SOLUTION PROCESSED ORGANIC LIGHT EMITTING DIODES

by

Kaustav Nag

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science, Electrical and Computer Engineering
University of Toronto

© Copyright by Kaustav Nag 2014
Solution Processed Organic Light Emitting Diode

Kaustav Nag
Master of Applied Science
Electrical and Computer Engineering
University of Toronto
2014

Abstract

Solution processed approaches provide numerous advantages for producing low cost, large area displays. This Master’s thesis investigates the suitability of solution processed ITO anodes for the fabrication of organic light emitting diodes. To that end this work has demonstrated that solution processed ITO films fabricated by spin casting, when subjected to rapid thermal annealing with temperatures up to 450°C can exhibit significantly improved conductivity. Furthermore when inkjet printed silver mesh was incorporated between two layers of ITO, the sheet resistance of the overall structure exhibits comparable performance to commercially available ITO. The effects of rapid thermal annealing on the organic semiconducting materials PEDOT:PSS and MEH:PPV layers are also investigated and shown to improve the performance and efficiency of the devices. Finally OLED devices were fabricated on ITO/Ag mesh/ITO stack and the device performance is comparable to devices fabricated on commercially available ITO.
Acknowledgments

The past two years in University of Toronto has been an immensely enjoyable experience. I would first like to thank Prof. Amr Helmy and Prof. Mohini Sain for providing me the opportunity to work in this interesting cross disciplinary project. The constant encouragement and helpful feedbacks provided by them have been of great help in solving all problems I have encountered.

I would like to thank Steven Rutledge for helping me out in overcoming challenges and clarifying my not so intelligent questions. I would like to express my gratitude to the numerous other members of my research group including Rajiv, Janahan, Yiwen, Charles, Herman, Nima and Dongpeng for being so helpful and going out of their way to help me solve my often encountered problems.

I would also like to thank Gagan, Peter, and Jaya Prakash for the immensely enjoyable coffee breaks which helped me unwind and get a fresh perspective.

Finally I would like to thank my parents, relatives and friends back home in India for constantly supporting me from the other side of the planet.
Table of Contents

Acknowledgments ........................................................................................................ iii
List of Tables .................................................................................................................. vii
List of Figures ................................................................................................................ viii
List of Acronyms .......................................................................................................... xiii

1 Introduction ................................................................................................................ 1
  1.1 Advantages of OLED .......................................................................................... 2
  1.2 Challenges in OLED ......................................................................................... 3
  1.3 Problem Statement ............................................................................................. 5
  1.4 Aim of the Project ............................................................................................... 6

2 Background ................................................................................................................. 8
  2.1 Structure of OLED ............................................................................................. 8
  2.2 Light Emitting Mechanism ............................................................................... 10
    2.2.1 Fluorescence .............................................................................................. 12
  2.3 Carrier Transport ............................................................................................... 13
  2.4 Inkjet Printing ................................................................................................... 14
  2.5 Solution Processed OLED ................................................................................ 18
  2.6 Incorporation of Metal Nanoparticles ............................................................... 19
  2.7 Flexible Substrates ............................................................................................. 20

3 Experimental Methodology ....................................................................................... 21
  3.1 Material Selection .............................................................................................. 21
  3.2 Preparation of Silver and ITO nanosuspension ................................................. 23
  3.3 Anodes fabricated using Spin Coating ............................................................... 24
  3.4 Inkjet Printing ................................................................................................... 25
  3.5 Fabrication of ITO/MEH-PPV/Al Devices ......................................................... 25
List of Tables

Table 5-1: Product specification of XEROX XCM-NS32 Silver nanoparticle ink...........57

Table 5-2: Conductivity measurement of inkjet printed lines of Xerox ink subsequent to heating at 175°C on a hot plate and at 200°C and 500°C of rapid thermal annealing...58

Table 6-1: Parameter values obtained from curve fitting of MEH-PPV based devices...68

Table 6-2: Parameter values extracted from curve fitting of PEDOT:PSS/MEH:PPV based devices.................................................................75

Table 6-3: Extracted parameter values of devices subjected to RTA after MEH:PPV spin coating........................................................................................................77

Table 7-1: Parameter values obtained from curve fitting J-V Characteristics.........84

Table 7-2: Sheet resistance and thicknesses of spin coated ITO anodes...............86

Table 7-3: Parameter values obtained from curve fitting J-V Characteristics.........88

Table 7-4: Parameter values obtained from curve fitting J-V Characteristics........90
List of Figures

Figure 1-1: A simple OLED structure (C- cathode, EL- Emissive organic layer, A: Anode)………………………………………………………………………………………………3

Figure 2-1: Structure of different OLEDs. Where C = cathode; EL = emitting layer; HTL = hole transport layer; HIL = hole injection layer; A= anode. ..............................9

Figure 2-2: Light emitting mechanism from an OLED device.........................................11

Figure 2-3: Possible physical process following absorption of a photon by a molecule. Taken from [4].................................12

Figure 2-4: Fujifilm Dimatix 2831 Printer. .................................................................15

Figure 2-5: Schematic of Inkjet printing......................................................................16

Figure 2-6: Schematic representations of common line morphologies. (a) individual drops, (b) scalloped, (c) uniform, (d) bulging, and (e) stacked coins. Drop spacing decreases from left to right. Taken from [45]. ......................................................17

Figure 3-1: Chemical structure of PEDOT (left) and PSS (right) .................................22

Figure 3-2: Chemical Structure of MEH-PPV.............................................................23

Figure 3-3: Intensity obtained on a spectrometer as a function of frequency..............29

Figure 3-4: Power observed in powermeter against the area under the curve obtained from spectrometer.........................................................30

Figure 3-5: Power observed in powermeter against the peak intensity of the curve at 585 nm obtained from spectrometer.........................................................31

Figure 3-6: Power observed in powermeter against the area under the curve obtained from spectrometer along with the error range.................................32
Figure 3-7: CIE (International Commission on Illumination) visual luminous efficiency distribution for phototopic vision. The function is normalized to unity at 555 nm. Taken from [68].

Figure 4-1: Sheet resistance and relative standard deviations as a function of Spin rate.

Figure 4-2: Effect of RTA on sheet resistance of single spin coated ITO films.

Figure 4-3: Effect of RTA on sheet resistance of twice spin coated films.

Figure 4-4: Effect of two step RTA on sheet resistance of ITO films.

Figure 4-5: Effect of RTA and conventional annealing on sheet resistance of ITO films.

Figure 4-6: SEM images of ITO coated films.

Figure 4-7: Optical transmission as a function of wavelength.

Figure 4-8: Average Sheet Resistance as a function of anneal time when heated at 160°C.

Figure 4-9: Average Sheet resistance as a function of spin rate at two different silver concentrations.

Figure 4-10: Average sheet resistance as a function of spin rate at 3 different annealing temperatures. Inset shows sheet resistance at 150°C.

Figure 4-11: Sheet resistance as a function of anneal temperature at two different concentrations of Silver for 15 minutes.

Figure 4-12: Sheet resistance as a function of anneal temperature at two different concentrations of Silver for 30 minutes.

Figure 4-13: SEM image of 8% spin coated Ag on silica substrate.
Figure 4-14: Sheet resistance of ITO/Ag stack and only ITO on silica. Spin rate of Ag kept constant at 1000 rpm.

Figure 4-15: SEM images of ITO/Ag stack on Silica

Figure 4-16: Sheet Resistance of ITO/Ag/ITO stack on silica substrate.

Figure 4-17: SEM of ITO/Ag/ITO stack structure on silica.

Figure 5-1: Optical image of printed line at 10 micron drop spacing at temperatures of 30, 45 and 60˚C respectively.

Figure 5-2: Variation of drop pitch 5, 10, 25, 50, 65 microns at constant substrate temperature of 60˚C.

Figure 5-3: Silver lines deposited on the edges of the line after being heated at 500˚C.

Figure 5-4: Profilometer measurement of cross section of inkjet printed silver lines demonstrating coffee drop effect.

Figure 5-5: Lines printed with Xerox ink of 1 layer and 5 layers after heating at 175˚C for 15 minutes respectively.

Figure 5-6: Profilometer reading of line cross section of Xerox ink.

Figure 5-7: PEDOT:PSS grid with 250 micron grid size.

Figure 5-8: Sheet resistance and relative standard deviation of PEDOT:PSS/Ag Grid/PEDOT:PSS as a function of grid size.

Figure 5-9: Sheet resistance and relative standard deviation as a function of Ag grid separation.

Figure 5-10: ITO/Ag/ITO grid with 250 micron spacing.

Figure 5-11: Sheet resistance as a function of annealing temperature for ITO/Ag Grid/ITO stack.
Figure 5-12: Optical transmission of Ag grid and ITO/Ag grid/ITO structure

Figure 6-1: Energy Diagram of ITO/MEH:PPV/Al devices

Figure 6-2: Current density Voltage characteristics of ITO/MEH-PPV/Al devices with varying MEH-PPV thicknesses

Figure 6-3: Curve fitting of MEH-PPV based diodes

Figure 6-4: Optical power as a function of applied bias. Arbitrary unit corresponds to counts of CCD detector

Figure 6-5: Optical power as a function of current density. Arbitrary unit corresponds to counts of CCD detector

Figure 6-6: Current density Voltage characteristics of devices subjected to RTA

Figure 6-7: Optical power - Voltage characteristics of devices subjected to RTA. Arbitrary unit corresponds to counts of CCD detector

Figure 6-8: Optical power as a function of Current density of devices subjected to RTA. Arbitrary unit corresponds to counts of CCD detector

Figure 6-9: Energy diagram of ITO/PEDOT:PSS/MEH:PPV/Al Devices

Figure 6-10: Post MEH:PPV Rapid Thermal Annealing of PEDOT:PSS/MEH-PPV based devices

Figure 6-11: Pre MEH-PPV current density voltage characteristics of devices subjected to RTA before MEH:PPV spin coating

Figure 6-12: Optical power-voltage characteristics of devices subjected to RTA after MEH:PPV spin coating. Arbitrary unit corresponds to counts of CCD detector

Figure 6-13: Optical power as a function of current density for devices subjected to RTA after MEH:PPV spin coating. Arbitrary unit corresponds to counts of CCD detector
Figure 7-1: Current Density Voltage characteristics of the devices with different anode structures. .................................................................83

Figure 7-2: Light emission as a function of voltage applied........................................85

Figure 7-3: Current density as a function of applied voltage for ITO with different thicknesses...........................................................................87

Figure 7-4: Optical power as a function of Voltage for different ITO thicknesses. Arbitrary unit corresponds to counts of CCD detector .........................89

Figure 7-5: Current density as a function of applied bias............................................90

Figure 7-6: Optical power as a function of applied bias. Arbitrary unit corresponds to counts of CCD detector ..............................................................................91

Figure 7-7: Optical power as a function of current density. Arbitrary unit corresponds to counts of CCD detector.................................................................92

Figure 8-1: Comparison of sheet resistances of different solution processed anodes...97

Figure 8-2: Comparison of Optical power vs voltage for different fabricated devices. Arbitrary unit corresponds to counts of CCD detector.................................99

Figure 8-3: Comparison of Optical power verses current density for different fabricated devices. Arbitrary unit corresponds to counts of CCD detector..........................100
List of Acronyms

LCD – Liquid Crystal Display

OLED - Organic Light Emitting Diode

PLED – Polymer Light Emitting Diode

Alq3 - Tris(8-hydroxyquino-line) Aluminum

PPV - Poly(p-phenylene vinylene)

PET - Polyethylene Terephthalate

BC - Bacterial Cellulose

PES - Polyethersulfone

ITO - Indium Tin Oxide

LUMO - lowest Unoccupied Molecular Orbital

HOMO - Highest Occupied Molecular Orbital

Ev – Electron Volt

HIL - Hole Injection Layer

HTL - Hole transport Layer

EL - Emissive layer:

ETL - Electron transport Layer

Φw - Work Function

RTA - Rapid Thermal Annealing

PEDOT:PSS - Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate
MEH-PPV - Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]

IJP - Inkjet Printing

RPM - Revolutions per Minute

Ag - Silver

J-V - Current density – Voltage

SEM - Scanning Electron Microscopy
1 Introduction

Electronic appliances are all pervasive in modern civilization. The technological advancements in fabrication of electronic devices be it sensors, integrated circuits, displays or lighting systems have improved leaps and bounds in the past several decades. These devices have not only become fundamental to industrial and scientific communities, it has touched all aspect of our daily lives. Notably display devices, of all kinds, are of paramount importance since they act as vehicle for information exchange. The conventional cathode ray tube which was ubiquitous in late nineties have given way to more efficient display technologies such as liquid crystal displays (LCD), plasma display panels and light emitting diodes.

Organic light emitting diodes (OLED) have garnered tremendous interest from various research groups across the world due to its promising nature in the field of display technology and lighting applications on account of its ease of fabrication, low power consumption, wide viewing angles and excellent contrast [1-4]. Organic electro luminance was first demonstrated by Pope and coworkers in 1963 using a single crystal of Anthracene [5]. However there were few improvements in these devices owing to difficulty in fabrication processes and high operating voltage. The breakthrough finally arrived in 1987 when double layered organic diodes was reported by Tang and Skylark based on tris(8-hydroxyquino- line) Aluminum (Alq3) deposited by thermal vacuum evaporation [6]. Soon after, Friend and coworkers developed polymer LEDS (PLEDs) based on poly(p-phenylene vinylene) (PPV) in 1990 [7]. These two seminal papers reinvigorated research and development of OLEDs which is continuing to this day. As a result there have been spectacular developments resulting in devices that can operate at brightness of 500cd/m² for over 200,000 hours [8]. Traditionally OLEDs are developed on glass substrates. By replacing glass with flexible substrates like
polyethylene terephthalate (PET), bacterial cellulose (BC), Polyethersulfone (PES) among others, results in OLEDs which are both flexible and lightweight [9-13]. The application of these flexible materials will facilitate the roll to roll manufacturing of printed electronics thereby reducing costs [14-15].

Organic Light Emitting Diodes (OLED) are widely regarded as the next display technology overshadowing LCD technology with hopes of achieving 40% market share of the mobile display market having an annual market value of 10 billion dollars by 2015, according to research firm Display Search. Research into the reduction of materials or manufacturing costs, as well as the development of novel platforms for display applications, is therefore an area attracting well-deserved interest. Recently launched products such as curved display televisions, from Samsung and LG, demonstrates the promising potential of OLEDs. The potential future size of the flexible OLED market could grow as fast as 151% to exceed $20 billion in 2020 [16].

1.1 Advantages of OLED

Although LCD and LED are currently dominating display markets, OLEDs offer a wide range of advantages over both these technologies. Unlike LCDs which require back lighting, OLEDs are electro luminescent i.e. they are able to generate light on its own. LCDs work by having a backlight which continuously generates white light which is selectively blocked to display an image on screen. So even when displayed images are completely black, the backlighting will still be consuming power and generating light. This is the reason why LCD display systems cannot produce true black. However since OLEDs can generate light themselves, they are capable of producing true black. Power consumption is also an area where OLEDs are much better than LCDs. Since OLEDs do not require backlighting they consume much less power compared to traditional LCD devices. The lower consumption of power will be especially beneficial for battery operated devices such as cell phones.
OLEDs comprise of organic layers stacked between two metal contacts. Since the organic layers are very thin, on the order of nanometers, the resultant OLED displays are also much thinner and lighter compared to LCDs. The substrate of an OLED can be flexible instead of being rigid. This has the potential to completely revolutionize display and lighting systems and usher in an era of flexible displays. Additionally OLEDs are compatible with roll to roll manufacturing. The roll to roll manufacturing process offers high throughput and significant reduction in cost. This will make OLEDs competitive with other display technologies.

1.2 Challenges in OLED

Although OLEDs have a lot of advantages compared to other display technologies such as LCD, plasma display, they are plagued by inherent technological challenges which impede their commercialization process.

1.2.1 Manufacturing:

OLEDs essentially comprise of organic media stacked between an anode and a cathode. These organic materials which are responsible for their electroluminance properties are quite susceptible to environmental conditions. As a result the preferred deposition techniques are vacuum based which increase production costs. The increased production cost is a major deterrent for commercialization of OLEDS. Also vacuum based thermal evaporation requires
shadow masks to pattern the OLEDs. This in turn causes excessive material wastage and leads to additional concerns of getting rid of the waste. A change in device pattern will require new masks which have to be fabricated and thereby increase costs. Finally scalability is as issue regarding the vacuum based deposition techniques since the display size is now limited to the size of the vacuum chamber. Ongoing research has focused on using wet processing techniques with additive patterning, such as inkjet printing, to reduce material wastage for fabrication of low cost display systems. Complex patterns can be printed with ease and no shadow masks are required. Solution processed OLEDs eliminate the need for vacuum based technologies which is a current bottleneck in fabrication of OLEDs.

1.2.2 Materials:

The organic layers used in the fabrication of OLEDs are very much sensitive to atmospheric condition primarily oxygen and moisture. The oxidation of these organic layers in time results in device degradation and failure. Hence the devices need to be packaged properly so as to avoid oxygen and water penetration. Transparent conducting anodes are also a limiting factor in the development of OLEDs. The most popular transparent conductive oxides used by manufacturers are indium tin oxide (ITO). Although it has very high optical transmission and excellent electrical properties, Indium is one of the rare elements and hence expensive. There has been lot of research focused on finding suitable alternatives to ITO. Solution processed ITO [17-19], conductive polymers [20-22], carbon nanotubes [23-25] and graphene [26-28] are all suitable candidates, but they are still years away from being manufactured in commercial scale.

1.2.3 Limited lifetime of blue emitters:

The three primary pigments for displaying colors are red, blue, and green. Although red and green emitting polymers have been synthesized having very high life times and efficiencies, the life time of blue emitting polymers have been
an area of concern [29]. Since OLEDs emit light by recombination of excitons, the wavelength of emitted light depends on the energy difference of excitons. Since a blue emitting polymer will require the energy difference between the excitons to be higher compared to red and green emitters, this inherent problem causes limited shelf life of the blue emitting polymers.

1.2.4 Flexible anodes:

OLEDs based on flexible substrates require flexible anodes. Since flexible substrates such as PET, PES and cellulose nanocomposite [9-13, 30] do not have high thermal stability, anodes such as ITO which are deposited using sputtering at high temperature, are not suitable. On the other hand solution processed anodes suffer from high sheet resistance (of the order of hundreds of Ohms/square compared to sputtered ITO which show sheet resistance of 4-8 Ohms/square) severely degrades device performances. Additionally ITO is quite rigid, and when flexed, it cracks resulting in pinhole formation which exhibit local field effects thereby causing device degradation. Polymeric anodes utilizing PEDOT: PSS although flexible, exhibit high sheet resistance.

1.3 Problem Statement

The inability of solution processed anodes to have low sheet resistance is a major bottleneck for fabrication of completely solution processed OLEDs. Solution processed ITO demonstrate very high sheet resistance which results in poor current injection and hence poor device performances. Once this drawback is alleviated, commercialization of completely solution processes OLEDs can be realized. Hence, there exists a void in development of OLED devices which are completely solution processed starting from fabrication of anodes to the organic layers. If such a technique can be demonstrated it will help reduce device cost by virtue of simplifying manufacturing processes since the organic layers and anodes can be deposited using the same equipments. Although such devices will not have very high current and luminous efficiencies as demonstrated by state of the art OLEDs, they can be utilized in low cost display applications which are less demanding performance wise. Completely solution processed devices can usher in
really low cost displays given they are compatible with roll to roll manufacturing. This will help drive down prices and make OLED devices economically viable in the commercial space, dominated by LCDs at this point of time.

1.4 Aim of the Project

The ultimate aim of this project is to develop an OLED using a solution processed mechanism compatible with flexible substrates which have a low temperature threshold. To achieve the goal, we first concentrate our efforts on developing a transparent conducting anode using ITO nano suspension. We investigate the effect of conventional as well as rapid thermal annealing on its sheet resistance. A silver film developed from silver nanoparticle suspension is incorporated between two ITO layers to further lower its sheet resistance. Since a continuous silver film is opaque and blocks light emanating from the organic media, inkjet printing which is an additive patterning technique compatible with roll to roll manufacturing is employed to get around this problem. Using an inkjet printer, a silver grid is printed instead of a continuous layer. Once the anodes are optimized, the organic media comprising of PEDOT:PSS as hole injecting layer and MEH:PPV as the emitting layer is spin coated on top of it. The performance of these devices will be compared with a reference device which is based on commercially available ITO coated glass and identical organic stack. The thicknesses of individual layers are optimized and then the effect of rapid thermal annealing on the emitting layer MEH:PPV is investigated. Rapid thermal annealing is similar to conventional annealing processes except for the fact that the ramp rate is very high (25°C per second) and the samples are heated for a very small duration. Although many research groups have investigated the ITO/PEDOT:PSS/MEH:PPV/Al structure in the past, they used commercially available ITO coated glass as the starting material [33]. These substrates have ITO deposited on them using sputtering which provides very good characteristics required for a transparent conducting anode. We focus our attention on wet processing techniques which can be used for deposition of anodes as well as organic layers to streamline manufacturing processes. As no vacuum based deposition is used in our case, our devices will not match the performances of state of the art OLEDs but they are more suitable for low cost displays which do not have high
performance criteria. In these experiments, a concerted effort is made to maintain temperatures below 200°C for all the fabrication processes to keep the manufacturing techniques compatible with flexible substrates. However in certain cases higher processing temperatures were used to obtain satisfactory device performances.
2 Background

In this chapter we discuss the fundamentals of OLED, their structure, light emission mechanism and carrier transport mechanism. Additionally a brief description of inkjet printing technology, various flexible substrates used and efficacy of solution proceeding technology is discussed.

2.1 Structure of OLED

The simplest OLED comprises of a single organic layer between the metal contacts. This organic layer must have very good electron and hole transport properties since light is emitted only when a hole combines with electron to form excitons. However such organic polymers which have good hole and electron transport properties are rare. Hence most of OLEDs comprise of two organic layers. The layer in contact with the anode has good hole conducting properties where as the other organic layer in contact with cathode has excellent electron conducting properties. The holes and electrons recombine at the interface to emit light. Similarly in a three layered OLED an extra emissive layer is sandwiched between the hole and the electron transport layers which acts as a site for recombination of holes and electrons. The difference in the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the emissive material determines the specific wavelength of light emitted. In more advanced OLEDs, layers for efficient injection of holes and electrons from anodes and cathodes respectively are utilized. These layers have their work function matched with the electrodes so as to reduce Schottky barrier which results in better carrier injection. The role of individual layers and most commonly used materials for them are as follows:

a. Substrate: A substrate can be either rigid like glass or flexible like synthetic
substrates such as PET, PES or organic substrates such as cellulose nanocomposite. It should be highly transparent in the visible wavelength regime.

b. Anode: This is a transparent electrode which has a high work function. This layer injects holes into the organic layers. Most commonly used anode is Indium tin oxide as it has a high work function (~4.8ev) high transparency ( >85%) and low sheet resistivity (4-8 Ohms/sq). However Indium is a rare and costly material and efforts are underway to develop cheaper anodes from conducting polymer [20-22], carbon nanotubes [23-25], graphene [26-28] etc.

c. Hole Injection Layer (HIL): The role of this layer is to facilitate efficient injection to holes into the subsequent organic layer. The primary requirement is that it should be transparent and the HOMO layer should match with the work function
of the anode. Commonly used HIL materials are PEDOT:PSS which has a work function of 5ev.
d. Hole transport Layer (HTL): This layer should be a good conductor of holes as well as block electrons so as to maximize the probability of electron and hole recombination at the subsequent emitting layer. PEDOT:PSS also serves as a good hole transport layer.
e. Emissive layer (EL): This layer is responsible for the electron and hole recombination and emission of light. The specific wavelength of emitted light depends upon the difference of energy levels between HOMO and LUMO.
f. Electron transport Layer (ETL): This primary function of this layer is to ensure efficient electron injection form the metal cathode and transporting the injected electrons towards the emissive layer. The Schottky barrier at the interface should be as low as possible so that the electrons can be easily injected into the organic media. Additionally this layer should provide good hole blocking functionality so that most of the holes are trapped in the emissive layers thereby enhancing the probability of recombination and light emission.
g. Cathode: Typically a low work function metal ($\phi_w \approx 2.9 - 4.0$eV) acts a cathode. Most of the reactive metals like calcium, magnesium have low work function. However they are highly unstable at atmospheric conditions owing to their reactive nature and hence are not suitable for application in OLEDs. So in addition to having low work function, the cathode has to be stable at room temperature and atmosphere. Aluminum, having a work function of 4.3ev, is one of the most preferred metals used as cathode in OLEDs.

2.2 Light Emitting Mechanism

OLEDs emit light through the phenomena of electroluminescence. It is based on the same principles of traditional semiconductors except for the fact that holes and electrons are transported through Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) respectively instead of valence and conduction band. When a voltage bias is applied across the organic stack, current flows through it. The cathode/anode injects electrons/holes respectively into the electron/hole
injection layer. This layer has a work function very closely matched to the cathode/anode but have low electron/hole mobility. These layers transfer the electrons/hole to the electron/hole transport layer which has better mobilities for carrier conduction. These layers transport the carriers into the emissive layer. In the emissive layer, the transported electrons and holes recombine forming excitons. These excitonic pairs return to the ground state by releasing excess energy in the form of photons. The wavelength of the light emitted depends upon the energy difference between LUMO and HOMO levels of the emissive layer. A large difference would imply greater energy transfer resulting in emission of light of shorter wavelength (towards the blue end of the spectrum) whereas a small difference would result in light emission of larger wavelength (towards the red end of the spectrum). The intensity or brightness of the OLED device depends upon the number of electron hole pairs recombination which in turn depends on the current passing through the device. A greater current would imply a greater number of holes and electrons available for recombination which would enhance the brightness of the device.

Figure 2-2: Light emitting mechanism from an OLED device
2.2.1 Fluorescence

A simple OLED comprises of either one or multiple organic layer sandwiched between electrical contacts (cathode and anode). While anodes provide the holes, the cathodes are responsible for injection of electrons. These electrons and holes combine in the organic media to form an excited state called excitons. These excitons can relax back to ground state by radiative or non radiative relaxation. In case of non radiative recombination, the excitons relax by dissipating the energy in the form of heat and thereby no emission is observed. Alternatively they can undergo conversion to triplet state (excited states where total angular momentum is one) whereby they slowly dissipate energy by delayed phosphorescence or undergo non radiative relaxation. When the excitons decay in to singlet state (excited states with total angular momentum of zero), light emission is observed as they relax by releasing excess energy in the form of a photon and returning to ground state. The lifetime of luminescence emission in case of florescence is $<10^{-8}$ seconds where as it is $>10^{-8}$ seconds in case of phosphorescence [4].

$$\text{Emission: } S_1 \rightarrow S_0 + h\nu_{\text{emitted}} + \text{heat}$$

where $S_1$ is the electronically excited state and $S_0$ is the ground state.

![Image of possible physical process following absorption of a photon by a molecule. Taken from [4]](image_url)

Figure 2-3: Possible physical process following absorption of a photon by a molecule. Taken from [4]
The internal quantum efficiency (IQE) which is defined as the ratio of number of photons generated inside the organic media to the number of electrons injected is at most 25% in case of florescent OLEDs. However by incorporating heavy metals (platinum, iridium, europium etc) into organic layers as dopants as is in the case of phosphorescent OLEDs, the triplet states can be harvested to emit light resulting in theoretical IQE of 100% [31].

2.3 Carrier Transport

Carrier transport in an organic media can be described as either injection limited or bulk limited. In case of injection limited transport, the carriers are efficiently transported away from the contacts into the bulk. As a result the rate limiting step is the injection of carriers from the contacts into the organic media. However in most of the organic media, carrier mobilities are vastly lower than their inorganic counterparts. Hence beyond a certain point there is a buildup of space charge at the interface since the organic media is unable to swiftly transport carriers away from the interface. This excess build up of charge is now the transport limiting step. The mobilities of holes and electrons in organic media differ because of the presence of traps.

In single carrier devices, the J-V characteristics can be modeled by three different equations. In the lower voltage regimes, transport follows an Ohmic behavior given by the following equation [34, 35]:

$$J = \frac{q\mu}{d} \frac{V}{d}$$  \hspace{1cm} (1)

where \( J \), is the current density through the device, \( q \), is the elementary charge, \( p \), is the volume density of holes or electrons, \( \mu \), is the carrier mobility of carriers (assuming single carrier transport), \( V \), is the applied voltage, and \( d \), is the thickness of the organic layer.

In the moderate voltage limit, trap dominated space charge limited current (SCLC) comes into play. The traps are assumed to be distributed exponentially in the energy space and the corresponding J-V characteristic can be modeled by the following equation assuming a zero Schottky barrier [32, 35]:

...
\[ J = q^{l-1}\mu N_V \left( \frac{2l+1}{l+1} \right)^{l+1} \frac{1}{(l+1)} \cdot \frac{\varepsilon}{H_B} \cdot \frac{V^{l+1}}{d^{2l+1}} \]  

(2)

In the above equations, \( N_V \) is the density of states in the valence band of the organic material, \( H_B \) is the total trap density, \( \varepsilon = \varepsilon_r \varepsilon_0 \), where \( \varepsilon_r \) is the relative permittivity of the organic and \( \varepsilon_0 \) is that of free space, \( l = T_C/T \), where \( T_C \) is the characteristic temperature of an exponential trap distribution in the material and \( T \) is the experiment temperature.

However in most of the practical cases, there is a non-zero Schottky barrier at the interface between the metal contact and the polymer. When we take into account this Schottky barrier, the J-V characteristic follows the following equation [32, 36]

\[ J = q^{l-1} \mu N_V \left( \frac{1}{l+1} \frac{\varepsilon}{H_B} \right)^{l+1} \times \frac{V^{l+1}}{(l+1)^{l+1} - C(2l+1)/(l+1)l+1)} \]  

(3)

Where \( C \) is an integration constant equal to

\[ C = J \left( \frac{1}{q\mu P(0)} \right)^{(l+1)/l} \left( \frac{\varepsilon}{qH_B} \right) \left( q\mu N_V \right)^{1/l} \left( \frac{1}{l+1} \right) \]  

(4)

With,

\[ P(0) \approx N_0 e^{-\phi_B/kT} \]  

(5)

\( P(0) \), is the injected charge density at the ITO contact, \( \phi_B \), is the injection barrier, \( k \), is Boltzmann’s constant, and \( T \) is temperature.

At higher voltages, the J-V characteristic follows the common \( V^2 \) Law [32,35]:

\[ J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} \]  

(6)

2.4 **Inkjet Printing**

An economical alternative to expensive thermal evaporation and vacuum deposition technique is the application of wet processing techniques like spin coating and inkjet printing. Although vacuum evaporation of organic polymers results in high performance OLED, it also results in lot of material wastage and is not compatible with roll to roll manufacturing. This is where solution processing techniques come into play. Spin coating is one of the most popular deposition techniques on account of its simplicity,
reproducibility and applicability over wide range of substrates and solutions. However there are two significant drawbacks of this process. There is a lot of material wastage since solutions spin off the substrate on account of the centrifugal force and also it is not compatible with roll to roll manufacturing since only one substrate can be coated at a time and has to be manually removed. Inkjet printing on the other hand has numerous advantages like a mask-less patterning, non contact processing, applicability on wide variety of substrates and efficient material usage and minimal waste generated.

Figure 2-4: Fujifilm Dimatix 2831 Printer
As a result complex patterns can be printed with ease on account of its ability to precisely deposit picolitre volumes of solutions using computer controlled translation stages. Since both polymer and metal nanoparticle inks can be utilized, inkjet printers can print both polymer and metal films which is ideal for flexible substrates.

Inkjet printers can be broadly categorized into continuous inkjet printer (CIJ) which produces a continuous stream of droplets from the nozzle and drop on demand printers (DoD) which ejects droplets when they are compelled to do so. DoD printers can be further classified as thermal printers which heat a small portion of ink thereby vaporizing it and creating a bubble which applies a high pressure (> 1 MPa) wave to the fluid inside the reservoir, forcing a drop out through the nozzle and peizo electric inkjet printers where a mechanical deformation of a small ink reservoir induces a pressure wave in the ink, forcing out a droplet. A broader range of ink formulations and materials can be
applied using piezoelectric inkjet printers since they avoid thermal cycling. By appropriately adjusting the voltage waveform applied at the nozzle, the size, shape, and speed of the droplet can be controlled. Drop pitch that is the distance between two successive droplets can be adjusted by angling the line of nozzles along the print head.

Figure 2-5: Schematic of Inkjet printing
The ink properties such as surface tension and viscosity play pivotal role in proper droplet ejection. Too low surface tension will prevent drop ejection since the drop will simply spread across the nozzle and cover it. Very high surface tension on the other hand will nullify the effectiveness of the pressure wave in the nozzle and prevent drop formations. Inks with high viscosity exhibit long, pronounced tails, which is why inks containing large proportions of polymers tend to display the extreme of this effect – the so called “bead on a string” [37]. The tail can either merge with the main drop during flight or form satellite droplets. If the satellite droplets do not deviate from path and strikes the substrate at the same point as the main droplet, printed pattern will be well defined. However if satellite droplets follow different trajectories, it will compromise print resolution and result in poor line and film definitions. The film parameters such as its morphology and homogeneity depends on a large number of printing parameters like substrate temperature [38], drop spacing [39], solute concentration [40], solvent system[41] among others. Each of these parameters needs to be optimized to obtain good film parameters.
Nevertheless there are some intrinsic limits on inkjet printing. For proper ejection of droplets, the ink must meet the viscosity and surface tension limits set by the printer. The droplets on the substrate exhibit “coffee drop effect” during the drying process [42]. Since the evaporation rate at the circumference is greater than that at the center, the fluids move towards the edge to replenish solvent lost through evaporation causing uneven distribution of solutes in the drop [43]. As a result the device efficiency and lifetime takes a hit. This problem can be alleviated by using a small fraction of a high boiling point solvent which generates a Marangoni flow that counteracts the formation of coffee drop effect [44].

![Schematic representations of common line morphologies](image)

**Figure 2-6:** Schematic representations of common line morphologies. (a) Individual drops, (b) scalloped, (c) uniform, (d) bulging, and (e) stacked coins. Drop spacing decreases from left to right [Taken from 45].

In the ink-jet printing process, coffee ring can be effectively prevented by using a mixture of two solvents with great difference in boiling points and uniform films can be gained [46-47]. Additionally in order to print multiple organic layers, the solvent systems
used for the individual layers need to be orthogonal i.e. a solvent used for one layer should not affect or dissolve the other layer [48].

2.5 Solution processed OLED

Most of the OLEDs reported in literature utilize vacuum processing in one form or another. Since OLEDs are quite susceptible to moisture and oxygen, the organic layers are deposited at high vacuum. However since vacuum deposition is an expensive process, the resulting OLEDs are quite expensive to be commercially competitive. One alternative is to use solution processed techniques such as spin coating and inkjet printing for the fabrication of the devices [49-52]. The solution processed OLEDs are not as high performing as the vacuum based ones, but they are relatively cheap and hence can be used as low cost displays in less demanding applications.

H. Gorter et al. [53] did a comparison between thermally evaporated and inkjet printed OLED devices. The device consists of a multilayer stack on ITO, coated with a hole-injection layer (PEDOT:PSS), a hole transport layer (α-NPD, N,N′-Di-[(1- naphthyl)-N,N′-diphenyl]-1,1′-biphenyl)-4,4′-diamine) and as an emitting layer (Alq3, Tris-(8-hydroxyquinoline)aluminum), with LiF/Al as the reflective cathode. When all the organic layers were thermally deposited the luminous efficiency was 4.2 cd/A whereas when the layers were inkjet printed the efficiency was much lower than even 0.1cd/A. This was due to the fact that the solvent systems used to dissolve one of the organic layers also dissolved the second deposited layer disrupting layer morphologies and interfaces causing device degradation.

Hua Zheng et al. in [54] reported a completely solution processed OLED on an ITO glass substrate using PEDOT:PSS as hole emitting layer, P-PPV as emitting layer and a blend of PFN and Epoxy as electron injection layer which doubles up as a moisture barrier to protect the organic layers. Finally the silver cathode was inkjet printed. They reported a maximum luminous efficiency of 7.29 cd/A and external quantum efficiency of 2.57% for inkjet printed cathode and 13.3 cd/A and 3.56 % for thermally evaporated Ba/Al cathode at 1000cd/m² brightness.

A full color passive matrix PLED has been fabricated in [55] with current efficiencies of 1.37, 9.5 and 1.44 cd/A, for red, green, and blue mono- chrome displays respectively.
with device structure as ITO/PEDOT/ Emissive layer/Ba/Al. The PEDOT:PSS layer was spin coated while the emissive layer was spin coated for monochrome displays and inkjet printed for multi color displays sequentially on top of each other with blue emitter at bottom to reduce leakage current. In [56] devices with structure ITO/PEDOT:PSS/MEH-PPV/LiF/Al was fabricated exhibiting maximum current density and luminance of about 97.5 mA/cm$^2$ and 55 cd/m$^2$ at 8 Volts. All the organic layers were spin coated.

2.6 Incorporation of Metal Nanoparticles

A lot of researchers have focused their attention on developing solution processed transparent conductive oxide (TCO) for ease of fabrication and applicability to flexible substrate. The current choice of TCO among OLED manufacturers is Indium tin oxide deposited by sputtering. However sputtering results in material wastage and also is incompatible with roll to roll manufacturing. Hence solution processed fabrication technique like inkjet printer has been employed to form ITO films which have sheet resistance of 202 Ohms/square, resistivity of $1.52 \times 10^{-2}$ Ohm-cm and transmittance of ~85% (500-550nm) after being thermally annealed at 450°C [57]. Such high sheet resistance (compared to sputtered ITO 4~8 Ohm/sq) will lower device performance while high temperature makes them incompatible with flexible substrate. A promising candidate is the semiconducting material PEDOT:PSS, which is highly transparent and can be easily produced from solution [58]. However, the sheet resistance of high conductive PEDOT:PSS is typically in the range of 100–200 Ohms/square which is two orders of magnitude higher than that of commercial ITO. One technique to further reduce the sheet resistance is application of a silver mesh structure using silver nanoparticles. Silver is one of the most conductive elements and stable silver suspensions have already been reported in literature. By printing a silver mesh structure is sandwiched between inkjet printed ITO layers, the sheet resistance was reduced to 3.4 Ohms/square [59]. The silver mesh will provide the conductive pathways while the ITO will ensure work function match for better device performances. However no OLEDs are fabricated on these structures and compared with devices with commercial ITO. In [60] ITO was replaced by conductive polymer PEDOT:PSS in conjunction with
electroplated gold metal grid. Incorporating the metal grid improved the device performance by 24% at 6 volts and 45% at 7 volts compared to the polymer electrode devices without a metal grid. Still the luminous efficiency at 100 cd/m² for the polymer with grid was 39.1 cd/A compared to 53.5 cd/A for devices on ITO.

2.7 Flexible Substrates

Present application dictates use of flexible substrates. There is also ongoing interest in using green materials in all walks of life. So a flexible substrate which is derived from green technology will be very promising.

Recently Legnani et al. used Bacterial cellulose (BC) membranes as flexible substrates for fabrication of OLED. ITO thin film was deposited using r. f. magnetron sputtering at room temperature and observed transmittance was 40%. In order to demonstrate the feasibility of devices based on BC membranes three OLEDs with different substrates were produced: a reference one with commercial ITO on glass, a second one with a Si-O thin film interlayer between the BC membrane and the ITO layer and a third one just with ITO deposited directly on the BC membrane [10]. The observed OLED luminance ratio was 1: 0.5: 0.25 respectively, with 2400 cd/m² as the value for the reference OLED. Ummartyotina et al. fabricated nanocomposite films composed of bacterial cellulose (10-50%) and poly-urethane resin [61]. The transmittance observed was 80% with thermal stability up to 150°C and CTE less than 20ppm/K. The resulting flexible OLED fabricated by thermal evaporation of organic media had a power efficiency of 0.09 cd/A at 200 cd/m². Si-O thin film was deposited on bacterial cellulose nanocomposite via plasma enhanced chemical vapor deposition (PECVD) as transparent barrier against water vapor. The Si–O layer had a uniform and highly smooth surface – more than 80% of the surface features the surface roughness of 15 nm. The water vapor transmission rate (WVTR) of the bacterial cellulose nanocomposite was evaluated as 9 × 10⁻² g/m²/day, but after the deposition of the Si–O barrier layer, the WVTR in the range of 10⁻⁴ g/m²/day was achieved.
3 Experimental Methodology

3.1 Material Selection

The first step in fabricating OLEDs is selection of the various layers which make the OLED stack. An OLED can be developed on a rigid substrate such as glass or on a flexible substrate such as PET, PES [10] or cellulose nanocomposite [61]. An OLED comprises of anode which acts as the positive contact injecting electrons. The second layer is the organic layer which acts as a hole transport layer. The third layer is the emitting layer where the electrons and holes combine to form exciton and emits photons. The final layer is the cathode which serves as negative contact and completes the circuit.

a. Substrates:

The essence of this project is to develop a fabrication technique which is compatible with flexible substrates. The flexible substrates are very temperature sensitive and degrade when heated above 200°C. Hence the upper limit for all processing steps in fabrication of OLEDs is 200°C. Glass is selected as the choice of substrate since it is easier to develop an OLED on rigid substrate since it is transparent and is abundantly available. Once the processes for OLED fabrication have been optimized, the process and the stack can then be developed on flexible substrates such as PET or cellulose nanocomposite substrate.

b. Anode:

As outlined earlier primary requirement of the anodes from OLED fabrication point of view is that it needs to be conductive and transparent. Two different anodes were used and the device performances were compared. The first
anode used in the fabrication of the devices was the commercially available ITO. ITO coated boroaluminosilicate slides were purchased from Delta Technologies which have a sheet resistance of 4-10 Ohms/sq and thickness of 150-200 nm. This acts as the reference device. Since the ITO coated glass is fabricated using sputtering where the temperature can go beyond 200˚C due to collisions, this method is not suited for flexible substrates. In order to alleviate this problem, solution processed ITO was fabricated using spin coating techniques. And finally to improve the conductivity of the ITO, a silver grid was inkjet printed between the spin coated ITO.

c. Hole transport layer:
PEDOT:PSS was selected as the hole transport layer owing to its close work function match with ITO and optical transparent nature. The PEDOT:PSS was obtained from H.C Stark under the brand name Clevios F HC with conductivity of 150 S/cm.

![PEDOT and PSS](image)

**Figure 3-1: PEDOT (left) and PSS (right)**

d. Emitting Layer:

MEH-PPV powder purchased from Sigma Aldrich was selected as the emitting layer since a lot of literature is available on it [56]. Its peak emission wavelength is at 585 nm. MEH-PPV suspension was obtained by dissolving
MEH-PPV powder in toluene at 0.5% by weight and then sonicating for 24 hours to disperse it properly.

**Figure 3-2: MEH-PPV Chemical structure**

e. Cathode:

Typically low work function metals like calcium and magnesium is used as the cathodes. However these metals are reactive at atmospheric condition and hence degrade quickly. Aluminum having a work function of 4.3 ev was selected to act as cathode. Aluminum pads of sizes 500 by 500 micron were evaporated at $10^{-6}$ Torr base pressure using a shadow mask resulting in formation of 300nm film to complete the device fabrication process.

### 3.2 Preparation of Silver and ITO nanosuspension

The ITO and silver nanosuspension were prepared in Faculty of Forestry, University of Toronto by Dr. Shawn Wang. The fabrication process is described below. ITO was synthesized by a controlled precipitation reaction from an aqueous solution of InCl$_3$ and SnCl$_4$·5H$_2$O followed by a forming gas treatment at 150°C resulting in an average particle size between 5 and 30 nm. The resultant ITO powder was then re-dispersed in a triple roller mill with the addition of 3,6,9-trioxadacananonic acid (TODA) as a surface modifier and a mixture of 2-isopropanol and (2-[2-butoxyethoxy]-ethyl)-acetate as solvents. The nanosuspension was prepared by diluting the ITO powder with 1-propanol as the principal solvent so as to obtain a final ITO content between 3 and 10 wt% with Poly-vinyl Alcohol (PVA) as stabilizer.
Similarly silver nanoparticle suspension was prepared by polyol synthesis [67]. It basically involves reducing AgNO$_3$ in ethylene glycol followed by dispersing it in various organic medium. Poly(vinyl pyrrolidone) (PVP) was added to prevent the agglomeration of the silver nanoparticles. The best results were obtained when it was mixed in Acetone. So all silver nanosuspension used in this project was dispersed in Acetone.

For inkjet printing a commercial silver ink form XEROX containing 32% by weight silver with viscosity and surface tension fine tuned for DMP 2831 Inkjet Printer was utilized.

### 3.3 Anodes fabricated using spin coating

To develop the anodes on glass substrate, first the glass substrate was cleaned using acetone, methanol and isopropyl alcohol followed by oxygen plasma etch to get rid of organic solvents. Then the ITO suspension was spin coated on the glass substrate with the spin coater and heated at various temperatures and duration to remove the organic solvents and prepare a continuous film.

Similarly Silver suspensions were filtered using a 0.22 micron filter and spin coated on glass substrate. Following which the samples were heated at various temperatures and durations on a hot plate to sinter the silver nanoparticles thereby forming continuous films. The surface morphology was analyzed using SEM and sheet resistance was experimentally obtained using 4-point probe model 101C. Each measurement was done at least 5 different points in the sample and reported value is the average of these measurements. Relative standard deviation in these samples are also reported which is defined as

$$\text{Relative Standard Deviation} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$  \hspace{1cm} (3.1)

Finally ITO/Ag/ITO grid was obtained by first spin coating ITO layer on a cleaned glass substrate followed by thermal treatment. Subsequently silver suspension was spin coated and sintered to form a continuous film. Finally the top ITO layer was spin coated on top of silver layer to complete the device structure and its sheet resistance was characterized.
3.4 Inkjet printing

When utilizing inkjet printing technique, first the droplet formation was optimized. The parameters such as firing voltage, substrate temperature and drop pitch which is the distance between two successive printed drops were optimized to obtain proper lines definitions. Once the printing conditions were optimized simple horizontal lines on a glass substrate were printed to test the conductivity. Two different inks were used for inkjet printing. One was fabricated in Department of Forestry while the other was purchased from XEROX Canada. The printed lines were heated at 150˚C to 400˚C for 15 minutes to sinter the nanoparticles and obtain conductive lines. Silver paste was applied at the endpoints of the line to facilitate as contacts. The current voltage characteristic was obtained using a probe station. Once the conductive lines were fabricated, silver grid patterns were printed on top of a spin coated PEDOT:PSS glass substrate. After the sintering step, the top PEDOT:PSS layer was spin coated and the samples were tested for the sheet resistance to verify the effect of Ag grid on sheet resistance using four point probe. Once a reasonable sheet resistance and optical transmission was obtained, the silver ink was then inkjet printed on top of spin coated ITO layer on a glass substrate in a square grid pattern. The size of the grid was varied and its effect on sheet resistance was observed. Finally the inkjet printed lines were heated at 150˚C for 15 minutes to sinter the nanoparticles and obtain continuous lines. The optical transmission was characterized using an ellipsometer.

3.5 Fabrication of ITO/MEH-PPV/Al Devices

Once the transparent conducting anodes were fabricated, those anodes were used to develop the OLEDS. Initially attention was focused to optimize the thicknesses of the emitting layer MEH-PPV. Devices were fabricated with ITO/MEH-PPV/Al structure on commercial ITO coated boroaluminosilicate glasses. The ITO substrate was cleaned using acetone, methanol and isopropyl alcohol followed by oxygen plasma etch. Then MEH-PPV was spin coated at various spin rates to yield different thicknesses and soft baked at 120˚C for 5 minutes to evaporate the solvent. Finally aluminum pads were thermally evaporated and the samples were again subjected to oxygen plasma etch to remove the exposed MEH-PPV. The current voltage characteristics were obtained using
a semiconductor parameter analyzer while light emission was measured using a spectrometer and power meter.

In another set of experiment RTA was performed using AnnealSys AS-ONE Rapid Thermal Processing Furnace after spin coating of MEH-PPV to observe its effect on MEH-PPV mobility. The samples were heated at 150°C, 175°C and 200°C with 25°C per second ramp rate. The electrical characterization was done using HP 4155 semiconductor parametric analyzer while optical characterization was done using Newport Power Meter Model 2931C.

3.6 Fabrication of ITO/PEDOT:PSS/MEH/PPV/AL devices with Rapid thermal annealing

After the thickness of MEH-PPV was optimized, devices were fabricated with ITO/PEDOT:PSS/MEH-PPV/Al structure to test the effect of rapid thermal annealing on the device performance of OLEDs. It is reported in literature that RTA at 200°C lowers the sheet resistance in PEDOT:PSS [62]. The reference ITO coated glass substrate was cleaned using acetone, methanol and iso propyl alcohol followed by oxygen plasma etch. Then PEDOT:PSS was filtered using 0.22 micron filters and was spin coated at 1500 rpm film and heated at 120°C for 5 minutes to evaporate the solvent and a 100 nanometer thick film was obtained. Then MEH-PPV was spin coated on top of PEDOT:PSS layer and was soft baked at 120°C to evaporate toluene. Rapid thermal annealing was performed at two different points. In first case, RTA was performed after depositing of PEDOT:PSS while in another set of experiment, it was performed after spin coating of MEH:PPV. The samples were annealed at three different temperatures of 150°C, 175°C and 200°C. The ramp rate was kept constant at 25°C per second and the duration of heating was 30 seconds. Finally aluminum pads were thermally evaporated and the samples were oxygen plasma etched to get rid of the exposed organic media. The current voltage characteristics were obtained using a semiconductor parameter analyzer while light emission was measured using a spectrometer.
3.7 Fabrication of ITO/PEDOT:PSS/MEH:PPV/Al devices with solution processed ITO

After fabricating devices on commercial ITO, the attention was focused on solution processed ITO. The ITO layer was spin coated at different spin rates from an ITO nanosuspensions followed by a soft bake at 175°C for 5 minutes. To make them conductive they were subjected to the rapid thermal annealing as is reported in literature [57]. The samples were heated to high temperatures (up to 550°C) to increase conductivity. After minimizing its resistance, the top PEDOT:PSS layer was spin coated at 1500 rpm to form 100 nm film. They were subjected to soft bake at 120°C. Then MEH-PPV was spin coated on top of PEDOT:PSS layer was heated at 120°C to evaporate toluene. Finally aluminum pads were thermally evaporated and the samples were oxygen plasma etched to get rid of the exposed organic media.

3.8 Fabrication of ITO/Ag grid/ITO PEDOT:PSS/MEH:PPV/Al devices

In the following set of experiments, an inkjet printed silver grid was incorporated to further enhance the conductivity of the anodes. After spin coating a bottom ITO layer and subjecting it to RTA, silver grid using commercial XEROX ink was printed of grid size 250 microns. Then the top layer ITO was spin coated and subjected to RTA. Finally the same organic stack was spin coated on top of it and device performances was measured in terms of current density-voltage and light output.

3.9 Light output measurement and calibration

Once the diodes were fabricated they were tested for light output. Since the cathode size is 500 by 500 micron which is very small, the devices could not be tested using integrating sphere as it was very difficult to make contacts with such small contacts. To get around this problem, a CCD detector and a spectrograph was used. The spectrograph permits a particular wavelength to strike the CCD camera and the intensity is recorded. Light from the diodes was collected by 10x Olympus M Plan objective lens with numeric aperture (NA) of 0.25.

\[
NA = \eta \sin \theta
\]  

(3.2)
Substituting NA=0.25 and \( \eta \) which is the refractive index of the media in which the objective lens operate which in this case is air with \( \eta =1 \), the value of \( \theta \) is obtained which is 14.47°. So the objective lens collects light form only 14.47°.

The total power emitted by the light source is given by [66]

\[
P_{\text{emitted}} = \int_0^{90°} I_{\text{air}} 2\pi r \sin(\phi) \ r \ d\phi
\]

Where \( P \) is the total power emitted by the light source, \( r \) is the distance from the source and \( I_{\text{air}} \) is given by

\[
I_{\text{air}} = \frac{P_{\text{source}} \eta_{\text{air}}^2}{4\pi r^2 s^2} \cos \phi
\]

Integrating equation 3.2 over 0 to 90 degrees gives the total power emitted

\[
P_{\text{detected}} = \int_0^{90°} I_{\text{air}} 2\pi r \sin(\phi) \ r \ d\phi
\]

And integrating it over 0 to 14.47 degrees gives the power detected by the objective lens.

Dividing equation (3.4) by equation (3.2) gives the percentage of power detected by the lens.

Solving the equation amount of light detected was found out to be

\[
\frac{P_{\text{detected}}}{P_{\text{emitted}}} = 0.0624
\]

However one problem with the system is that the intensity measured is in arbitrary units. So this system works well for comparative assessment of different samples but it cannot be used to compare light emission to other reported literatures. So a Newport Power meter (Model 2931-C) was utilized to detect the actual power from the diodes. However one issue with the power meter is that it is good in detecting power in those devices which have a narrow emission spectrum like a laser as it can be calibrated at a
particular wavelength. But in the fabricated diodes, the MEH-PPV emits a fairly broad band spectrum from 550 nm to 700 nm with a peak at 585 nm. Hence there will be a residual error in the measured power output. The calibrating frequency of the power meter was kept at 585 nm and the reading was noted. Then the calibrating frequency was changed to 550 nm and 700 nm and the power meter reading was noted. The difference in reading is range of error.

A typical graph obtained from the spectrometer is shown in the following figure

![Graph showing intensity vs frequency](image)

**Figure 3-3:** Intensity obtained on a spectrometer as a function of frequency
A crude way of determining power from the above graph is integrating to find the area under the curve. Once the area is determined it can be equated to the powermeter reading to determine the relation between the intensities observed using the spectrometer and the powermeter.

![Graph showing linear fit between Power and Area](image)

**Figure 3-4: Power observed in powermeter against the area under the curve obtained from spectrometer**

It is observed that there exists a linear fit to the data. The relationship between the peak intensity and the power reading from power meter was explored. Since the area under the curve is proportional to the peak intensity, it is expected that there will be a similar linear relationship.
Figure 3-5: Power observed in powermeter against the peak intensity of the curve at 585 nm obtained from CCD Camera

Next the error range of the measurements was studied. As discussed earlier that the powermeter is mostly used for narrow band emission with the calibrating wavelength selected at as the central wavelength. However the diode devices are broad band emitters and hence the photon energy will be vastly different from the calibrating frequency. Hence an extra reading keeping the calibrating wavelength at the edges of the MEH-PPV emission spectrum was made so as to obtain the error bars.
Figure 3-6: Power observed in powermeter against the peak intensity at 585 nm detected by the CCD camera along with the error range.

The sensitivity of human eye varies with wavelength. It is maximum at 555 nm and decreases as one move away from it as described in figure-3.7 which illustrates the visual luminous efficiency distribution for phototropic vision.
Most of the light measurements are taken in phototropic units which take into account the variation of sensitivity of human eye. Luminous flux ($\varphi_v$) is related to radiant flux $\varphi(\lambda)$ by the following equation [68].

$$\varphi_v = K_m \int \varphi(\lambda)V(\lambda)d\lambda$$ (3.7)

Where $K_m$ is the maximum spectral efficacy of radiation for photopic vision and is equal to 683 lm/W [69] and $V(\lambda)$ is visual luminous efficiency distribution. Luminance in cd/m$^2$ can be obtained by calculating luminous flux per unit area per steradian. The area of our device is 250,000 $\mu$m$^2$ and the total solid angle of emission is a hemisphere (2$\pi$). Since the peak of emission spectra of MEH-PPV spectra is at 585 nm which is quite close to 555 nm, further assumption can be made that the value of $V(\lambda)$ is unity. After the simplification, luminance in cd/m$^2$ can be calculated by the following equation.

$$\frac{Watts}{m^2sr} = 683 \frac{cd}{m^2}$$ (3.8)
4 Conducting Anodes by Spin Coating

One of the major challenges in the fabrication of organic light emitting diodes is obtaining a transparent conducting anode with low sheet resistances utilizing wet processing techniques. Currently the most popular technique of fabricating anodes is sputtering of ITO with sheet resistances of the order of 4-10 Ohm/sq and transmission above 90% in the visible regime. Solution processed techniques have an advantage over sputtering since the same techniques can be used in depositing organic layers. In this chapter ITO films fabricated via spin coating and various techniques were investigated through which the sheet resistance can be lowered to make its performance at par with commercially available sputtered ITO. Characterization of the sheet resistance and surface morphology of the stack comprising of a spin coated silver layer sandwiched between two spin coated ITO layers was performed. Although such stack will be opaque and will not transmit light, the idea is to see its efficacy and then use inkjet printing to fabricate silver grids instead of a continuous film which is discussed in the next chapter.

The effectiveness of an anode can be measured in terms of its sheet resistance, surface morphology and work function match with adjacent organic layers. A low sheet resistance indicates that the material readily allows movement of charge carriers. Similarly surface morphology plays a key role in determining efficient carrier injection into the subsequent organic layers on account of absence of spikes and pinholes which causes local high electric field effects. Another important characteristic of anode is its work function. ITO has a work function of 4.8ev which matches closely with that of PEDOT:PSS (5ev) thereby reducing barrier height. On the other hand Silver has a work function of 4.2ev meaning holes have to overcome high barriers to be successfully injected into the PEDOT:PSS.
4.1 **Spin coated ITO films**

The efficacy of solution processed anodes is investigated in this chapter. The silver nano suspensions are varied in terms of concentration, spin rate, temperature and duration of annealing. The spin coated ITO layer is subjected to conventional annealing and rapid thermal annealing and the films are characterized in terms of thicknesses, sheet resistance and surface morphologies.

4.1.1 **Conventional annealing of ITO films**

ITO nano suspension is spin coated on cleaned glass substrates followed by annealing at 200°C for 2 hours to sinter in a conventional oven. The anneal temperature was kept below 200°C because that is the maximum temperature the nano cellulose substrate can withstand without degrading. Then their sheet resistances are measured using a four point probe. The results are illustrated in Figure 4-1. It can be clearly observed that the sheet resistances are of the order of $10^4$ Ohms/sq which is three order of magnitude higher than the commercial ITO available on glass substrate deposited by sputtering. Such high resistances clearly show that sintering of ITO using conventional oven baking at temperatures below 200°C is not an option for developing OLEDs which require sheet resistance of the order of 10 Ohms/sq for optimal performances.

![Figure 4-1: Sheet resistance and relative standard deviations as a function of Spin rate](image-url)
4.1.2 Rapid Thermal Annealing of ITO films

The effect of rapid thermal annealing on sintering of ITO is investigated in this section. It has been observed in [57] that RTA is very effective in lowering sheet resistances of ITO films when annealed at 450˚C for 5 minutes. The ITO films were spin coated at 2000 rpm on a glass substrate and then subjected to RTA at various temperatures for duration of 5 minutes. The ramp rate was kept constant at 25˚C per second. The results are outlined in the figure 4-2.

As can be observed from the graph, RTA does indeed sinter the ITO and reduce the sheet resistances to 223 Ohm/sq when annealed at 450˚C. This clearly demonstrates that RTA is an effective tool for sintering of ITO.

Figure 4-2: Effect of RTA on single spin coated ITO films

The effect of RTA on twice spin coated ITO films was investigated and the results are shown in Figure 4-3. The twice spin coated films show even lower sheet resistances as expected since sheet resistance is a function of film thickness. Spin coating ITO twice at 2000 rpm results in films which are almost twice as thick and hence lowers the sheet resistances to 56 Ohms/sq for films annealed at 450˚C.
So in the next set of experiments the ramp rate was reduced to 10°C per second and samples were heated to temperatures above 450°C albeit for only 10 seconds. Then the temperature was lowered and held at 400°C for 5 minutes to see if any improvement in sheet resistances can be observed.
As can be seen from the above figure, although the sheet resistance eventually lowers, there is no remarkable improvement in sheet resistances when two step RTA is performed. So in conclusion RTA at 450°C for 5 minutes gives the optimum sheet resistances.

4.1.3 Comparison of Rapid thermal Annealing with Conventional Annealing

In the previous set of experiments the ITO was subjected to high temperature RTA. In this section, the devices were subjected to the same temperature but in a hot plate. The idea is to investigate whether the improvement in sheet resistance is due to rapid thermal annealing of the samples. Figure 4-5 illustrates the resultant sheet resistance on samples with twice spin coated ITO films at 2000 rpm. The samples are then heated on a hot plate for 2 hours. It can be clearly observed that performing RTA for 5 minutes at elevated temperatures results in one order of magnitude lower sheet resistances compared to annealing on a hot plate at the same temperature for 2 hours.

![Figure 4-5: Effect of RTA and conventional annealing on ITO films](image-url)
4.1.4 Surface Morphology

One important property of transparent conducting anodes is the surface roughness. Jagged surfaces can lead to local high electric field effects which results in device degradation. The surface morphology of the ITO films by spin coating ITO layer on top of a cleaned silica substrate was characterized by SEM images.

![SEM images of ITO coated films](image)

**Figure 4-6: SEM images of ITO coated films**

As can be observed from the above images, the surfaces are relatively smooth although few bumps are observed. However no spikes are seen which can prove detrimental to OLED performances. However at this junction we are unable to quantify the surface roughness because we do not access to Atomic force microscope (AFM) which works with metallic materials..

4.1.5 Optical Transmission

The effect of spin rate on the optical transmission of the ITO film was investigated. The measurements were done using an ellipsometer by Steven Rutledge of our group. Spinning at higher spin rate results in lower film thickness which results in better optical transparency. When spun at lower rate, the optical transmission reduces since film thickness increases.
4.2 Spin coated Silver films
The sheet resistance of the spin coated Ag films depends on anneal temperature, time and the thickness of the film. The thickness of the film in turn depends on the spin rate. A higher spin rate indicates a lower thickness and hence a higher sheet resistance. In this section the effects of these factors are studied.

4.2.1 Effect of anneal time on sheet resistance
8% Silver nanoparticle suspension was spin coated on a glass substrate at 3000 rpm for 45 seconds following which it was annealed in a thermal oven at 160°C for different time duration. The anneal time was varied from 10 minutes to 5 hours to figure out exactly after how much time does it take for Ag nanoparticles to coalesce and form conductive pathway. From the figure 4-8, it can be seen that there was hardly any change in sheet resistance in the first hour. It was because of the presence of organic solvents like acetone and PVP which prevented the formation of a continuous silver film. After one hour, it was observed that sheet resistance decreased drastically from $10^6$ Ohm/sq to 0.5 Ohm/sq as the organic compounds began to evaporate leaving behind

Figure 4-7 Optical transmission as a function of wavelength. (2000/2000 rpm implies twice spin coated ITO layers at 2000 rpm).
only Ag nanoparticles which begin to coalesce. The sheet resistance reached a minimum after 3 hour duration after which it plateaued as all the organic compounds had evaporated and hence no further improvement was observed. Similar was the case with relative standard deviation which was lowest at 180 minutes after which it plateaued.

![Graph showing sheet resistance and relative standard deviation over time.](image)

**Figure 4-8: Average Sheet Resistance as a function of anneal time when heated at 160˚C**

### 4.2.2 Effect of concentration and spin rate on sheet resistance

Similar to duration of anneal time, the concentration of Ag nanoparticles in the suspension has a great impact on the sheet resistance of the spin coated film. Three different suspensions which had concentration 8%, 6% and 3% Ag by weight in acetone was prepared. Each suspension was spin coated on a glass substrate at different spin rates followed by annealing for 3 hours at 160˚C. It is expected that higher concentration of Ag nanoparticles will result in better sheet conductivity. On the flipside, it will also result in more opaque film. So a trade-off is necessary. It was observed that the 3% Ag film was not conductive since it showed a sheet resistance of the order of $10^{10}$ Ohms/sq on account of inadequate amount of Ag nanoparticles for formation of
conductive pathways. Also as the spin rate was increased, the film thickness decreased which resulted in lower conductivity.

![Graph showing sheet resistance vs. spin rate](image)

**Figure 4-9: Average Sheet resistance as a function of spin rate at two different silver concentrations.**

As can be seen from the figure, the 8% Ag suspension provides a lower sheet resistance. It exhibited sheet resistance lower than 0.5 Ohm/sq. The 6% Ag nanosuspension had a sheet resistance one order of magnitude greater than the 8% suspension but it was still lower than the commercial ITO (4-8 Ohm/sq).

### 4.2.3 Effect of temperature on sheet resistance

Temperature plays a paramount role in sintering of Ag nanoparticle film. Although glass can withstand high temperatures, the flexible substrates are quite temperature sensitive and cannot withstand high temperatures. So figuring out the lowest sintering temperature is quite important. The 8% Ag in acetone was heated to different temperatures (150°C, 158°C, 165°C and 200°C) for 3 hours.
From the figure 4-10, it can be observed that at 150°C, the sheet resistance is very high indicating the absence of conductive pathway on account of presence of organic compounds. However when the samples were heated to 158°C and 165°C the sheet resistance decreased drastically. Furthermore there was not much change in resistance at 165°C and 200°C. Also with increasing spin rate, sheet resistance increased since the film thickness decreased resulting in more resistance for the flow of charge carriers.

4.2.4 Effect of Rapid Thermal Annealing on sheet resistance

RTA is an heating process where temperature is increased at a very rapid rate. Two solutions 6% Ag in acetone and 8% Ag in Acetone were rapid thermally annealed from 250°C to 350°C for 15 minutes. The ramp time was 25 °C per second. The observed sheet resistance is shown in figure 4-10. It was observed that with increasing temperature, the sheet resistance of 6% solution decreases until 300°C after which sheet resistance increases.
Figure 4-11: Sheet resistance as a function of anneal temperature at two different concentrations of Silver for 15 minutes

However the sheet resistance was still two orders of magnitude higher than those annealed in a hot plate. Hence the duration of annealing was increased to 30 minutes. As can be seen from the figure 4-12, the sheet resistance decreased till 250°C after which it plateaued.
Figure 4-12: Sheet resistance as a function of anneal temperature at two different concentrations of Silver for 30 minutes

From this experiment it was clear that the sintering of silver nano particles depended more on the duration of heating rather than the rate of heating. As there was no pronounced improvement in sheet resistance with RTA, conventional annealing techniques were preferred.

4.2.5 Surface Morphology
Although spin coated silver films showed superior conductivity, they have a high work function mismatch which results in increased barrier heights. Only carriers which have enough energy to overcome this barrier can be injected into the subsequent organic layers. Hence it is of paramount importance to lower the charge barrier to maximize carrier density. ITO on the other hand results in lower charge barrier but has a very high sheet resistance. To overcome this challenge, an ITO/Ag/ITO stack is developed
whereby the middle Ag layer provides a parallel conductive path and the underlying ITO decreases the charge barrier for efficient injection.

The following figure shows the surface morphology of 8% Ag spin coated on a silica substrate and annealed at 160°C for 3 hours. The surface roughness was very high which would cause local high electric field effects and result in degradation of device performance.

![SEM image of 8% spin coated Ag on silica substrate](image)

**Figure 4-13: SEM image of 8% spin coated Ag on silica substrate**

### 4.3 ITO/Ag/ITO Structure

The ITO/Ag stack structure on silica was developed to measure the sheet resistance of the compound structure.
Figure 4-14: Sheet resistance of ITO/Ag stack and only ITO on silica. Spin rate of Ag kept constant at 1000rpm

It was observed that the sheet resistance is dominated by the silver layer rather than ITO layer. The current experiences lesser resistance in silver layer owing to its higher conductivity. Hence the Ag and ITO layer acts as two resistors in parallel and current flows through the lower resistive layer (in this case Ag).

Figure 4-15: SEM images of ITO/Ag stack on Silica
SEM images show the thickness of individual layers as well as the top surface morphology. As expected the top silver layer is quite rough and would adversely affect the OLED. In order to match the work function, a top ITO layer is required.

![Graph showing sheet resistance and relative standard deviation](image)

**Figure 4-16: Sheet Resistance of ITO/Ag/ITO stack on silica substrate.**

There is about one order of magnitude increase in sheet resistance compared to ITO/Ag stack structure which is due to the addition of top ITO layer. SEM images in Figure 4-16 show a very smooth top contact which will enhance carrier injection into the organic layers.
4.4 Concluding Remarks

From the results above, it can be seen that spin coated ITO has a very high sheet resistance unless it is subjected to annealing. When the solution processed ITO is heated in a conventional oven at high temperatures such as 500°C, the observed sheet resistance is around 500 Ohms/sq which is two orders of magnitude higher compared to commercial ITO. This will not only lead to poor device performance but will also increase the operating voltage since higher current will be required to inject carriers into the organic layers. Hence it was clear that some processing techniques other than conventional oven baking would be required to lower sheet resistance and improve device efficiency. Hence rapid thermal annealing was used to decrease the sheet resistance. Rapid thermal annealing is a process where samples are heated to a high temperature in a relatively short period of time. The spin coated ITO samples were subjected to 450°C for 5 minutes with a ramp rate of 25°C/sec and the sheet resistance was measured. Remarkably the sheet resistance decreased to 50 Ohm/square which is just one order of magnitude higher than the commercially available ITO. This is even better than the one reported in literature which had rapid thermally treated ITO sheet resistances of 202 Ohm/sq [57]. Another merit of rapid thermal annealing is that it is compatible with roll to roll manufacturing since the samples are heated for a very short
duration of time. This will help drive down prices and make OLEDs and FOLEDs ubiquitous. However since the flexible substrates cannot withstand temperatures as high as 500°C, it is of paramount importance that techniques are figured out to try to achieve same sheet resistance albeit using low temperature processes.

Hence attention was focused on using a silver layer sandwiched between a top and bottom ITO layers. Silver layer does not require such high temperatures to form conductive pathways and is also much more conductive than ITO. The role of this layer is to efficiently inject carriers into the solution processed ITO uniformly. The obtained sheet resistances look very promising since they are even lower than 1 Ohms/sq. However the SEM images of spin cast silver films show very rough surface which in turn can cause device degradation by creating pin holes and local high electric field effects.

For proper operation of OLEDs, it is imperative that the anodes have a smooth surface morphology. Additionally the work function mismatch between silver and PEDOT:PSS will increase device operation voltages since an extra barrier height is created which needs to be overcome by charge carriers in order to inject into the organic media. To maintain work function match a top ITO layer was spin coated since the work function of ITO matches very closely to that of PEDOT:PSS. This also helps in smoothing out the top silver layer. SEM images of ITO demonstrate that surface profile is very smooth. The observed sheet resistance of the entire stack was found out to be less than 2 Ohms/sq which is lower than the commercial ITO.

However one of the problem of using spin coated silver layer is the fact that they are optically opaque to light and hence the light emitted by the organic layer will not be able to escape the device. This is an important challenge which needs to be addressed before OLEDs can be fabricated on solution processed anodes. This challenge can be overcome by fabricating silver grid lines instead of a complete layer. The gaps in the mesh will provide a path for the generated light to escape the device while the silver grid will enhance carrier injection into the ITO. However spin coating cannot be used to fabricate the grid structure as it is not an additive patterning technique and can only be used to fabricate a complete layer. Hence inkjet printing was utilized as it is a very efficient method to print patterns with very little material wastage as opposed to spin
coating where a lot of material is wasted as it spins off the surface. Another major advantage is inkjet printing is its compatibility with roll to roll processing. Hence it can be used in roll to roll fabrication of OLEDs. One important restriction placed by the printer is that the ink must satisfy viscosity and surface tension constraint specified by the printer for proper jetting of the droplets through the nozzle. In the next chapter inkjet printing of silver grids is described in detail.
5 Inkjet Printed Anodes

In the previous chapter it was demonstrated that the spin coated silver nanoparticle layer achieved remarkable conductivity. However optical transmission was negligible because of the fact that silver is not transparent. Hence the silver layers would absorb all the light emitted by the active layers resulting in poor light emission from the device. So a method to utilize the high conductive property of silver without sacrificing on optical transmission was required. One technique to realize this goal is to fabricate silver grid like structures instead of a complete layer. This will enable light to escape from the space between the grids while current will conduct through the silver grids into the ITO layer. This grid structure requires use of additive patterning technology such as inkjet printing. Inkjet printing has garnered a lot of interest from researchers because of the fact that it is an additive patterning technique which does not require expensive masks, and there is very little material wastage. On the other hand it places lot of constraints on the inks used to pattern in terms of viscosity and surface tension since jettability of the ink depends on these physical properties. The film parameters such as its morphology and homogeneity depend primarily on the following factors: substrate temperature [38], drop spacing [39], solute concentration [40], and solvent system [41]. Each of these parameters needs to be optimized to obtain good film parameters which are discussed in the following sections.

5.1 Substrate Temperature

Substrate temperature during inkjet printing plays an important role in the line registration. Substrate temperature essentially determines the drying rate of the droplets. At low substrate temperature, the solvent has more time to evaporate. Since the rate of evaporation is faster at the periphery compared to center, solvents move outward resulting in movement of solute towards the edges and deposition of the
solute along the edges. As a result it can be seen the hollow profile in the middle when deposition is done at room temperature. However when the substrate is kept at higher temperature, the solvent evaporates quickly. There is no time for movement of solute towards the periphery and hence they are uniformly deposited throughout the profile.

Figure 5-1: Optical image of printed line at 10 micron drop spacing at temperatures of 30, 45 and 60˚C respectively

As can be observed from the optical microscope images, when silver suspension is deposited at room temperature, most of the silver nano particles coalesce at the periphery while the centre is mostly devoid of it. This is due to the fact that drying rate is slow which in turn is responsible for slower evaporation of solvent. Since the rate of evaporation at the periphery is greater than that at the center, a convective flow is established which moves the silver nano particles towards the periphery. Since the rate of evaporation is slower, the convective flow plays a dominant role and results in a hollow center. However as the substrate temperature is increased to 45˚C, the rate of evaporation goes up. In this scenario there is not much time for the convective flow to play a dominant role and hence silver is uniformly deposited throughout the line. This effect is even more evident when substrate temperature is increased to 60˚C.
5.2 Drop Spacing

Drop spacing or pitch is defined as the distance between two successive droplets ejected by the printer. Too high drop pitch will result in isolated droplets unable to form a contiguous line. Too low drop pitch in turn will result in very high overlap of droplets causing bulging. So it is important to find the sweet spot between these two extremes. For this experiment, the substrate temperature and firing voltage was kept constant at 60°C and 25 volts respectively.

Figure 5-2: Variation of drop pitch 5, 10, 25, 50, 65 microns at constant substrate temperature of 60°C
As is evident from the figure, at very low drop spacing of 5 microns, there is extensive drop overlap which results in line formation describing stacked coin feature. There is bulging and contraction evident along the edges. At the drop spacing of 10 and 25 microns, the line edges are relatively smooth with not much bulging is observed. However when the drop spacing decreases to 50 microns, there is insufficient overlap and hence the lines are scalloped. On further elevation of drop pitch to 65 microns, the drops become isolated and there is no line formation.

5.3 Conductivity measurements
When samples of inkjet printed lines on glass substrate was heated at high temperatures to sinter the silver nanoparticles, no evident improvement in conductivity was observed. It is because of the fact that on heating, the evaporation rate of the solvents at the periphery is higher than that at the center. To compensate the faster solvent loss at the edges of the lines, the solvents from the center move towards the periphery thereby depositing the silver ink on the edges. As a result the silver deposition is not uniform along the cross section of the lines. The following figures demonstrate this effect. The samples were heated at 500˚C for three hours and the resultant optical images are shown in the following figures. This is the classic “coffee stain effect” which can be resolved using two system solvent instead of one solvent where the boiling point of one solvent is higher than that of the other solvent [44]. This counteracts the solvent flow towards the periphery during evaporation resulting in proper line profile.

Figure 5-3: Silver lines deposited on the edges of the line after being heated at 500˚C
Due to this effect the observed conductivity of the lines was almost $10^7$ times higher compared to that of bulk silver. Since this problem revolves around the chemistry of the ink and is beyond the scope of the thesis, it was decided to utilize a commercial ink which has been optimized for proper printing using DMP 2831 printer.

![Profilometer measurement of cross section of inkjet printed silver lines demonstrating coffee drop effect](image)

**Figure 5-4: Profilometer measurement of cross section of inkjet printed silver lines demonstrating coffee drop effect**

### 5.4 Commercial Xerox Ink

The commercial silver nano suspension XCM-NS32 was obtained from Xerox. Its physical parameters are listed in the following table.
Table 5-1: Product specification of Xerox XCM-NS32 Silver nanoparticle ink

The ink was jetted using a customized waveform provided by Xerox Inc. and the substrates were heated to 40°C prior to printing. It was observed that the line width was 100 microns and line height was 100 nm for a single printed line. The samples were heated at 175°C for 15 minutes using a hot plate to sinter the solvent. Additionally rapid thermal annealing of the samples was employed to see its effect on the conductivity of the printed lines.

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (Color)</td>
<td>Metallic Blue</td>
</tr>
<tr>
<td>Appearance (Form)</td>
<td>Liquid</td>
</tr>
<tr>
<td>Silver Content</td>
<td>30.22%</td>
</tr>
<tr>
<td>Viscosity (cps)</td>
<td>2.99</td>
</tr>
<tr>
<td>Average particle size (nm)</td>
<td>&lt;12</td>
</tr>
</tbody>
</table>

Figure 5-5: Lines printed with Xerox ink of 1 layer and 5 layers after heating at 175°C for 15 minutes respectively
The below figure illustrates the line morphology of silver lines printed using Xerox ink. As can be seen the silver is deposited uniformly throughout the cross section and does not show any coffee stain effect as can be confirmed by the profilometer measurements.

![Profimeter measurement of line cross section of Xerox ink](image)

**Figure 5-6: Profilometer measurement of line cross section of Xerox ink**

The 5 mm printed lines were then used to measure the conductivity using the probe station and the results are outlined in the below figure.

<table>
<thead>
<tr>
<th>Sintering Conditions</th>
<th>Resistivity (Ohm-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot plate 175°C for 15 minute</td>
<td>4.27E-8</td>
</tr>
<tr>
<td>RTA at 200°C for 1 minute</td>
<td>1.80E-2</td>
</tr>
<tr>
<td>RTA at 500°C for 1 minute</td>
<td>1.07E-7</td>
</tr>
<tr>
<td>Bulk Silver</td>
<td>1.59E-8</td>
</tr>
</tbody>
</table>

**Table 5-2: Conductivity measurement of inkjet printed lines of Xerox ink subsequent to heating at 175°C on a hot plate and at 200°C and 500°C of rapid thermal annealing**
It can be clearly seen that heating on hot plate for 15 minutes gives us the best result compared to rapid thermal annealing where samples are subjected to 200˚C or 500˚C for 1 minute only with a ramp rate of 25˚C per second. This demonstrates the fact that duration of heating is more important than the temperature for sintering of silver nano particles.

5.5 PEDOT:PSS/Ag Grid/ PEDOT:PSS

In order to investigate the effect of the inkjet printed silver lines on the sheet resistance of PEDOT:PSS, a PEDOT:PSS/Ag grid/ PEDOT:PSS device was fabricated. On an acetone cleaned oxygen plasma treated glass substrate, PEDOT:PSS was spin coated to form a 100 nm layer. Then silver ink from Xerox was used to inkjet print horizontal and vertical lines with varying degree of separation. The distance between the lines was varied from 0.5mm to 2mm. Having lines closer to each other would reduce sheet resistance but on the other hand would decrease optical transmittance and vice versa. After printing of silver mesh, the samples were cured at 175˚C for 15 minutes on a hot plate to silver the silver nano particles to improve electrical conductivity. Finally a top layer of PEDOT:PSS was spin coated to complete the structure.

![PEDOT:PSS grid with 250 micron grid size](image)

**Figure 5-7: PEDOT:PSS grid with 250 micron grid size**

Sheet resistance was finally measured and is presented in the following figure.
From the above figure, it can be concluded that sheet resistance decreases as the line separation is decreased. The relative standard deviation is less than 20% for each of the samples. It is worth mentioning that for grid spacing of 0.5 mm and 1 mm, the sheet resistance is less than that of commercial sputtered ITO which is around 7-8 Ohms/sq.

5.6 ITO/Ag Grid/ITO Stack

Instead of using the PEDOT:PSS layer, attention was turned to using solution processed ITO to build the ITO/Ag/ITO stack. The ITO layer is spin coated at 2000 rpm and sintered at 175°C for 3 hours resulting in a sheet resistance of $10^4$ Ohms/sq. Ag grid of different sizes (0.5, 1, 1.5, 2 mm) are printed using the Xerox ink and sintered at 175°C for 15 minutes on a hot plate. Finally the top ITO layer is spin coated like the bottom ITO layer.
Figure 5-9: Sheet resistance and relative standard deviation as a function of Ag grid separation

It was observed that at lower grid sizes, the sheet resistance was comparable to commercial ITO however at larger grid size, the non-conductive ITO dominates the sheet resistance. Since the aluminum deposited using shadow mask has dimensions of 500 by 500 microns and the width of the silver lines is around 100 microns, the grid size was fixed at 250 microns to ensure there is adequate overlap between the pads and Ag grid and enough void in between for the light to escape out of the devices.

Figure 5-10: ITO/Ag/ITO grid with 250 micron spacing.
The ITO layer was sintered using two different processes. In first case, after spin coating ITO at 1000 rpm, the samples were sintered using a conventional hot plate at 300, 350 and 400°C. In second case instead of using hot plate, rapid thermal annealer was used to sinter it at the same temperatures for 5 minutes with ramp rate of 25°C per second. After the inkjet printing of the grid, the top ITO layer was spin coated and the same heating techniques were used. The results are outlined in the following figure.

As can be observed, in case of heating on hot plate, the resistances are of the order of 40 Ohms/sq when annealed at 400°C. This is due to the fact that the ITO itself is having a sheet resistance of $10^4$ Ohms/sq. However on employing RTA, the resistances are down to 10 Ohms/sq since the ITO have sintered and formed conductive pathway thereby improving conductivity. Incorporating silver grid further lowers the sheet resistance to less than 10 Ohms/sq.
The optical transmission of the ITO/Ag/ITO grid is shown in the following figure. It can be seen that the transmission reduces further to 0.48 at 550 nm since the silver lines are opaque.

Figure 5-12: Optical transmission of Ag grid and ITO/Ag grid/ITO structure

5.7 Concluding Remarks

In the preceding chapter, the potential of spin coating for fabrication of transparent conducting anode was discussed. Although good results were obtained in terms of low sheet resistance, optical transmission became an issue since spin coated silver layer is opaque. So rather than spin coating a complete silver layer, a silver grid would make much more sense in obtaining a conductive anode without compromising optical transmission. Hence an inkjet printer was used to print a silver grid. The opaque silver lines would make the anodes more conductive while the space between the grids would be optically transparent to allow light escape from the devices. Initially silver grids from
silver nanosuspensions developed at Faculty of Forestry were tested. Although the ink was jetting properly and the substrate temperature, drop pitch were optimized for proper printing, the silver lines were fairly non-conductive since the silver concentration in the nanosuspensions was quite low. On increasing the silver concentration, the silver ink did not disperse well in the solvent. Hence commercial XEROX ink which was optimized for the Dimatix DMP 2831 printer specifications was utilized. After printing the silver grids, the samples were sintered at 175°C for 15 minutes to make them conductive. The conductivity was found to be 4.27E-8 Ohm meter which is one order of magnitude lower than bulk silver.

Then anodes were fabricated where Ag grid was sandwiched between spin coated ITO layers or spin coated PEDOT:PSS layers. PEDOT:PSS has been demonstrated to be an efficient anodes for OLEDs [63]. When the Ag grid was incorporated between PEDOT:PSS layers, the sheet resistance was found to be dependent on the grid size. The lowest sheet resistance of 5 Ohms/sq was obtained when grid size was set at 500 microns which is two order of magnitude improvement on just PEDOT:PSS sheet resistances. The added benefit of the PEDOT:PSS/Ag grid/PEDOT:PSS anode is that the maximum temperature the samples had been subjected to was 175°C which would be compatible with flexible substrate.

Anodes with silver grids sandwiched between spun on ITO layers were fabricated. The ITO layers which were treated with conventional oven baking had high sheet resistance (~ 50 Ohms/sq) while those which were treated with RTA showed much lower sheet resistance (~ 10 Ohms/sq).
In the previous chapters the fabrication of solution processed anodes were discussed. In this chapter optimization of the organic stack will be studied. The commercially available ITO coated glass is used as the substrate. Organic layer typically comprises of an emitting layer sandwiched between an anode and a cathode. However to enhance hole injection which is one of the limiting factors for OLED performance, a hole injecting layer is used in between the emitting layer and the anode. PEDOT:PSS is one of the most common hole injecting layer because of its high optical transmission, stability and is inexpensive. MEH:PPV is one of the most frequently used emitting material and has been thoroughly researched. The devices are fabricated using the aforementioned organic materials.

**6.1 Single Layered Devices**

The devices were fabricated comprising of ITO coated glass acting as anode, MEH:PPV as the emitting layer and thermally evaporated Aluminum as the cathode.

![Energy Diagram of ITO/MEH:PPV/Al devices](image.png)

**Figure 6-1: Energy Diagram of ITO/MEH:PPV/Al devices**
MEH-PPV is among the most common emitting layer used in the fabrication of OLED because of its ease of processing. Since it can be obtained in solution form, spin coating is an effective and economic technique for film formation. Thickness of the emitting layer is one of the most important process parameter which needs to be optimized for fabrication of efficient OLEDs. In the next section devices were fabricated having different thicknesses of MEH-PPV.

6.1.1 Optimization of MEH-PPV layer thickness

Devices were fabricated having the structure ITO/MEH-PPV/Al. MEH-PPV was spin coated on cleaned ITO coated glass and Aluminum was thermally evaporated on top of MEH-PPV. The spin rate of MEH-PPV was kept constant at 1000 rpm which gave a film thickness of 45 nm as observed by the profilometer measurement. To achieve different thicknesses, the number of layers was varied from one to three. After spin coating each layer, the samples were heated at 125˚C for 5 minutes to evaporate the solvent. After achieving the required thicknesses, 300 nm of Aluminum was deposited at 10⁻⁶ Torr pressure to act as cathode.

After the fabrication of the devices, the electrical performance of the devices was measured using a semiconductor parameter analyzer. The obtained current density-voltage characteristics is shown in the following figure. As can be observed, the 45 nm thick MEH-PPV device reached maximum current density at lower voltages compared to 90 nm and 135 nm thick devices. It was because thinner devices require lower voltages to reach the same electric field magnitudes required to drive current. Similarly the thicker 135 nm device required maximum voltage to reach the same current densities.
Figure 6-2: Current density - voltage characteristics of ITO/MEH-PPV/Al devices with varying MEH-PPV thicknesses

Since current density is inversely proportional to the device thickness, it was expected that for same voltage bias, current density would be lower in the thicker. The experimental data is curve fitted to the following equation to extract the mobility, L and hole trap density parameters.

\[
J = q^{1-1} \mu N_v \left( \frac{2^{l+1}}{l+1} \right)^{l+1} \left( \frac{1}{l+1} \cdot \frac{\varepsilon}{H_b} \right)^{l} \cdot \frac{V^{l+1}}{d^{2l+1}}
\]  

(6.1)
Figure 6-3: Curve fitting of MEH-PPV based diodes

For curve fitting purposes it was assumed that the density of state (N_v) was constant at $10^{19}$ cm$^3$. The mobility value agreed quite well with reported literature [33].

<table>
<thead>
<tr>
<th>Device thickness (nm)</th>
<th>L</th>
<th>Mobility (cm$^2$/V s)</th>
<th>Hole trap density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>5.73</td>
<td>2.02E-05</td>
<td>2.38E18</td>
</tr>
<tr>
<td>90</td>
<td>5.75</td>
<td>2.81E-5</td>
<td>9.19E17</td>
</tr>
<tr>
<td>135</td>
<td>5.19</td>
<td>2.80E-5</td>
<td>4.75E17</td>
</tr>
</tbody>
</table>

Table 6-1: Parameter values obtained from curve fitting of MEH-PPV based devices

Following the electrical characterization, the light emission from the devices was measured. It is expected that since the highest current densities are the same in all the devices, the maximum optical power will also be the same. And this is exactly what is seen in the following figures. The optical powers were same for all the devices but they occurred at different voltages since their thicknesses varied which in turn affected their electric field. Also at higher voltages, there was substantial decrease in luminance. This
was because of the fact that at high voltages, due to very high current densities, resistive heating occurred which caused oxidation of the organic polymer and hence resulted in device degradation.

![Graph showing optical power as a function of applied bias.](image)

**Figure 6-4:** Optical power as a function of applied bias. Arbitrary unit corresponds to counts of CCD detector.

As can be observed from the figure 6-5, the light output is most efficient for devices of 90 nm thickness since they required lower current densities compared to the 45 nm and 135 nm devices to achieve same level of optical power. This can be explained by the principle that below a certain thickness, the hole electron pair recombination was not optimal since there was not enough width of emitting layer thickness. As a result there was not enough charge carrier recombination and hence lower light emission. However for thicknesses above 100 nm although now there was enough space for charge recombination, the photons had to travel longer distances to escape the devices. This resulted in loss of optical power due to re absorption of emitted photons and also due to
interference between the source and the virtual image formed by the cathode which acted as a mirror [65].

![Graph showing optical power as a function of current density.](image)

**Figure 6-5**: Optical power as a function of current density. Arbitrary unit corresponds to counts of CCD detector.

### 6.1.2 Effect of Rapid thermal annealing

After optimizing the thickness of MEH-PPV layer, rapid thermal annealing was performed to observe its effect on device efficiencies. After the spin coating of MEH-PPV layer, the samples were subjected to RTA at different temperatures (150°C, 175°C and 200°C). One of the samples acted as control and was not subjected to RTA. As can be seen from the current density and voltage characteristics there was no change in forward bias regime. However when the reverse bias regime was studied, it was seen that the leakage current is maximum in case of samples annealed at 200°C. Since leakage current does not contribute to light emission, a higher leakage current will degrade the devices quickly since it would result in unnecessary heating effect. It is
important to note that samples annealed at 150°C and 175°C showed lower leakage current which in turn pointed to the fact that these devices would not suffer from heating effects as much as the un annealed and the sample annealed at 200°C.

Figure 6-6: Current density Voltage characteristics of devices subjected to RTA

Figure 6-7 depicts the optical power as a function of applied voltage. As can be observed the optical power did not vary much with annealing. There was not much difference in optical powers between the annealed samples and the control.
Optical power as a function of current densities is shown in the below figure. Compared to un annealed samples the annealed samples could handle the higher current densities better and did not get burned up quickly. This could be attributed to the fact that leakage current in annealed samples was lower compared to un annealed samples and hence the heating rate of the devices was slower. Hence they were optically active at higher current densities.
Figure 6-8: Optical power as a function of Current density of devices subjected to RTA. Arbitrary unit corresponds to counts of CCD detector.

6.2 Double Layered Devices

Single layered devices suffered from a high carrier injection barrier between ITO and MEH:PPV which limited carrier conduction. To decrease the hole injection barrier, PEDOT:PSS was utilized which enhanced hole injection and transport. Figure 6-9 shows the energy diagram of the device.

Figure 6-9: Energy diagram of ITO/PEDOT:PSS/MEH:PPV/Al Devices
6.2.1 Post MEH-PPV Rapid Thermal Annealing

In this set of experiment, RTA was performed after spin coating 90 nm of MEH-PPV on top of the PEDOT:PSS layer. The current density voltage characteristics are shown in the following figure. It can be observed that the current densities of devices annealed at 150°C and 175°C were higher compared to that of unannealed samples at higher voltages in forward bias regime. Also an interesting point is the fact that under reverse bias condition, samples heated at 200°C show higher leakage current compared to the other samples. As the leakage current plays no role whatsoever in light emission, this suggests annealing at 200°C results in degradation in MEH-PPV layer. Also compared to the ITO/MEH-PPV/Al structure, these devices had reverse bias current densities almost two orders of magnitude lower. This indicates that these devices would not suffer from heating effects as much as the previous set of devices.

![Current density vs Voltage graph](image)

**Figure 6-10: Post MEH:PPV Rapid Thermal Annealing of PEDOT:PSS/ MEH-PPV based devices**
The experimental data was fitted to equation (6.1) to obtain the L, mobility and hole trap density parameters under the assumption that density of states is constant at $10^{19} \text{ cm}^{-3}$. The values are listed in the following table. It can be observed that the mobility remains constant in annealed and unannealed samples but the L value which represents the slope of the line is 11% higher for 150°C sample compared to the unannealed samples. This suggest that RTA at 150°C resulted in better carrier conduction.

<table>
<thead>
<tr>
<th>RTA Temperature (°C)</th>
<th>L</th>
<th>Mobility (cm²/V s)</th>
<th>Hole trap density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un</td>
<td>3.39</td>
<td>1.85E-05</td>
<td>1.65E18</td>
</tr>
<tr>
<td>150 °C</td>
<td>3.74</td>
<td>1.67E-05</td>
<td>7.04E18</td>
</tr>
<tr>
<td>175° C</td>
<td>3.53</td>
<td>1.73E-05</td>
<td>2.49E18</td>
</tr>
<tr>
<td>200° C</td>
<td>3.23</td>
<td>1.82E-05</td>
<td>2.04E18</td>
</tr>
</tbody>
</table>

Table 6-2: Parameter values extracted from curve fitting of PEDOT:PSS/MEH:PPV based devices

6.2.2 Pre MEH-PPV Rapid Thermal Annealing

In the following section effect of RTA on just the PEDOT:PSS layer is discussed. The RTA was performed after the spin coating of 100 nm of PEDOT:PSS and prior to spin casting of MEH:PPV. The current density voltage characteristics are outlined in the figure 6-11. In these devices, once again the sample annealed at 150°C showed higher current densities than the control sample at higher voltages like the previous case but the difference is not that prominent. However in reverse bias regime, it was observed that annealed samples showed higher leakage current compared to control sample. Hence annealing after deposition of MEH-PPV gave better set of devices in terms of J-V characteristics.
Figure 6-11: Pre MEH-PPV current density voltage characteristics of devices subjected to RTA before MEH:PPV spin coating

As in the previous section, the experimental data is fitted with the equation (6.1) to calculate the L, hole density and mobility values. It can be observed that the slope value (L) increased till 175°C and then decreased for devices annealed at 200°C. This is in close agreement with groups previous result where degradation of PEDOT:PSS was observed when annealed at 200°C [64]. A consistent decrease in mobility values with increasing annealing temperature was also observed.
<table>
<thead>
<tr>
<th>RTA Temperature (˚C)</th>
<th>L</th>
<th>Mobility (cm²/V s)</th>
<th>Hole trap density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un</td>
<td>3.42</td>
<td>1.87E-05</td>
<td>1.51E18</td>
</tr>
<tr>
<td>150 ˚C</td>
<td>3.59</td>
<td>1.71E-05</td>
<td>1.49E18</td>
</tr>
<tr>
<td>175 ˚C</td>
<td>3.89</td>
<td>1.71E-05</td>
<td>1.52E18</td>
</tr>
<tr>
<td>200 ˚C</td>
<td>3.33</td>
<td>1.68E-05</td>
<td>2.85E18</td>
</tr>
</tbody>
</table>

Table 6-3: Extracted parameter values of devices subjected to RTA after MEH:PPV spin coating

6.2.3 Light emission

The light emission was observed from the post MEH:PPV annealed samples and the obtained optical powers are plotted as a function of voltage in the following figure. It can be observed that the samples annealed at 150˚C perform better compared to other samples.
Figure 6-12: Optical power-voltage characteristics of devices subjected to RTA after MEH:PPV spin coating. Arbitrary unit corresponds to counts of CCD detector.

This was due to the fact that the current densities required to obtain the maximum intensities were attained at lower voltages for 150°C samples due to the steeper increase in current density as confirmed from the above table. Also important to note is the fact that the drop in optical power at higher voltages was more prominent for 150°C samples since it exhibited higher carrier conduction and hence was more prone to the resistive heating effects. The optical power as a function of current density is plotted in the below figure 6-13.
Again the 150˚C samples outperformed the other devices in terms of current efficiencies. The 150˚C samples required lower current densities to reach the same optical power compared to the other samples. Finally at high current densities all devices show lowering of light emission because of the resistive heating effect which degrades the polymers.

6.3 Concluding Remarks

The effects of rapid thermal annealing on the organic layers were investigated in this chapter. Firstly the thicknesses of MEH:PPV was optimized by fabricating devices with different thicknesses sandwiched between ITO and Al which acted as the metal contacts. It was observed that 90 nm thick MEH:PPV performs better than the 45 nm and 135 nm film. MEH:PPV with low thickness although has lower operating voltages,
the current efficiency is lower compared to the 90 nm films. It was because there was less recombination path for the injected electrons and photons thereby resulting in lower recombination. However when the thickness of MEH:PPV layer increases beyond 100nm, the virtual light source due to the cathode interferes which causes loss in optical output [65]. Once the device thickness was optimized, the ITO/MEH:PPV/Al samples were subjected to RTA to investigate its effects on device performances. It was observed that although the forward bias current density remained the same, the reverse bias or the leakage current decreased with increasing annealing temperature initially but at 200°C, the leakage current was higher. This demonstrated some sort of breakdown in the diodes and hence the anneal temperature was kept below 200°C. When the experimentally obtained J-V characteristics were curve fitted to equation (6.1), the resultant parameter values of mobility matched quite closely to that reported in literature [36]. Then devices were fabricated with the addition of hole transport layer PEDOT:PSS to improve hole conductivity. The samples were subjected to RTA after deposition of MEH:PPV and the resultant J-V characteristics showed higher current densities for 150°C and 175°C devices. When RTA was done prior to deposition of MEH:PPV, the devices showed almost identical J-V characteristics except for 200°C devices which showed lower current densities due to breakdown in PEDOT:PSS. This clearly demonstrated that whatever improvement in PEDOT:PSS mobility was observed in ITO/PEDOT:PSS/Al devices were not carried forward when MEH:PPV was incorporated. Finally the light emission was measured with the help of a spectrometer. The luminance was best in case of samples subjected to RTA at 150°C which was supported by the fact that the current density was higher at the same voltage compared to the other samples.

All the devices in this chapter were fabricated with commercial ITO fabricated using sputtering. In the preceding chapters, solution processed ITO and with Ag grid and their conductivities were demonstrated. In the following chapter devices with identical organic stack are fabricated on the solution processed anodes and its device performances are compared to those fabricated in the preceding sections of the current chapter.
7 OLED devices on solution processed anodes

So far the device performances of OLEDs fabricated on ITO coated glass slides available commercially were discussed. However one chief limitations of these ITO coated glass slides in that the deposition process of ITO is expensive. Typically the ITO layer is deposited on substrates using sputtering. Wet solution processed ITO has the added advantage that the same techniques can be used to deposit the organic layers thereby streamlining manufacturing processes. ITO anodes developed using solution processed mechanism for low cost displays has been described in chapter 4 and 5. In chapter 4 it was demonstrated that by subjecting spin coated ITO to rapid thermal annealing, the sheet resistance can be brought down to 57 Ohms/sq. And in chapter 5 by incorporating an Ag grid sandwiched between ITO layers, the sheet resistance was further reduced to 10 Ohm/sq. Using these samples as the starting point, the rest of the organic stack was fabricated and the light emission and current densities were measured. The device configuration essentially remains the same. On top of solution processed anodes, a layer of PEDOT:PSS was spin coated to enhance the hole conduction above which two layers of MEH:PPV was spin coated resulting in thicknesses of 90 nm which acts as emitting layer and finally thermally evaporated Aluminum of thickness 300 nm was deposited at $10^{-6}$ Torr.

7.1 Anodes with conventional annealing

In this section devices featuring anodes without undergoing any rapid thermal annealing are studied. Essentially in these devices ITO has been heated at 200°C using a conventional oven to maintain compatibility with flexible substrates which cannot withstand higher temperatures. The devices fabricated are as follows:
Device A: ITO spin coated twice at 2000 rpm and subjected to annealing on a hot plate at 200°C for 2 hours

Device B: PEDOT:PSS spin coated at 2000 rpm and heated at 125°C on a hot plate

Device C: ITO spin coated twice at 2000 rpm and annealed at 200°C for 3 hours followed by inkjet printing of Ag grid with grid size of 250 micron. Finally top ITO layer is spin coated at 2000rpm and heated at 200°C for 2 more hours

Device D: PEDOT:PSS is spin coated at 2000 rpm and heated at 125°C for 5 minutes followed by inkjet printing of Ag grid with grid size of 250 micron. Finally top PEDOT:PSS layer is spin coated at 2000 rpm and heated at 125°C for 5 minutes.

The organic stack in all the layers is essentially same. On top of each of the anodes, PEDOT:PSS is spin coated at 2000 rpm followed by a soft bake at 125°C for 5 minutes. Then two layers of MEH:PPV is spin coated at 1000 rpm to form a 90 nm film and soft baked at 125°C. Finally the Aluminum contact is thermally evaporated to form a 300 nm aluminum pad of 500 micron by 500 micron size.

The resultant current density as a function of voltage is plotted in figure 7-1
It can be observed that incorporation of Ag grid increases the current density by almost 3 orders of magnitude. Device A performs the worst since the ITO has very high sheet resistances. On incorporating the solver grid its current density increases but no light emission is observed. PEDOT:PSS based devices perform slightly better although device D shows very high leakage current which might be due to the fact that there is short circuit in the devices due to exposed Ag grid not conformably covered by PEDOT:PSS layers.
<table>
<thead>
<tr>
<th>Device</th>
<th>L</th>
<th>Mobility (cm²/V s)</th>
<th>Hole trap density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/Ag/ITO</td>
<td>2.91</td>
<td>2.17E-05</td>
<td>1.56E18</td>
</tr>
<tr>
<td>PEDOT/Ag/PEDOT</td>
<td>0.91</td>
<td>4.31E-05</td>
<td>1.10E19</td>
</tr>
<tr>
<td>PEDOT</td>
<td>1.92</td>
<td>3.13E-05</td>
<td>3.41E19</td>
</tr>
<tr>
<td>ITO</td>
<td>2.5</td>
<td>3.66E-05</td>
<td>2.62E19</td>
</tr>
</tbody>
</table>

Table 7-1: Parameter values obtained from curve fitting J-V Characteristics

The mobility values shown in above table closely resemble those of devices developed in previous chapter based on commercial ITO anodes. However the L value which closely relates to the slope of the curves is lower compared to the commercial ITO based devices which were around 3.3. This reveals that the current density does not increase as rapidly as the commercial ITO based devices with increasing voltage. This is expected since the anodes have high sheet resistances.

Except for Device D, none of the other devices showed any detectable light emission. Even device D shows very weak light emission and at very high voltages. From this experiment it is clear that in order to fabricate better devices, the ITO layer has to be subjected to rapid thermal annealing to lower the initial sheet resistance. Only then can the devices have acceptable current density and light emission.
Figure 7-2: Light emission as a function of voltage applied. Arbitrary unit corresponds to counts of CCD detector.

7.2 ITO Anodes with RTA

ITO anodes are developed on a glass substrate by spin coating ITO nano-suspensions at various rates and subjecting them to rapid thermal annealing. As it was observed that rapid thermal annealing at 450°C gives us the lowest sheet resistance which is an essential criterion for good device performances, all devices were subjected to RTA at the aforementioned temperatures.

In this section devices developed at different spin rates to investigate the effect of ITO thickness on device performance is elucidated. A higher spin rate ensures smoother surface morphologies and higher optical transmission however at the price of higher sheet resistance. The set of devices fabricated have the following anodes:

Device 1: ITO spin coated at 2000 rpm
Device 2: ITO spin coated at 6000 rpm

Device 3: ITO spin coated at 2000 rpm twice

Device 4: ITO spin coated at 6000 rpm twice

All the devices were then subjected to rapid thermal annealing at 450°C for 5 minutes with temperature ramp rate of 25°C/sec. The sheet resistance and thickness of the spin coated ITO anodes are listed on the table below along with that of commercial ITO for reference.

<table>
<thead>
<tr>
<th>Device</th>
<th>Sheet Resistance (Ohms sq⁻¹)</th>
<th>Thickness (microns)</th>
<th>Resistivity (Ohms cm)</th>
<th>Transmission at 580nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO-2000</td>
<td>220</td>
<td>1.2</td>
<td>2.64E-2</td>
<td>0.57</td>
</tr>
<tr>
<td>ITO-6000</td>
<td>765</td>
<td>0.75</td>
<td>5.73E-2</td>
<td>0.91</td>
</tr>
<tr>
<td>ITO-2000+2000</td>
<td>57</td>
<td>2.4</td>
<td>1.36E-2</td>
<td>0.48</td>
</tr>
<tr>
<td>ITO-6000+6000</td>
<td>335</td>
<td>1.5</td>
<td>5.02E-2</td>
<td>0.87</td>
</tr>
<tr>
<td>ITO commercial</td>
<td>10</td>
<td>0.20</td>
<td>2.00E-4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 7-2: Sheet resistance and thicknesses of spin coated ITO anodes

Following the RTA, PEDOT:PSS was spin coated at 2000 rpm followed by soft baking at 125°C followed by twice spin coating of MEH:PPV at 1000 rpm resulting in the formation of 90 nm film. Another soft bake was done at 125°C to evaporate out the solvent. Finally the 300 nm of aluminum was thermally evaporated at 10⁻⁶ Torr to act as cathode.

The obtained current density-voltage characteristics are shown in the following figure.
Figure 7-3: Current density as a function of applied voltage for ITO with different thicknesses. (2000/2000 rpm implies twice spin coated ITO at 2000 rpm)

The reverse biased leakage current for all the devices are same which leads to the conclusion that thickness of anode does not affect the leakage current. It can also be noticed that the current density peaks at different voltages for the devices. In thicker anodes which have lower sheet resistance, the current density peaks are observed at lower voltages. This is because of the fact that lower sheet resistance facilitates better carrier injection to the organic layers and lower voltage bias is required to attain high current densities.
<table>
<thead>
<tr>
<th>Device (rpm)</th>
<th>L</th>
<th>Mobility (cm$^2$/V s)</th>
<th>Hole trap density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO-2000</td>
<td>3.48</td>
<td>1.60E-05</td>
<td>1.34E18</td>
</tr>
<tr>
<td>ITO-6000</td>
<td>3.31</td>
<td>1.67E-05</td>
<td>3.05E18</td>
</tr>
<tr>
<td>ITO-2000/2000</td>
<td>4.56</td>
<td>1.55E-05</td>
<td>6.80E17</td>
</tr>
<tr>
<td>ITO-6000/6000</td>
<td>3.79</td>
<td>1.91E-05</td>
<td>1.69E18</td>
</tr>
</tbody>
</table>

**Table 7-3: Parameter values obtained from curve fitting J-V Characteristics**

In these devices, the L values which reveals how fast current density increases with applied bias are quite similar to those obtained with commercial ITO devices. Since rapid thermal annealing decreases sheet resistance and thus makes the anode better carrier injector to the organic layers.

The devices are then characterized in terms of light emission as a function of applied bias. The following graph demonstrates the obtained results. As expected the devices which reach higher current densities at lower bias yields higher optical power at lower voltages. The twice coated ITO at 2000 rpm achieves peak optical power at 9 volts compared to the device with a single spin at 6000 rpm which has its peak at 18 volts. Also the peak power of each device decreases with increasing surface resistances. Another important observation is the fact that the twice spin coated at 2000 rpm samples show light emission almost twice as high as the devices fabricated on commercial ITO. This is even more startling because of the fact that the solution processed ITO anodes have much lower optical transmission. This can be attributed to the fact that sputtered ITO has very smooth surface compared to solution processed ITO which have slightly granular surface. Thus there is more area in contact with the PEDOT:PSS which improves carrier injection and hence leading to higher carrier recombination.
Figure 7-4: Optical power as a function of Voltage for different ITO thicknesses. Arbitrary unit corresponds to counts of CCD detector. (2000/2000 rpm implies twice spin coated ITO at 2000 rpm).

7.3 Devices on ITO/Ag grid/ITO Anodes

The efficacy of incorporation an Ag grid in between the two layers of spin coated ITO is discussed in this section. The devices are fabricated in the following manner. Firstly a layer of ITO is spin coated on glass slide followed by rapid thermal annealing at 450°C. Then a silver grid is inkjet printed on top of the ITO layer using the Xerox ink. The grid size is kept constant at 250 microns while the drop spacing is 25 microns. After patterning the grid, the samples are heated on a hot plate at 175°C for 15 minutes to sinter the silver nanoparticles to form conductive pathways. Finally the top ITO layer is coated at 2000 rpm followed by rapid thermal annealing at 450°C. The organic layers are deposited in the same way as discussed in the previous section.
The devices are tested and compared with spin coated ITO only anode devices in terms of current densities and optical power. The above figure plots current densities as a function of applied bias. It can be clearly observed that leakage current is almost two orders of magnitude lower in case of ITO/Ag/ITO anodes compared to ITO only devices. On the forward bias side, the ITO/Ag/ITO devices closely mimic the ITO only devices although it attains a higher current density at slightly lower bias voltages.

<table>
<thead>
<tr>
<th>Device</th>
<th>L</th>
<th>Mobility (cm²/V s)</th>
<th>Hole trap density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>4.56</td>
<td>1.55E-05</td>
<td>6.8E17</td>
</tr>
<tr>
<td>ITO/Ag/ITO</td>
<td>4.78</td>
<td>1.71E-05</td>
<td>6.9E17</td>
</tr>
</tbody>
</table>

Table 7-4: Parameter values obtained from curve fitting J-V Characteristics
The optical power is plotted as a function of applied bias and is shown in the following figure. As can be expected devices which have Ag grid in between the ITO layers show higher optical power compared to only ITO devices. It can be explained by the fact that since silver is a better conductor of charge carriers compared to ITO, the carrier density injected into the organic layers is higher compared to that of ITO only anodes.

Figure 7-6: Optical power as a function of applied bias. Arbitrary unit corresponds to counts of CCD detector.

As higher current densities are observed at lower voltages, the number of electron holes recombination occurring in the organic media also increases and thus the increased optical power. However the peak power is still higher in case of ITO albeit at higher voltages. This might be due to the fact that optical transmission in ITO/Ag Grid/ITO structure is lower compared to ITO only anodes.
On analyzing the light emission as a function of current densities, it can be observed that only ITO devices have better efficiencies compared to ITO/Ag/ITO anodes. The ITO/Ag/ITO anodes have the opaque silver grid lines which lower the optical transmission and decrease the current efficiency of the devices.

### 7.4 Concluding Remarks

The devices fabricated on solution processed anodes were discussed in this chapter. To keep the fabrication process compatible with low temperature threshold flexible substrate, RTA was avoided in the first set of experiments. The devices were fabricated with ITO/Ag Grid/ITO, PEDOT:PSS/Ag Grid/PEDOT:PSS anodes along with only ITO and PEDOT:PSS anodes. The spin on ITO was subjected to 200°C heat treatment in a conventional oven. However the electrical measurements revealed that current densities were much lower compared to the devices on commercial ITO. This was...
expected since sintering ITO at 200°C does not decrease sheet resistance adequately. Only the PEDOT:PSS /Ag Grid/PEDOT:PSS devices have high enough current density to have light emission at high voltages (20V). It was obvious that RTA on ITO was required to improve the current injection into the organic media in order to have light emission. So the second sets of devices were fabricated on ITO with different thicknesses which had been subjected to RTA. The current densities improved drastically by almost three order of magnitudes. The devices with thicker ITO reached the same current densities at lower voltages compared to devices with less thick ITO. It was because the thicker ITO provided more conductive pathways for the charge carriers and hence efficiently injected current into PEDOT:PSS. Finally anodes with the Ag grid sandwiched between ITO were used to fabricate the PLEDs. Although utilizing the Ag grid improved current density in forward bias, there was a huge decline in reverse bias or leakage current. Hence the diode characteristics are much better for devices with Ag grid although the reasons for such behavior are still unknown. The light emission was observed for devices with Ag grid. The current efficiency was still better in case of ITO only devices since the certain amount of light was lost due to opaque silver lines.
8 Conclusion

8.1 Summary

The advent of organic media in the optoelectronic devices has stirred a lot of interest in recent years. One of the most promising areas for the application of the organic compounds is in the field of display technologies. OLEDs have advantages over competitive display technologies such as LCDs and Plasma owing to the fact that their fabrication processes are compatible with roll to roll manufacturing, low power consumption and ability to be incorporated in flexible displays on account of its thin and light nature. However one of the reasons why OLEDs have not caught up with the commercial successes of the other display technologies is because of their high cost. Although the organic media are very sensitive to the atmospheric oxygen and moisture, they can be developed by solution processing techniques to fabricate low cost devices where performance criteria are not stringent. Furthermore for development of flexible displays using compatible roll to roll manufacturing, it is imperative that an alternative be found to the sputtered process for deposition of ITO. Sputtering although provides very good quality of ITO films in terms of smooth surface morphology, conductivity and optical transmission, it complicates manufacturing processes opposed to wet processing techniques where the same equipments can be used to deposit anode and the organic polymers. In this thesis, anodes developed by spin coating of ITO nano suspension and incorporating Ag grid fabricated by inkjet printing of Ag nano suspensions have been studied in detail. The effects of rapid thermal annealing on the organic media to see if there is any improvement in device performances were also investigated. Finally the device performance of devices fabricated on the solution processed anodes was analyzed and the results were compared with the devices fabricated on traditional ITO coated glass.
The first part of the thesis focused on obtaining solution processed anodes with sheet resistance comparable to that of commercially available ITO (4-10 Ohms/sq). In order to achieve this goal ITO nanosuspensions and silver nano suspensions were fabricated in Faculty of Forestry. ITO thin films were obtained by spin coating the ITO nanosuspensions on a cleaned glass substrate. In order to form conductive pathway in the ITO films, it is imperative to subject them to thermal treatment so that the solvents can evaporate and ITO nanoparticles in the film can coalesce. Finally the sheet resistance and the optical transmission were characterized. The films were first heated on a hot plate at 200˚C in order to be compatible with processing on flexible substrates. It was observed that after heating the samples for 2 hours the sheet resistance was 8118 Ohm/sq which is 3 orders of magnitude higher than that of commercial ITO. So the samples were further heated to 400˚C and the resultant sheet resistance was 452 Ohms/sq which is still two orders of magnitude higher than commercial ITO. It was apparent that conventional heat treatment was not the way forward for sintering of spin cast ITO films. So the effects rapid thermal annealing was investigated on the ITO films. Rapid thermal annealing differs from conventional oven annealing process in the sense that the process is greatly accelerated. The samples are subjected to high temperatures for a very short time span but the ramp rate is very steep (25˚C/second). One of the advantages of RTA is that since it is done for short time duration, it is compatible with roll to roll processing. When the ITO films were subjected to RTA at 450˚C for 5 minutes, the sheet resistance lowered to 56.4 Ohms/sq which is just one order of magnitude higher than commercial ITO. The optical transmission at 580 nm wavelength was observed to be 0.87 for 750 nm thick ITO layers and 0.48 for 2.4 micron thick ITO layers.

Although the sheet resistance was drastically reduced, such high temperatures are not compatible with flexible substrates which have low temperature thresholds. Hence to lower the sheet resistances, silver nanoparticle films were incorporated in the anodes. But since there is a huge work function mismatch between silver and PEDOT:PSS which would increase barrier for charge injection, an ITO layer was spin coated on top of the Ag layer to reduce the charge injection barrier. The sheet resistance of the entire
stack was measured and the lowest sheet resistance observed was around 0.06 Ohms/sq which is two order of magnitude lower than that of commercial ITO. The SEM images of the stack showed that the top ITO layer smoothened out the rough Ag surface which would improve device performance. However one issue with spin casted silver films was that because of their opaque nature, the optical transmission was very low. So instead of a complete layer, fabricating silver grid structure made more sense. The current conduction will be improved by the opaque silver grids while light can escape the devices through the space between the grids. But in order to print a silver mesh, an additive patterning technique was required. So an inkjet printer in Chemical Engineering Department, University of Toronto was used to print the mesh. Once the driving voltage, substrate temperature and waveform were optimized silver grids were printed. However one of the issues with the ink from Faculty of Forestry was that it showed sever coffee stain effects. Coffee stain effect is described as phenomenon where most of the nano particles are deposited non uniformly. Due to increased rate of evaporation of solvent along the edges of the line, the solvent from the centre of the line moves towards the edges to compensate the evaporation loss. This leads to deposition of all the nano particles along the edges causing non uniformity. Due to the non uniformity, the conductivity of the lines was very low. Therefore a commercial ink from Xerox was purchased and used to fabricate the grid structure. The sintering condition for the commercial ink was heating on a hot plate at 175°C for 15 minutes. Utilizing the grid spacing of 250 microns, the sheet resistance of the ITO/Ag mesh/ITO structure was decreased to 27 Ohm/sq for the devices where ITO was subjected to conventional annealing and to 7 Ohm/sq for the devices where ITO was subjected to RTA at 450°C.
After obtaining anodes with respectable performance criteria, attention was focused on the organic media. MEH-PPV which was selected to the emissive layer was optimized in terms of thicknesses. Most efficient devices were obtained for thicknesses of 90 nm. The MEH-PPV based devices were also subjected to rapid thermal annealing at 150°C, 175°C and 200°C to investigate its effect. The forward bias J-V characteristics were identical but the reverse bias current was minimum in case of devices annealed at 150°C and 175°C. The luminance was characterized for devices subjected to RTA at different temperatures. It was observed that the un-annealed samples had higher luminance at lower voltages while samples annealed at 150°C showed higher luminance at higher voltages. With the introduction of PEDOT:PSS layer, it was observed that the current density required for the same luminance decreased by an order of magnitude compared to MEH-PPV only devices due to better hole injection into
the emissive layer. There was a marked increase in luminance for samples annealed at 150°C compared to other devices. Till this point all the OLEDs were fabricated on commercial ITO. So now attention was focused on OLEDs fabricated on the solution processed anodes. The ITO samples which had not been subjected to RTA had current density one magnitude lower than the one developed on commercial ITO. As a result no luminance was observed with these devices. However the OLEDs fabricated on RTA annealed ITO showed better device performance to those of the commercial ITO. The ITO only devices and ITO/Ag/ITO devices had lower current densities and required lower operating voltages to obtain the same luminance thereby improving current efficiency. The devices fabricate on solution processed ITO had optical powers almost twice to that of devices fabricated on commercial ITO. This despite the fact that the optical transmission of solution processed anodes is less than 0.5 at 580nm. The solution processed anodes reached their peak optical powers at lower voltages compared to commercial ITO devices. Since these devices have higher current densities compared to commercial ITO devices, they get burnt out quickly due to the heating effect of excessive charge carriers.
Figure 8-2: Comparison of Optical power verses voltage for different fabricated devices. Arbitrary unit corresponds to counts of CCD detector.

On analyzing the optical power as a function of luminance shown in figure 8-3, it can be clearly observed that solution processed anodes outperform the devices fabricated on conventional sputtered ITO anodes. The luminous efficiency of solution processed ITO only devices is 0.048 cd/A while that of commercial sputtered ITO based devices hovers around 0.024 cd/A.
Figure 8-3: Comparison of Optical power verses current density for different fabricated devices. Arbitrary unit corresponds to counts of CCD detector.

8.2 Future work

This work clearly demonstrates that solution processed anodes can perform just as well as commercial sputtered ITO. Devices can now be manufactured on flexible substrates using roll to roll manufacturing processes since all the fabrication steps are compatible with it. These devices will have much lower manufacturing cost enabling low priced OLED display products. Although the result show that devices with solution processed anodes have same luminance at lower current densities similar to commercial ITO based devices, the ITO in the anodes had to be subjected to temperatures of 450°C.
Flexible anodes cannot withstand such high temperatures. Hence some other route has to be figured out to lower the sheet resistances at lower sintering temperatures. This might be possible by increasing ITO concentration. Once this obstacle is overcome, devices can be fabricated on flexible substrates.

Another alternative technique to lower processing temperatures would involve application of a more conductive PEDOT:PSS as a substitute for ITO in the anode structure. In the thesis devices fabricated with PEDOT:PSS/Ag grid/PEDOT:PSS did not work out as good as solution processed ITO. It might be because of the fact that there is a high barrier to carrier injection due to work function mismatch. This problem could be offset to an extent by using more conductive PEDOT:PSS. Since PEDOT:PSS does not require high sintering temperatures, such anodes would be compatible to flexible substrates. This will usher in the era of flexible OLED devices which can revolutionize the electronic world.

Another technique to improve optical transmission will be to use just the silver grid instead of the ITO/Ag/ITO structure. Although the work function match between PEDOT:PSS and Ag grids is high, the improvement in the current spreading from incorporating the silver grid might offset the work function mismatch.

Another area of improvement could be the use of inkjet printing for the deposition of organic layers. This will require careful consideration to the viscosity and surface tension of the MEH:PPV and PEDOT:PSS solvents so as to achieve a better drop formation and jetting profile. Additionally ITO could also be inkjet printed to make the complete anode fabrication process based on inkjet printing.
9 References


