

Fabrication of Organic Solar Cells Using Embedded Matrix Obtained Via Insitu Growth of CdS Nanoparticles in P3HT

A Project Report submitted in partial fulfillment of the requirements for the award of degree of

Master of Technology In Nanoscience and Technology

Submitted by

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Submitted to

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CERTIFICATE

This is to certify that the project report entitled “**Fabrication of Organic Solar Cells Using Embedded Matrix Obtained Via Insitu Growth of CdS Nanoparticles in P3HT**” which is being submitted by **Mr. Jalaj Kumar Singh (Enrollment No. 2K9/MT/FT/NST/01)** to “**Department of Applied Physics, Delhi Technological University, Delhi**” for the award of degree of **Master of Technology (NanoScience and Technology)** is a record of bonafide work carried out by him under our supervision.

The project work has been carried out from 10th July 2010 to 31st March 2011.

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STUDENT'S DECLARATION

I hereby certify that the work which is being presented in this project report entitled “**Fabrication of Organic Solar Cells Using Embedded Matrix Obtained Via Insitu Growth of CdS Nanoparticles in P3HT**” submitted to the Department of Applied Physics, Delhi Technological University in fulfillment of the requirement of the degree of **Master of Technology (NanoScience and Technology)** is an authentic record of my own work. I have not submitted the matter embodied in this dissertation for the award of any other degree elsewhere.

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JALAJ KUMAR SINGH

1. INTRODUCTION



Organic Solar Cells

The present 'Global Warming' up phenomenon has changed the world energy scenario to focus on the importance of Renewable Energy sources for augmenting power production worldwide. Of these, Solar and wind power are the most important sources. The Solar photovoltaic (PV) industry experienced a healthy growth rate of over 40% in the last 5 years. The cumulative total of PV systems installed in India is 250 MW in the year 2006 including export of 160 MW. India position was 4th in the world in 2004 in solar production. India had started country wide Solar Photovoltaic Program for about two decades and has installed an aggregate 1.3 million systems.

The expansion trend of the photovoltaic (PV) industry as one of the most promising renewable energy sources is observed majorly in Japan, United States and Europe. More than 85% of the current world productions of PV cells involve crystalline silicon. Nevertheless, after several years of intensive research and development, a new generation of devices is in transition from small to large-scale production. This one is based on inorganic materials like CdTe and CuInSe (CIS), etc. But beyond this second generation, a third one is intensively

considered. These latter calls upon an entirely new type of materials, namely, the organic semiconductors. Interest in organic solar cells stems primarily from the promise of ease of processing. This is because, to date, many organic solar cell devices have used polymers as integral parts of their construction. For example, conjugated polymers often participate as electron donors and hole conductors in the active layer of the organic solar cells. Since the science of polymer processing is well developed, it is hoped that one day conventional processing steps such as roll-to-roll processing can be employed to make large-area inexpensive organic solar cells on flexible substrates which can be used in countless ways, from handheld electronics to commercial power production. However the research on organic solar cell still have a long way to go to compete with inorganic solar cells. The efficiency of inorganic solar devices is upto 20% and the development of inorganic thin layer and multi junction devices will likely lead to even better performance. In contrast, the optimum efficiency of organic solar cell based on the bulk heterojunction concept is 4-5%. Another problem with these devices is the stability, as they degrade much faster than the inorganic one and hence performance of the devices decreases with the time. As per our M.Tech curriculum, during the final semester which is totally research oriented we have worked on above problems and to meet some improvement in those areas and hence to achieve the better performance of the organic solar cell, we have learnt the working and fabrication process and then worked on efficiency and stability.

2.PHOTOVOLTAIC TECHNOLOGIES

2.1 A BRIEF HISTORY OF PHOTOVOLTAICS

With concerns about rising oil prices and climate change spawning political momentum for renewable energy, solar electricity is poised to take a prominent position in the global energy economy. Global energy demand will more than double by 2050 and will triple by the end of the century. At the same time, an estimated 1.64 billion people, mostly in developing countries, are not yet connected to an electric grid.

A solar cell or a photovoltaic cell is a device which converts sun's radiation into electricity. In general, a solar cell that includes both solar and non solar source of light(such as photons from incandescent bulbs) is termed as photovoltaic cell.

The story of photovoltaic started in 1839 when Becquerel discovered the photovoltaic effect from a silver coated platinum electrode immersed in an electrolyte radiated with light. The number of early thin film cell had already been developed in the 1930s, based on the schottkey barrier device, using a semitransparent metal layer deposition on top of selenium that provides the asymmetric junction. At that time, scientists were interested in the photoconductive current which being proportional to the frequency of the incident light, could function as a reliable photographic light meter.

As early as 1967, the first thin film CdS cell deposited on plastic was ready; while soon after a number of new photovoltaic materials were discovered, stimulated by theoretical work, including GaAs, InAs and CdTe, indicating that these materials would offer higher efficiency. The strategies for higher energy of multiple bandgap designs and tandem cells were also established at that time. Adding to the surprise,

the use of thin films that is nowadays changing the PV industry on a global scale was conceived by Chapin at the very beginning of the modern solar PV. Then, in the 1970s, scientists taking part in the US PV Research and Development Program developed thin films of crystalline Si and a whole range of new semiconductor materials (CIS, CdTe, InP, Zn3P2, Cu2 Se, WSe2, GaAs, ZnSiAs), that is, almost all the alternative materials used by today's new PV industry, including polycrystalline and amorphous silicon, and organic semiconductors.

Finally, in the early 1980s, Barnett developed the polycrystalline silicon thin film cell; while Martin Green replaced the silicon serigraphy with a silicon solar cell with greater surface area to catch the sun's rays with tiny, laser etched grooves in which the wires (contacts) that carry the electric current are buried, leading to 20% efficient cells. In 1997 the first modules using a triple junction amorphous silicon cell were commercialized by Sharp and also in 2007 Sanyo achieved an efficiency of 22% at the research level with its HIT solar cells. The HIT (heterojunction with intrinsic thin layer) solar cell is composed of a single thin crystalline silicon wafer surrounded by ultra thin amorphous silicon layers. The structure of the HIT cell enables an improvement in the overall output by reducing recombination loss by surrounding the energy generation layer of single thin crystalline silicon with high quality ultra thin amorphous silicon layers. In the meanwhile, highly efficient GaAs cells were developed to power spacecraft that now, exploiting the recent discovery of the near perfect growth of GaAs crystals as well as quantum well solar cells based on the same material, are likely to open the way to third generation solar cells.

2.2 PHOTOVOLTAIC TECHNOLOGIES

- 1839: Photovoltaic effect was first recognized by French physicist Alexandre-Edmond Becquerel
- 1883: First solar cell was built by Charles Fritts, who coated the semiconductor selenium with an extremely thin layer of gold to form the junctions (1% efficient).
- 1946: Russell Ohl patented the modern solar cell
- 1954: Modern age of solar power technology arrives - Bell Laboratories, experimenting with semiconductors, accidentally found that silicon doped with certain impurities was very sensitive to light.

❖ First Generation

- Single crystal silicon wafers (c-Si)

❖ Second Generation

- Amorphous silicon (a-Si)
- Polycrystalline silicon (poly-Si)
- Cadmium telluride (CdTe)
- Copper indium gallium diselenide (CIGS) alloy

❖ Third Generation

- Nanocrystal solar cells

- Photoelectrochemical (PEC) cells
- Grätzel cells
- Polymer solar cells
- Dye sensitized solar cell (DSSC)

❖ **Fourth Generation**

- Hybrid - inorganic crystals within a polymer matrix

2.2.1 FIRST GENERATION

First generation photovoltaic cells are the dominant technology in the commercial production of solar cells, accounting for more than 86% of the solar cell market.



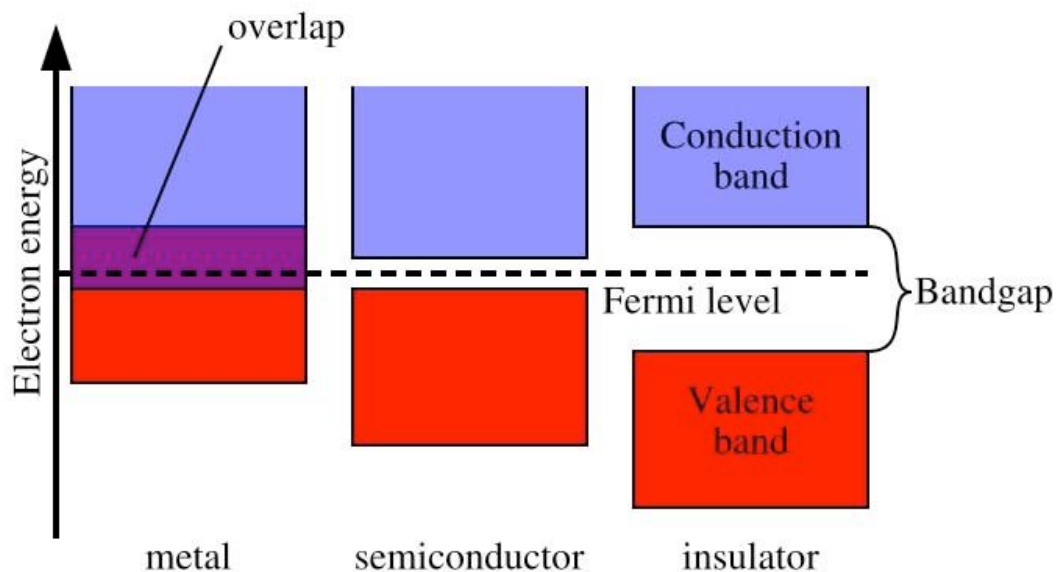
- ❖ Cells are typically made using a crystalline silicon wafer.
- ❖ Consists of a large-area, single layer p-n junction diode.
- ❖ Approaches
 - Ingots can be either monocrystalline or multicrystalline
 - Most common approach is to process discrete cells on wafers sawed from silicon ingots.
 - More recent approach which saves energy is to process discrete cells on silicon wafers cut from multicrystalline ribbons
- ❖ Band gap ~ 1.11 eV

Advantages

- Broad spectral absorption range
- High carrier mobilities

Disadvantages

- Requires expensive manufacturing technologies
- Growing and sawing of ingots is a highly energy intensive process
- Fairly easy for an electron generated in another molecule to hit a hole left behind in a previous photoexcitation.
- Much of the energy of higher energy photons, at the blue and violet end of the spectrum, is wasted as heat.



2.2.2 SECOND GENERATION

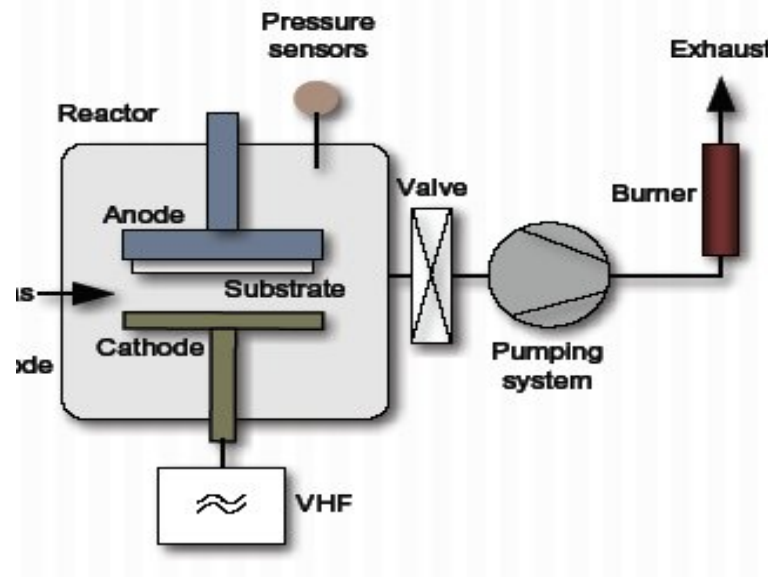
Thin-film Technology

- Based on the use of thin-film deposits of semiconductors.
- Using of thin-films reduces mass of material required for cell design.
- Contributes greatly to reduced costs for thin film solar cells.
- Several technologies/semiconductor materials currently under investigation or in mass production
- Deposition of thin layers of non-crystalline-silicon materials on inexpensive substrates using PECVD.
- Devices initially designed to be high-efficiency, multiple junction photovoltaic cells.

Plasma Enhanced Chemical Vapor Deposition

- **Thin-film deposition**
 - Technique for depositing a thin film of material onto a substrate.
 - Layer thickness can be controlled to within a few tens of nm.
 - Single layers of atoms can be deposited
- **Chemical vapor deposition (CVD)**

- Chemical process using a gas-phase precursor.
 - Often a halide or hydride of the deposited element.
- **PECVD - Plasma Enhanced CVD**
- Uses an ionized vapor, or plasma, as a precursor
 - Relies on electromagnetic means (electric current, microwave excitation) to produce plasma.



Advantages

- Lower manufacturing costs
- Lower cost per watt can be achieved
- Reduced mass
- Less support is needed when placing panels on rooftops
- Allows fitting panels on light or flexible materials, even textiles.

Disadvantages

- Typically, the efficiencies of thin-film solar cells are lower compared with silicon (wafer-based) solar cells
- Amorphous silicon is not stable
- Increased toxicity

2.2.3 THIRD GENERATION

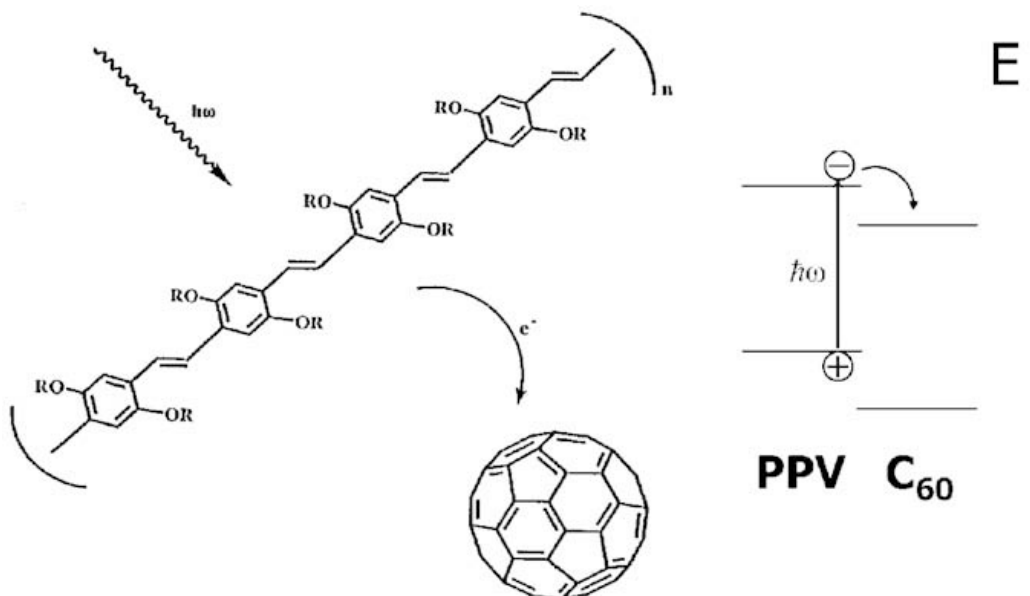
Different Semiconductor Technology

- Very different from the previous semiconductor devices
- Do not rely on a traditional p-n junction to separate photogenerated charge carriers.
- Devices include:
 - Nanocrystal solar cells
 - Photoelectrochemical cells

- Grätzel Cell
- Dye-sensitized hybrid solar cells
- Polymer solar cells

Polymer solar cells

- Bulk heterojunctions' between an organic polymer and organic molecule as electron acceptor.
- Fullerene embedded into conjugated polymer conductor
- Lightweight, disposable, inexpensive to fabricate, flexible, designable on the molecular level, and have little potential for negative environmental impact.
- Present best efficiency of polymer solar cells lies near 5 percent
- Cost is roughly one-third of that of traditional silicon solar cell technology
- **Band gaps $\geq 2\text{eV}$**



- After excitation in photoactive polymer, the electron is transferred to the C_{60} due to its higher electron affinity
- Photoinduced quasiparticle (polaron P^+) formed on the polymer chain and fullerene ion-radical C_{60}

Advantages

- Low-energy, high-throughput processing technologies
- Polymer cells - solution processable, chemically synthesized
- Polymer cells - low materials cost
- Grätzel cells - attractive replacement for existing technologies in "low density" applications like rooftop solar collectors
- Grätzel cells - Work even in low-light conditions
- DSSC - potentially rechargeable => upgradeable?

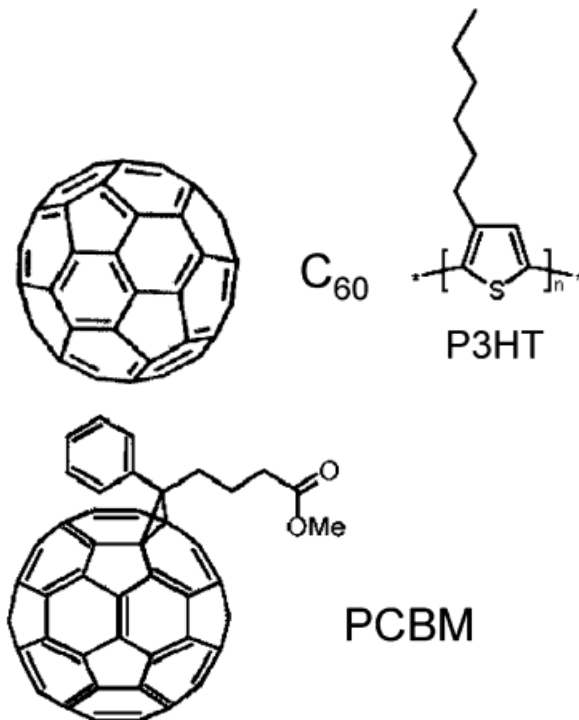
Disadvantages

- Efficiencies are lower compared with silicon (wafer-based) solar cells
- Polymer solar cells:
- Degradation effects: efficiency is decreased over time due to environmental effects.
- High band gap
- PEC cells suffer from degradation of the electrodes from the electrolyte

2.2.4 FOURTH GENERATION

Use of polymers with nanoparticles mixed together to make a single multispectrum layer.

- Significant advances in hybrid solar cells have followed the development of elongated nanocrystal rods and branched nanocrystals
- More effective charge transport.
- Incorporation of larger nanostructures into polymers required optimization of blend morphology using solvent mixtures.
- Cell Design:
 - Solid state nanocrystals (Si, In, CuInS₂, CdSe)
 - Imbedded in light absorbing polymer (P3HT)
 - p-type, polymeric conductor, such as PEDOT:PS, carries 'holes' to the counter electrode.
 - Coated on a transparent semi-conducting oxide (ITO)



Advantages

- Solution processable

- Lower materials cost (polymer)
- Self-assembly
- Printable nanocrystals on a polymer film
- Improved conversion efficiency (potentially)

Disadvantages

- Efficiencies are lower compared to silicon (wafer-based) solar cells
- Potential degradation problems similar to polymer cells
- Optimize matching conductive polymers and nanocrystal

2.2.5 ORGANIC SOLAR CELLS

The first generation of organic photovoltaic solar cells was based on single organic layers sandwiched between two metal electrodes of different work functions. The rectifying behavior of single layer devices was attributed to the asymmetry in the electron and hole injection into the molecular π^* and π -orbitals, respectively, and to the formation of a Schottky-barrier between the p -type (hole conducting) organic layer and the metal with the lower work function. The power conversion efficiencies reported were generally poor (in the range of 10^{-3} to $10^{-2}\%$), but reached remarkable 0.7% for merocyanine dyes in the early days. In this case, the organic layer was sandwiched between a metal–metal oxide and a metal electrode, thus enhancing the Schottky-barrier effect [metal-insulator semiconductor (MIS) devices]. The next breakthrough was achieved by introducing the bilayer heterojunction concept, in which two organic layers with specific electron or hole transporting properties were sandwiched between the electrodes. Tang reported 1986 about 1% power conversion efficiency for two organic materials (a phthalocyanine derivative as p -type semiconductor and a perylene derivative as n -type semiconductor) sandwiched between a transparent conducting oxide and a semitransparent metal electrode. This result was for many years the outstanding benchmark and was surmounted only at the turn of the millennium.

Hiramoto and co-workers did pioneering work introducing the concept of an organic tandem cell structure by stacking two heterojunction devices. They also developed a three layer p - i - n like structure with a co-deposited interlayer between the p -type (hole conducting) and n -type (electron conducting) layers. In the meantime, the field of conjugated polymers grew mature, and the first single layer devices based on these newly developed materials were presented. But also, these polymer single layer devices were showing only power conversion efficiencies of less than 0.1%. The observation of a photoinduced electron transfer from optically excited conjugated polymers to the C60 molecule and the observation of highly increased photoconductivities upon C60 addition to the conjugated polymers led to the development of polymer–fullerene bilayer heterojunction and bulk heterojunction devices incorporating C60 and C60-derivatives with enhanced solubility.

The photoinduced electron transfer occurs when it is energetically favorable for the electron in the S₁- excited state of the polymer to be transferred to the much more electronegative C60, thus resulting in an effective quenching of the excitonic photoluminescence of the polymer. Because the electron is transferred from a p -type hole conducting polymer onto the rather n -type electron

conducting C60 molecule, the notation of donor (D) and acceptor (A) with respect to the electron transfer was introduced. The photoinduced charge transfer is depicted schematically in Fig. 1 together with the energetic description.

A further approach was lamination of two polymer layers, leading to a diffusive interface between D and A moieties, and calculated power conversion efficiencies approaching 2% were reported.

The organic solar cell development gained momentum in the past years: Conversion efficiencies between 1.5 and 4% have been achieved for evaporated bilayer devices, bulk heterojunction polymer–fullerene. Conceptually similar to the bulk heterojunction, there is a wide research field of dye sensitized, electrochemical solar cells. The early steps in the development were largely improved by the Graetzel group. However, in recent years, by the introduction of organic hole conductors as replacement for the liquid electrolytes in electrochemical solar cells and by the exchange of the electron conducting acceptor materials in organic heterojunction devices with inorganic nanocrystals, electrochemical and organic photovoltaic research directions are gradually merging together.

3. ORGANIC SOLAR CELL

a) BASICS:

Organic solar cell is a photovoltaic device which converts photons into electricity, as an active layer where charge separation takes place organic semiconductor material is used. The glass substrate is used as a base and on this substrate the INDIUM TIN OXIDE(ITO) is coated which works as an electrode(anode). On this ITO film we deposit the organic material (single, double or multi layer) which works as an active layer, finally the aluminium coating is done which works as another electrode(cathode).

Unlike in an inorganic crystalline PV cell material, with its band structure and delocalized electrons, excitons in organic photovoltaics are strongly bound with an energy between 0.1 and 1.4 eV. This strong binding occurs because electronic wavefunctions in organic molecules are more localized, and electrostatic attraction can thus keep the electron and hole together as an exciton. The electron and hole can be dissociated by providing an interface across which the chemical potential of electrons decreases. The material that absorbs the photon is the donor, and the material acquiring the electron is called the acceptor. In Fig. 2, the polymer chain is the donor and the fullerene is the acceptor. After dissociation has taken place, the electron and hole may still be joined as a geminate pair and an electric field is then required to separate them.

After exciton dissociation, the electron and hole must be collected at contacts. However, charge carrier mobility now begins to play a major role: if mobility is not sufficiently high, the carriers will not reach the contacts, and will instead recombine at trap sites or remain in the device as undesirable space charges that oppose the drift of new carriers. The latter problem can occur if electron and hole mobilities are highly imbalanced, such that one species is much more mobile than the other. In that case, space-charge limited photocurrent (SCLP) hampers device performance.

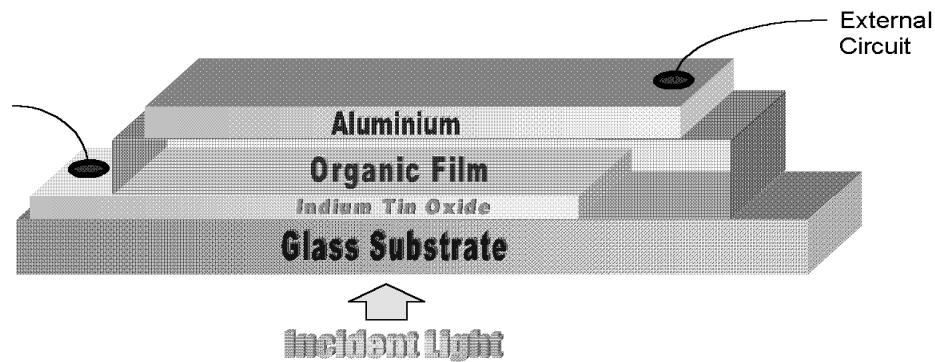
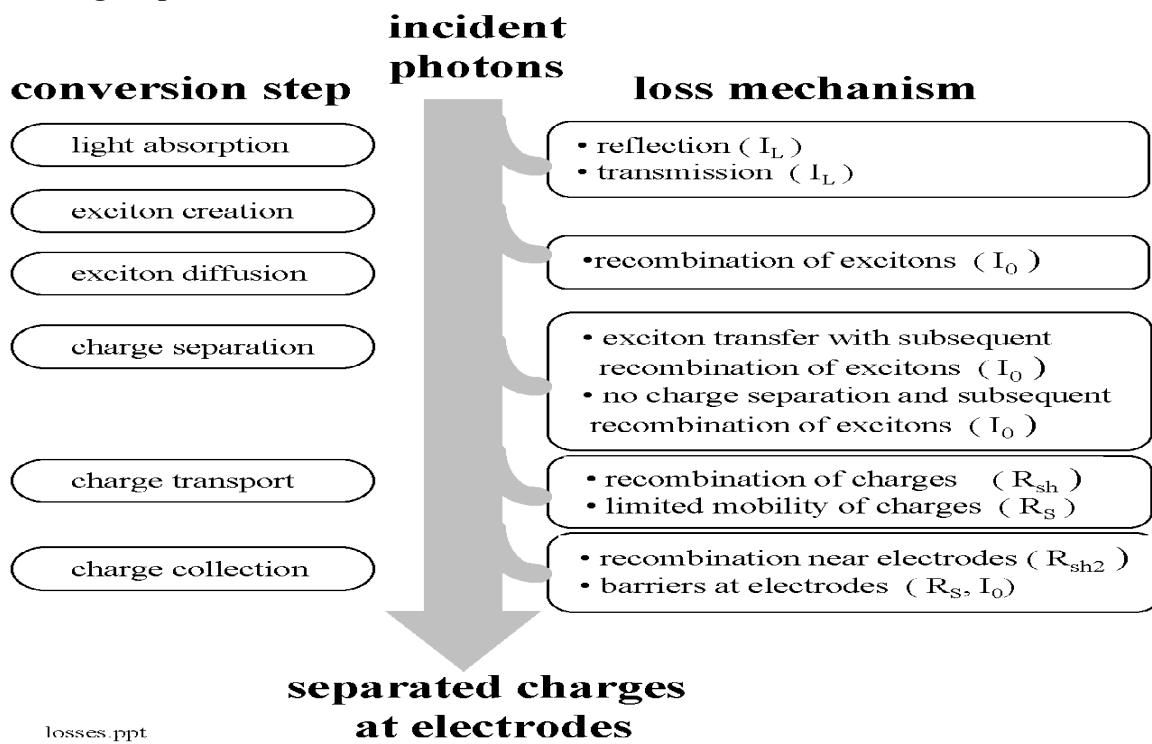


Fig3.1 Device Structure(taken from Phd thesis of Dipl.Ing. Klaus Petri)

Working Steps:



losses.ppt

Fig 3.2 working mechanism(taken from Phd Thesis of Dipl.Ing. Klaus Petritsch)

Device Physics:

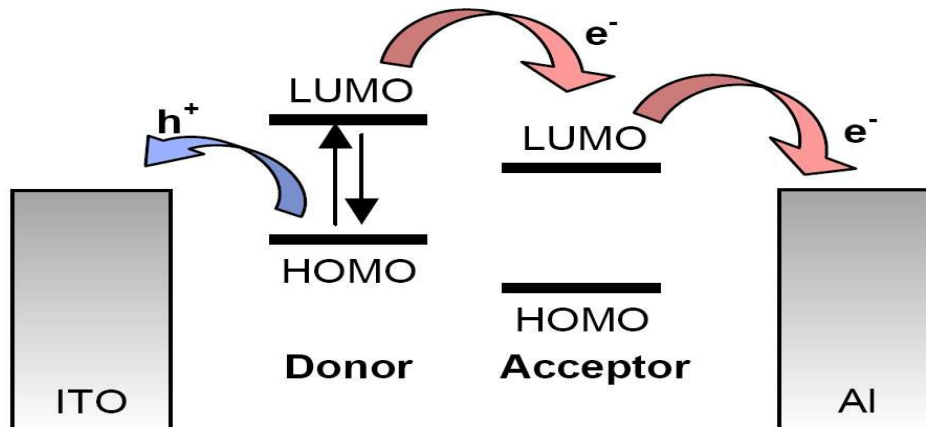
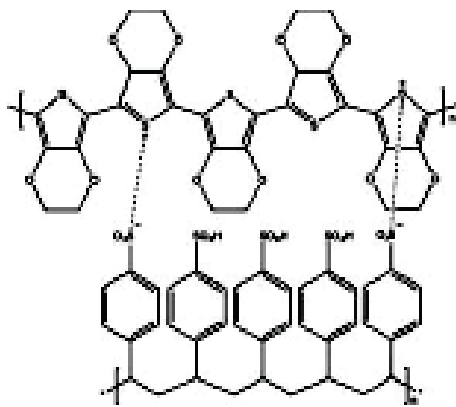


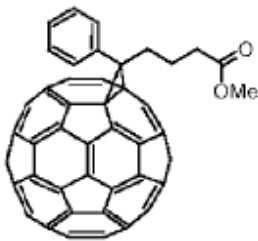
Fig 3.3 exciton transfer mechanism (by Daniel Lehmann, 11.01.2005)

b) MATARIALS USED:

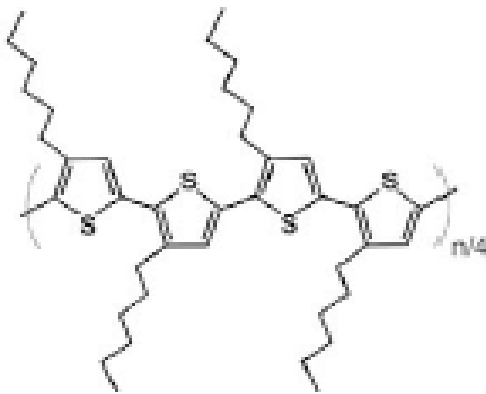
we have used Poly(3,4ethylenedioxythiophene):poly(styrenesulfonate)— Baytron PH(PEDOT:PSS) for smoothness of rough ITO surface and as a exciton blocking layer[1] . We have used P3HT and PCBM mixture as polymer blend having specifications as follows:



[PEDOT:PSS](#)

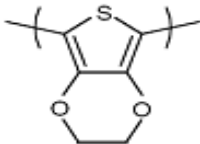
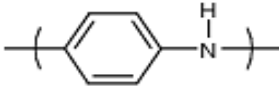



PCBM



P3HT

Examples of Electrochromic Conjugated Polymers

Name	Chemical Structure	Colors	Notes
Poly(3,4-ethylenedioxythiophene) (PEDOT)		Oxidized: faint blue Reduced: deep blue	Highly conductive when oxidized (even partially) Doped state is especially stable Commercially available in many forms, including aqueous suspensions
Poly(aniline) (PANI)		Neutral: colorless Oxidized 1: green Protonated oxidized 1: blue Oxidized 2: blue Protonated oxidized 2: violet	Commercially available in many forms Not conducting in neutral state
Poly(3-hexylthiophene) (P3HT)		Oxidized: clear Neutral: red-pink	Commercially available Not conducting in neutral state Other alkyls can be substituted for hexyl group Need at least butyl for polymer to be soluble

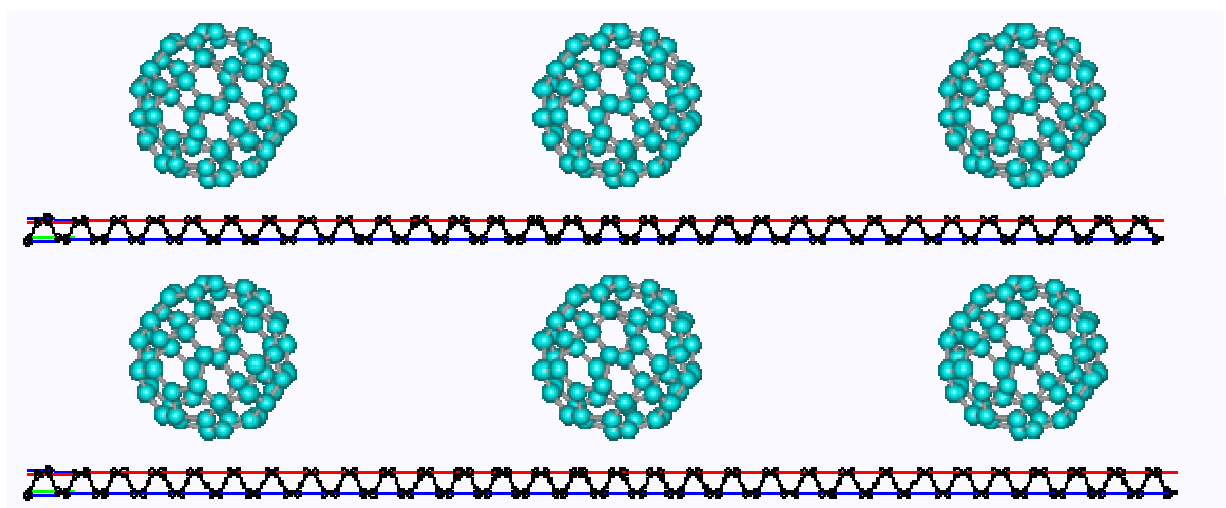


Fig 3.4 PCBM(C₆₀):P3HT BLEND

e) FABRICATION PROCESS:

Apparatus used:-

I. SPIN COATING SYSTEM

Spin coating is a technique by which very thin films are deposited onto a solid substrate. To fabricate thin polymer films, the polymer is first dissolved in a volatile solvent (e.g. toluene for polystyrene). If a drop of solution is placed on a substrate, it can flow to form a metastable, continuous film or form a droplet on the surface, depending on the "wettability" of the substrate. By spinning the substrate, the droplet is forced to spread out while the solvent evaporates. If deposition conditions such as choice of solvent, solution concentration and spin speed are chosen correctly, a thin film of uniform thickness is deposited on the substrate. Spin coating is a procedure used to apply uniform thin films to flat substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. A machine used for spin coating is called a spin coater, or simply spinner. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. Spin coating is widely used in microfabrication, where it can be used to create thin films with thicknesses below 10 nm.

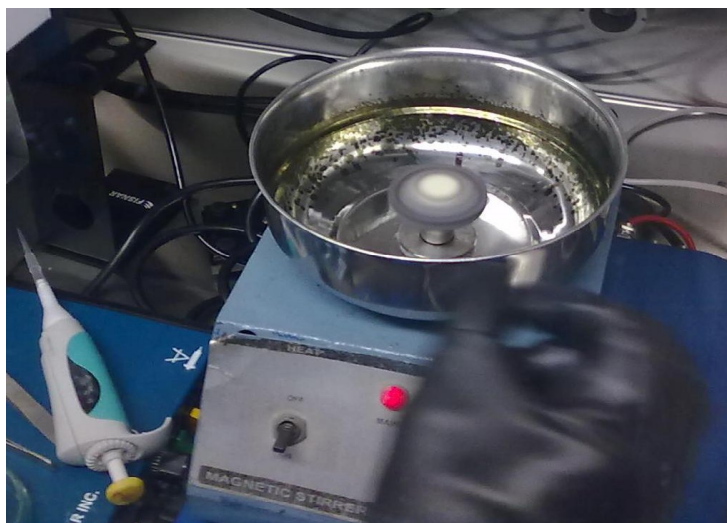


Fig 3.5 Spin Coater

II. ULTRASONIC BATH

An ultrasonic bath, is a cleaning device that uses ultrasound (usually from 15–400kHz). In an ultrasonic bath, the object to be mixed is placed in a chamber containing a suitable ultrasound conducting fluid (an aqueous or organic solvent, depending on the application). An ultrasound generating transducer built into the chamber, or lowered into the fluid, produces ultrasonic

waves in the fluid by changing size in concert with an electrical signal oscillating at ultrasonic frequency. This creates compression waves in the liquid of the tank which 'tear' the liquid apart, leaving behind many millions of microscopic 'voids' or 'partial vacuum bubbles' (cavitation). These bubbles collapse with enormous energy; temperatures of 10,000 K and pressures of 50,000 lbs per square inch have been reported. Transducers are usually piezoelectric material (e.g. lead zirconate titanate or barium titanate), and sometimes magnetostrictive (made of a material such as nickel or ferrite).



Fig 3.6 Ultrasonic Bath

III. GLOVE BOX

A glovebox (or glove box) is a sealed container that is designed to allow one to manipulate objects while being in a different atmosphere from the object. Built into the sides of the glovebox are two gloves arranged in such a way that the user can place his or her hands into the gloves and perform tasks inside the box without breaking the seal or allowing potential injury. Part or all of the box is usually transparent to allow the user to see what is being manipulated. Two types of glove boxes exist: one allows a person to work with hazardous substances, such as radioactive materials or infectious disease agents; the other allows manipulation of substances that must be contained within a very high purity inert atmosphere, such as argon or nitrogen. It is also possible to use a glovebox for manipulation of items in a vacuum chamber.

Inert atmosphere work

The argon in a glove box is pumped through a series of treatment devices which remove solvents, water and oxygen from the gas. Heated copper metal (or some other finely divided metal) is commonly used to remove oxygen, this oxygen removing column is normally regenerated by passing a hydrogen/nitrogen mixture through it while it is heated, the water formed is passed out of the box with the excess hydrogen and nitrogen.



3.7 Old Glove box (manually operated)

IV. THERMAL EVAPORATOR

Evaporation is a common method of thin film deposition. The source material is evaporated in a vacuum. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. Evaporation is used in microfabrication, and to make macro-scale products such as metallized plastic film. Evaporation involves two basic processes: a hot source material evaporates and condenses on the substrate. It resembles the familiar process by which liquid water appears on the lid of a boiling pot. However, the gaseous environment and heat source are different.

Evaporation takes place in a vacuum, i.e. vapors other than the source material are almost entirely removed before the process begins. In high vacuum (with a long mean free path), evaporated particles can travel directly to the deposition target without colliding with the background gas. At a typical pressure of 10^{-4} Pa, an 0.4-nm particle has a mean free path of 60 m. Hot objects in the evaporation chamber, such as heating filaments, produce unwanted vapors that limit the quality of the vacuum.

Evaporated atoms that collide with foreign particles may react with them; for instance, if aluminium is deposited in the presence of oxygen, it will form aluminium oxide. They also reduce the amount of

vapor that reaches the substrate, which makes the thickness difficult to control. Evaporated materials deposit nonuniformly if the substrate has a rough surface. Because the evaporated material attacks the substrate mostly from a single direction, protruding features block the evaporated material from some areas. When evaporation is performed in poor vacuum or close to atmospheric pressure, the resulting deposition is generally non-uniform and tends not to be a continuous or smooth film. Rather, the deposition will appear fuzzy. Any evaporation system includes a vacuum pump. It also includes an energy source that evaporates the material to be deposited. Many different energy sources exist:

In the thermal method, the source material is placed in a crucible, which is radiatively heated by an electric filament. Alternatively, the source material may be hung from the filament itself (filament evaporation).

Optimization

- Purity of the deposited film depends on the quality of the vacuum, and on the purity of the source material.
- The thickness of the film will vary due to the geometry of the evaporation chamber. Collisions with residual gases aggravate nonuniformity of thickness.
- In order to deposit a material, the evaporation system must be able to melt it. This makes refractory materials such as tungsten hard to deposit by methods that do not use electron-beam heating.

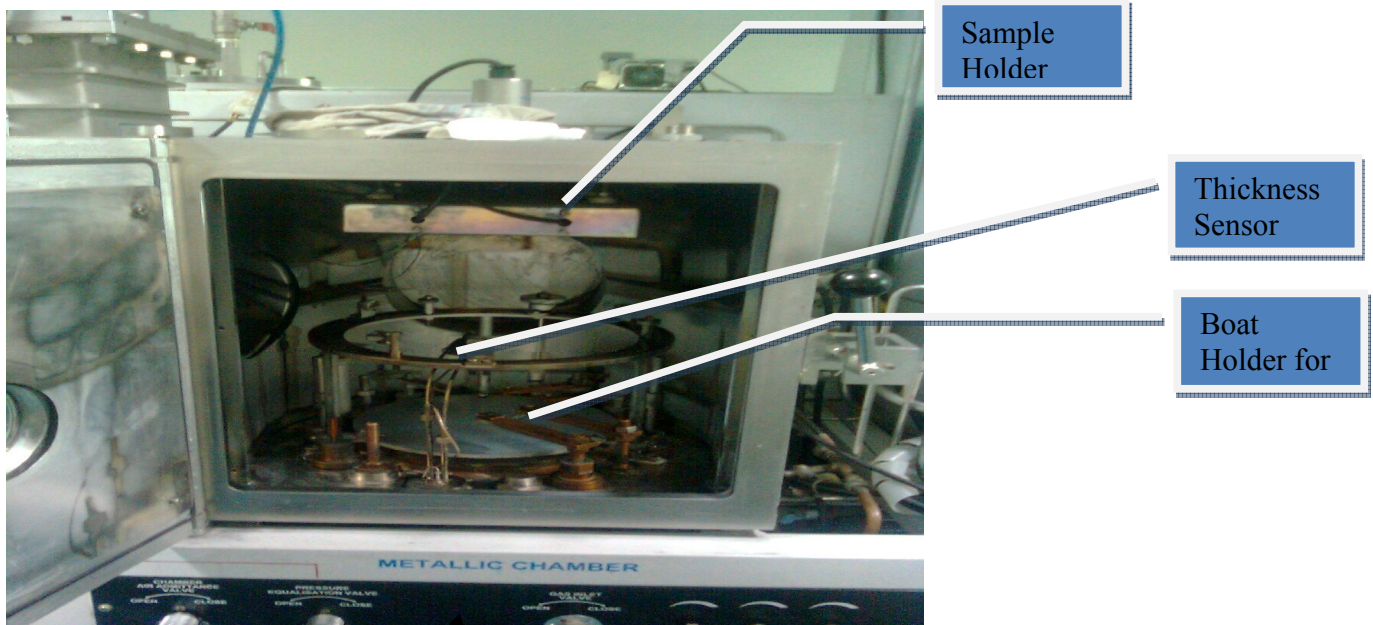


Fig 3.8 Metallic Chamber

Steps involved:-

The following steps were followed for the laboratory preparation of organic solar cells at the National Physical Laboratory, Delhi, India.

- 1.** First, a substrate for the solar cells is used, in this case a transparent electrode made of Indium-Tin-Oxide covered glass. These glass plates are conducting only on one side.
- 2.** The substrates are cut to the appropriate sizes.
- 3.** A number is scratched onto the glass to mark the non-conductive side.
- 4.** The Indium-Tin-Oxide (ITO) electrode should be removed from some parts of the glass side to avoid shorts. This is done by etching the ITO in an acidic bath.
- 5.** To avoid etching away all the ITO, we have to cover parts of the glass slide with a mask. This is done with black/brown adhesive tape which covers only the parts of the glass, where the ITO coating should stay.
- 6.** To etch the ITO away, the substrates are immersed in 1:1 solution of hydrochloric acid and water i.e. 50% solution of acid in water. To speed up the reaction the zinc powder is added (5mg in 50ml HCl).
- 7.** After the etching process, the substrates are rinsed with deionized water to remove the acid. Under the adhesive tape, the ITO was not etched; it now covers an area of the intended shape and size.
- 8.** Now, the substrates are cleaned for half an hour in special cleaning soap solution. For better results this is done in a heated Ultrasonic bath.
- 9.** Because of the extremely small thickness of the active layers in the organic solar cell, a very thorough cleaning is necessary to avoid shorts or bad contacts between the layers.
- 10.** So a further cleaning is done. ITO coated plates are washed in acetone heated at 100⁰C. This is followed by cleaning in trichloroethane followed by propanol at 100⁰C.
- 11.** The spatula is washed with acetone and P3HT, PCBM, are weighed on the butter paper (after noting its weight).

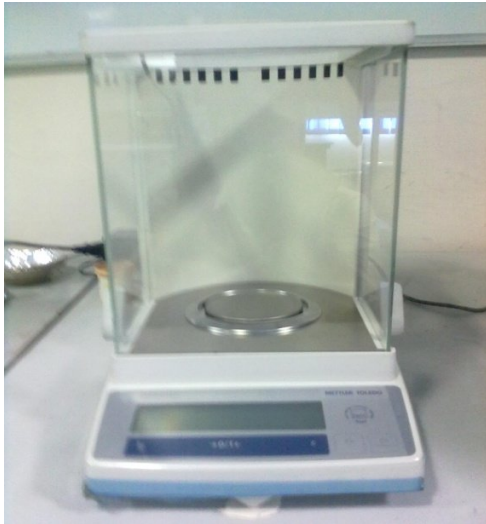


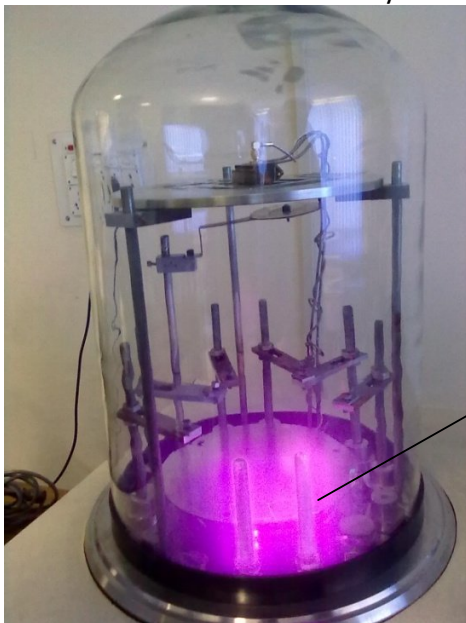
Fig 3.9 Digital Weighing machine

12. After weighing at different ratios according to our need and for getting better result they are each transferred into a vial containing few ml of chlorobenzene according to our specifications (mg/ml).

13. The vials are then kept in an ultrasonic bath for half an hour. The frequency set is 35kHz for making nano-solutions.

14. The plates are then allowed to dry in an oven at 120°C for 30minutes.

15. ITO coated plates are subjected to plasma in a plasma thermal evaporator(fig 3.10) for 5 minutes for the removal of any leftover dirt or particles and surface smoothness.



Plasma
Glow

Fig 3.10 Plasma chamber

16. ITO covered side of the substrates is now coated with PEDOT:PSS. This a transparent conductive polymer which is needed to enhance the contact between the ITO electrode and the active layer. To get a good film quality, the PEDOT: PSS solution has to be filtered.

17. The optimal film thickness is between 50 and 100 nm. This is achieved by using spin coating technique. In this method the polymer solution is distributed evenly on a glass substrate (Fig 3.11) which is subsequently rotated at 2000rpm for 2 minutes. Due to centrifugal forces, a very thin and homogeneous film of the polymer is coated on the surface of the substrate.

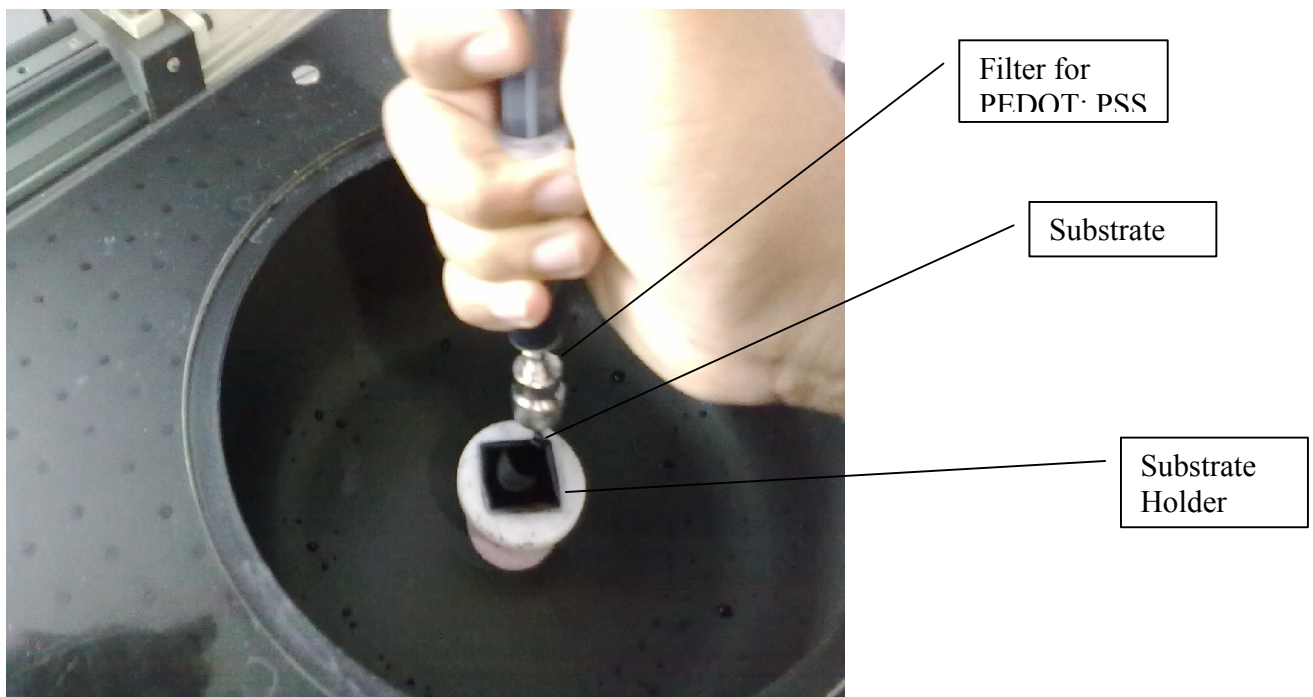


Fig3.11 Coating of PEDOT: PSS in spin coater

18. First, P3HT (Poly-hexyl-thiophene), a p-type semi conducting polymer is weighed to give a final solution concentration of 15mg/ml. Then, PCBM is weighed to give the same final solution concentration. PCBM is soluble derivative of Buckminster fullerene C60.

19. The active layer is also deposited by the spin coating technique in inert atmosphere inside the Glove Box (Fig 3.12). After that heating of the substrate to 120°C for 30 min on a hot plate inside the glove box ensures a fast evaporation of the solvent.



Fig 3.12 Coating inside glovebox

20. When the solvent has evaporated completely, a thin film of P3HT and PCBM with a thickness of about 200nm remains on the surface of the substrate.

21. To finish the solar cells, the metal back electrode has to be evaporated. A mask is aligned to the substrate, so that the metal electrode is deposited only on the area where it is needed.

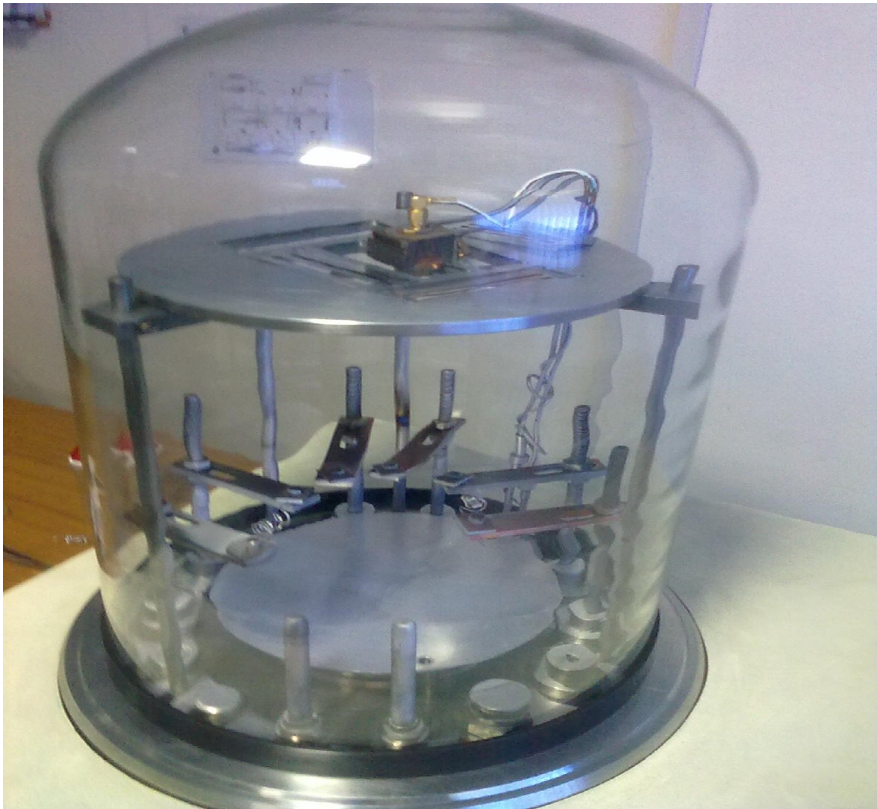


Fig 3.13 Al deposition unit

22. As the active layer of the solar cell is sensitive to atmospheric oxygen and water, the next steps are performed in inert environment glove box.

23. The transfer from and to the glove box is done via an air lock. The lock containing the substrates is evacuated and then filled with nitrogen.

24. The evaporation of the metals is done from a small tungsten boat containing the desired metal (aluminum) on which a high current is applied. Thus the boat is heated up and the material evaporates.

25. The process is done in high vacuum, so that the evaporated metal can condense on the substrates as thin films without colliding with gas molecules in between. The film thickness is monitored by a quartz crystal microbalance.

26. The metal electrode is an approx. 100 nm thick layer of aluminum.
27. To optimize the performance of the solar cells, they have to be heated for a few minutes after the final deposition.
28. In darkness, the solar cell current-voltage (short-I-V) characteristic behaves like a diode.
29. If a negative bias is applied, a small negative current is flowing. At positive applied voltages, the current is much higher. Under illumination, the I-V curve is shifted so in some range the current is negative, even though a positive voltage is applied. In this range, the solar cell generates power. The maximum of power is generated in the maximum power point. The maximum power output divided by the power of the incoming light is the overall power efficiency of the solar cell.
30. Solar cells can only convert some parts of the solar spectrum.
31. To measure the dependency of the conversion efficiency and the wavelength of the incoming light, the solar cell is illuminated with light of different wavelengths and the resulting current is measured at the same time.

4. AREAS OF IMPROVEMENT

4.1 EFFICIENCY:

The first area on which we have worked, is efficiency improvement of organic solar cell. Efficiency can be calculated as follows:

$$J_{sc} = (I_{sc} / \text{pixel Area})$$

$$\text{Fill Factor} = \frac{V_{max} \times I_{max}}{V_{oc} \times I_{sc}}$$

$$\text{Efficiency } (\eta\%) = \frac{V_{max} \times I_{max}}{P_{in}}$$

or

$$= FF \frac{V_{oc} \times I_{sc}}{P_{in}}$$

Where: I_{sc} -> short circuit current, V_{oc} -> open circuit voltage, FF-> fill factor
 So it clear from above equations that to improve the efficiency of the organic solar cell we have to improve either I_{sc} or V_{oc} , hence ultimately we have to improve the fill factor. We have used different ratios of P3HT:PCBM and found difference in efficiency and finally get the optimum ratio according to our laboratory. After that we developed the CdS nanoparticles via in-situ growth and using the matrix we have improved the efficiency further.

4.2 DEGRADATION/STABILITY:

Once the device fabrication is complete and we get good efficiency as well, the next thing we have to work upon is the lifetime of the solar cell. As we are using organic semiconductors in these devices, they are degradable with the atmosphere i.e the performance of these materials decreases with the time, as the large lifetime of a device the more stable the device will be . To check degradation we have to take measurements at different time intervals and compare the V_{oc} and J_{sc} . For getting higher stability we have tried different thickness of PEDOT: PSS and P3HT and different annealing temperature.

4.2 CHARGE TRANSPORT:

After exciton generation the most important thing is the easy transport of the exciton till the electrode (i.e. good carrier lifetime), as much number of carrier will be transported more will be the efficiency. So we have to choose such organic semiconductor which shows very good carrier transport hence we have to study the transport characteristics before using the semiconductor.

5. EFFICIENCY IMPROVEMENT

After learning device fabrication steps, I have repeated all of them several times by fabricating many devices for a good practice and then we have started the work for efficiency improvement. As we have discussed in previous chapter that for efficiency improvement we have to increase the V_{oc} and J_{sc} , so we have tried the same by two ways. In first experiment we have tried different ratios of P3HT: PCBM and in second we synthesized CdS nanoparticles and fabricate the device.

5.1 USING DIFFERENT RATIOS OF P3HT:PCBM

Experiment 1:-

**P3HT: PCBM (1:0.5) , Solution (25mg/ml) , Device Configuration:
ITO/PEDOT:PSS/P3HT:PCBM/AL**

The amount of both materials according to above ratio and solubility is as follows-

Volume	P3HT	PCBM
0.3 ml	5 mg	2.5 mg

by using this combination we have fabricated the device and we found V_{oc} of the device 0.436 and $J_{sc} = 2.57 \times 10^{-03}$ and efficiency was 0.429. Results for two samples with same ratio and configuration are listed below-

	J_{sc}	V_{oc}	Efficiency

Sample 1	-2.57×10^{-03}	0.436	0.429
Sample 2	-2.54×10^{-03}	0.476	0.484

I-V Curve

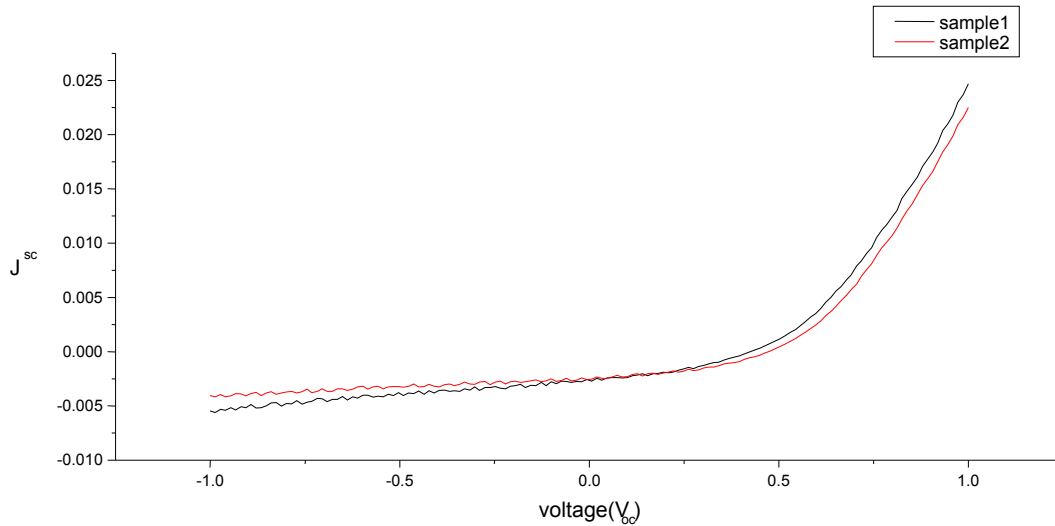


Fig 5.1.1 comparison of I-V Curve of both samples

Experiment 2:-

**P3HT: PCBM (1: 1.5) , Solution (30mg/ml), Device Configuration:
ITO/PEDOT:PSS/P3HT:PCBM/AL**

The amount of both materials according to above ratio and solubility is as follows-

Volume	P3HT	PCBM
0.3 ml	4.5 mg	6.75 mg

by using this combination we have fabricated the device and we found V_{oc} of the device 0.531 and $J_{sc} = -4.43 \times 10^{-03}$ and efficiency was 0.825 and Results for two samples with same ratio and configuration are listed below-

	J_{sc}	V_{oc}	Efficiency
Sample 1	-4.43×10^{-03}	0.531	0.825
Sample 2	-5.10×10^{-03}	0.470	0.731

I-V Curve

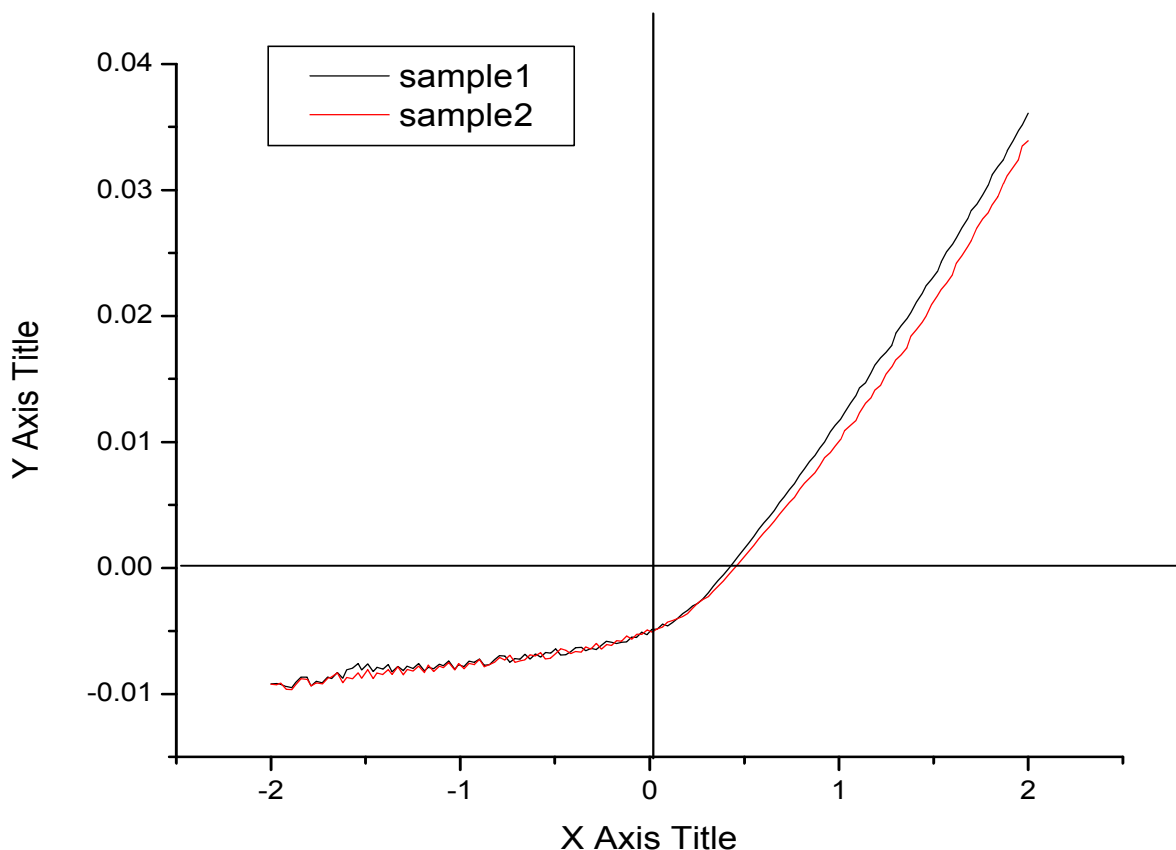


Fig 5.1.2 comparison for I-V curve for sample 1 and 2 for exp. 2

Experiment 3:-

P3HT: PCBM (1: 1) , Solution (30mg/ml), Device Configuration:

ITO/PEDOT:PSS/P3HT:PCBM/AL

The amount of both materials according to above ratio and solubility is as follows-

Volume	P3HT	PCBM
0.3 ml	4.5 mg	4.5 mg

by using this combination we have fabricated the device and we found V_{oc} of the device 0.464 and $J_{sc} = -7.45 \times 10^{-03}$ and efficiency was 1.57 and Results for two samples with same ratio and configuration are listed below-

	J_{sc}	V_{oc}	Efficiency
Sample 1	-9.77×10^{-03}	0.443	1.43
Sample 2	-7.45×10^{-03}	0.464	1.57

I-V Curve

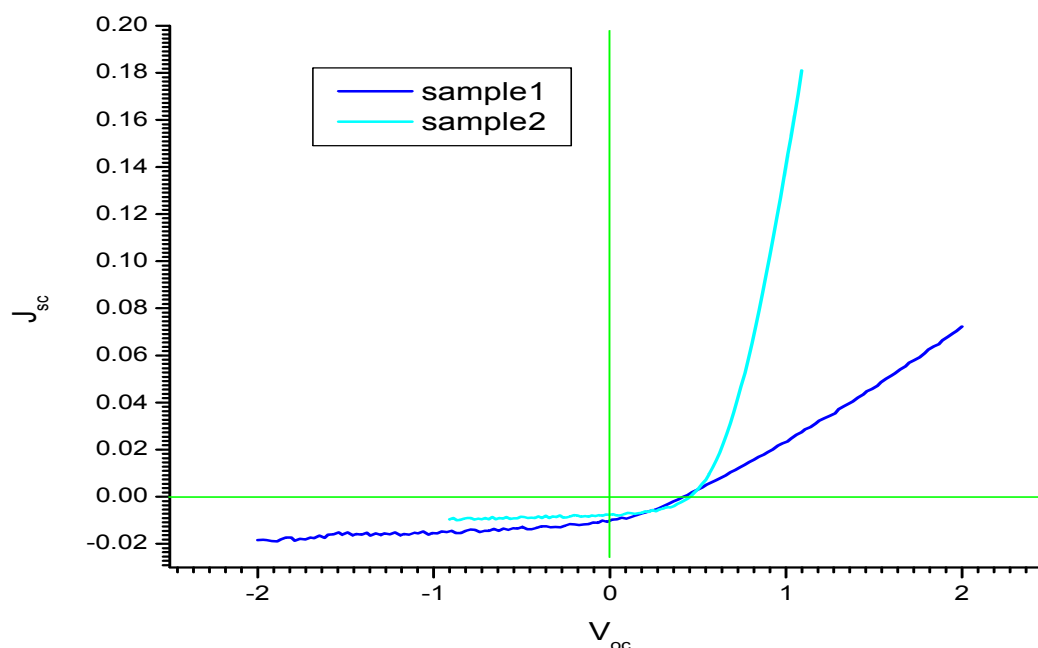


Fig 5.1.3 Comp of I-V for both samples

Results of Experiments under 5.1:-

We got highest efficiency with ratio 1:1 so this comes out to be an optimum ratio for the device fabrication using our available facilities and hence for our further experiments we will use the same ratio of P3HT:PCBM.

5.2 USING CdS NANOPARTICLES

5.2.1 Fabrication by In-situ growth of CdS nanoparticles via P3HT:

5.2.1.1 Synthesis of nanoparticles

In a three-neck round-bottom flask which is equipped with a magnetic stirring bar and condenser, we have taken 16 mL of DCB, 8mL of DMSO, 0.02 g of cadmium acetate dihydrated, and 0.02 g of P3HT and this mixture was heated to 100 C and after that we have degassed it with nitrogen for 30 min. In a second vial, 0.004 g of sulfur was dissolved in 2 mL of anhydrous DCB. Both solutions were heated to the temperature of the reaction (between 120 and 180 C) depending on the composite and conditions of reaction. Then we have injected 2 mL of the sulfur solution swiftly into the cadmium precursor solution. The solution was allowed to react for 30 min, during this reaction degassing was removed. The mixture of CdS and conducting polymer was purified by removing any cadmium, sulfur ions, and DMSO by adding anhydrous methanol to form the precipitate. After centrifugation, the

supernatant was then removed and the composite dissolved in DCB and kept for further synthesis.

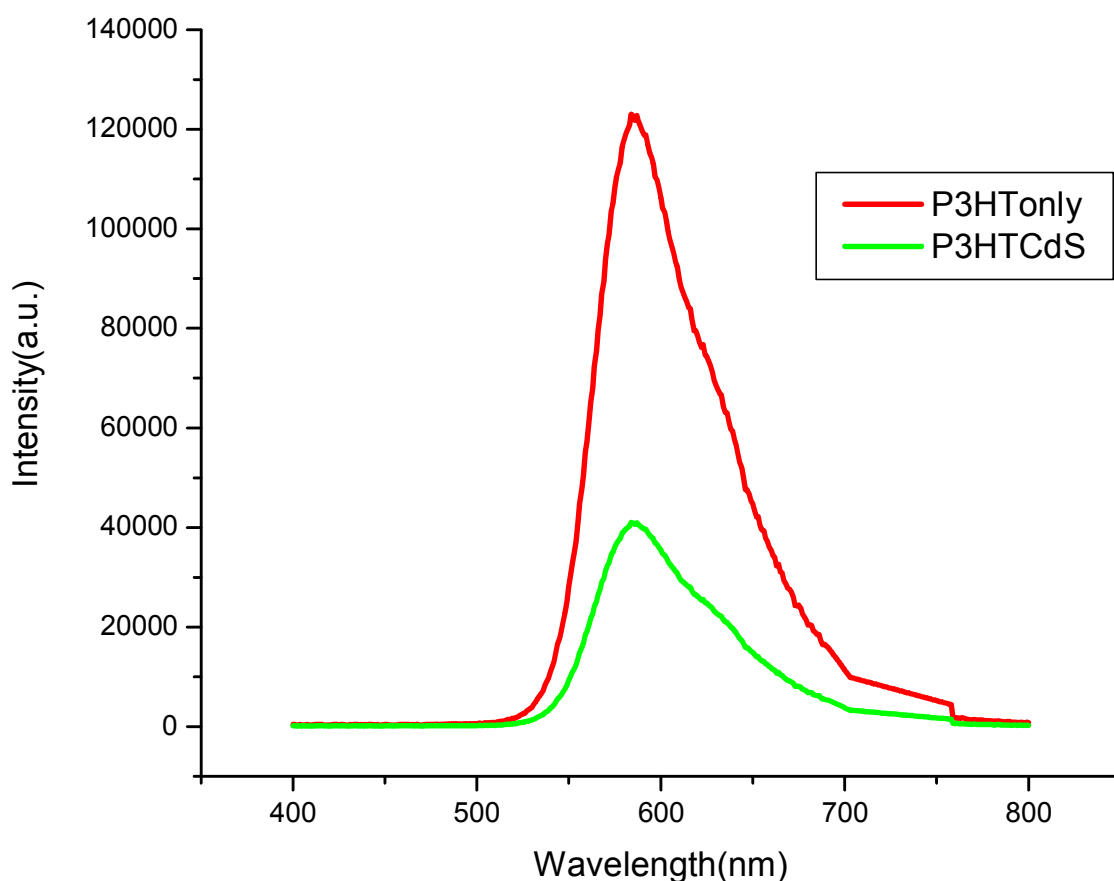


Fig 5.2.1 Photoluminescence emission spectra of P3HT and CdS:P3HT

Above Figure 5.2.1 shows the photoluminescence emission spectra of P3HT and CdS/P3HT composites in DCB. In agreement with previous work^[18], a reduction in the spectral intensity of the composites relative to the reference P3HT sample was observed. This reduction of PL intensity is due to photo generated charge transfer between the CdS and P3HT^[19]. According to previous studies, the decreased photoluminescence intensity of the composites is related to an improvement in photovoltaic performance^[20]. The photoluminescence quenching can be also used as a powerful tool for evaluation of charge transfer efficiency in the donor-acceptor blend composites^[21, 22]. Once the photo generated excitons are dissociated, the probability for recombination should be significantly reduced. This is a well known effect of the ultrafast electron transfer from the donor to acceptor, and it is expected to increase the exciton dissociation efficiency in photovoltaic devices^[21-23]. Thus, the synthesis of the composites with CdS nanoparticles provides a significant interest and encourages for further investigations onto the photoconductivity assessment for solar cell use.

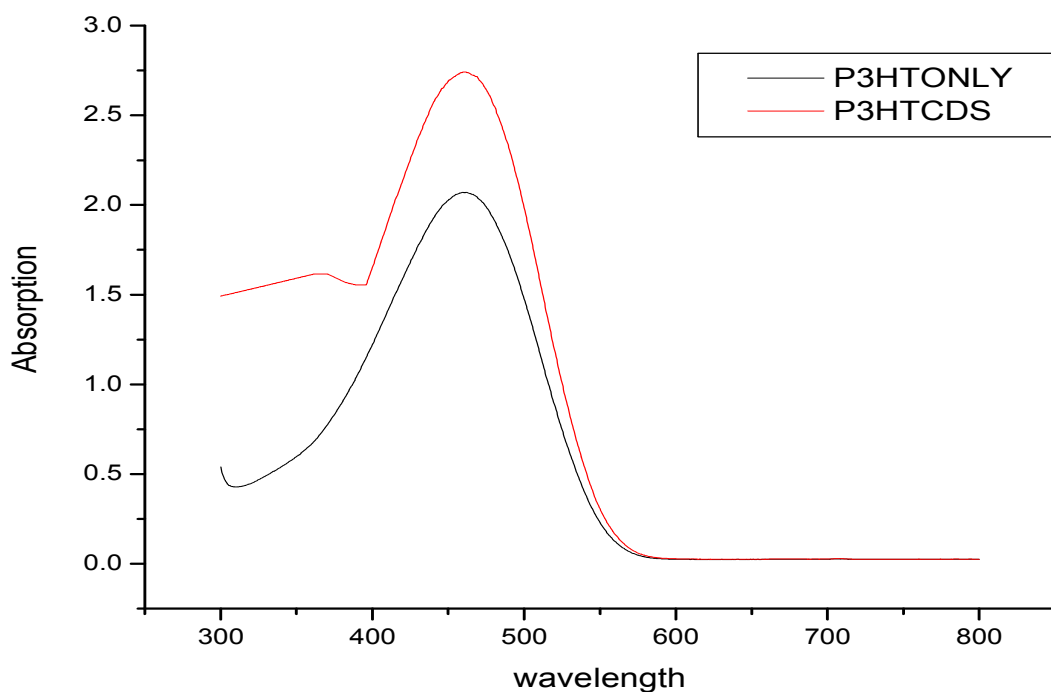


Fig 5.2.2 Comparison of UV spectra of P3HT and P3HT: CDS

The UV-vis absorption spectra of CdS/P3HT composite film obtained at 150⁰C shows the exciton peak behind the polymer exciton absorption peak at 385 nm due to the presence of CdS nanocrystals, as shown in Figure 5.2.2. Hence it is the confirmation of the CdS nanoparticles inside P3HT.

The presence of CdS nano particles in P3HT has also been confirmed by Transmission Electron Microscopy (TEM). Fig. 5.2.3 shows the high resolution TEM (HRTEM) image of CdS nano particles dispersed in the P3HT matrix. These particles were synthesized in the P3HT matrix with stirring. The nano-particles can easily be seen in the HRTEM image. The size of the nano-particles was ~ 6-10 nm. Fig. 5.2.4 shows the HRTEM image of the CdS nano-particles in the P3HT matrix synthesized without stirring. The size of the particles in this case was relatively small compared to those synthesized in the matrix with stirring.

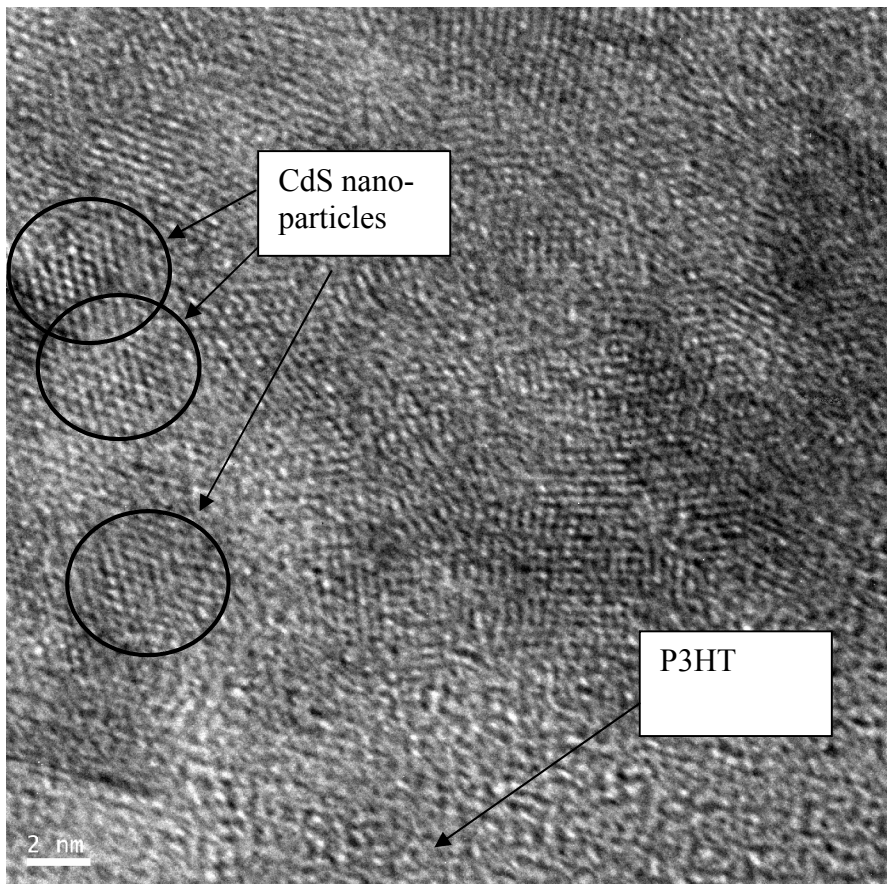


Fig 5.2.3 HRTEM image of P3HT:CdS matrix synthesized with stirring

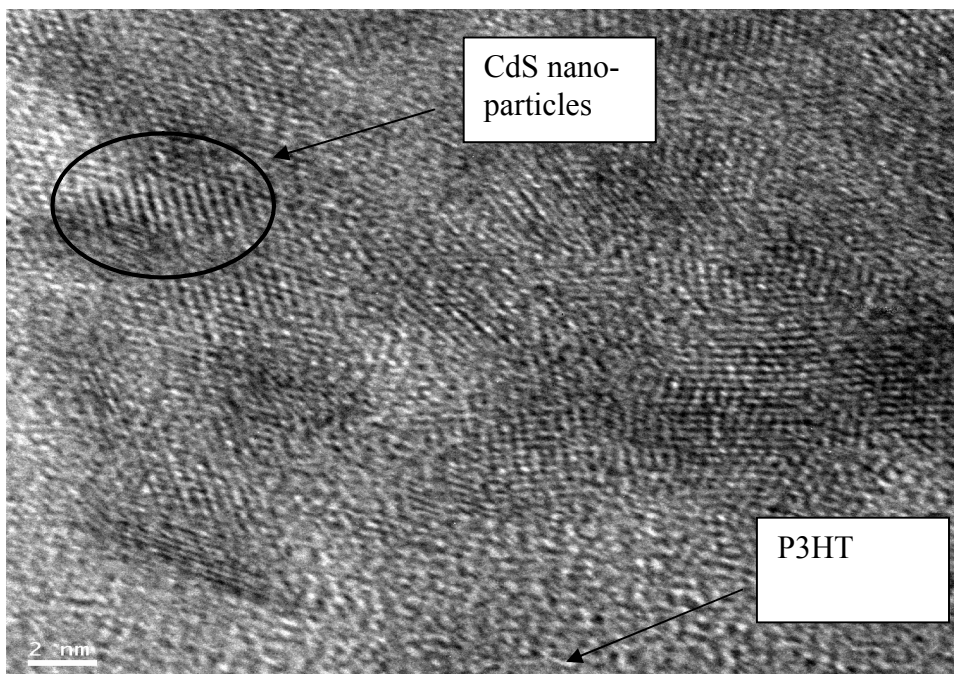


Fig 5.2.4 HRTEM image of P3HT:CdS matrix synthesized without stirring

5.2.1.2 Fabrication of device

We have used the indium tin oxide (ITO)-coated glass with the resistivity of ~ 15 ohms/sq. We have cleaned this ITO-coated glass with acetone and then by using plastic tape we have

made a pattern on this substrates so that during etching step the non covered area of ITO could be removed and two ITO strips on which taping was done remains there and then we cleaned the substrates by acetone. Now we have performed various cleaning steps as first of all cleaning with soap solution then rubbing by soap and cotton, after that cleaned with tap water and then distilled water and then put the substrate in distilled water in ultrasonicator so that soap can be removed completely. Then we have performed the boiling steps for making substrate very clean, in this sequence we have firstly boiled it in acetone for 15 minutes and after that in dichloroethelene and iso-propanol for 15 minutes each. After the cleaning steps we kept the substrate in oven for drying and after 15 minutes we treated the substrates with plasma in vaccum chamber at high tension and dry it again in oven for 30 minutes.

After plasma those substrates are ready to use for layer deposition and then we deposited PEDOT:PSS layer of about 100nm by spin coating for 120 sec at 2000 rpm and then annealed them at temp 120 degree for 30 minutes so that the layer can be fixed completely. While annealing period we prepared one solution of chlorobenzene and CdS-P3HT polymer matrix (15 mg/mL) and other of CB and P3HT only(15 mg/ml) and then in glove box inert atmosphere we have done the polymer coating at 1500 rpm and annealed at 120 C for 30 min.

After annealing the polymer layer we have done the aluminum coating for electrode purpose by using a mask and thermal evaporation inside a chamber of high vaccum and the device is prepared for measurement.

We have taken the I-V curves for both the devices and found that in case of P3HT only the V_{oc} of the device was 0.131 volts and the I_{sc} for the same device was 1.4×10^{-6} Amp. When we taken the measurements for the device fabricated with CdS: P3HT matrix, we found the V_{oc} was 0.33V and I_{sc} was 1.31×10^{-6} Amp. Hence there was significant increment in the V_{oc} of the device in case of the CdS while current was near about same. The device with CdS nanoparticles exhibited better efficiency. The enhances V_{oc} in the CdS:P3HT system compared to only P3HT can be attributed to introduction of donor-acceptor interface, since V_{oc} in polymer solar cells is controlled by the different of HOMO and LUMO energy levels of donor and acceptor respectively. The current can be increased by using PCBM with P3HT polymer and hence we can achieve higher efficiencies in that case. This comparison is shown in the fig below.

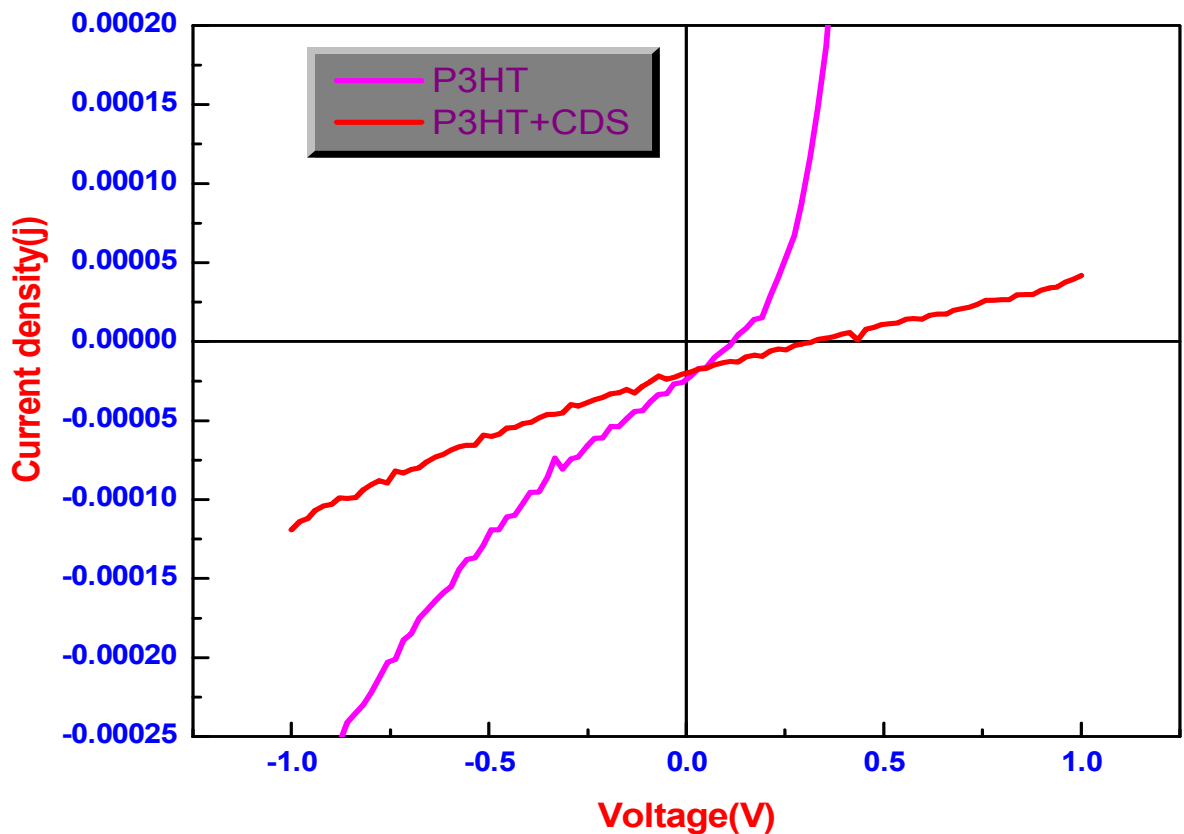


Fig.5.2.5. Comparison of I-V curves of P3HT only and with CdS particles

We have also plotted and compared the I-V curves in dark which are shown in figure below and it is easily observed that the curve for CdS particle embedded matrix is linear for whole scale while for P3HT only it is bending in first quadrant. Fig. 5.2.6 shows the dark J-V characteristics of P3HT and P3HT:CdS devices on log-log scale. The device with CdS nanoparticles exhibited low current compared to that of pure P3HT. This reduction in current on doping of CdS nanoparticles can be attributed to the introduction of traps for charge carriers. The CdS nanoparticles work as electron traps and reduce the current.

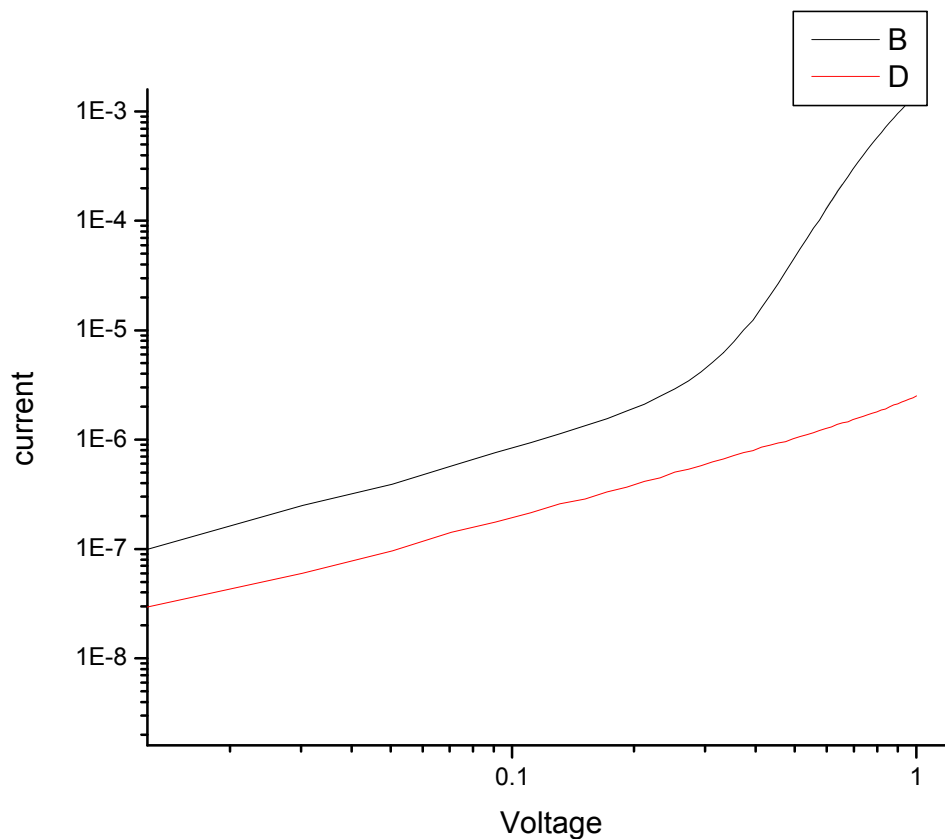


Fig.5.2.6. Comparison of I-V in Dark

Results and conclusion for chapter 5.2:-

After going through all the results and graph comparisons shown in above section we can conclude that as we have expected, the CdS particles when synthesized inside the polymer matrix, are increasing the photovoltaic effect in solar cell and significant increments in V_{oc} and Efficiency of the device are also achieved.

6. DEGRADATION STUDY

The Degradation of the solar devices is mainly concerned with how long a device takes to degrade its efficiency hence what is the life time of the device and here we work how to improve the life time by lowering the degradation. Lifetimes observed for polymer-based photovoltaic are very short compared to inorganic silicon-based solar cells with lifetime in excess of 25 years. For polymer solar cells the lifetime is most often defined as the time it takes for the efficiency to reach half its initial or maximum value. The lifetimes that have been reported are very short when the devices are operated in the atmosphere, and typically the values are in the range of minutes to a few days^[16].

6.1 BY USING DIFFERENT THICKNESS OF PEDOT:PSS USED WITH P3HT:

It is reported in past studies the Cells prepared without the PEDOT:PSS layer degraded relatively slower^[17]. The authors conclusion was that the hygroscopic PEDOT:PSS layer takes up water from the atmosphere increasing sheet resistance. Only relative values for the efficiency of most of the cells tested were reported, however, so direct comparisons may be difficult. The time span used in these experiments was also limited to 8 h with cells degrading to 50% of the initial efficiency over 1–2 h.

So we have tried to get the stability as good as possible with variation of thickness of PEDOT: PSS layer in following manner-

In our experiment we have taken two samples one has thin layer and another has thick layer of PEDOT: PSS over ITO and after that P3HT:PCBM layer was deposited.

We have done measurements of the both devices after different time intervals (two hours each) and compared the results which are as follows-

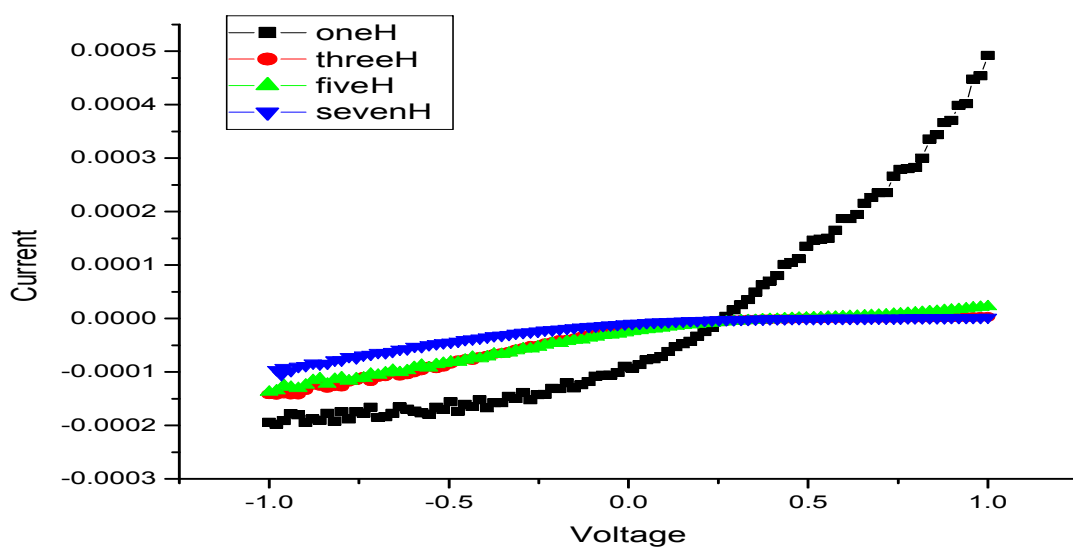


Fig 6.1 Degradation after two hour interval with device configuration ITO/PEDOT: PSS (Thin) / P3HT: PCBM / AL

In the above graph measurements of the thin layer device were taken in the light and it has been observed that device was degraded in the manner that V_{oc} of the device was increased slowly and I_{sc} was decreased. Hence overall efficiency was decreased with the time.

Now we have taken measurements of the thick layer device in the same way and get following results-

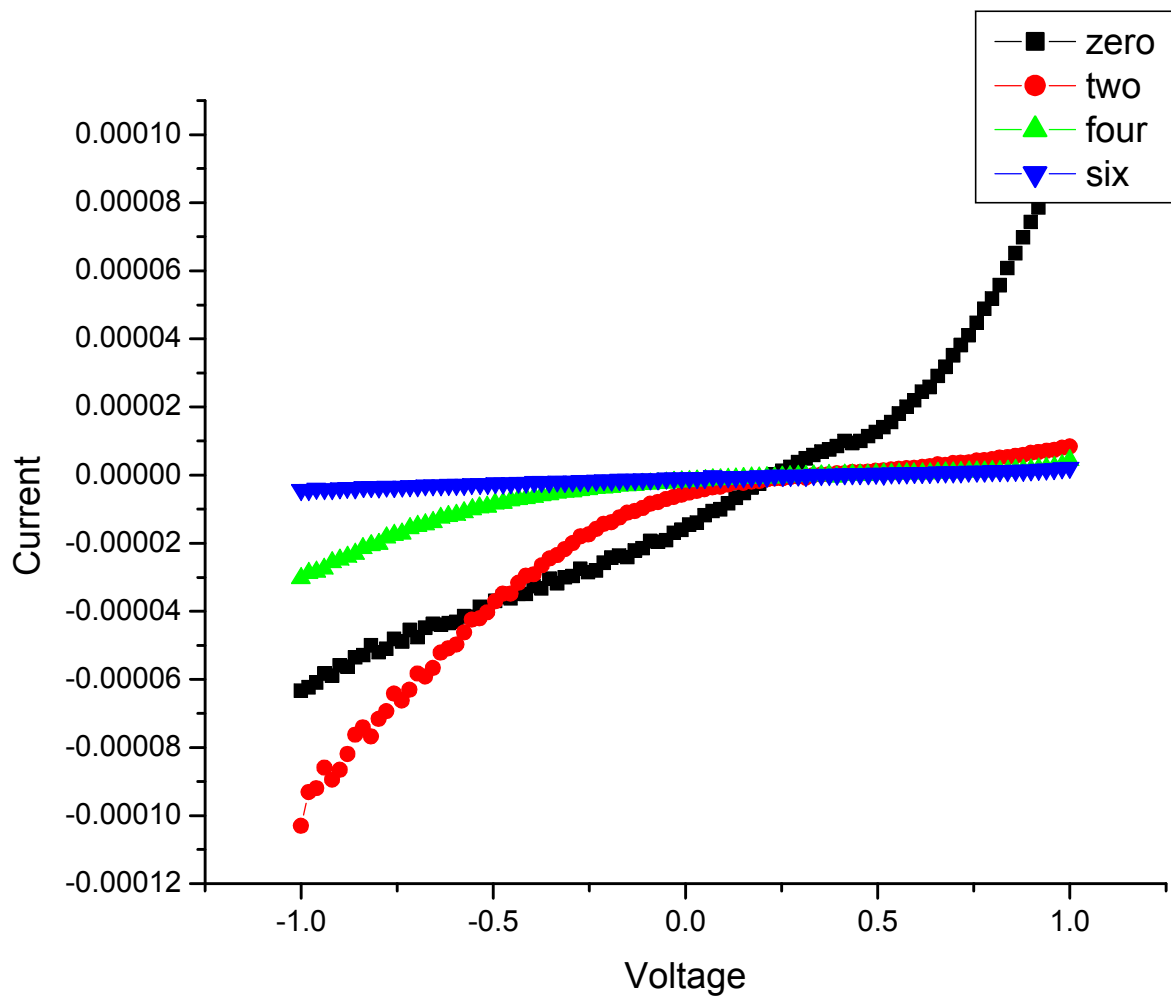


Fig 6.2 Degradation after two hour interval with device configuration ITO/PEDOT: PSS (Thick) / P3HT: PCBM / AL

It is observed from thick layer results that degradation was much faster in this device in comparison to thin layer and device was degraded in random manner.

When the measurement was taken a day after then device has almost lost its PV effect in following way-

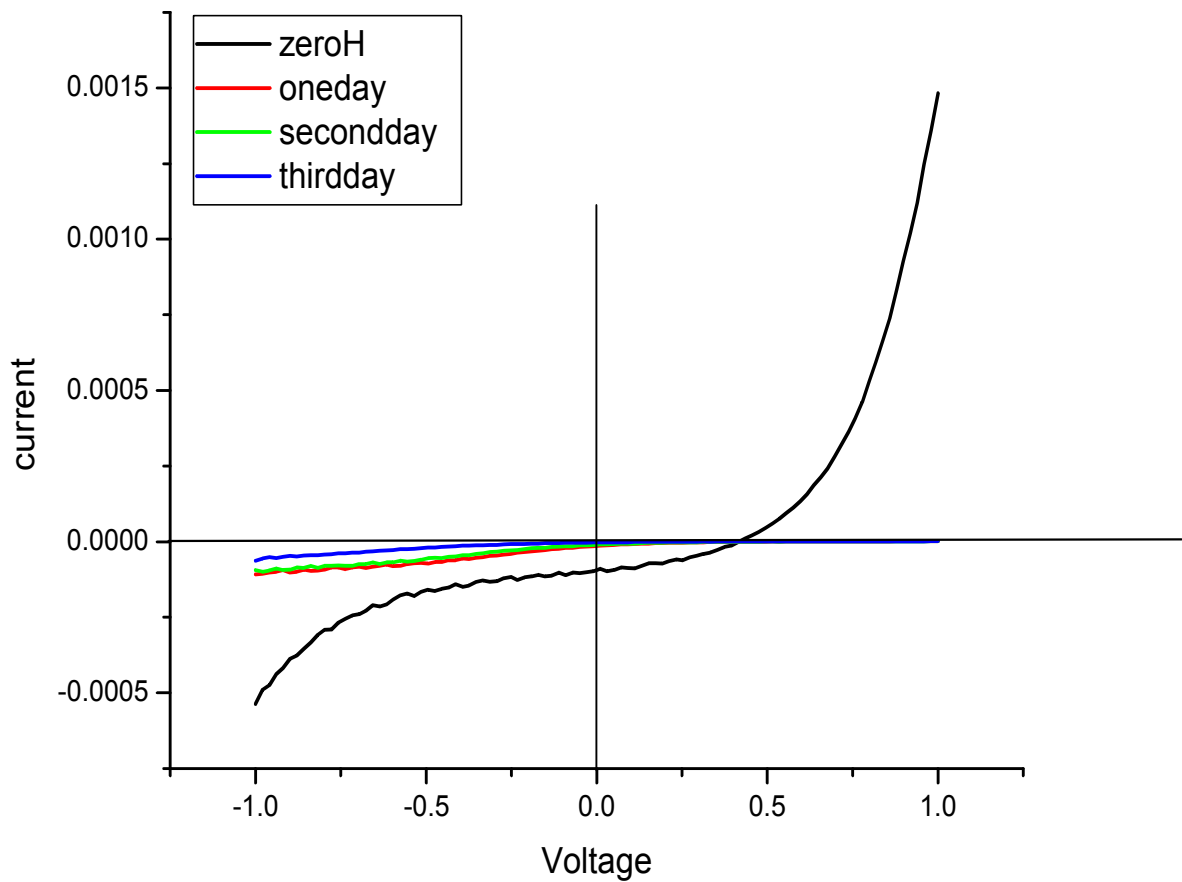


Fig 6.3 Degradation after one day interval with device configuration ITO/PEDOT: PSS (Thin) / P3HT: PCBM / AL

Hence this degradation was observed probably due to the layer of PEDOT: PSS because degradation is increasing as we increased the thickness of the layer. To confirm this result we have decided to fabricate a device without using PEDOT: PSS layer which will be discussed in next topic.

6.2 WITHOUT USING PEDOT: PSS (i.e. P3HT ONLY):

In this experiment we have fabricated the device by using only P3HT:PCBM and device configuration was ITO/P3HT:PCBM/AL and then we took measurements after two hours duration each as we have done in last chapter and got the following results-

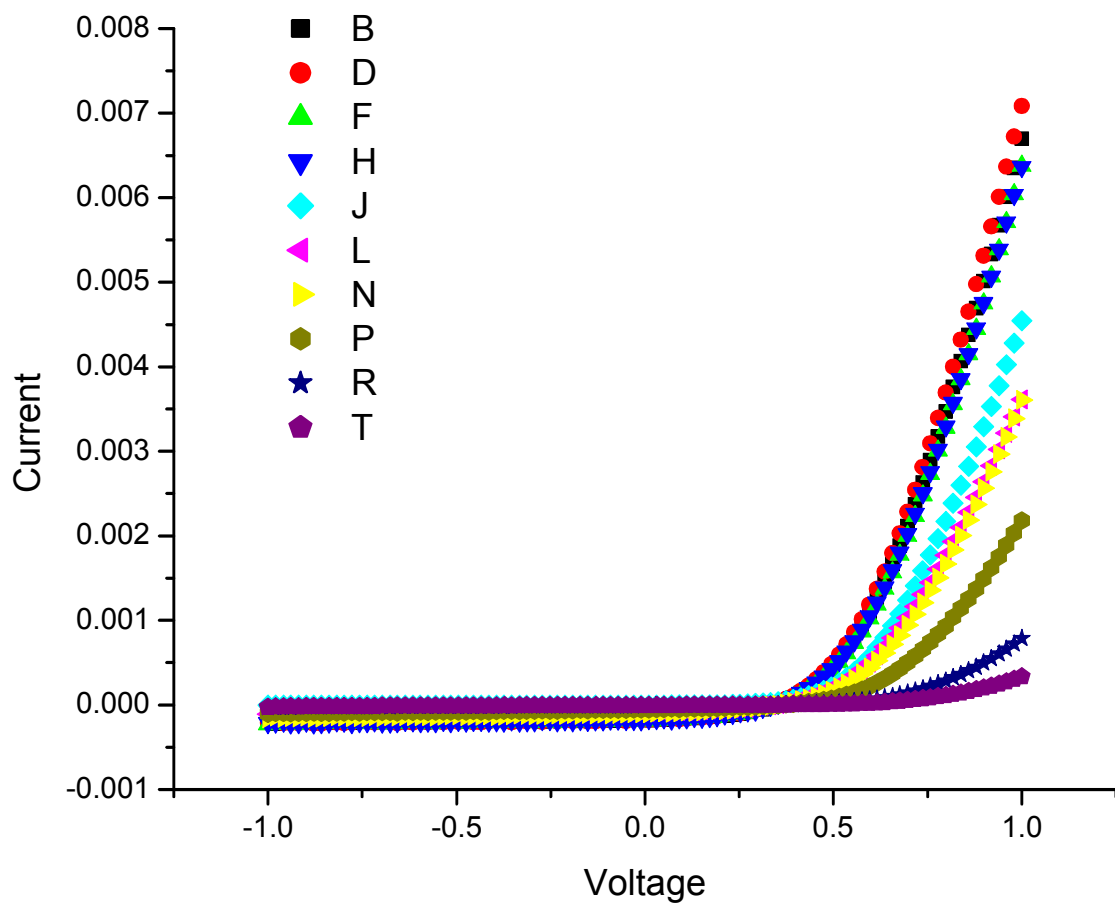


Fig 6.4 Degradation after two hour interval with device configuration

ITO / P3HT: PCBM / AL

These measurements were taken in the light and it is clear from the diagram that in this device degradation is much slower and uniform in comparison to PEDOT: PSS so we have decided to took the readings in dark also and seen the lower degradation in dark. This is shown below-

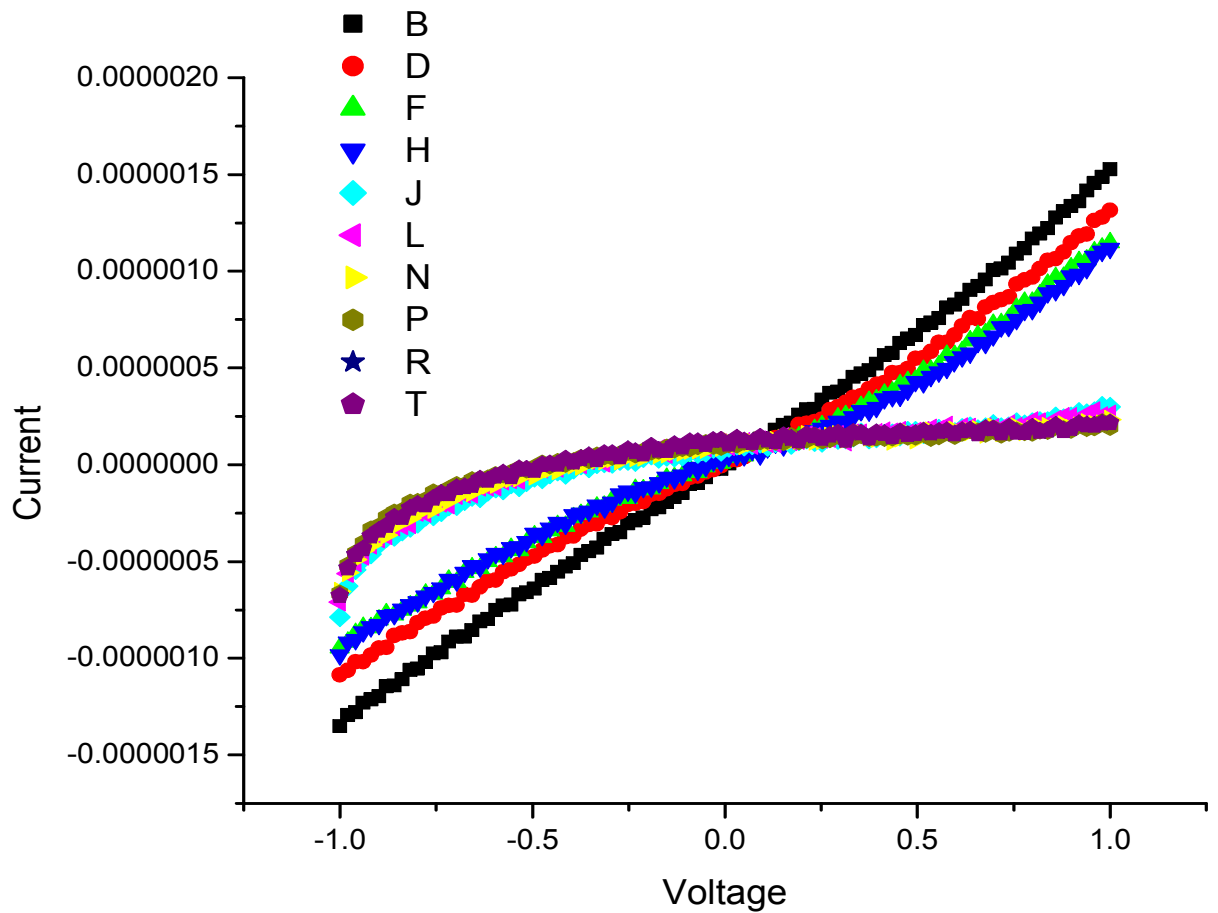
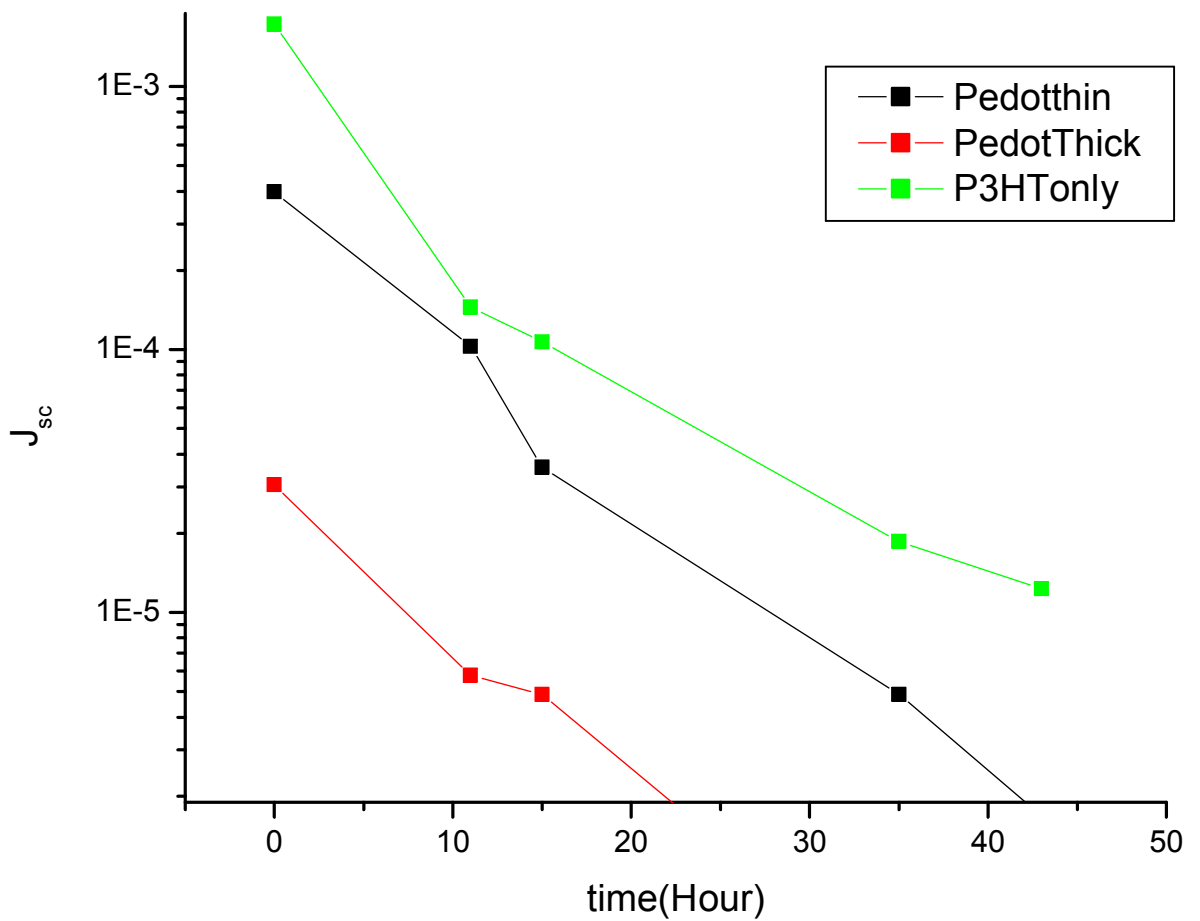


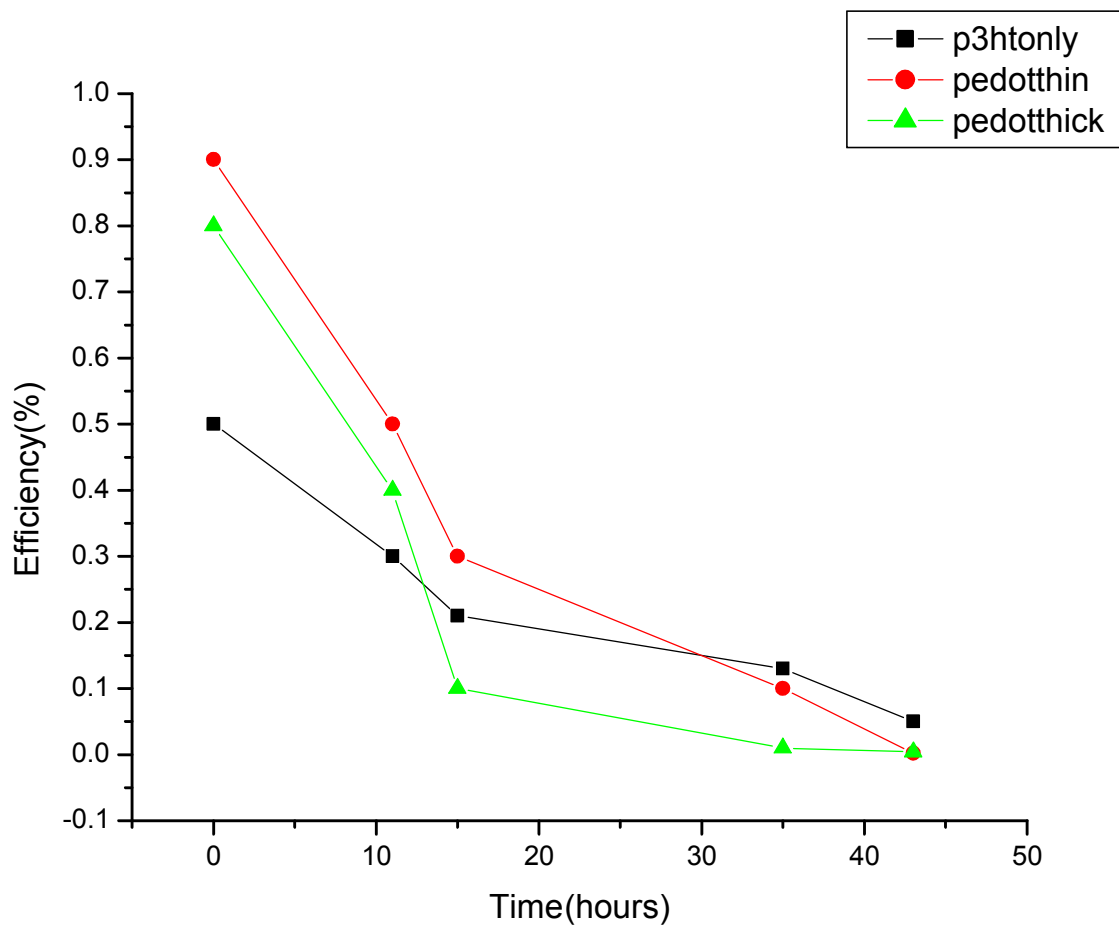
Fig 6.5 Degradation after two hour interval in dark with device configuration ITO / P3HT: PCBM / AL

Hence after observing both cases we have come to the conclusion that PEDOT: PSS is making the degradation faster because it affects the ITO surface and absorbs the water from the atmosphere. Now to compare both the cases together we have calculated the J_{sc} for each measurement of all devices and plotted the results as follows:



It is clear from above figure that P3HT device is degrading slower than the PEDOT: PSS thin and thick and PEDOT: PSS thick is degrading faster than both.

After comparing the J_{sc} we have calculated the Efficiency for all Measurements of PEDOT: PSS thin, thick and P3HT only and results are shown in following figure:



So final result is that we get long life of devices when we fabricate them without PEDOT: PSS but at the same time we get the lower efficiency hence if we want good life time with good efficiency as well then we have to search the alternative of PEDOT: PSS which can be some other C_{60} derivatives or growth of nanoparticles inside the polymer as we have discussed in chapter 5. So this can be future work in the field of organic solar cells.

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