerable performance improvements expected.

Cleaning previously used substrates eventually provides the impetus for the stronger and more prolific etching of previously used substrates; however, initially, the variety of cleaners altering the PLED drew a minute locus of transient responses to the different cleaning agents. Windex ® on previously used substrates yields the most promising results, since substrates treated with Windex ® eclipsed the performance of control substrates. The vast majority of cleaning agents lowered brightness or efficiency or both, compiling a list of substances not to use on PLEDs. Because Windex ®

primarily finds applications with glass, perhaps improving transmission of light, rather than simply generating more light, requires an entire thesis devoted to the topic.

Aging OC1C10 foments more questions than it answers. Continued experimentation wrought the idea for aging polymers before deposition, more out of a curiosity for characteristics and limits of the primary materials of PLED construction than expected device improvements. Even though data consistently resemble a benefit to device fabrication, at no time does any mechanism appear either in empirical data or published article to explain the heightened luminance and efficiency. Aging the polymer creates the project's only unwarranted success.

From researching various books, articles, and other published techniques, etching presents the most likely and feasible option to improve PLED performance with the greatest accuracy and minimal resources^{19,20,14}. That etching which grants the increases in performance generates no surprise, though some of the longer etches were expected to degrade device performance more that actually occurs. Previously published works describing etches longer than 20 seconds state blatant PLED deterioration results from such an "extended" etch, but our 50 second KOH etch results in pixels that simply lack improvements to the extent others did, rather than emit far less light or operate grossly inefficiently. Though other researchers did use substrates with lower resistances at 10 Ohms, the correlation between substrate resistance and greater etching "endurance", if any, is unclear¹⁷. Nonetheless, etching previously used substrates creates increases in luminance and efficiency precisely matching goals set at the project's outset.

One of the main research goals consists of exploring PLED possibilities; this leads to a broad range of topics covered over the course of several experiments. The

results of each experiment merely suggest potential learning from that particular experimental configuration. Slight variations of each experiment may yield more certainties in terms of result confirmation, and experimental “tuning.”

Choosing to move forward, despite discovering a technique or property that ostensibly showed genuine promise for PLED improvement, allowed the discovery of more possible improvement methods. From the outset, the thesis project design shunned experimental regressions in favor of maximum research exposure. Many discrete exploratory experiments built the framework upon which multiple future theses and senior projects could begin.

Future Experiments For Other Students

Trying any of the previous experiments with a new polymer presents the most obvious suggestion for future experiments. Annealing experiments appear the most likely candidates to export to another polymer. With a new polymer, the effect and degree of change in performance become even more important with a previous set of data for comparison.

The annealing experiments with materials underneath substrates in the UV reactor could vary the materials. Numerous experiments tuning the temperature for the most promising materials could yield device improvements greater than those described in chapter 2. Any additional experiments would reveal if the silicon wafer or altered manufacturing caused the luminance in the 60-70 cd/m² range.

Additional re-use experiments could try new types of cleaners, possibly focusing on surfactants, oxidizers, or enzymes. Since Windex ® provides some data with improved performance, using industrial strength ammonia, alone or mixed with other agents, could also provide new leads. Experiments with new household substances like lime juice could also present many avenues for material characterization. None of the tested substances improved performance, but a significant improvement from a common substance could provide large gains for little cost.

Cleaning agent sequence provides another promising experimental variable. When proceeding with agents such as the homemade Windex ®, the ingredient order could present clues to subtle enhancement mechanisms; these characteristics may remain hidden until certain sequences of cleaning agents or actions uncover them.

Experiments testing polymers from 2002, 2003, or 2005-2010 could verify if the increased performance yields a linear relationship with age. Since OC1C10 showed improvement after aging 1 week, this experiment could yield useful data for another polymer if performed over the course of several months to a year.

Lastly, a variety of etching experiments with different etchants and time intervals could also yield useful data, both for OC1C10 or other polymers. Temperature, concentration, and etching angle may add complexity to the design of experiment.

References

1. HJ Round; Note on Carborundum *Electron. World* 19:309-310, 1907.
2. A Bernanose, M Comte, and P Vouaux, A new method of emission of light by certain organic compounds, *J. Chim. Phys.*, 50:64-68, 1953
3. N Holonyak Jr. and SF Bevacqua, Coherent (visible) light emission from Ga(As_{1-x}P_x) junctions, *Appl. Phys. Lett.*, 1:82-83, 1962.
4. M Pope, H Kallman, and P Magnante, Electroluminescence in organic crystals, *J. Chem. Phys.*, 38:2042-2043, 1963.
5. RH Partridge, Radiation Sources, U.S. Patent 3,995,299, 1976.
6. CW Tang and SD VanSlyke, Organic electroluminescent diodes, *Appl. Phys. Lett.*, 51:913-915, 1987.
7. H Shirakawa, AG Macdiarmid, AJ Heeger, et al., *Chem. Commun.*, 16:578-580, 1977.
8. BR Weinberger, SC Gau, A polyethylene:aluminum photodiode, *Appl. Phys. Lett.*, 38:555-557, 1981.
9. H Tomozawa, D Braun, SD Phillips, AJ Heeger, and H Kroemer, Metal-polymer Schottky barriers in cast films of soluble poly(3-alkylthiopenes), *Synth Met.*, 22:63-69, 1987.
10. JH Burroughes, RH Friend, et al., Light-emitting diodes based conjugated polymers, *Nature*, 347:539-541, 1990.
11. D Braun, AJ Heeger, Visible Light emission from semiconducting polymer diodes, *Applied Physics Letters*, 58:1982-1984, 1991.
12. Z Li, et al. *Organic Light-emitting Materials and Devices*. CRC Press, Boca Raton, p.4, 2007.
13. Z Li, et al. *Organic Light-emitting Materials and Devices*. CRC Press, Boca Raton, p 474, 2007.
14. U Scherf, et al. *Organic Light-Emitting Devices*. Wiley, New York, p 170, 2006.
15. D Braun, <http://courseware.ee.calpoly.edu/~dbraun/courses/courseinfo/PolymerLab/Manual/index.html> Date Accessed 6.2.08.
16. M Cecchi. "Experimental design and analysis of polymer based light emitting diodes using statistical methods." MS Thesis California Polytechnic State University,

San Luis Obispo, 2001.

17. Z Li, et al. *Organic Light-emitting Materials and Devices*. CRC Press, Boca Raton, 2007. 494.
18. T.P. Nguyen, et al. *Synthetic Metals* 138 (2003) 113-117.
19. C.J. Huang, Y.K. Su, S.L.Wu, *Materials Chemistry and Physics*. 2004, 84, 146-150.
20. G Liu, J Kerr, S Johnson, *Synthetic Metals*. 2004, 144, 1-6.