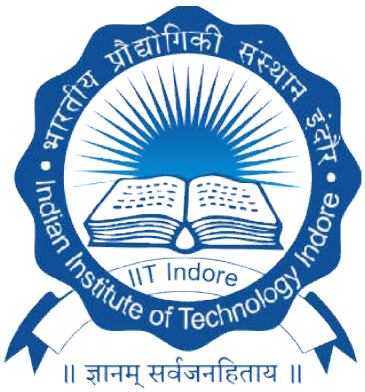
B. TECH. PROJECT REPORT

On

Development of Photo Induced Memory Device

BY

AMEYA BHARATI



DISCIPLINE OF ELECTRICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY INDORE

NOVEMBER 2016

DEVELOPMENT OF PHOTO INDUCED MEMORY DEVICE

A PROJECT REPORT

Submitted in partial fulfillment of the
requirements for the award of the degrees

of
BACHELOR OF TECHNOLOGY
In
ELECTRICAL ENGINEERING

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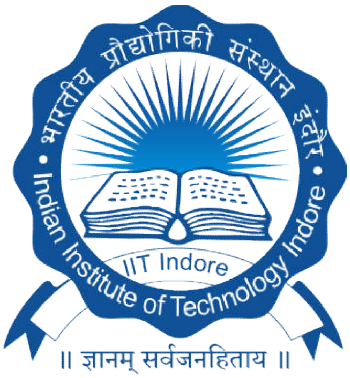

INDIAN INSTITUTE OF TECHNOLOGY INDORE
NOVEMBER 2016

CANDIDATE'S DECLARATION

I hereby declare that the project entitled **"Development of Photo Induced Memory Device"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Electrical Engineering' completed under the supervision of **Dr. Vipul Singh, Assistant Professor, Department of Electrical Engineering,** IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

AMEYA BHARATI

(1200203)

CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the students is correct to the best of my/our knowledge.

Dr. Vipul Singh

Assistant Professor

Department of Electrical Engineering

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Preface

This report on "Development of Photo Induced Memory Device" is prepared under the guidance of Dr. Vipul Singh.

Through this report, I have tried to develop, optimize, and characterize organic semiconductor based photo induced memory devices. I have characterized thin films of different solutions achieve optimized characteristics and better charge transport within the device.

I have also studied the effect of different annealing temperatures on these thin films, thus figuring out the best combination to choose for the fabrication of photo induced memory devices. Readings and graphs at all steps have been added to make the report more comprehensive and illustrative.

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Acknowledgements

I wish to thank Dr. Vipul Singh for his kind support and valuable guidance.

It is his help and support, due to which I became able to complete the design and technical report.

I would also like to thank Dr. Kshitij Bhargava and other PhD students in the MNRG lab, who were always there to help me out whenever I needed it.

Without their support, this report would not have been possible.

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Abstract

Organic semiconductor based electronics are called the technology of the future, owing to their versatile and innovative use in new age electronics. With the use of conducting organic polymers instead of conventional electronic components, new age electronics can be fabricated with a large number of advantages. Conductive polymers are lighter, more flexible, and less expensive than inorganic conductors. This makes them a desirable alternative in many applications. It also creates the possibility of new applications that would be impossible using copper or silicon.

Organic electronic devices are quickly making their way into the commercial world, with innovative thin mobile devices, high-resolution displays, and photovoltaic cells. The future holds even greater potential for this technology, with an entirely new generation of ultralow-cost, lightweight and even flexible electronic devices, which will perform functions traditionally accomplished with much more expensive components based on conventional semiconductor materials, such as silicon.

For working towards these futuristic technological advances, basis strategies to improve and optimize memory behaviour in Photo Induced Memory Devices (PIMDs) have been undertaken in this project.

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List of abbreviations

PIMD	Photo Induced Memory Devices
P3HT	Poly (3-hexylthiphene 2,4-diyl)
OLED	Organic Light Emitting Diodes
OFET	Organic Field Effect Transistors
WORM	Write Once, Read Many times
HMDS	Hexamethyldisilazane
UV	Absorption
PL	Photo Luminescence
P3OT	Poly (3-octylthiophene, 2,4-diyl)
P3DT	Poly (3-decylthiophene, 2,4-diyl)
Al	Aluminum

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CHAPTER 1

Introduction

1.1 Overview

Organic electronics is a field of materials science which involves the design, synthesis, and characterization of organic compounds like polymers. These polymers show conductivity and other desirable electronic properties. Developed in the context of organic chemistry, these conducting polymers are formed out of carbon based small molecules with long chains, giving them the unique characteristics that they possess. The establishment of high-tech products relying on organic semiconductors demonstrates the remarkable technological maturity and competitiveness of these materials. Some basic steps for improving the performance of conducting molecular systems and polymers that make them attractive for an ever-growing range of technological applications are explored in this project.

Some of the many applications of organic electronics include Organic Light Emitting Diodes (OLEDs), Organic Field Effect Transistors (OFETs), and Organic Solar Cells. For the fabrication of all these devices, Organic Photo Induced Memory Devices (PIMDs) are required. These PIMDs can be optimized, and charge transport within them can be improved by changing the surface characteristics of their components. Memory characteristics within the PIMD can be improved by tweaking the solutions and fabrication conditions.

1.2 Objectives

The main objective of this project is to characterize thin films of a solution of conducting polymer. Different annealing temperatures will also be used to see which combination is optimum for fabricating the devices.

The obtained thin films would then be used to develop PIMDs. These are then characterized and measurements would be taken to confirm light influenced memory behaviour.

1.3 Methodology

Firstly, thin films of solutions of a conducting polymer are formed. The polymer used in this project is Poly (3-Hexylthiophene 2,4- Diyl), abbreviated as P3HT. Four different organic solvents are used for making these solutions.

Further, the samples that are made from these solutions are annealed at different temperatures to see the effects on their characteristics. Absorption and Photoluminescence spectra are measured to see which solution and temperature show the best characteristics.

This solution is then used for the thin films in the fabrication of PIMDs.

1.4 Report Layout

This report is organized as follows:

- **Chapter 2 (Theory and Design):** This chapter outlines the theory and functioning of thin films and PIMDs. It also talks about their use in organic electronics, and the concept design of the devices being fabricated in this project.
- **Chapter 3 (Experimentation and observation):** A number of experiments have been conducted in the course of this project. This chapter outlines all the experiments conducted and the observations obtained in its course.
- **Chapter 4 (Working and conclusion):** This chapter includes possible explanations of how the fabricated PIMDs work and the basis behind their functioning.
- **Chapter 5 (Future applications and scope):** This chapter outlines the large number of real life technological applications of PIMDs, and the scope of this technology in the future.

CHAPTER 2

Theory and Design

2.1 Theory

Write Once Read Many times (WORM) PIMDs have been fabricated by using P3HT thin films, gold electrodes, and aluminum coating. The characterization of these devices is undertaken by shining a green laser light on them for a particular period of time, and then switching off the light. A significant increase in the current is observed as soon as the light is shone, and the memory effects of this increase in current last after the light is switched off. This proves that the device shows light induced memory characteristics.

Conductive polymers are often typically intrinsically conductive or at least semiconductors. They sometimes show mechanical properties comparable to those of conventional organic polymers. Both organic synthesis and advanced dispersion techniques can be used to tune the electrical properties of conductive polymers, unlike typical inorganic conductors. The most well-studied class of conductive polymers include polyacetylene, polypyrrole, polyaniline, and their copolymers. Poly (p-phenylene vinylene) and its derivatives are used for electroluminescent semiconducting polymers. Poly (3-alkythiophenes) are also a typical material for use in solar cells and transistors. The compound Poly (3- Hexylthiophene 2,4 Diyl) is used in this project.

P3HT is an organic polymer, which ensures that it is soluble in organic solvents. Chloroform ($CHCl_3$), Toluene ($C_6H_5CH_3$), Chlorobenzene (C_6H_5Cl), and Dichlorobenzene $C_6H_4Cl_2$) are used as solvents for the fabrication of thin films. P3HT is seen to be highly soluble in chlorinated compounds like Chloroform, Chlorobenzene, and Dichlorobenzene.

Annealing is a process of heating a glass substrate coated with a thin film. The process of annealing is crucial to the fabrication of these devices, as it causes a change in the physical and chemical properties of the substrate. A uniform morphology in the thin film can be achieved by heating the substrate at a particular temperature for a particular time. Annealing improves and enhances the characteristics of the thin film,

improves its homogeneity, and prepares the substrate for further use. This ensures that the film is better suited for charge transport and for carrying out the planned experiments.

A highly conducting metal is used to make the electrodes in a PIMD. In this case, gold electrodes are used. The development of photo induced memory characteristics require a depletion layer on top of the thin film. An aluminum layer of very low thickness can be used as a good way to achieve these characteristics.

2.2 Design

Gold electrodes are used in the development of these PIMDs. On top of the electrodes, a thin film of a P3HT solvent is coated. This substrate is then annealed and coated with a thin layer of aluminum.

The structure of the PIMDs fabricated in this experiment is best shown in the figure below.

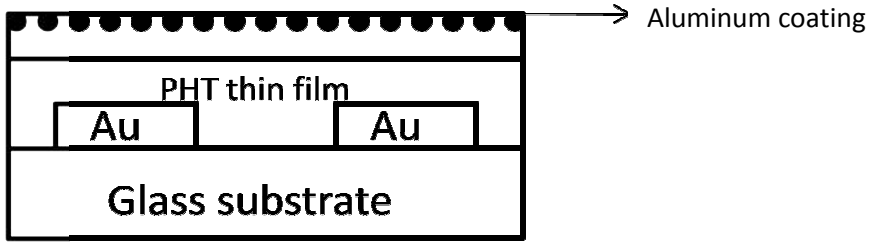

Fig 1: Structure of PIMD

1% solutions of P3HT are used with different solvents to prepare the thin film as shown in the picture. The thin films are made on cleaned glass substrates with the help of a Spin Coater.

The gold electrodes and aluminum film deposition is carried out on the glass substrate with the help of vacuum metal deposition. Channel length between the two Au electrodes is taken to be 100 nm. The thickness of all thin films is kept constant, so is the thickness of the glass, electrodes, and aluminum coating.

CHAPTER 3

Experimentation and Observations

A number of experiments have been carried out in this project before the actual fabrication of PIMDs. As the channel length and thickness of electrodes and aluminum film has been kept constant, the characteristics of the thin films were optimized to improve the characteristics of the final PIMD.

The factors that were changed to achieve optimum characteristics were:

1.) Choice of solvent
2.) Annealing temperature of the substrates

The following steps were taken to perform the initial experiments:

3.1 Thin film analysis

3.1.1. Experimentation

The following steps were taken for making thin films:

(Caution: Some of the materials used in the lab can be corrosive or harmful to your body. Make sure that you use safety goggles, rubber gloves, and masks whenever necessary to ensure your safety.)

1.) Cleaning of glass slides:
    a. 12 glass slides of 1.5 cm x 1.5 cm are cut using a diamond tipped cutter.
    b. These glass slides are cleaned by ultrasonication with Acetone, and then Isopropyl Alcohol for 10 minutes each. This is to ensure that no stray particles are left behind on them.
    c. A solution of H_2O_2, NH_4OH, and Deionized water in the ratio 1:1:5 is used, and the glass substrates are dipped in them. This solution is covered and heated for 10 minutes at 60 °C. This is done for making the glass substrates hydrophilic in nature.

d. After doing this procedure, the substrates are taken out from the solution and cleaned with DI water, and dried with the help of a hair blower.
e. To make one surface of the glass substrates hydrophobic, a drop of Hexamethyldisilazane (HMDS) is dispensed on top of it. (Caution: Safety goggles should always be worn while handling HMDS.)
f. The glass substrates are now ready for thin film coating.

2.) Forming P3HT solutions:
   a. 12 samples of 1 mL HPLC vials are cleaned by filling them with acetone and isopropyl alcohol in turn. These are ultrasonicated for 10 minutes each.
   b. These vials are kept in the oven for ten minutes at 110 °C for drying them.
   c. Using an electric weighing machine, 10 mg P3HT is measured. (For a 1% solution, 10 mg of P3HT is dissolved in 1 mL of solvent.)
   d. 10 mg of P3HT is added to 1 mL of Chloroform. A small magnetic bead is put in this solution, and left for stirring overnight so that the polymer dissolves uniformly in the solvent.
   e. These solutions are then filtered, and taken in 1 mL syringes.

3.) Spin coating:
   a. Using a vacuum pump, the cleaned glass slides are fixed in the spin coater.
   b. Using the syringe filled with the solution, the solutions are dispensed on the hydrophobic part of the glass slide.
   c. The settings are set to 1500 rpm for 20 seconds, and thin films are created.

4.) Annealing:
   a. Three samples are made with Chloroform solution. These samples are annealed separately at 60 °C, 80 °C, and 100 °C, for 60 minutes each.

The process is repeated by taking different solvents.

Toluene ($C_6H_5CH_3$), Chlorobenzene (C_6H_5Cl), and Dichlorobenzene ($C_6H_4Cl_2$) are used as solvents, and three samples are made with each solution. The absorption spectra and photoluminescence spectra of all these samples are measured.

3.1.2 Observations

The UV and PL spectra that are measured for the given samples are graphed, and compared to figure out which combination of solvent choice and annealing temperatures gives the best UV and PL characteristics. The graphs for all of these are shown below:

1.) UV Spectra for Chloroform solution:

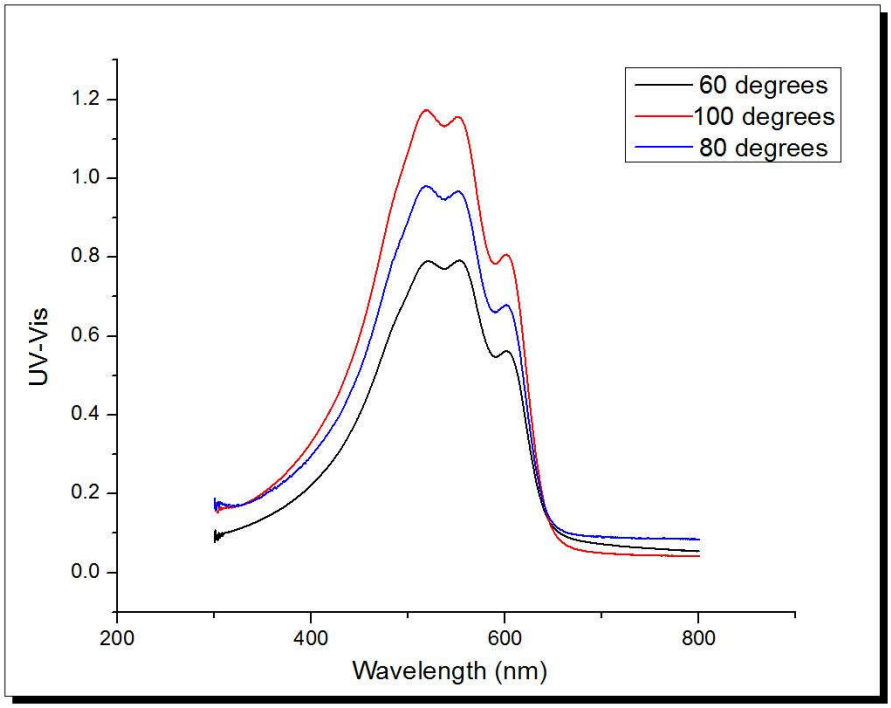

Fig 2: UV Spectra for Chloroform solution

2.) PL Spectra for Chloroform solution:

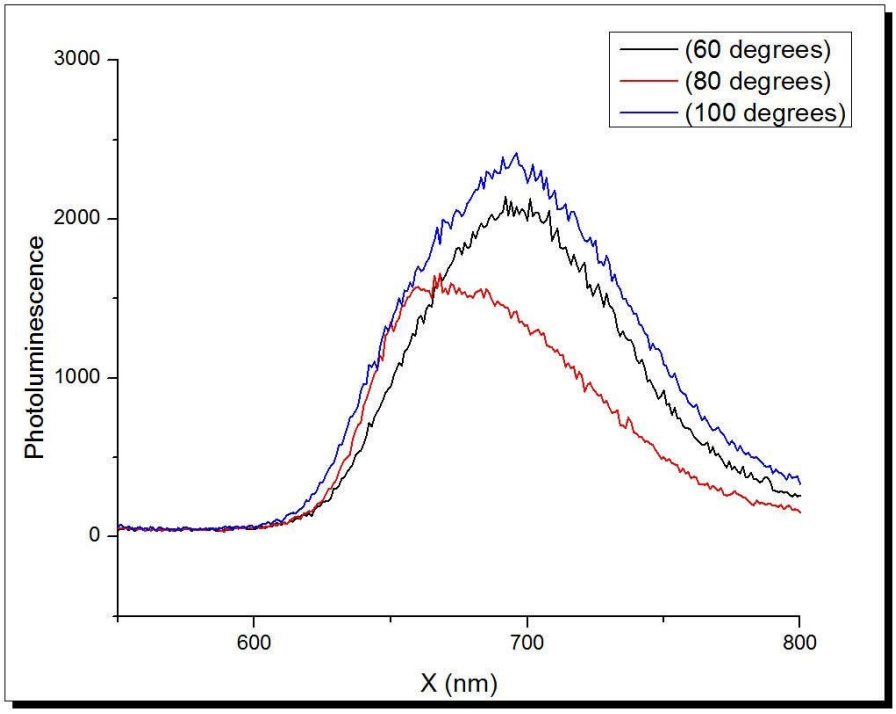

Fig 3: PL Spectra for Chloroform solution

3.) UV Spectra for Chlorobenzene solution:

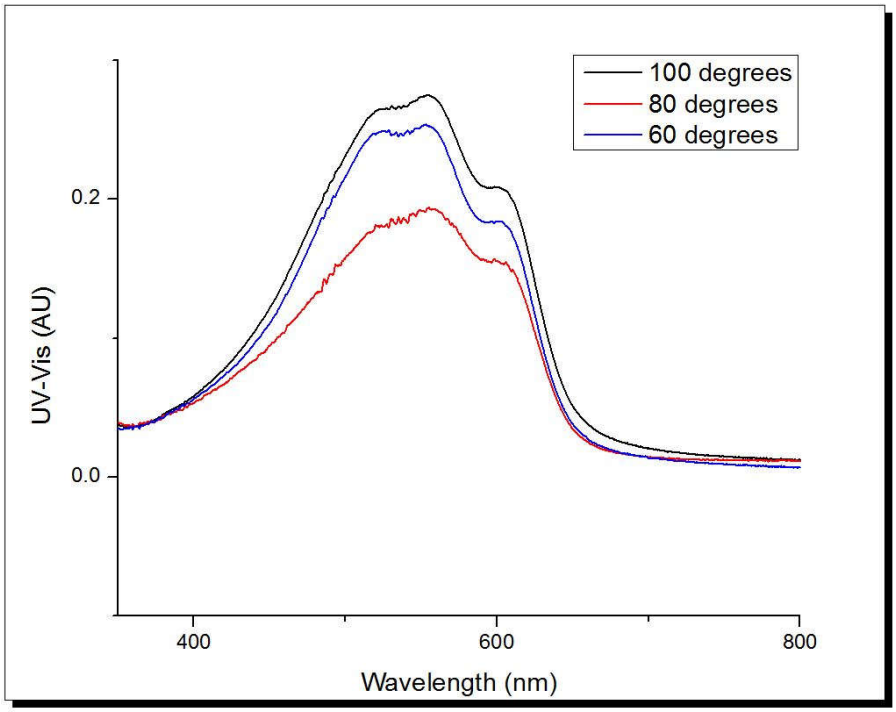

Fig 4: UV Spectra for Chlorobenzene

4.) UV Spectra for Dichlorobenzene solution:

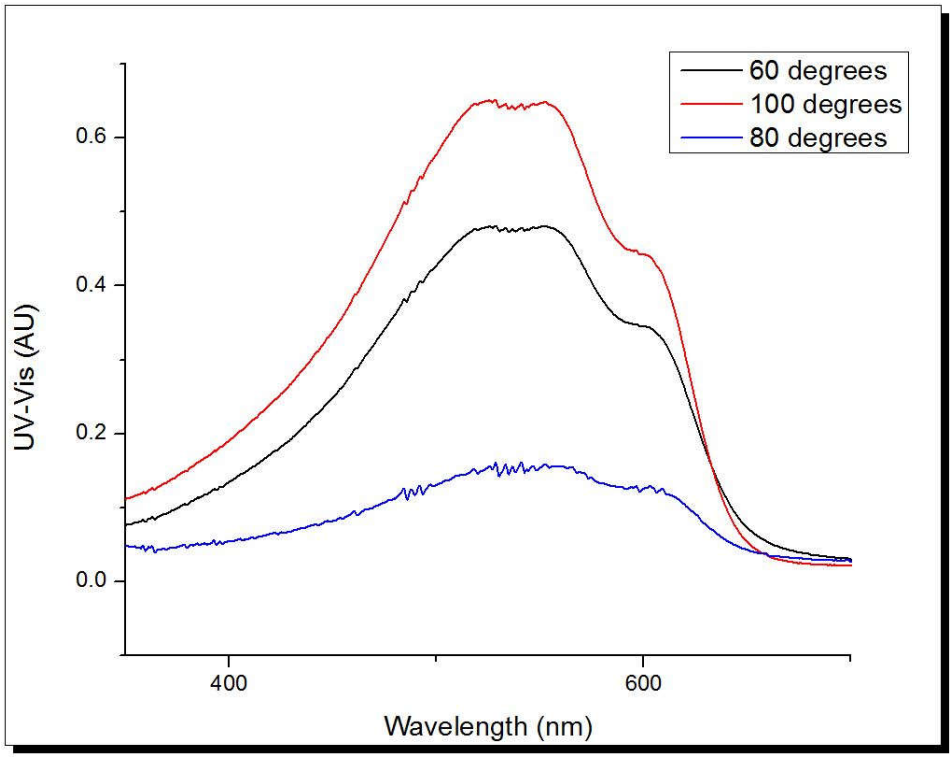

Fig 5: UV Spectra for Dichlorobenzene solution

5.) UV Spectra for Toluene solution:

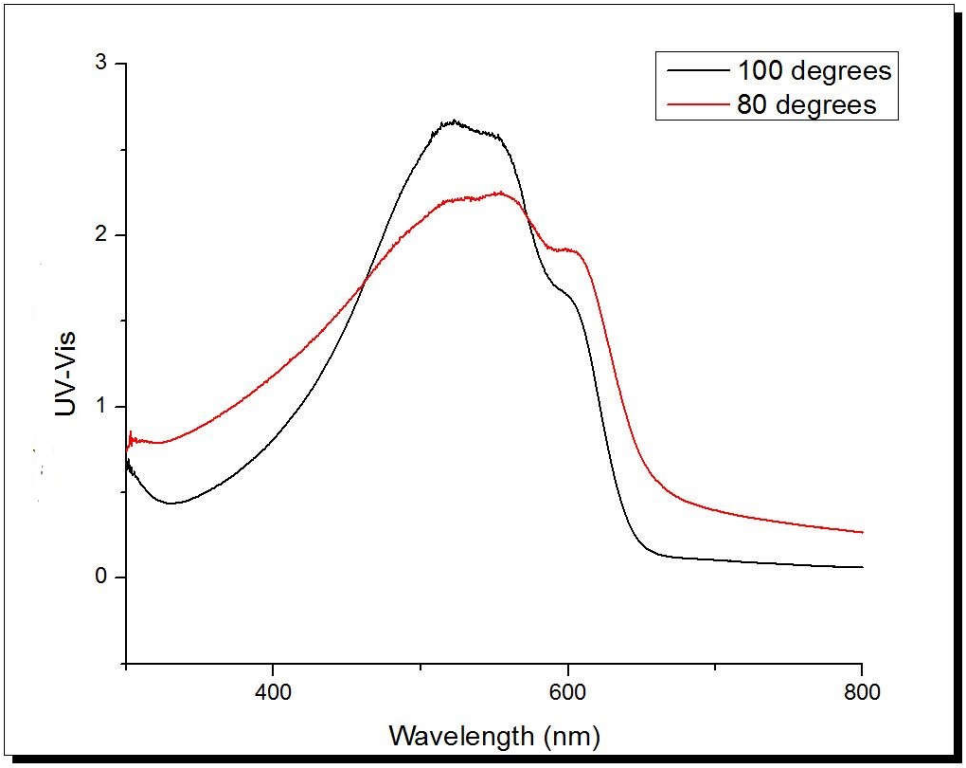

Fig 6: UV Spectra for Toluene solution

6.) PL Spectra for Toluene solution:

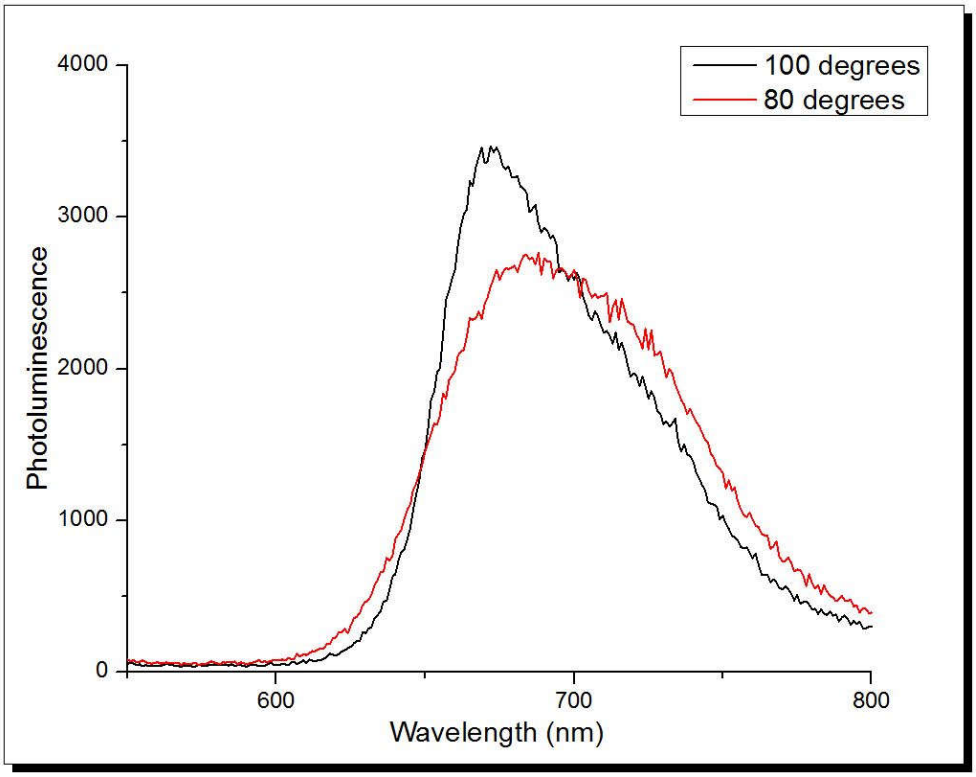

Fig 7: PL Spectra for Toluene Solution

The solubility of P3HT in the solutions taken was seen to be:

Dichlorobenzene > Chlorobenzene > Chloroform > Toluene

The best characteristics were observed for P3HT in Chloroform solution, annealed at 100 °C.

This combination is further used in the fabrication of PIMDs.

3.2 Fabrication of PIMDs

3.2.1 Experimentation

After characterizing thin films and obtaining the best combination using UV and PL Spectra, the following steps are conducted for the fabrication of PIMDs.

1.) Glass samples are cleaned using acetone and isopropyl alcohol.

2.) 1 wt% Chloroform solution is prepared with P3HT, P3OT (Poly (3-octylthiphene 2,4-diyl)), and P3DT (Poly (3-decylthiophene 2,4-diyl)).
3.) Hydrophobic and hydrophilic treatment is carried out on the glass substrates, and the samples are washed and dried.
4.) Using a vacuum metal deposition technique, gold electrodes with a channel length of 100 nm are deposited on top of the glass substrates.
5.) These glass substrates are spin coated with a 1% solution of P3HT and Chloroform for 20 seconds at 1500 rpm.
6.) These substrates are then annealed at 100 °C for 60 minutes.
7.) On top of these, vacuum metal deposition is carried out, and a thin film of aluminum is coated.

The PIMDs are ready for characterization.

8.) Green laser light (Diameter of beam: 3mm. Wavelength of light: 650 nm) is shone on these samples for 10s. V-I characteristics are measured. The light is then switched off for 60s, and VI characteristics are measured again.
9.) Similarly, light is shone on these samples for 60s. V-I characteristics are measured. The light is then switched off for 120s, and VI characteristics are measured again.

After these experiments, transient readings of current with respect to time are taken by changing the voltage and conducting cycles of 50s ON, 100s OFF. The observations obtained are as follows.

3.2.2 Observations

The graphs of all the measurements and readings taken above are given below:

1.) P3HT, 10s ON, 60s OFF:

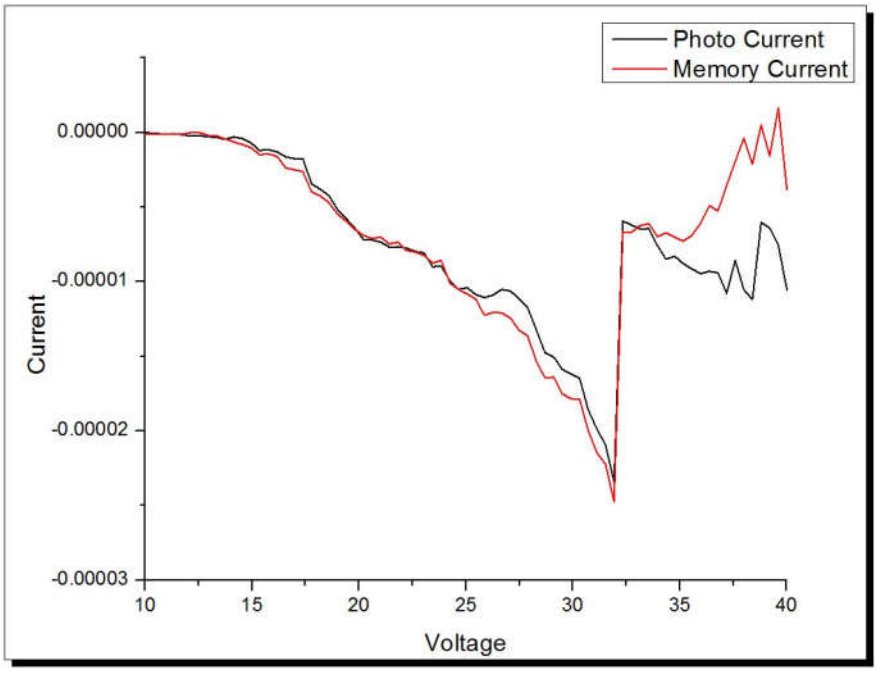

Fig 8: P3HT, 10s ON, 60s OFF

2.) P3HT, 60s ON, 120s OFF:

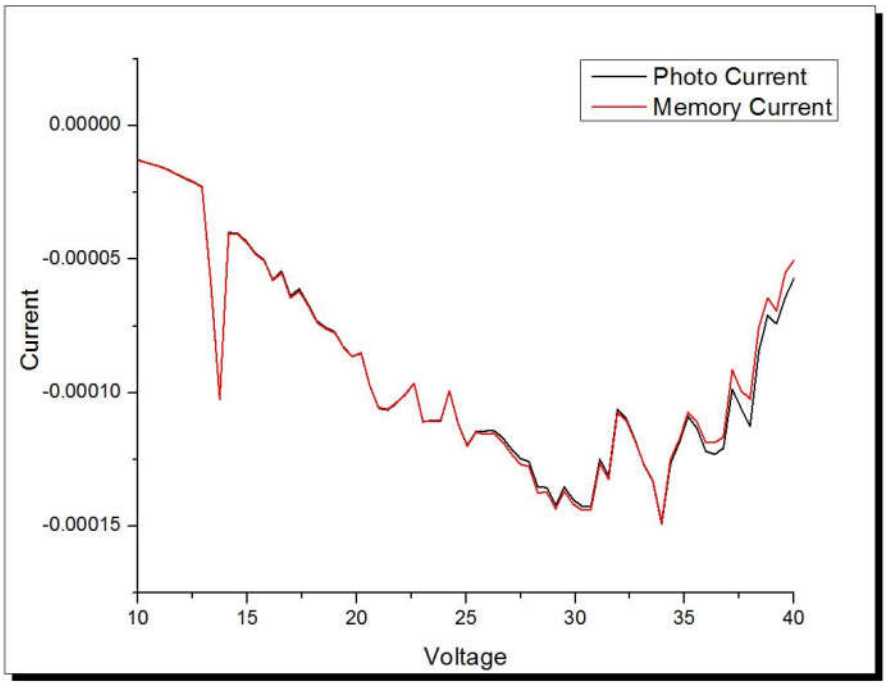

Fig 9: P3HT, 60s ON, 120s OFF

3.) P3OT, 10s ON, 60s OFF:

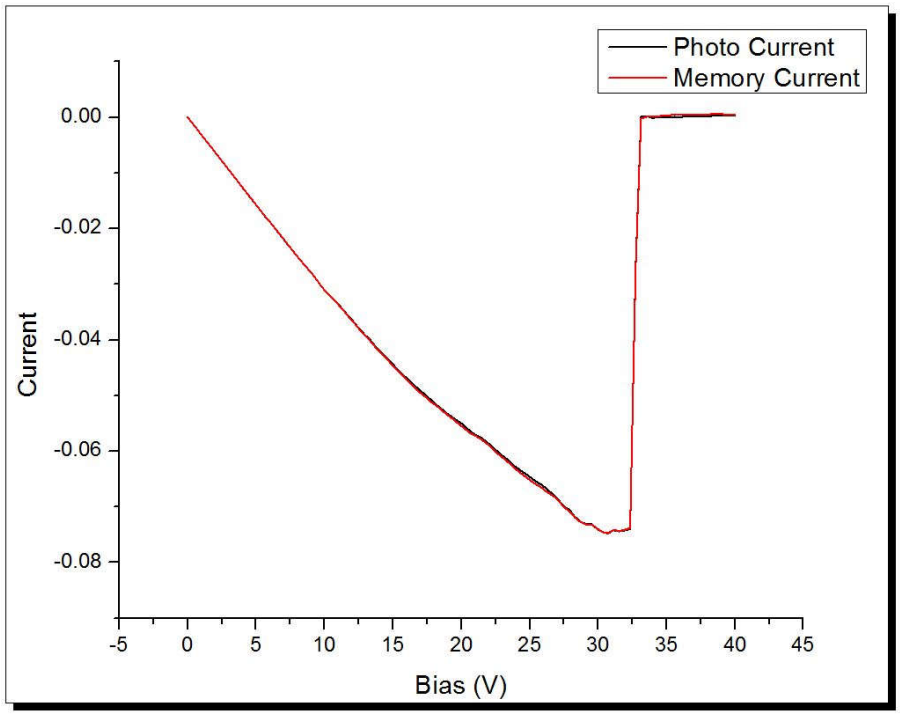

Fig 10: P3OT, 10s ON, 60s OFF

4.) P3OT, 60s ON, 120s OFF:

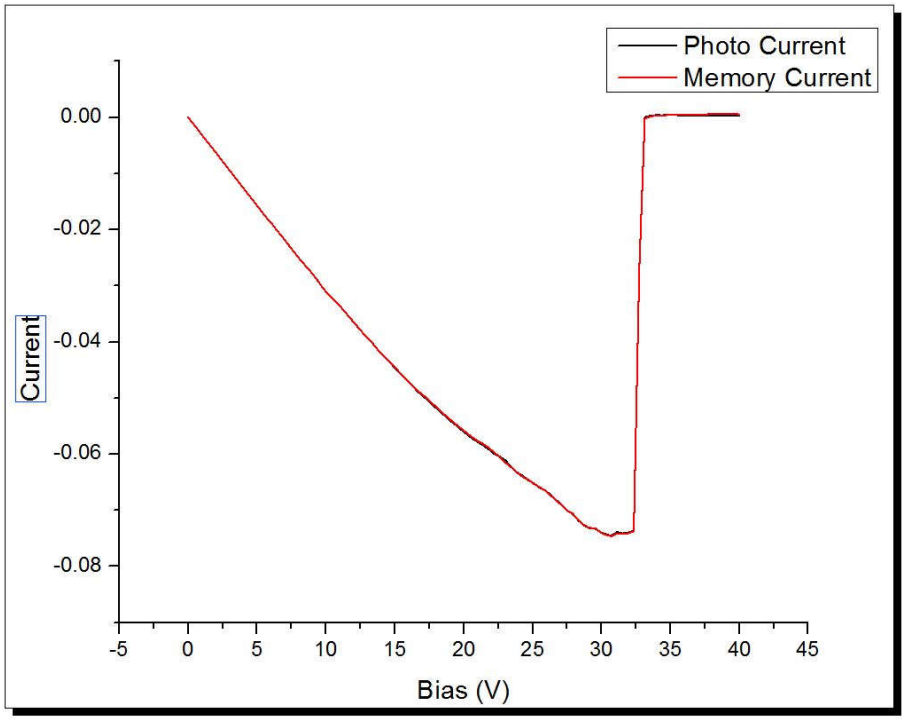

Fig 11: P3OT, 60s ON, 120s OFF

5.) P3DT, 10s ON, 60s OFF:

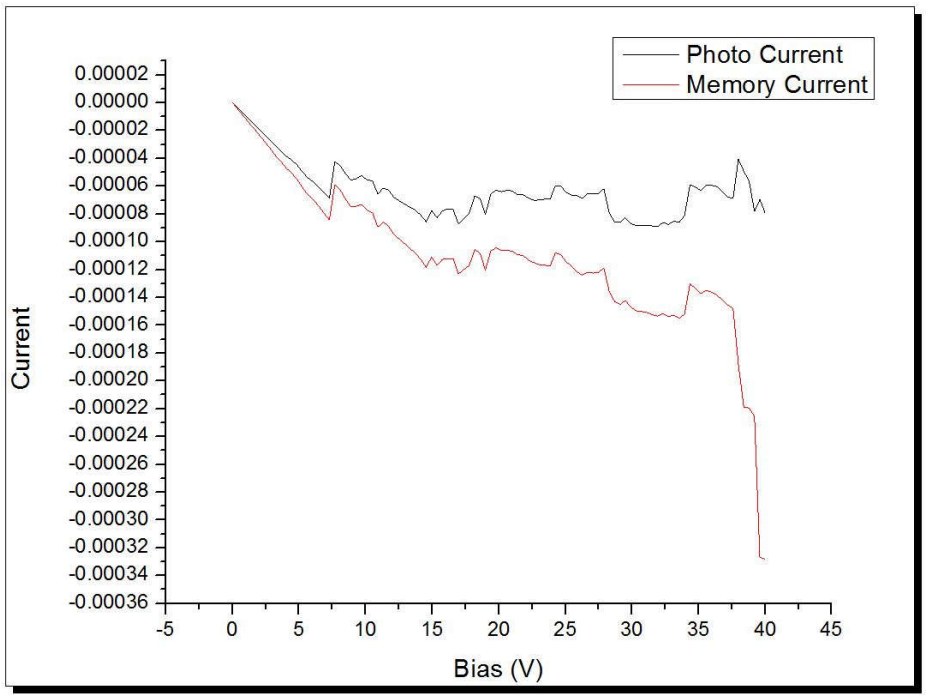

Fig 12: P3DT, 10s ON, 60s OFF

6.) P3DT, 60s ON, 120s OFF

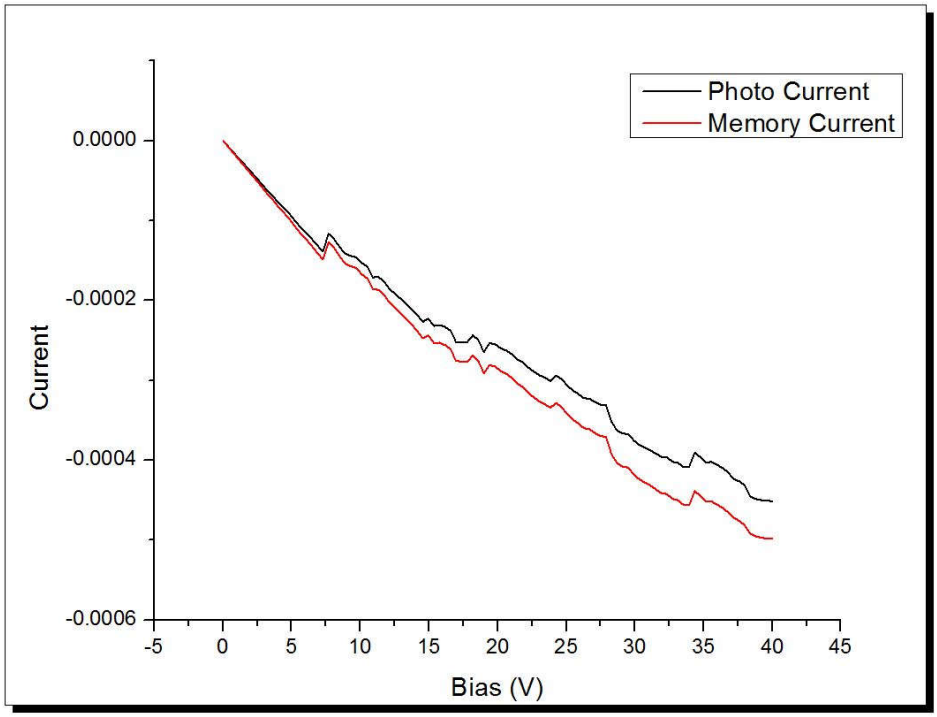

Fig 13: P3DT, 60s ON, 120s OFF

The transient readings are taken at 10V, 20V, 30V, and 50V. For 50V, the readings are also taken over 4 cycles.

The following graphs are obtained as observations:

1.) 10V:

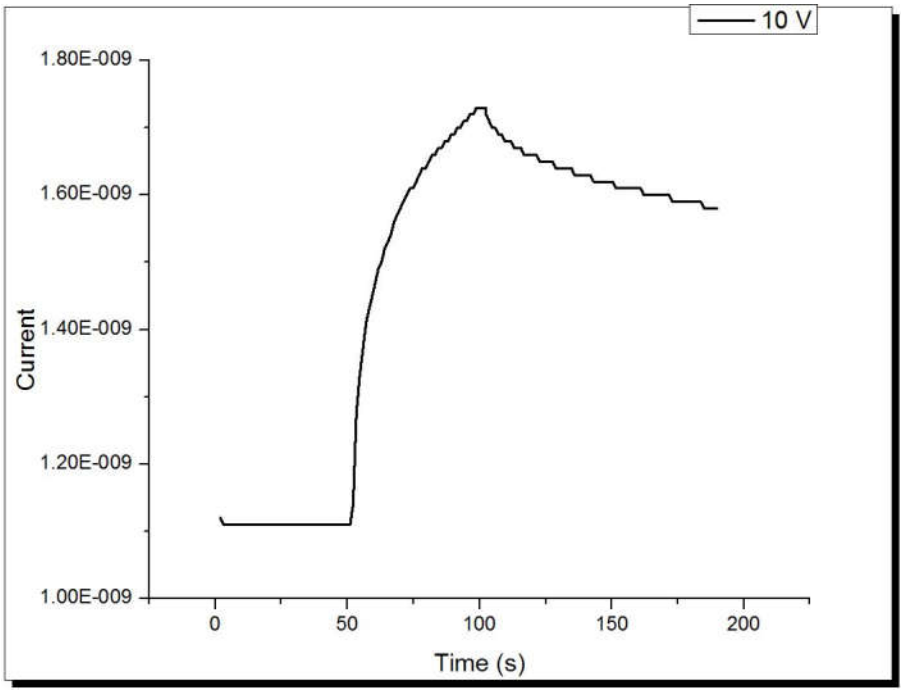

Fig 14: Transient readings for 10V

2.) 20V:

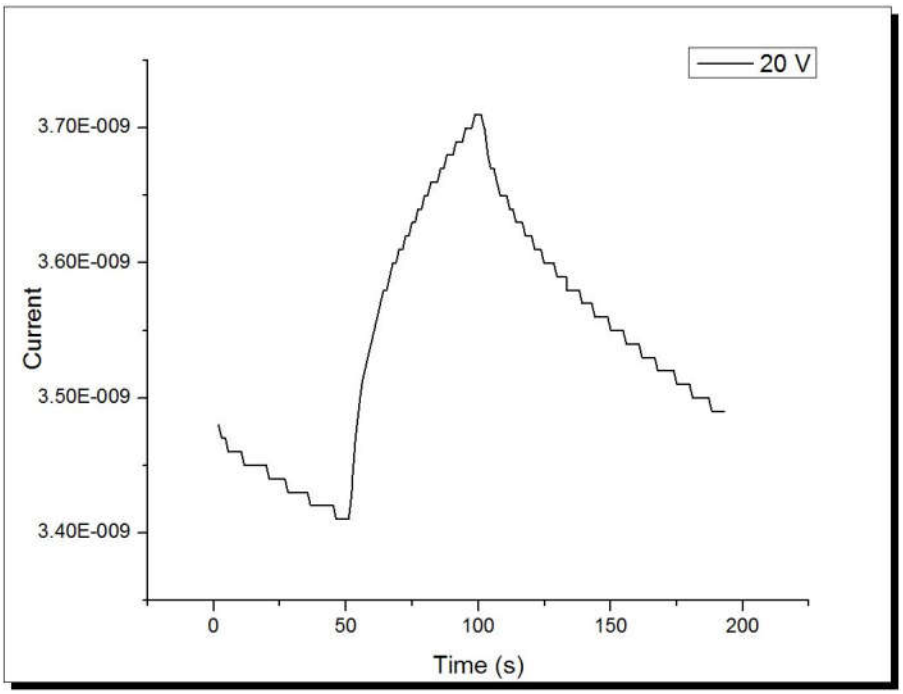

Fig 15: Transient readings for 20V

3.) 30V:

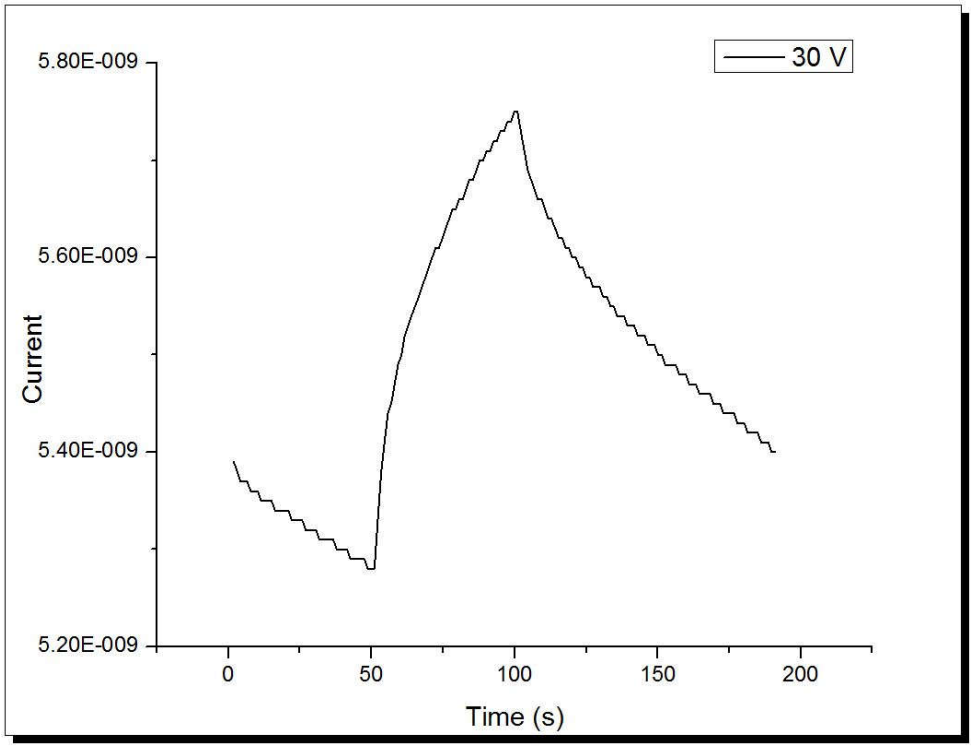

Fig 16: Transient readings for 30V

4.) 50V:

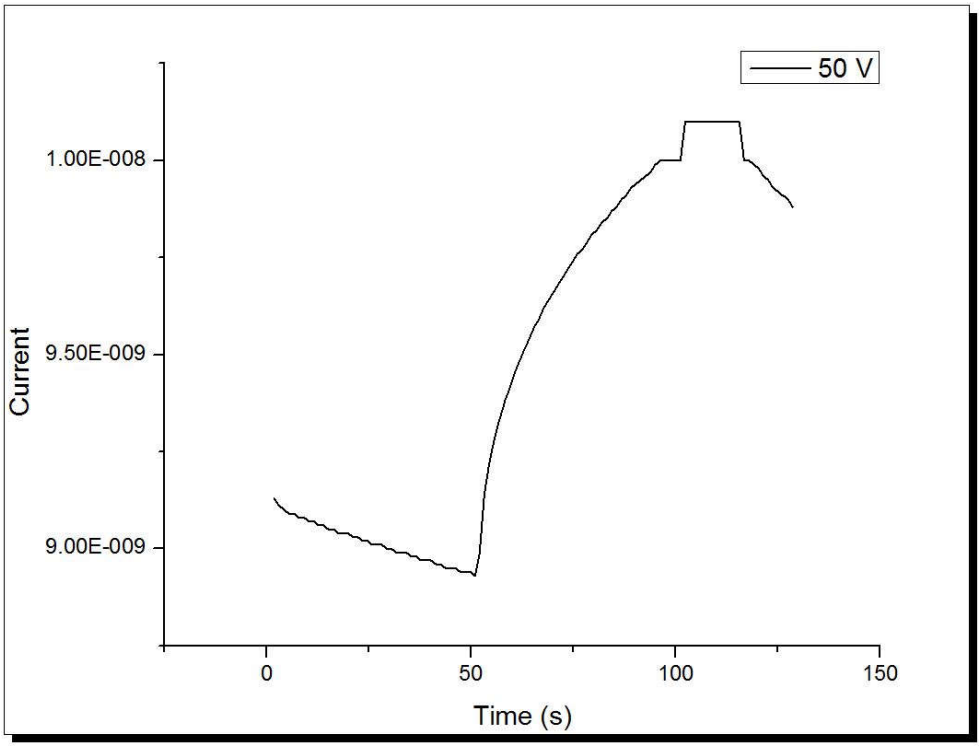

Fig 17: Transient readings for 50V

5.) 4 cycles at 50V:

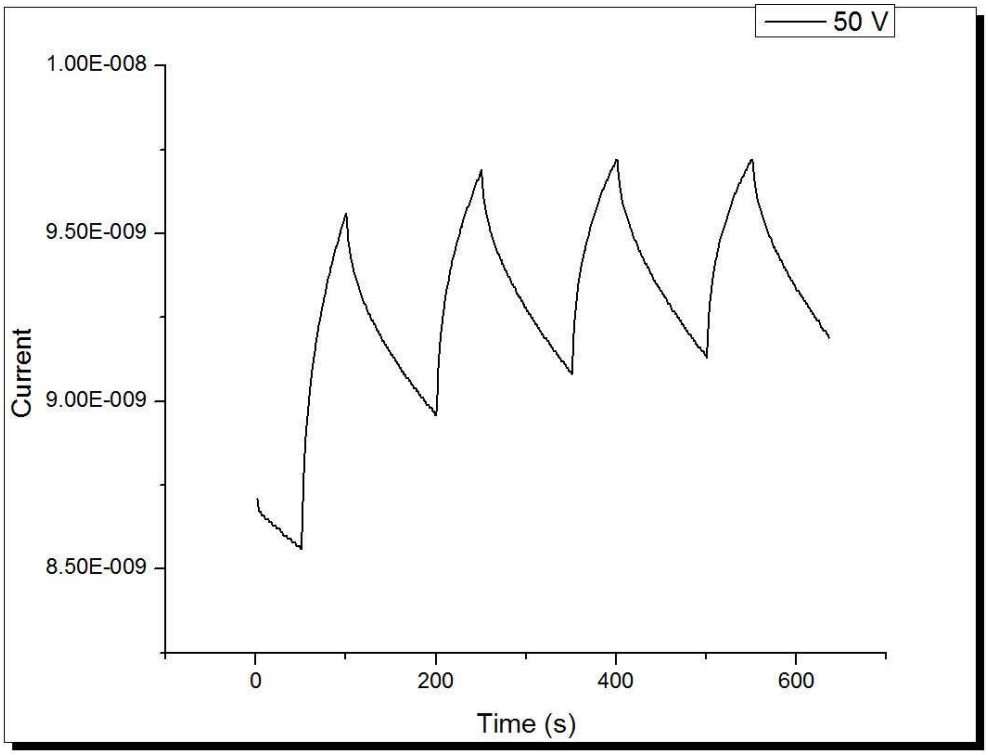

Fig 18: Transient readings for 50V, 4 cycles

These are the observations obtained for the various measurements carried out through this project. The conclusions and possible explanations for photo induced memory behaviour are discussed in the next chapter.

CHAPTER 4

Working and conclusion

4.1 Working

A possible explanation of the observation of photo induced memory behaviour in the fabricated device can be found by taking the depletion layer present in between the thin films and Aluminum coating into consideration.

In this theory, it is explained that due to the smaller work function of Al compared to P3HT, electrons transfer from Al to acceptors in P3HT, resulting in loose of the conductivity and formation of depletion layer. The origins of acceptors are associated with the trace of catalyst or oxygen.

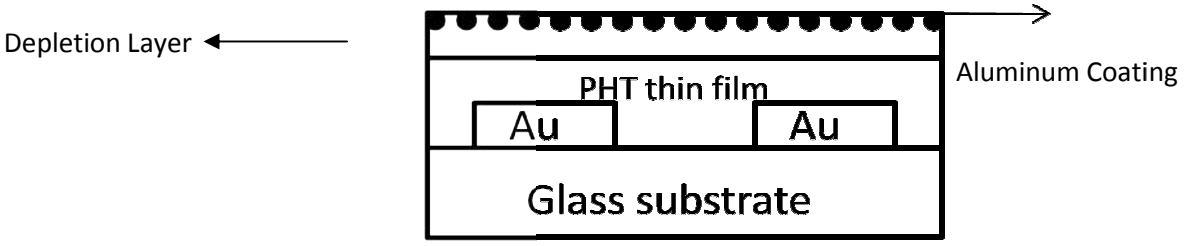

Fig 19: Formation of depletion layer in the PIMD

The resistance of depletion layer must be large enough for the long retention of the charges stored in Al particles.

When light is illuminated on the, the photo carrier generation is explained by the assistance of the internal field around the aluminum particles coated on top of the device. The photo carriers of electrons migrate to the Al, and the holes migrate to the bulk sides.

Electrons get trapped at the site of Aluminum particles for a long time after the light is switched off. So even after the light influenced excitation is stopped, these trapped electrons give rise to photo induced memory effects.

4.2 Conclusion

Through the experiments carried out in this project, we can see that organic semiconductors show properties that can be used in the fabrication of PIMDs. By characterizing thin films to give the best possible characteristics, these devices can be fabricated. Using the properties of depletion layer and the trapping of charges between the polymer thin film and aluminum coating, light induced memory characteristics can be effectively achieved.

Conducting polymers do not dissolve equally in different organic solvents, and show different UV and PL characteristics for different solvents and varied annealing temperatures. By studying the effects of varying these parameters on the standards of measurements, thin films can be optimized. Charge transport in a PIMD can be improved by changing and improving the surface characteristics of the thin films being coated on top of the substrates.

A possible explanation can be given by giving credit to the coating of aluminum, which causes a depletion layer in the device, in turn giving to memory characteristics. These devices show a large increase in current flow when light is shone on them, and continue to show a distinct increase in current (as compared to dark current) after the light has been switched off, pointing towards light induced memory behaviour.

CHAPTER 5

Future applications and scope

Organic electronics are the technology of the future. A large number of organic electronic devices, such as Organic Light Emitting Diodes (OLEDs), Organic Field Effect Transistors (OFETs), and Organic Solar Cells employ the use of PIMDs in their functioning. The number of advantages and opportunities that organic electronics provide to modern technology can be exploited in numerous ways, and can only be limited by imagination.

The principle advantages of organic semiconductors are:

1.) They are light in weight, compared to inorganic semiconductors which are often bulky and take a lot of space.
2.) Inorganic semiconductors need extreme fabrication test conditions, with clean rooms and temperatures of over a 1000 °C. Organic electronics can be fabricated in moderate conditions like at room temperatures.
3.) Organic semiconductors are a lot cheaper than their inorganic counterparts, which will play a huge role in bringing down the price of expensive technology.
4.) Organic semiconductors can be coated on flexible displays, and do not always need a crystalline structure.

Due to these reasons, organic semiconductor based electronics find use in a lot of technological advancements and futuristic applications. Some of this technology has already reached market maturity, and is used efficiently with OLEDs, leading to technology like flexible display films. These flexible display films are transparent when turned off, which means that foldable televisions could soon be a reality.

Similarly, thin film solar cells made from organic semiconductors can be used as panels for windows. These cells are transparent, and can be embedded directly into the windows of your house; producing electricity when light falls on them. A similar application is also proposed for transparent solar back panels for

mobile phones, which will drastically improve the battery life of modern smartphones. In a wafer thin layer, electronic components can be flawlessly integrated and applied to different carrier materials. These materials easily and flexibly adapt to surfaces, requiring much little space than the present day bulky, rigid electronics. It is even possible to produce coatings with ink-jet printers using electronic ink.

In a field like organic electronics, new breakthroughs are happening every day, and the possibilities of innovation are endless.

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