2011

Schottky behavior of organic solar cells with different cathode deposition methods

Laxman Anishetty

The University of Toledo

Follow this and additional works at: http://utdr.utoledo.edu/theses-dissertations

Recommended Citation
http://utdr.utoledo.edu/theses-dissertations/509

This Thesis is brought to you for free and open access by The University of Toledo Digital Repository. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of The University of Toledo Digital Repository. For more information, please see the repository's About page.
A Thesis

entitled

Schottky behavior of organic solar cells with different cathode deposition methods

by

Laxman Anishetty

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of Science Degree in Electrical Engineering

Dr. Rashmi Jha, Committee Chair

Dr. Mansoor Alam, Committee Member

Dr. Vijay Devabhakthuni, Committee Member

Dr. Maria R Coleman, Committee Member

Dr. Patricia R. Komuniecki, Dean
College of Graduate Studies

The University of Toledo
May, 2011
Copyright 2011, Laxman, Anishetty

This document is copyrighted material. Under copyright law, no parts of this document may be reproduced without the expressed permission of the author.
An Abstract of

Schottky behavior of organic solar cells with different cathode deposition methods

By

Laxman Anishetty

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the
Master of Science Degree in Electrical Engineering

May 2011

During the last decade, organic photovoltaic research has attracted attention and power
conversion efficiencies have shown strong growth. This growth has attracted economic
and scientific interest towards organic solar cell. This attention was possible due to the
introduction of new polymer materials, inorganic molecules, sophisticated methods of
fabrication, and improved material technologies. Bulk-Hetero Junction solar cells
achieved 7 % efficiency with the introduction of inorganic small molecules in organic
polymers. Organic solar cells of 12% efficiency are targeted. However, the degradation
of organic semiconductors due to the environment and the effect of cathode deposition
make the organic solar cells inferior to silicon solar cells. In this thesis, the effect of
cathode deposition with various deposition methods was studied.

The Dark Capacitance-Voltage characteristics and Capacitance-Frequency
characteristics Of MEH PPV (Poly (p-phenylene vinylene) (PPV)) Solar cell with
sputtering and thermal evaporation of the aluminum cathode are reported here.
Capacitances are measured at different temperatures using cryogenic testing. Interface state densities and their time constants are calculated and analyzed. The variance of depletion width, interface state densities and time constants with two different processes is discussed here. The observations indicated that rf sputtering deposition of cathode is introduces greater interface densities compared to thermal evaporation devices.
To my grandparents, parents, uncle, family members and friends, who have been ever supportive of me, guiding and encouraging me through my endeavors.
Acknowledgement

I wish to express my deepest gratitude to my advisor Dr. Rashmi Jha for her great support, guidance, financial support and encouragement, without which it would not have been possible to succeed in my research. I would also thank Branden Long, Madhumita Chowdery and Jorhan Ordosgoitti for working with me and helping in analyzing my data. And I would like to thank Jacob Tom for his technical help in my research.

I am also thankful to the E.E.C.S Department for generously supporting my graduate studies. I would like to thank Dr. Maria R. Coleman, Dr. Mansoor Alam and Dr. Vijay Devabhakthuni for serving on my thesis committee. I thank the University of Toledo, my home for the last two years, for providing me with a wonderful life experience.

Special thanks to all my friends for their enthusiastic and generous support through my research study.

Above all, I wish to express my deep appreciation to my family, and friends who with their love and encouragement have made all this possible. Last but not the least, my humble obeisance to my grandparents and parents, with whose blessings I have achieved so much.
Table of contents

Abstract........................................................................................................................................... ii

Table of contents ........................................................................................................................... vii

List of Figures .............................................................................................................................. x

List of Tables............................................................................................................................... xii

1 Introduction.............................................................................................................................. 1

2 Organic Solar Cells ................................................................................................................ 4

  2.1 Solar cell working Principle ......................................................................................... 4

  2.2 Generations of Solar cells............................................................................................ 7

  2.3 Organic solar cell devices............................................................................................ 9

    2.3.1 Basic working Principle .................................................................................... 9

    2.3.2 Single layer devices......................................................................................... 10

    2.3.3 Bilayer Solar cell.............................................................................................. 12

    2.3.4 Bulk Hetero Junction Devices......................................................................... 15

3 Materials, Fabrication and Characterization ...................................................................... 19

  3.1 Materials....................................................................................................................... 19

    3.1.1 Substrates ......................................................................................................... 19

    3.1.2 Silver Epoxy..................................................................................................... 20
4.4 Study of MEH PPV and SI NC blends ............................................................... 52

4.5 Simulation of Grooves....................................................................................... 54

Conclusions and Future Work.................................................................................. 57

References ............................................................................................................... 58

Appendix ................................................................................................................... 60
List of Figures

Figure 2-1  Solar cell working principle [4]............................... 4
Figure 2-2  Solar cell equivalent circuit [6]............................... 5
Figure 2-3  solar cell IV characteristics [4]............................... 6
Figure 2-4  Solar cell efficiency graph [5]............................... 7
Figure 2-5  Single layer solar cell device [9]........................... 10
Figure 2-6  Band diagram of single layer solar cell device a). MIM picture b) schottky . 11
Figure 2-7  schematic diagram Bilayer solar cell device [9]........ 12
Figure 2-8  band diagram of organic material and band diagram of bilayer device [23] .. 13
Figure 2-9  Bulk hetero junction solar cell structure..................... 15
Figure 2-10  schematic diagram of Bulk hetero junction device [17]........ 16
Figure 3-1  Structure of PEDOT PSS 20
Figure 3-2  Chemical structure of MEH PPV ................................ 21
Figure 3-3  Silicon Nano Particles [14]........................................ 23
Figure 3-4  structure of Chloro benzene....................................... 24
Figure 3-5  spin coater................................................................. 27
Figure 3-6  Schematic Illustration of the Spin coating Technique [17]............. 28
Figure 3-7  Sputtering Deposition [25]........................................ 29
Figure 3-8  E beam evaporation [28]............................................ 32
Figure 3-9  Solar cell device ............................................................. 33
Figure 3-10  Device configuration of organic solar cell [30]............ 34
Figure 4-1  Current vs. Voltage characteristics of device after fabrication and annealed sample after exposing to light.............................................. 37
Figure 4- 2 Current vs. Voltage characteristics of device after exposing to light............ 37
Figure 4- 3 Capacitance vs. Voltage characteristics of device without silver epoxy....... 39
Figure 4- 4 Capacitance vs. Voltage characteristics of device with silver epoxy.......... 40
Figure 4- 5 Dark current vs. Voltage characteristics of devices ................................. 41
Figure 4- 6 Capacitance vs. Voltage characteristics of device of sputtered cathode ...... 43
Figure 4- 7 Capacitance vs. Voltage characteristics of device of sputtered cathode ...... 44
Figure 4- 8 Doping Density vs. Depletion width of device with sputtered cathode ...... 46
Figure 4- 9 Doping Density vs. Depletion width of device with evaporated cathode .... 46
Figure 4-10 Capacitance vs. Frequency characteristics of Devices ............................... 48
Figure 4-11 $G_p$ vs. $\omega$ characteristics of two devices .......................................... 50
Figure 4-12 $G_p/\omega$ vs. $\omega$ characteristics of evaporated cathode device at different temperatures ................................................................. 50
Figure 4-13 $G_p/\omega$ vs. $\omega$ characteristics of sputtered cathode device at different temperatures ............................................................................................. 51
Figure 4-14 Capacitance vs. Voltage characteristics of device with active layer MEH PPV and SI NC ........................................................................................................... 52
Figure 4-15 $G_p/\omega$ vs. $\omega$ characteristics of MEH PPV solar cell and MEH PPV- SI NC blend solar cells ........................................................................................................... 53
Figure 4-16 Organic groove solar cells structure ............................................................ 54
Figure 4-17 Ray tracing of the groove solar cells ......................................................... 55
List of Tables

Table 3. 1 Properties of PEDOT: PSS......................................................................................... 21
Table 3. 2 Properties of MEH PPV polymer.................................................................................. 22
Table 3. 3 Properties of Chloro Benzene [21]............................................................................. 24
Table 3. 4 Sputtering Process conditions .................................................................................... 30
Chapter 1

1 Introduction

The consumption of energy has been increasing over the years. Traditionally energy is supplied from fossil fuels and nuclear energy. These energy sources are limited and will have serious scarcity in future generations. Renewable energy sources will play a key role in supplying electricity to future generations. Biomass energy, geothermal energy, wind energy and solar energy are the main renewable energy sources utilized today. The sun is the most sustainable and reliable energy source. This resource makes photovoltaic devices an obvious candidate for energy consumption. Furthermore, this method of energy conversion has environmental benefits. The amount of energy received by earth per day is very large and 1000 times greater than the world’s energy needs. However, only a small percentage of the energy is being utilized for world energy needs. This difference leads to efforts to improve existing technologies.

Photovoltaic cells harvest solar energy from the sun and convert it into electrical energy. The conversion of energy into electrical energy is an important challenge. Traditionally, the solar cell industry has been dependent on inorganic solar cells. Silicon and CdTe are the main semiconductors employed for the fabrication of inorganic solar
cells. Inorganic silicon solar cells have achieved efficiencies of 25% [1]. But the high cost of silicon solar cells has led to the investigation of low-cost alternative photovoltaic materials and devices.

Many improvements have been taken and new materials for solar cells have been explored over the years. Research has now reached the stage of using organic polymer semiconductors in solar cells. The low cost, mechanical flexibility, large scale fast production and easy modification of properties make organic solar cells a replacement for the high cost inorganic solar cells. However, organic solar cells typically demonstrate much lower efficiency than the Si Solar cells. Furthermore, organic polymer degrades in the environment with prolonged exposure. A cost-effective, low-damaging, and large-area scalable electrodes deposition technique on organic materials is also unknown. In order to overcome these issues, there have been tremendous research efforts in the areas of organic photovoltaic devices [1]. Organic solar cells have been showing strong improvement in device characteristics. This recent development in efficiency and stability of organic solar cells makes them candidates for future generations.

Organic solar cells have attracted much attention due to their low cost and easy fabrication. Bulk-Hetero Junction solar cells achieved 7% efficiency with the introduction of inorganic small molecules in organic polymers [2]. Significant research is going into improving the efficiency of the organic solar cells and also the stability of the devices to atmosphere. The devices should have a larger area for commercial purposes.
The thermal evaporation process is employed in deposition of the cathode for a solar cell. Even though this process is a controllable process, it is not applicable to a large area device fabrication. In most organic solar cells, the sputtering method is not employed for cathode deposition because sputtering damages the polymer layer. Plasma and high energy argon particles may penetrate into the organic polymer layer and also creates defects at the interface [3]. The study of defects and their effects on performance is useful for implementation of the sputtering deposition method. This thesis outline is a study of the influence of RF sputtering and thermal evaporation methods on organic solar cells. Furthermore, it discusses the influence of silicon nano particles with RF sputtering cathode deposition.

The organic solar cells have potential application in power supplies for mobile consumer electronics. Organic solar cells can be used in power supplies for sensor networks. It can also be used in radio frequency tags, laptop computers and iPods.
Chapter 2

2 Organic Solar Cells

2.1 Solar cell working Principle

Photovoltaic devices are designed to convert solar energy into electric energy. By using the right type of semiconducting materials in a photovoltaic device, it can effectively convert the energy. Semiconducting materials creates electrons and holes by absorbing incoming light.

![Figure 2-1 Solar cell working principle](image)

Figure 2-1 Solar cell working principle [4].
A solar cell is a photodiode, which consists of p and n type semiconductors. When these two semiconductors come together, a depletion region is formed. Electron hole pairs are generated in the device when light is incident on the solar cell. The electron hole pairs generated near to the depletion region in the open circuit condition tend to recombine. This phenomenon leads to a decrease in the depletion region charge and depletion region. This reduction is equivalent to applying forward voltage to the device. Hence, this reduction in depletion width tends to develop a voltage across the terminals of the diode [5]. Maximum voltage can be developed across the terminals after complete elimination of complete depletion region. This is called open circuit voltage. If the device is short circuited, all of the electrons and holes generated will flow through the device. The current generated by the flow of photons is called short circuit current [6].

![Solar cell equivalent circuit](image)

**Figure 2-2 Solar cell equivalent circuit [6].**
The equivalent circuit model of a solar cell is shown in Figure 2-2. \( I_L \) represents short circuit current (current generated by photoelectric effect), \( I_d \) represents current through the diode. Voltage through the shunt resistor \( R_{SH} \) gives the open circuit voltage. Series resistance in the device is represented by \( R_s \). There is a voltage drop across series resistance. Therefore, the maximum voltage across the terminals is less than open circuit voltage across the diode. Under illumination, current flows opposite to the dark current driven by forward bias. Thus, the device operates in the fourth quadrant and makes the product of current and voltage negative. As a result, the device generates power using illumination.

![Solar Cell IV Characteristics](image)

Figure 2-3 solar cell IV characteristics [4].

The basic parameters of a photovoltaic device can be extracted from the graph shown in Figure 2-3. External current is measured as a function of applied external voltage. The
characteristics are plotted inverted about voltage axis. Ideality factor and reverse saturation current of the devices are calculated in dark condition. Short circuit current, open circuit voltage and efficiency are calculated under illumination. The characterization of the cells is discussed in Chapter 3. The cell produces no power at short circuit and open circuit conditions. The cell produces maximum power where the product of I and V is maximum.

2.2 Generations of Solar cells
Solar cells have been classified into three different generations. At present, first generation solar cells are highly represented in commercial productions. Concurrent research is going on in all three generations. Efficiencies of solar cells in different generations are shown in Figure 2-4.

First generation solar cells consist of high quality, large area, and single junction silicon devices. Fabrication of the devices involves high energy and labor costs. First generation solar cells dominate the solar panel market with 86% of the total solar cell market [7]. Despite high manufacturing costs, silicon solar cells dominate the market due to high efficiency compared to other generation devices.

Second generations cells, thin film solar cells, are significantly cheaper than first generation solar cells but have low efficiencies. Thin film solar cells have the advantage of flexibility and light weight over silicon solar cells. Cadmium telluride (CdTe), amorphous silicon, copper indium gallium selenide (CIGS), and micro amorphous silicon are the most successful materials for the second generation solar cells. Thin film solar cells dominate the residential solar market as the new, higher-efficiency cell. A trend towards shifting to thin film solar cells from silicon solar cells is growing.

Third generation solar cells consists of a wide range of innovations including polymer solar cells, dye-sensitized and nano crystalline solar cells. These solar cell technologies are being developed to enhance poor performance of thin film solar cells with low production costs. Still in the research phase, these solar cells are the cutting edge in technology. These solar cells include solar cells that do not need the P-N junction
necessary for first generation solar cells. The organic solar cells are targeted to achieve efficiencies of 12%.

2.3 Organic solar cell devices.

2.3.1 Basic working Principle

The conversion process of light energy to electric current in organic solar cells is accomplished by four sequential steps [8].

1. Absorption of light photon leads to the formation of excited state, the electron-hole pair.
2. Diffusion of exciton to the region where dissociation may occur
3. Dissociation of electron hole pair to form free charges
4. Charge transport of holes and electrons

Light absorption in conjugated polymer excites electrons to a state above band gap. This results in the formation of excitons. In this state, electrons and holes are tightly bonded by columbic attraction forces. The binding energy of excitons is 0.4 ev [23]. These excitons can diffuse through the polymer in the range of 10nm before vanishing. These excitons must be dissociated in order to obtain free charge carriers before they vanish. To break up the excitons, an electric field of energy greater than the binding energy of the electron hole pair is required. Dissociation of excitons at a hetero junction interface can generate free charge carriers. Combinations of acceptor and donor conjugated materials, conjugated material/metal layer and conjugated material/inorganic
particles blend act as good interfaces for efficient dissociation of excitons due to the formation of an electric field at the junction.

2.3.2 Single layer organic solar cell devices

Single layer organic solar cells are the simplest form of organic solar cells. These solar cells are fabricated by sandwiching a layer of conjugated material between two metallic conductors. The basic structure of the device is shown in Figure 2-5. The device consists of a polymer active layer sandwiched between a high work function Indium Tin Oxide (ITO) electrode and a low work function Al or Mg or Ca electrode. The selection of the electrodes determines the characteristics of the solar cell. Work function of the devices is the key parameter in analyzing the device behavior. The difference in the work functions of electrodes creates the electric field to dissociate the excitons. Work function is the energy difference between the vacuum level and Fermi
level of the material. The rectifying behavior of the device is explained by using a MIM (metal insulator metal) picture or schottky barrier as shown in Figure 2-6.

![Figure 2- 6 Band diagram of single layer solar cell device a). MIM picture b) Schottky](image)

When polymer absorbs the light photons, electrons are excited to LUMO (lowest unoccupied molecular orbital) level and leave holes in HOMO (Higher occupied molecular orbital) level. The work function difference between the electrodes sets up an electric field. Band bending occurs at the junction of the schottky barrier formed between the low work function metal and the polymer layer due to the electric field generated by the work function difference. The excitons are dissociated in the depletion region of the schottky barrier.

Single layer organic solar cells demonstrate low efficiencies. These types of cells have quantum efficiencies less than 1% and power conversion efficiencies of less than 0.1% efficiency. These low efficiencies are due to the inefficient dissociation of excitons. The electric field generated between the electrodes is not sufficient to dissociate the
excitons. Frequently, generated holes recombine with the electrons before reaching the electrodes.

2.3.3 Bilayer organic solar cell devices

![Figure 2-7: Schematic diagram of a bilayer solar cell device][9]

A bilayer solar cell includes two different organic layers sandwiched between the two conductive electrodes. Figure 2-7 shows the basic structure of the device. These solar cells are also called as planar-donor-acceptor-hetero junction solar cells. The Donor and acceptor planar interface acts the location for the exciton dissociation. These materials are chosen so that the materials have different ionization potentials and electron affinities. These differences create electrostatic forces at the interface. Donor and acceptor materials are chosen to make the differences large enough, so these electric fields are strong, which
may break up the excitons more efficiently than the single layer devices do. Acceptors have higher electron affinity and ionization potentials than the donor material does.

Figure 2- 8 band diagram of organic material and band diagram of bilayer device [23]

Upon absorption of incoming light by the donor layer, electrons in the donor material are excited from HOMO level to LUMO level and form excitons. If an acceptor molecule is in proximity of this exciton, the excitons can transfer to the LUMO of the acceptor and can be dissociated at the interface. This transfer can occur when the ionization potential \( I_D' \) of excited state of donor satisfies the following non linear equation.

\[
I_D' - A_A - U_C < 0
\]

\( A_A \) = Electron affinity of acceptor material

\( U_C \) = Effective columbic interaction.
The energy diagram shown in Figure 2-8 depicts the maximum voltage that can be obtained from the device. Absorption of photons leads to the excitation to a high energy level whereas the charge separation at the planar interface lowers the energy of the charge carriers gained from the absorption. As shown in Figure 2-8 the maximum energy obtained is the difference between the LUMO level of the acceptor material and the HOMO level of the donor material. This energy difference is often called the effective band gap $E_{g,eff}$ of the planar junction.

Mono molecular transport is the biggest advantage of bi layer devices over single layer devices. After the excitons are dissociated at the heterojunction interface, electrons pass through n type material and holes pass through p type material to the external circuit. Electrons and holes are effectively separated from each other, and hence, carrier recombination is greatly reduced. This recombination only depends on the trap densities. Traps are the vacancies which absorbs the electrons and holes.

The main problem of these heterojunction devices is the short diffusion length of exciton in these materials. The diffusion length of excitons in polymers is in the order of 10nm. For effective dissociation of excitons, the thickness of the layers must be in the same range as this diffusion length. However, the organic material layer needs a minimum thickness of 100nm to absorb enough photons. At 100nm thickness, only a
small percentage of excitons reach the interface junction. Bulk hetero junction devices were designed to address this problem.

### 2.3.4 Bulk Hetero Junction Devices

![Bulk Hetero Junction Solar Cell Structure](image)

Figure 2-9 Bulk hetero junction solar cell structure [9].

In this type of device, electron acceptor and donor materials are mixed together, and forms a polymer blend. If the length of the blend is same as that of the diffusion length of excitons, then most of the generated excitons will reach the donor and acceptor interface. This phenomenon leads to efficient dissociation of excitons. Holes move to the donor domains then are transported through the device and collected by the anode, and electrons are transported in the opposite direction and collected at the cathode. The bulk hetero junction structure is similar to the bi layer structure with respect to donor to acceptor concept, but it has largely increased the interfacial area where exciton dissociates. For transportation of charges, acceptor and donor phases have to form an interpenetrating and bicontinuous network. So the performance of the device is highly dependent upon the nano morphology of the blend.
The excitons created by absorption of photons are everywhere in the bulk. These excitons are in proximity to the interface between the materials. Therefore, efficient dissociation of excitons and charge separation can occur everywhere in the bulk of the hetero junction layer. In Figure 2-10, the energy levels of donors are shown in dark dashed lines and the energy levels of acceptors are shown in light dashed lines. Electrodes have to be chosen such that the work function of one electrode is close to the LUMO level of the acceptor and the other electrode forms good contact with the HOMO level of donor material. And the maximum voltage obtained from the device is the difference of LUMO of acceptor and HOMO of donor.
Generally, bulk hetero junction solar cells can be achieved by co deposition of the acceptor and donor pigments or solution casting of polymer/molecule, polymer/polymer, and molecule/molecule.

Various combinations of acceptor and donor materials have been used as a sandwiched layer in bulk heterojunction solar cells. One of the most significant combinations are fullerene, C60 as acceptor and semiconducting polymer as donor. An important achievement in efficiencies is reached by Shaheen et al. who indicated that the solvent used has a significant effect on the performance of bulk heterojunction solar cells [13]. An efficiency of 2.5% was obtained by optimizing the processing conditions. This 2.5% efficiency has been achieved for BHJ solar cells based on PCBM as acceptor and MDMO PPV as donor material. The best device contains 1:4 (w/w) ratios of MDMO PPV and PCBM. But the absorption spectrum of the MDMO PPV polymer is a poor match to spectra of incident light. MDMO PPV has low carrier mobility values. P3HT has higher carrier mobility values than MDMO PPV polymer. And the absorption spectrum of P3HT is a good match to spectra of incident light [15]. P3HT has been considered as a replacement of MDMO PPV to use with PCBM in BHJ solar cells. P3HT/PCBM solar cells showed great performance compared MDMO PPV/PCBM solar cells. Photovoltaic devices of P3HT/PCBM blend shows power conversion efficiency of 3.85%. These higher efficiencies were achieved by annealing the device after fabrication.
Acceptor materials are also considered for modification. The absorption coefficient of the fullerene, C60 PCBM acceptor is very low in visible region of spectrum. C70 PCBM was used as a substitute for C60 PCBM with the combination of MDMO PPV. This MDMO PPV and C70 PCBM combination shows high efficiency due to the high absorption coefficient of C70 PCBM [15]. However, the lower mobility values, environmental degradation, and processing methods renders further increase in efficiency.

Inorganic particles were introduced in the solar cells for effective electron transportation. Inorganic nanocrystals such as silicon nanocrystals, TiO2 nanocrystals, and ZnO nanocrystals offer several advantages such as high absorption coefficient, high electron mobility, and size tunability [12]. Bulk heterojunction solar cells with organic polymer as donor material and inorganic nanocrystals as acceptor materials deserve deep investigation. The performance of these solar cells can be enhanced by controlling morphology of the blend which is significantly influenced by conditions like blend composition, spin coating speed and type of solvents. Therefore, the investigation of the effect of processing conditions on the fabrication and characterization of hybrid organic solar cells is crucial.

In this work, we investigated the effect of different processing methods on the fabrication and characterization of organic solar cells.
CHAPTER 3

3 Materials, Fabrication and Characterization

This chapter discusses the fabrication of Organic Photovoltaic Devices that were used in my research. The materials used in the fabrication of organic solar cells and their key material properties are discussed. The essential preparation steps required in the fabrication are discussed. The typical characterization methods used in the analysis is also discussed.

3.1 Materials.

3.1.1 Substrates

Indium Tin Oxide (ITO) is commonly used as the substrate for the fabrication of solar cells. Indium tin oxide (ITO) is a composite solid solution of indium oxide (In$_2$O$_3$) and tin oxide (SnO$_2$), typically 90% In$_2$O$_3$, 10% SnO$_2$ by weight [16]. The melting point is 1800–2200 K, and density is 7120–7160 kg/m$^3$ at 293 K. ITO was purchased from Delta technologies Limited. The size of the substrate is 25×25×1.1mm with a sheet resistance of 4-10 ohms. Electrical properties and transparency of ITO are high compared to other conducting oxides. ITO films were deposited on Corning glass by physical vapor
deposition, sputter deposition and the evaporation process. However, ITO is costly compared to other conductive materials.

### 3.1.2 Silver Epoxy

Silver epoxy was used to form high strength conductive bonds from back contact ITO to testing probes. Silver epoxy adhesive adheres to the ITO substrate. Silver epoxy is purchased from MG Chemicals. Silver epoxy gives good electrical conductivity and conductive bonding. The conductive silver epoxy comes in 7g syringes. The mixture of two syringes gives the proper epoxy.

### 3.1.3 PEDOT: PSS

ITO is commonly used as the anode for organic solar cells, but due to its roughness it cannot form good contact with the spin coated polymer. PEDOT: PSS is transparent and highly conductive, and it makes ITO surface smooth. PEDOT: PSS is used to form good contact with the polymers. The work function of the PEDOT PSS is 5.1ev, so it can form ohmic contact with the polymers and it can be act as good hole collecting layer.

![Figure 3-1 Structure of PEDOT PSS](image)

Figure 3-1 Structure of PEDOT PSS
Table 3.1 Properties of PEDOT: PSS

<table>
<thead>
<tr>
<th>Composition</th>
<th>PEDOT content, 0.5 wt. %</th>
<th>PSS content, 0.8 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>1.3 wt % dispersion in H₂O</td>
<td></td>
</tr>
<tr>
<td>Band gap</td>
<td>1.6 ev</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>1 S/cm</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1 g/mL at 25 °C (lit.)</td>
<td></td>
</tr>
</tbody>
</table>

Chemical structure of PEDOT: PSS is shown in Figure 3.1. The mixture of two ionomers PEDOT and PSS gives the polymer mixture. PEDOT [poly (3,4-ethylenedioxythiophene)] is a conjugated polymer that carries positive charge and is based on polythiophene. PSS [poly(styrenesulfonate)] is based on sulfonated polystyrene. Part of sulfonyl groups are deprotonated and carry a negative charge [18]. Table 3.1 shows the characteristics of PEDOT PSS.

### 3.1.4 MEH PPV

![Chemical structure of MEH PPV](image)

Figure 3-2 Chemical structure of MEH PPV
MEH PPV is used as an electron donor material in organic solar cells. MEH PPV is one of the derivative of PPV. Fig 3.2 shows the chemical structure of the MEH PPV polymer. Poly (p-phenylene vinylene) (PPV) is a conducting polymer that has been significantly used in the fabrication of organic electronic devices.

MEH PPV has small optical band gap. This band gap and its fluorescence make MEH PPV to be used in many electronic applications like Photovoltaics and Light emitting diodes. Though MEH PPV is insoluble in water it can be processed using aromatic solvents. MEH PPV is vulnerable to oxygen degradation which is detrimental for OPV (organic photovoltaic) device performance. With presence of a small amount of oxygen, energy is transferred to oxygen molecules from excited polymer molecules and singlet oxygen is formed. Singlet oxygen attacks the structure of the polymer, leading to its degradation [19]. Properties of MEH PPV are shown in Table 3.2 [20]. Nc, Nv are the occupied densities in conduction band and valence band.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap</td>
<td>2.1 ev</td>
</tr>
<tr>
<td>Permittivity</td>
<td>3.0</td>
</tr>
<tr>
<td>Nc</td>
<td>2.5E19 cm⁻³</td>
</tr>
<tr>
<td>Nv</td>
<td>2.5E19 cm⁻³</td>
</tr>
</tbody>
</table>
3.1.5 Silicon Nano Particles

Silicon nanoparticles were used as an acceptor material in hetero junction solar cells. Silicon Nanoparticles of 5nm size were supplied form Meliorum Technologies. Silicon nano particles were blended with MEH PPV and used as the active layer. Nanoparticles of size 5nm diameter were used to form a blend. Nano particles are allotropic form of silicon with paracrystalline structure similar to amorphous silicon. These were fabricated from Bulk silicon by PECVD process. Bulk silicon is an indirect gap semiconductor, which means it is an inefficient source of light. Properly prepared Silicon nanoparticles acts as a direct band gap semiconductor. Figure 3.3 shows the Silicon nanoparticles. It has high electron mobility values.

3.1.6 Chlorobenzene Solvent

Chlorobenzene is an aromatic compound, used as a solvent for the polymers. It is a colorless, flammable liquid and a widely used as an intermediate solvent in the manufacture of other chemicals.
Chloro Benzene structure is shown in fig 3.4. 1wt% of MEH PPV was mixed in Chloro Benzene and the solution is sonicated for uniformity.

<table>
<thead>
<tr>
<th>Table 3. 3 Properties of Chloro Benzene [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Melting Point</td>
</tr>
<tr>
<td>Boiling Point</td>
</tr>
<tr>
<td>Solubility ( water )</td>
</tr>
<tr>
<td>Solubility in solvents</td>
</tr>
</tbody>
</table>

Other aromatic compounds like toluene, chloroform are also used as solvents.

3.1.7 Cathode
The most commonly used cathode for organic solar cells is Aluminum (Al). Aluminum has a work function of 4.3. It forms schottky junction with organic polymers. Titanium,
tungsten and manganese were also used to study the morphology of polymer with sputtering deposition. The metal electrodes used in this project had a circular shape with the area about 0.2 cm².

3.2 Fabrication

The fabrication of planar solar cells were done in 4 steps. (1) Cleaning of substrate, (2) Spin coating of PEDOT PSS, (3) Spin coating of MEH PPV and (4) sputtering Deposition or Thermal evaporation.

3.2.1 Cleaning of Substrate

Preparation of solvents and cleaning of substrates was done in fume hood. ITO coated glass substrate were cleaned with Micro 90 solution. Micro 90 is a cleaning solution used for cleaning of glass substrates. 100ml of deionized water is taken into one cleaned glass container. Few drops of micro 90 solution were added into the glass container. The solution is sonicated for 60min using an Ultra sonicator. Glass container was kept on hot plate after completion of sonication. The solution was heated at 100°C for 20 min. Substrate was taken from the container and cleaned with DI water and heated at 100°C for 2 min. Silver epoxy was put on one corner of the substrate and is allowed to become dry for 1 hour.
3.2.2 Preparation of Polymer solution

MEH PPV was dissolved in the chlorobenzene solvent to form active layer solution. 0.5wt% to 5 wt% of MEH PPV in chlorobenzene was preferred. 100mg of MEH PPV was mixed in 10mg of Chloro Benzene. And the solution was sonicated in Ultra sonicator for 60 min and kept in the refrigerator.

Si Nc and MEH PPV blend was prepared in the Chloro Benzene solvent. 5 mg of silicon Nano particles were mixed with 400mg of 0.5wt% MEH PPV solution. 200mg of the solution was transferred to another container and stored in the refrigerator. And the remaining solution was sonicated in Ultra sonicator for 60 min and kept in the refrigerator. The sonicated solution is assumed to be uniform and the non sonicated solution is assumed to be non uniform.

3.2.3 Spin coating

3.2.3.1 Spin Coating technique

Spin coating technique is widely used for the preparation of organic solar cells. This is the main technique employed for the deposition of organic polymers. This technique is very economical [22] and can form very uniform films.
Figure 3- 5  spin coater

The Figure 3.6 shows the typical spin coater. Laurell WS 400 model spin coater was used. This technique consists of three steps deposition, spin up, and spinoff [23]. Substrate is fixed to the chuck.

The deposition of solution on the substrate was the first step. An excess amount of solution was needed as compared to what remains in the final film. At this step the chuck stays at stand still position. The solution is dispensed to spread all over the surface.

Spin up step is the second step in the process. The chuck is accelerated to a chosen rotational speed in order to spread the fluid by centrifugal force. Excess amount of solution was ejected and uniform amount was present on the stage. This step does not affect the outcome of the thickness from the final step. The third step affects the outcome of the thickness.

The final step spin off is very crucial step in spin coating. In the final step, the chuck is rotated at the constant speed and gradual thing of the film occurs because the liquid flows radially outward and off the substrate. Thickness is obtained depending upon the speed.
3.2.3.2 Coating of PEDOT PSS and MEH PPV

PEDOT PSS serves as a hole collecting layer and makes ITO substrate smooth. PEDOT PSS was spin coated at a constant speed of 2500 rpm for 30sec on the cleaned glass substrate. The substrate was taken from spin coater and heated on a hot plate for 10min at 120°C. Annealing made the PEDOT PSS layer crystalline. After annealing the substrate was cooled for 5 min at room temperature and taken to next step.

MEH PPV or MEH PPV and Si NC blend acts as an active layer. The polymer solution was taken and spin coated on the PEDOT PSS coated sample at a speed of 1500 rpm. The sample was heated on a hot plate at 140°C for 30min [24]. Cathode was deposited using sputtering deposition or thermal evaporation.
3.2.4 Sputtering Deposition Principle

Sputter deposition is a vapor deposition method of depositing thin films by ejecting source target atoms onto the substrate, such as silicon [25]. An important advantage of sputter deposition is that even materials of high melting points can easily be sputtered.

![Figure 3-7 Sputtering Deposition](image)

Targets are usually magnetrons that utilize strong magnetic and electric fields to observe electrons close to the surface of the targets. Sputtering deposition methods are several types. They are ion beam sputtering, reactive sputtering, ion assisted deposition, high power impulse magnetron sputtering (HIPMIS), high target utilization sputtering, and gas flow sputtering [25]. Sputter deposited films have a chemical composition close to that of the source material.

The sputtering deposition process is shown in the Figure 3.8. The first step in RF sputtering is to place the substrate material in the vacuum chamber. Then argon gas is allowed to flow through the chamber and increase the pressure in the vacuum chamber.
An electrical field was created in the chamber by turning on the RF guns. Electrical field intensity depends upon the power set up on the RF guns. The outer shell free electrons are moved by this electrical field out of the gas atoms. These electrons are moved away from the negatively charged target. This leaves the gas atom electrically unbalanced and becomes a positively charged ion [26]. Gas ions are accelerated towards the negatively charged target source. The source material is excited by the arriving ions via energy transfer. And the particles are ejected in the form of neutral particles. These particles are travelled upwards to cot substrate with the neutral ions. The No of gas ions generated increased with an increase in the electrical field. So the deposition rate depends upon the power input given to the RF gun. Aluminum cathode was deposited on top of the organic polymer by using sputtering. The typical parameters used for the process are shown in Table 3.4

<table>
<thead>
<tr>
<th>Table 3. 4 Sputtering Process conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Deposition time</td>
</tr>
<tr>
<td>Height of substrate</td>
</tr>
<tr>
<td>Rotation speed</td>
</tr>
</tbody>
</table>
3.2.5 Evaporation

In evaporation process the substrate was placed inside a vacuum chamber, in which the source material is placed. Source material is heated to a point where it gets evaporated. The molecules were freely evaporated in the vacuum and condensed on the substrate. Vacuum was required to remove the vapors other than source material before evaporation of source material begins. This principle is the same for all evaporation methods [27]. The only thing change in all evaporation methods is the way of heating the source material. There are two widely used evaporation techniques. They are E beam evaporation and resistive evaporation. In resistive evaporation, tungsten boat, containing the target material, is heated electrically by applying high power to evaporate the material. Aluminum is difficult material to be deposited using resistive evaporation, so that E beam evaporation is typically used to deposit aluminum metal on substrate.

In the E Beam evaporation method, source material was bombarded with an electron beam, produced by a charged tungsten filament under high vacuum. These atoms were transformed to gaseous state by electron beam. These atoms condense into solid form, coating everything in the vacuum chamber with the source material.
Figure 3-8 E beam evaporation [28]

The schematic picture of the E beam evaporation is shown in Figure 3.9. The deposition rate in this technique is very high compared to other deposition techniques.

3.2.6 Thickness determination of the active layer

Atomic force microscope was used to measure the thickness of active layer. The thickness of active layer is very crucial in understanding of the behavior of a solar cell. An AFM consists of a cantilever with a sharp tip at its end that is used to scan the surface. When the tip is closely brought to a sample surface, the cantilever is deflected due to the forces generated between the tip and the sample surface. The deflection of cantilever is measured using a laser spot reflected from the top surface of the cantilever [29]. Depending upon the deflection, the height between two layers is measured. AFM can be operated in three different modes, namely contact mode, non contact mode and Tapping mode. Tapping mode was used to find out the thickness of the film.
3.3 Characterization of Devices

The photovoltaic performance and electrical behavior of solar cells can be calculated by recording current as a function of applied voltage under light bias (illumination), which results in an IV-curve. Keithley 4200 Semiconductor characterization system (4200-SCS) was used for the study of solar cells in dark condition. The 4200-SCS is a measurement system that has instruments for both capacitance vs. voltage (C-V) and current vs. voltage (I-V) measurements, as well as software, graphics, and mathematical analysis capability. The software includes tests for making I-V and C-V measurements specifically on solar cells and deriving common PV cell parameters such as short circuit current and open circuit voltages from the test data.

Solar cells were fabricated and soldered on a chip board for probing purpose. A sample mounted on a chip board is shown in Figure 3.10. Samples were probed in Lakeshore cryogenic probe station for Electrical characterization. Probe station was maintained under vacuum pressure of $1 \times 10^{-4}$ m Barr. Dark CV and dark IV s were measured using
a Keithley 4200 Semiconductor Characterization System (SCS) at Room Temperature and for Cryogenic, the testing temperatures are maintained at 100K, 200K, 300K and 400K.

![Device configuration of organic solar cell](image)

Figure 3-10 Device configuration of organic solar cell [30]

The device follows diode equation while characterizing in dark condition.

\[ I = I_S(e^{qV/kT} - 1) \]  \hspace{1cm} \text{Equation (1)}

\( V \) is the applied voltage across the device, \( T \) is the temperature, \( q \) is electron charge, \( k \) is Boltzmann’s constant and \( I_S \) is current due to diode saturation.

And the current under illumination is given by

\[ I = I_S(e^{qV/kT} - 1) - I_L \]  \hspace{1cm} \text{Equation 2}

Where \( I_L \) is current due to photo generation [30].

Several factors determine the efficiency of a solar cell, including the maximum power point (Pmax), the energy conversion efficiency (\( \eta \)), and the fill factor (FF).
Fill factor is the measure of the difference between ideal and actual cells.

\[
FF = \frac{I_{\text{max}} V_{\text{max}}}{I_{\text{sc}} V_{\text{oc}}}
\]

Equation 3

Where \( I_{\text{max}} \) is current at maximum power output, \( V_{\text{max}} \) is voltage at maximum power output, \( I_{\text{sc}} \) is short circuit current and \( V_{\text{oc}} \) is open circuit voltage. These parameters are calculated from the current vs. voltage characteristics under illumination.

Capacitance vs. Voltage and Capacitance vs. Frequency characteristics are measured in the dark condition. Depletion width, doping Density and interface density calculations are shown in the next chapter.
Chapter 4

4. Results and Discussions

In this chapter, results obtained from this project will be discussed. The solar cells that were analyzed in this project were mainly fabricated by RF magnetron sputtering. The effect of high intensity light on the devices and comparison of sputtering and thermal evaporation techniques will be discussed. More than five devices per sample were analyzed in order to achieve the statistically viable results. The sputtering method employed is not the actual method used for fabrication of organic solar cells, so the results are based on statistics from five devices per sample. The active materials were mainly MEH PPV and MEH PPV-SI NC blend and chlorobenzene was used as the solvent. The cathode deposition method had a strong influence on the performance of devices. Therefore, two methods were used in this stage: (1) sputtering, (2) thermal evaporation. Current vs. Voltage, Capacitance vs. Voltage, Capacitance vs. Frequency and interface density characteristics of all type of devices will be discussed.

4.1 Effect of High Intensity Light and Thermal Treatment

Solar cells were exposed to AM 1.5 solar spectrums after fabrication. The effect of high intensity light will be discussed in this section. The samples were annealed at 140 C for 30 min on a hot plate after exposing to light. Annealing is a heat treatment to cause the changes in the properties of the device.
Figure 4-1 Current vs. Voltage characteristics of cathode sputtered device after fabrication and annealed sample after exposing to light.

Figure 4-2 Current vs. Voltage characteristics of cathode sputtered device after exposing to light.
RF magnetron sputtering of aluminum on top of the active layer can damage the top layer of the polymer [31]. Organic polymer generates electrons and holes after exposing to light. Figure 4.1 shows the current vs. voltage characteristics of the device. The saturation current in the reverse bias is in the order of mA. This behavior is similar to leaky diodes. RF sputtering created high energy aluminum ions and plasma ions. These high energy ions collide with the weak bonds of the polymer molecules. These collisions create trap sites at the interface. So the diode has a very leaky characteristics. With high power sputtering there is a greater damage and increase in the interface trap density.

Figure 4.2 shows the current characteristics after exposure to light. The reverse saturation current is very high compared to the actual device. The reverse saturation is 2mA. Where as for the actual device, the reverse saturation current is 0.2mA. This shows the shunting of the device. Electrons and holes are generated in the polymer under illumination. Interface traps act as recombination centers for the generated carriers. After exposing light on the devices the recombination path through the structural defects increases and it causes shunting of the device. MEH PPV polymer lost its effectiveness and crystalline nature. Hence, IV characteristics were not ideal diode characteristics.

The devices were thermally annealed at 140 °C for 30 min and tested. Annealing current characteristics are shown in Figure 4.1. The reverse saturation current is lower than the condition after exposing to light. The forward current in the high voltage region is lower than the actual device. Sputtering damages the crystallinity of polymer which is critical for semiconducting characteristics, whereas annealing helps in building crystalline nature of the polymer. So annealing right after device fabrication improves the
characteristics and makes the device as stable but not as that of the device after fabrication.

4.2 Influence of Silver epoxy

In order to form low resistance contact to the ITO, the polymer layer in the corner is removed by using mechanical scratching. And tip of the probe contacting this corner makes the back contact. But the removal of the polymer layer is not achieved completely, due to inefficiency of the mechanical scratching. This leads to highly resistive contact between the probe tip and ITO.

![Capacitance vs Frequency](image)

Figure 4-3 Capacitance vs. Voltage characteristics of sputtered cathode device without silver epoxy.
Sputtering leads to the low shunt resistance and the ineffective back contact leads to high series resistance. The series resistance measured in the device is $1\text{K}\Omega$-$100\text{K}\Omega$. The Figure 4.3 shows the capacitance characteristics of device without silver epoxy. The device has negative capacitance. This negative capacitance supports the assumption that the contact is not perfect. Before depositing MEH PPV, one corner of the ITO substrate was protected by silver epoxy. This makes it easy to probe the tip on to silver epoxy. Since silver epoxy is conductive, the probe makes ohmic contact with the ITO. The
Figure 4.4 shows capacitance characteristics of device with epoxy. It has positive capacitance and also the series resistance of this device measured to be 100Ω-300Ω.

4.3 Study of Cathode deposition

4.3.1 Device Performance

The space-charge limited conduction (SCLC) model is widely used for the analysis of Organic schottky diodes in forward bias. This model assumes the density of free carriers injected into the active region to be larger than the number of acceptor levels [32]. This model is applicable only in low electric field region.

Figure 4-5 Dark current vs. Voltage characteristics of devices with two different cathode deposition methods.
In a high electric field space charge dies out and current is proportional to the square of the applied electric field. In SCLC model current density is given by

\[ J = \frac{9}{8} \varepsilon \varepsilon_0 \mu p \frac{V^2}{L^3}. \] \hspace{1cm} \text{Equation 4}

\( V \) is applied Voltage, \( L \) is thickness of the film [32].

Current density is inversely proportional to the \( L^3 \).

Dark current characteristics are shown in Figure 4.5. Dark current of the device with sputtered cathode has high reverse current compared to the thermally evaporated cathode.

For the non ideal Schottky diodes the current is given by

\[ I = I_S (e^{qV/nkT} - 1). \] \hspace{1cm} \text{Equation 5}

\( V \) is the applied voltage across the device, \( T \) is the temperature, \( q \) is electron charge and \( k \) is Boltzmann’s constant. \( I_S \) = current due to diode saturation and \( n = \) ideality factor.

For ideal diodes \( n=1 \) and for non ideal diodes \( n>1 \). The voltage barrier in devices is 0.5V from Figure 4.5. Ideality factor for the above devices is calculated using equation 5.

For the sputtered cathode device ideality factor is 17.3 and for the thermally evaporated cathode ideality factor is 13.5. Typical range of ideality factors are lies in 10.5 to 13 [32].

Hence the sputtered cathode device is highly non ideal where as thermally evaporated device is comparatively ideal. Using the SCLC condition and equation 3 the
thickness of the devices are calculated. The sputtered device has active layer thickness of 60 nm whereas the evaporated device has active layer thickness of 100 nm.

### 4.3.2 Capacitance vs. Voltage characteristics

MEH PPV and aluminum contact forms Schottky diode at the interface. MEH PPV polymer region is depleted depending upon applied reverse bias voltage. At some point the entire polymer region is depleted and capacitance stays constant with an increase in reverse bias voltage. This depletion width gives the physical thickness of the polymer.

The capacitance vs. voltage characteristics of the two devices are shown in Figure 4.6 and Figure 4.7.

![Dark Capacitance vs Voltage](image)

Figure 4-6 Capacitance vs. Voltage characteristics of device of evaporated cathode
The capacitance of the diode is given by

\[ C = \varepsilon \varepsilon_0 \frac{A}{d} \] \hspace{1cm} \text{Equation 6}

The area of the Device is \( A=0.2cm^2 \).

\( \varepsilon = 3 \) is the dielectric constant of polymer, \( \varepsilon_0 \) is permittivity of free space.

And depletion width is given by

\[ d = \varepsilon \varepsilon_0 \frac{A}{C} \] \hspace{1cm} \text{Equation 7}

\( C \) is capacitance in the depletion region.

\[ \begin{array}{cccccc}
& & 9.17 \times 10^{-9} & & & \\
& 9.16 \times 10^{-9} & & & & \\
& 9.15 \times 10^{-9} & & & & \\
& 9.14 \times 10^{-9} & & & & \\
& 9.13 \times 10^{-9} & & & & \\
& 9.12 \times 10^{-9} & & & & \\
\end{array} \]

Voltage (V)

\[ \begin{array}{cccccc}
-2 & -1.5 & -1 & -0.5 & 0 & 0.5 & 1 & 1.5 \\
\end{array} \]

Capacitance (F)

Figure 4-7 Capacitance vs. Voltage characteristics of device of sputtered cathode
The capacitance characteristic for the thermally evaporated cathode device is shown in Figure 4.6. The capacitance in the reverse bias condition is $5.32 \times 10^{-9}$ F and the device is completely depleted. Depletion width calculated from the equation 7 is 100nm. The physical thickness of the polymer before deposition of Aluminum is 100nm.

The capacitance characteristic for the sputtered cathode device is shown in Figure 4.7. The capacitance in the reverse bias condition is $9.12 \times 10^{-9}$ F and the device is completely depleted. Depletion width calculated from the equation 7 is 59nm. This capacitance is very high compared to the previous device and this value is not comparable with the physical thickness of the polymer before sputtering. This change in thickness with thermal evaporation is explained by sputtering effect. Aluminum ions are penetrated into the polymer layer during sputtering [3]. Top layer of the polymer consists of a mixture of polymer and aluminum ions and effective thickness of polymer is less compared to the evaporated cathode device.
Doping density of the Schottky diode is given by
\[ N(a) = \frac{2}{q\varepsilon \varepsilon_0 A^2 \left[ \frac{d(\frac{1}{x})}{dx} \right]} \] ............................ Equation 8

Where \( q \) is electron charge, \( \varepsilon \) is the dielectric constant of polymer, \( \varepsilon_0 \) is permittivity of free space. \( A \) is area of the device. \( C \) is measured Capacitance, \( V \) is applied Voltage.

Doping density profiles of devices are shown in Figure 4.8, Figure 4.9. The doping density of sputtered cathode device lies in the range of \( 10^{18} \)-\( 10^{19} \) cm\(^{-3}\), whereas doping density of evaporated device lies in the range of \( 5 \times 10^{17} - 3.5 \times 10^{18} \) cm\(^{-3}\). Sputtered cathode device has high doping density due to the penetration of aluminum ions in to polymer region.
4.3.3 Interface State Density

Capacitance vs. Frequency characteristics of two devices are shown in the Figure 4.10. The capacitance value of the sputtered cathode device is higher than the evaporated cathode device. At frequency of 500 KHz the capacitance values are in the range $9\times 10^{-9}$ F for sputtered device and $5\times 10^{-9}$F for evaporated device. The peaks in Figure 4.10 indicate the presence of defects with small trap time constant ($\tau$). The sputtering device has high peak and three times higher than the evaporated cathode device.

Interface trap Densities are measured using conductance method [33]. This technique is based on measuring the equivalent parallel conductance $G_p$ of capacitor as a function of bias voltage and frequency. Conductance represents the loss mechanism due to the
interface trap capture and emission of captures. The conductance is measured as a function of frequency and plotted as $\frac{Gp}{\omega}$ vs. $\omega$ and is given by

$$\frac{Gp}{\omega} = qD_{it} \frac{\ln(1+(\omega \tau_{it})^2)}{2\omega \tau_{it}}$$  \hspace{1cm} \text{Equation 9}$$

$Gp$ = measured conductance of device

$D_{it}$ = interface state density

$q$ = electron charge

$\omega$ = frequency

$\tau_{it}$ = time constant of traps

$\frac{Gp}{\omega}$ has maximum at $\omega = 1/\tau_{it}$ and at that maximum interface state density is given by

$$D_{it} = \frac{2.5}{q} \left(\frac{Gp}{\omega}\right)_{\text{max}}$$  \hspace{1cm} \text{Equation 10}$$

$\frac{Gp}{\omega}$ Vs. $\omega$ graphs are shown in Figure 4-11. And the plots contain characteristics at three different voltages. Figure 4-11 represents the characteristics of sputtered device and evaporated device. Values of $D_{it}$ for the Sputtered device and evaporated devices are respectively $4.3 \times 10^{11}$ and $1.8 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1}$. The defects density is high for the Sputtered device due to collision of ions with polymer interface.
Figure 4-11 $G_p/\omega$ vs. $\omega$ characteristics of two devices

Figure 4-12 $G_p/\omega$ vs. $\omega$ characteristics of evaporated cathode device at different temperatures
Cryogenic testing is done on the devices at 140K, 200K, and 300K temperatures. Activation energy is calculated from $\tau$ values of the temperatures based on following equation.

$$\tau = 1 / [v_{th}\sigma_p N_A \exp\left(\frac{-q\phi_S}{kT}\right)]$$ ..........................Equation 11

$T$ is the temperature, $v_{th}$, $\sigma_p$ and $N_A$ are constant for two processes [34].

The activation energy ($q\phi_S$) of traps in the sputtered device is -0.07ev and for thermally evaporated device is 0.016ev. This shows the presence of deep level traps in sputtered and thermally evaporated devices.
4.4 Study of MEH PPV and Si NC blends

In this section organic solar cells with active layer of MEH PPV and SiNC blend (1:1) were discussed.

Cathode aluminum was deposited by sputtering method. CV profiling of the devices were done in dark conditions. Active layer forms schottky junction at the aluminum interface. The completely depleted region in the reverse bias gives depletion capacitance. The MEH PPV device has 60nm thickness of MEH PPV polymer when it is spin coated at 1500rpm. The area of the Device is $0.2cm^2$. In the reverse bias, capacitance is almost constant at $1.64 \times 10^{-8}F$. The Dielectric constant of the SiNC blended device is calculated from

Figure 4-14 Capacitance vs. Voltage characteristics of device with active layer MEH PPV and Si NC
equation 7. The Dielectric constant $\varepsilon$ of the SiNC blended polymer is calculated to be 5.55.

![Diagram](image)

Figure 4-15 $G_p/\omega$ vs. $\omega$ characteristics of MEH PPV solar cell and MEH PPV- Si NC blend solar cells.

The Dit values calculated from the equation 10 for the MEH PPV and SiNC blended MEH PPV devices are $3.8\times10^{11}$ and $6.4\times10^{11}$ cm$^{-2}$eV$^{-1}$ respectively. The Figure 4.15 shows the characteristics of three devices MEH PPV, SI NC, SI NC non uniform. SiNC non Uniform is a device whose active layer is assumed to consist of agglomerated SiNC in the MEH PPV polymer. The interface state density in this device is $11.3\times10^{11}$ cm$^{-2}$eV$^{-1}$. This device contains high amount of interface State densities compared to other devices.
4.5 Simulation of Grooves

Organic polymers are vulnerable to the traditional cathode deposition methods. Groove is a structure where polymer solution is poured into a V shaped device.

Figure 4- 16 Organic groove solar cells structure

In the structure shown in Figure 4.16 groove solar cell is V shaped. The walls of the V shaped grooves are the electrodes of the devices, and the base of the groove is the substrate. The active layer polymer (i.e. MEH PPV or pentacene) is poured in to the gap between the walls. The simulation of this device was done by TCAD Simulation software. The models used for the simulation of this device are Carrier continuity equation, exciton dissociation model, recombination model and hopping mobility model. The carrier continuity equation model is used for the transportation of carriers in the
materials without defects.

Organic polymers absorb photons which have energy greater than the band gap of the polymer. These absorbed photons generate exciton. These excitons are dissociated near the metal contacts in the single polymer layer. In case the polymer is mixed with acceptors then excitons are dissociated near the acceptor and donor interface. Once electrons and holes dissociate from the Singlet’s, they experience built-in electric fields. They are then separated and detected at the electrodes. Exciton dissociation model is used to determine the rate of dissociation. Recombination of generated carriers is explained by the Recombination model. The defects transportation is given by the hopping mobility model.

Figure 4- 17 Ray tracing of the groove solar cells
The light is illuminated on normal to the surface of the grooves cell. Light incident on the walls of the cells is reflected and absorbed by the polymer. The light absorption efficiency is high compared to the normal devices. In planar devices, the reflection of light at the contacts is lower than groove solar cells and hence, absorption efficiency is less. However, the fabrication of these cells is complicated compared to traditional organic solar cell devices.
Chapter 5

Conclusions and Future Work

This study indicates the sensitivity of the polymers towards the cathode deposition methods. For the same processing conditions the sputtered device has a smaller effective active layer than the samples with electrode deposited using evaporation. This indicates that high energy ion deposition creates damage at the polymer and cathode interface. Because of this damage, poor schottky characteristics of organic solar cell device were observed. Sputtered devices indicated a high amount of interface densities compared to the thermally evaporated device. These studies have indicated that the damage to the organic semiconductor due to the electrode deposition techniques needs to be minimized to improve the performance of the OPV device.

Thermally evaporated buffer layer before sputtering may effectively decrease the damage of sputtering. The future research should be with double layer cathode and with low power sputtering deposition. Also, groove organic solar cells shows good absorption of light. Further simulation study of the groove organic devices is needed to understand the conduction behavior of carriers.
References


[4]. www.nd.edu/~gsnider/EE698A/Yogesh_Solar_cells.ppt, Solar cells presentation by Yogesh Wakchaure

[5]. Master thesis on “modeling of solar cells” by balaji padmanabhan.


[12]. Toong Way, “Fabrication and Morphological Characterization of Hybrid Polymeric Solar Cells Based on P3HT and Inorganic Nanocrystal Blends”.


[15]. René Janssen, “Introduction to polymer solar cells”


[27]. http://www.memsnet.org/mems/processes/deposition.html

[28]. http://www.ece.utep.edu/research/cdte/Fabrication/index.htm


[30]. En Chung Chang, “Enhancing the Efficiency of MEH-PPV and PCBM Based Polymer Solar Cells via Optimization of Device Configuration and Processing Conditions”, Wiley Inter Science, 2005


[33]. Semiconductors physics and characterization by S M Sze.

Appendix

Process flow of fabrication

Steps

1. Substrate cleaning
   I. Take a beaker with DI water
   II. Add 5 to 6 drops of Micro 90 in to the DI water
   III. Put the ITO coated Glass substrate in to the Beaker
   IV. Heat the Beaker at 100 c for 20 min under a fume hood
   V. Put the beaker into ultra-sound bath under a fume hood for 60 min.
   VI. Dry substrates by N2 gun and put the substrate on sample holder

2. Deposition of PEDOT PSS
   I. Put substrate onto spin-coater and press vacuum button to hold substrate.
   II. The spinning rate and time of spin-coating were 2500 rpm for 30 sec for 100nm thickness
   III. Drop PEDOT: PSS onto the substrate and start spin coating.
   IV. Press vacuum button to release substrate and take it away from spin-coater.
   V. Clean spin coater using DI water and tissues.
   VI. Bake it on hotplate at 120c for 10min
3. Spin coating of MEHPPV

   I. 50 mg of MEH PPV is mixed in 10g of chlorobenzene and sonicated for 60 min

   II. Put substrate onto spin-coater and press vacuum button to hold substrate

   III. Drop MEH PPV solution on top of substrate.

   IV. Spin coating is performed at a speed of 1500rpm for 30 sec for 100 nm.

   V. Press vacuum button to release substrate and take it away from spin-coater.

   VI. Evaporate the solvent at 140c for 30 min.

4. Aluminum Deposition

   I. Shadow mask is placed on the substrate

   II. Process conditions: Power: 100 watts Pressure:5 mtorr Time: 45min Substrate height: 10mm

   III. Sputtering of Al of thickness 100nm
Figure 1 Dark current vs. voltage characteristics of sputtered cathode device at high power 100W

Figure 2 Dark current vs. voltage characteristics of sputtered cathode device at low power of 20W
Figure 3 Capacitance vs. Voltage characteristics of sputtered cathode device at high power of 100W.

Figure 3 Capacitance vs. Voltage characteristics of sputtered cathode device at low power of 20W.
Figure 5 Dark current vs. voltage characteristics of Titanium sputtered cathode device

Figure 6 Dark current vs. voltage characteristics of Manganese sputtered cathode device
Figure 7 Dark Current vs. Voltage characteristics of thermally evaporated cathode device.

Figure 8. Dark current vs. Voltage characteristics of silicon nanocrystal and MEH PPV blend device