

EIT KIC InnoEnergy Master's Programme

Renewable Energy - RENE

MSc Thesis

Fabrication and Characterization of Small Molecule Organic Solar Cells

Author: Mulugeta Ayele Birhanu

Principal supervisor: Dr. Joaquim Puigdollers Gonzalez

Session: July 2013



Escola Tècnica Superior
d'Enginyeria Industrial de Barcelona

UNIVERSITAT POLITÈCNICA DE CATALUNYA

MSc RENE is a cooperation between

Abstract

With increasing price of natural gas and petroleum products and their environmental concerns, alternative energy sources are required i.e. renewable energy sources. Solar energy is the abundant form of renewable energy. In addition to that, the total amount of solar power that incident on earth for an hour can cover the world's annual electric power demand. Hence capturing even fraction of this abundant power source is vital. The technologies used to capture solar power are the photovoltaic systems which, through the photovoltaic effect in semiconductors in the solar cells comprising the system; convert the energy in the photons of the sunlight directly to electric power. The system with silicon solar cells has high production cost because of which it has been difficult for the system to be in to grid parity.

The best alternative that attracted the attention of many researchers in the world is to use organic solar cells. Unlike their inorganic counterparts; the organic solar cells are easy and cheap to fabricate, light weighted, flexible, the semiconductors are tuneable with respect to their functions, colourful, can absorb light in cloudy days and semitransparent. The amount of semiconductor material required is very small (i.e. in 100nm). Because of these, even with half efficiency of inorganic ones can make them economical. The other advantage is that they can be used in areas where silicon solar cells haven't been used and properties like light weightiness, flexibility and colourfulness are required. This could be in the sports, agriculture, medical sector However, they have disadvantages: low efficiency and shorter life span due to degradation of the semiconductors.

Some of the factors that determine performance of solar cell are the type of structure used for the active layer of the solar cell and its thickness. The two kinds of structures we used in the lab were the bi-layer and bulk-junction photoactive layer. The performance of the bulk-junction solar cells increase with thickness of the photoactive layer up to certain point due to high intimacy of contact between the donor and acceptor and from this point on wards the performance decreases as recombination starts to dominate the effect of the intimacy of contact.

Comparison of the bi-layer and bulk-junction solar cells for certain thickness tells that the bi-layer has higher fill factor and open circuit voltage than the bulk-junction due to relatively low recombination and density of states. The efficiency of organic solar cells is increasing at higher rate recently as researches have been taking place even in big named companies. The degradation of the organic semiconductors is due to oxygen and water vapour from air which can be avoided by encapsulation of the solar cells.





Table of Contents

ABSTRACT	1
TABLE OF CONTENTS	3
1. INTRODUCTION	5
1.1. Photovoltaics	6
1.2. History of Organic Solar Cells	7
1.3. Motivation	9
2. ORGANIC SOLAR CELLS	13
2.1. Basics of Organic Solar Cells	13
2.1.1. Conjugated π -bondings systems	13
2.1.2. Generation of Electric Current from the Organic solar cells	15
2.2. Types and Structures of Organic Solar Cells	22
2.2.1. Types of Organic Solar Cells	23
2.2.2. Structure of Organic Solar cells	25
2.3. Materials Used for Fabrication	30
2.4. Characteristics of Organic Solar Cells	34
3. FABRICATION OF ORGANIC SOLAR CELLS	45
3.1. Substrate Preparation and Cleaning	45
3.2. Deposition and the Glove Box	47
3.2.1. The Glove Box	47
3.2.2. Deposition of the organic and metallic layers	48
3.3. Factors Affect Effectiveness or Performance of the Solar Cells	54
3.3.1. Due to Properties of Materials	54
3.3.2. Due to Fabrication	57
4. CHARACTERIZATION OF ORGANIC SOLAR CELLS	60
4.1. I-V Curve	60
4.2. Quantum Efficiency (QE) Measurements	61
4.3. Variable Illumination Intensity Measurement (VIM)	62
4.4. Absorption	63
5. EXPERIMENTAL	64
5.1. Effect of Thickness of Bulk-Junction layer on Performance of Small Organic Solar Cells made of DBP: C70 (1:1 rate ratio)	64



5.2. Performance comparison of the Bi-layer and bulk-Junction (1:1 rate ratio) solar cells made of DBP: C70.....	69
5.3. Degradation of Small Organic solar Cell whose active layer is made of DBP: C70 (1:1 rate ratio).....	73
6. CONCLUSIONS	79
7. RECOMMENDATIONS	80
8. FUTURE WORKS	81
8.1. Laboratory Works	81
8.2. Business opportunities	81
ACKNOWLEDGEMENTS	84
REFERENCES	85



1. Introduction

Solar Energy is one of the most abundant forms of energy in nature ^[28]. In fact it is the source of all energy on earth. Plants, animals and we, human beings get warmth and food from sun. To utilize this energy human beings have different mechanisms to extract the different forms of energy that exist in various forms. Plants can extract energy from the sun through photosynthesis and store it in different parts. This energy used directly by animals and human being as food and fuel or this plants and animals which have accumulated this energy will decay in million years and through various biological and physical transformations converts into fossil fuel which is used for transportation, electricity production and heat. The other outcome of solar energy is the wind energy. The solar variation on different part of the earth creates wind current which can be extracted either wind mills or wind turbines to deliver mechanical or electrical energy. Solar energy is also the source of hydropower in which water from various water bodies evaporates, goes up, cool down to condense and comes back as a rain on the mountains which makes rivers and lakes to be full and human beings utilize its potential energy to generate electricity ^[28].

Electricity played a huge role in the development of this world, in fact the leading role. Generation of electricity through the above mentioned mechanisms requires numbers of huge machines have some direct environmental problems associated to them. All the above mentioned forms of energies are indirect. A rather elegant way of extracting the sun's energy is to convert it directly to electricity. This will be the smartest way as solar energy is the most abundant form of energy. This is possible through the good electrical properties of semiconductors. The semiconductors are used to make photovoltaic cells which when eliminated with sun light can convert electrical energy directly to electricity.

The earth receives 174×10^{15} (PW) of solar radiation at the upper atmosphere although 30% of it reflects back and 70% goes to heat cloud, water bodies and landmass. The majority of the spectrum of sun light is in the visible and near infrared ranges with small part in the near ultraviolet region of the spectrum. The water bodies and the land mass of the earth receive 122×10^{15} (PW) equivalent to 3.85×10^{24} Joules per year which in 2002, the amount of energy received by the earth surface for one hour is greater than the total amount of energy required by the whole world in one year. ^[30]

This shows that extracting even a fraction of this solar power using efficient technologies, one can get enormous amount of power from the sun. That is why people are trying to capture this solar energy and try to generate electric power either through direct methods or indirect methods.



Grid parity is starting to be achieved already in Germany, Southern Italy, Netherlands and Spain in 2012; they should be followed by Northern Italy, Portugal and Austria in the next two years and then progressively by other countries. By the end of the decade, depending on how prices will evolve but also the cost of financing, grid parity could be achieved in all target countries.

Solar power can be used either directly to generate electricity using photovoltaic systems or indirectly using concentrated solar power. In the later case lenses or mirrors are used to focus the sun light towards a thermal fluid which through heat exchanger systems, thermal storage systems and turbines will convert thermal power to electric power. The thermal fluid receives the heat from the sun light and evaporates to a high pressure steam which can drive a steam turbine coupled to generator which ultimately generates the electricity. In the Photovoltaic systems the solar power is directly in to electric power.

1.1. Photovoltaics

Photovoltaic is electrical method of generating electrical power directly from sun light using Photovoltaic or solar cells without the involvement of any moving parts like Generator and engines which are required for most conventional power generating processes. Instead it uses arrays of solar cells which are capable of extracting the energy contained by the photons of the sun light and use it to excite their electrons to generate current through photovoltaic effect. ^[27]

The solar cells are made of specific materials called semiconductors. These semiconductors, when illuminated with sun light; they absorb the energy in the photons of sunlight and use this energy to excite their electrons which under the influence of electric field generate electricity. The excited electron then jumps from its lower energy level to higher energy level and starts to move freely. If electron can move freely in materials and got some potential difference in a circuit it can produce current. ^{[30] [27]}

In exact scientific words, solar cells are diodes which are electronic devices having very low series resistance and high parallel resistance for the current to flow and allow current to flow only in one direction. ^[27]

A solar cell is made of semiconductors. The most utilized semiconductor in electronics is silicon as polycrystalline, single crystalline and amorphous silicon solar cells. Silicon is also used to fabricate thin film solar cells to get flexible solar cells in addition to other materials like CdTe, Cu(In, Ga)Se₂. The organic solar cells are the newly immersing solar cells with low efficiency but with promising advantages and bright advancements.



The Voltage and current of a solar cell is very low compared to the ones in the transition cables, sources, electric equipment requirements. To get a very high voltage and current of required values these cells should be connected in series and parallel to increase the voltage and current respectively. Hence, to achieve these, commonly 36 cells, are connected in series and parallel and considered as a panel. Many panels on the other hand will be connecter in series and parallel so as to still increase those parameters ultimately to form an array. The array of photovoltaic panels then connected to electrical elements like Inverters, controller, Battery, Grid, and loads.

The combination of these electrical parameters (Battery or Grid, Loads) with the photovoltaic panels or arrays is called the photovoltaic system. The photovoltaic system is of two types: Stand alone or grid connected. The photovoltaic system generates DC current. Hence it is important to have inverter to be able to convert the DC current to AC current. The Grid connected photovoltaic system directly supplies power to the grid with the help of inverter and controller. The, stand-alone photovoltaic system on the other hand supplies power to a system isolated from the Grid. In this case a battery is required to store energy to enable utilize it later when there is no sun light.

1.2. History of Organic Solar Cells

The first studies on organic semiconductors concerning dark and photoconductivity (e.g. anthracene) were done in the early 20th century. In the 1960s, motivated by the discovery of the electroluminescence of thin films, molecular crystals were intensely investigated (e.g. optical excitation and charge carrier transport) by many Groups. In spite of the demonstration of the working principle of organic electroluminescent diodes, researchers had to struggle with many drawbacks (e.g. insufficient current, high operating voltage, low light output, and device stability) which prevented early success and commercial device application^[28].

In the 1970s, a second important class of organic semiconductors was established by the successful synthesis and controlled doping of conjugated polymers, and honoured later with the Nobel Prize in chemistry in 2000 for Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa. The conducting polymers initiated the first applications of organic materials (e.g. organic photoconductors, conductive coating, and photoreceptors in electro-photography. Although photovoltaic effects have been observed a long time ago, the breakthrough of the first thin film organic hetero-junction solar cell was achieved in 1986 by Tang and van Slyke. The basic principle is that two materials (n- and p- conducting) in a double layer structure are sandwiched between two electrodes.^[30]

In 1991 Hiramoto invented the bulk hetero-junction solar cell by mixing both materials to a blend layer. This approach was then further improved by Pfeiffer et al. through the possibility



of organic doping of wide gap transport materials, leading to a real p-i-n structure. Using this method, efficient p-i-n tandem solar cells have been realized. Organic solar cells can be classified into two major classes according to their working principle, the dye sensitized solar cells (DSSCs) firstly shown by Grätzel in 1991 and hetero-junction solar cells (HJSCs). The DSSCs achieved quite high power conversion efficiencies of around 12%, but they still suffer from corrosive nature and complex two-electron redox chemistry achieving long term stable devices. The HJSCs can further split up into solution and vacuum processed devices. Currently standard materials for solution processing are polythiophenes as electron donor and fullerene derivatives as electron acceptor. The standard materials for small molecule hetero-junction cells are phthalocyanines as donor and fullerene as acceptor. ^{[30] [35]}

Concerning the hetero-junction solar cells, a competition is currently going on between polymer based (solution processed) and small molecule (vacuum and thermal evaporation processed) solar cells. The Heliatek GmbH (<http://www.heliatek.com>) and IAPP (Dresden, Germany) achieve production-relevant efficiency record of 8.3% for organic photovoltaic cells in 2010. Later in the same year Konarka Technologies Inc. (<http://www.konarka.com>) (Lowell, USA) achieved the same power conversion efficiency for a polymer based single-junction solar cell. While Konarka is already selling products on the market, Heliatek is planning to produce in the start of 2012. ^{[14] [35]}

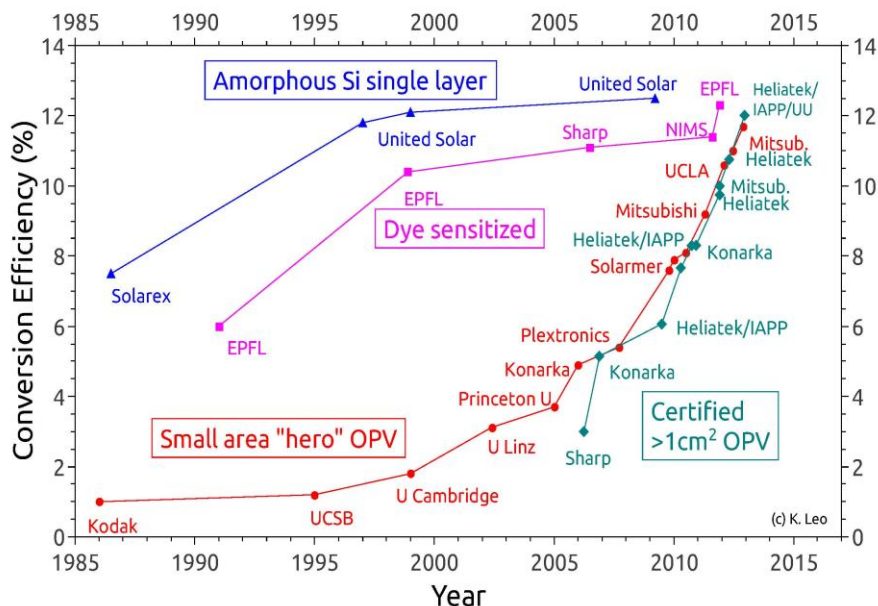


Figure 1: Evolution of the efficiency of Organic Solar Cells



As shown in the figure above the growth of the efficiency of organic solar cells is sloppy and it is touching the 10% and 11% marks for the single organic solar cells and tandem organic solar cells respectively. However, through the huge potential of chemical syntheses, in the future we will have materials absorbing in the near or infrared sun spectrum allowing new niche applications and design studies.

1.3. Motivation

Currently, More than 80% of the world energy demand is covered by fossil fuels. However utilization of fossil fuels for energy generation has so many problems associated to it.

Generation of electricity from fossil fuels releases carbon-dioxide to the environment which destroys the well being of our environment. The world demand for energy is exceedingly increasing. So there is no way out of environmental disasters like Tsunami which lead to explosion of petroleum plants and distraction of nuclear plants due to environmental pollutions.

The cost of fossil fuels is increasing and there is no reason for it to reduce as the scarcity of these fuels and the demand for energy is increasing. This is becoming a real concern as it is becoming the cause of some political conflicts between nations and nationalities; the cause of economical crisis for many countries in the world. This is the cause for international conflicts and economic crisis.

Fossil fuels are not sustainable. The demand for electricity is expected to double in the near future while the fossil fuel deposit in the world is on its way to be exploited.

All this reasons force us to search for other alternative energy generating systems. The alternative energy generating system should have no or very less of the above disadvantages faced by utilization of fossil fuels for energy generation. Renewable energies are the right answer to solve the above problems namely: Biofuels, Wind power, Hydropower, Geothermal power, Tidal power and solar Photovoltaic power and solar thermal power. All of these alternatives are in their best investigation levels to commercialize them and put them in to action.

The sun irradiation on the earth has a potential to cover the whole of world's electricity demand even if a small fraction of it is captured. With the additional advantage of converting the energy in sun light directly to electricity using photovoltaic, the potential is enormous. The abundance in the availability of the energy in the sunlight and the advancement and sophistication of photovoltaic technology are the most important factors for the dream to come true. The only small problem associated with photovoltaics was the fact that solar photovoltaic power generating systems had been under their infant stages of their Grid



parity. To make them competent with other conventional electricity generating systems, a lot of research has been taking place and the results are very good and in many countries like India, Italy, Germany, Netherlands, photovoltaic systems reached to a level of grid parity and many other countries are going to join these countries in the near future.^{[30] [40]}

The reason for photovoltaic not to reach grid parity was the fact that the production cost had been very high. Now due to lots of effort done on advancing and sophistication of the technology for the production of Photovoltaic panels, the world has reached to the level of producing competitive solar panels.

The photovoltaic systems that are commercialized and which are in their grid parity stage are those whose panels are made of inorganic semiconductors (mainly silicon).

However, there are still better hopes in other branch photovoltaic that deals with compounds called Organic semiconductors which are used to fabricate Organic Solar cells. Organic solar cells, although they are in their infant stage of research for high efficiency and commercialization, they have many advantages to their inorganic counterparts. Even with less than half the efficiency of inorganic solar cells, they can reach grid parity level so easily.^{[14] [35]} this is because:

The production processes of organic compounds and polymers are very simple and cheap unlike the inorganic solar cells. Production of silicon and its purification to the required standard is a very expensive process.

Very thin layer of organic material like in nanometres can absorb sunlight and generate electricity as their absorption coefficient is very high unlike the inorganic semiconductors. Hence, the amount of material required to fabricate the Organic solar cell is very small for hundreds of Angstrom or tens of nanometres of active layer. During organic solar cell fabrication, deposition of around 30nm of the P-type and around 50nm of the N-type thin films is enough to give current and voltage during solar cell test.

Since organic solar cells are composed of thin layers of active layers and can be deposited so easily with high flexibilities of organic products, a flexible organic solar cell can be fabricated. This will widen the application areas for photovoltaic solar cells.

The chemical composition of organic semiconductors can be varied in the advantage of good performance of the Organic solar cell as the process is simple although it requires a lot of effort to try various compounds to acquire this advantage. Therefore, through research one can modify a P-type or/and N-type semiconductors so as to make the solar cell has higher Voc, high Isc and high fill factor as this increase the efficiency of the solar cell. In addition to altering chemical composition we can carry of different kinds of depositions (bi-



layer, co-evaporations and PIN- layers) so as to optimize those important variables and of course ultimately the efficiency of the Organic solar cells. Even the band gap of the solar cell can be altered so that a wide range of the solar spectrum could be absorbed.

Their flexibility, light weightness semi-transparency and colourfulness give a lot of opportunity to use them in the areas where photovoltaics weren't used before. These widen the dimension of using organic solar cells and increase the market opportunity.

With these concrete advantages of Organic Solar cells over the inorganic ones it is very interesting to do research in this area so that we fabricate efficient, flexible and cheap Organic solar cells. The first three advantages enable the solar panels recover their costs in a short period of time.

Besides doing this one should also have to think about the challenges associated with organic solar cells the like

Degradation of the organic materials with oxygen and water. This is a challenge as the solar panel should stay for long time keeping its required characteristics nearly constant.

Low efficiency of the Organic solar cells should be improved so that panels made of Organic solar cells would be commercialized so soon.

They have a relatively high band gaps. This causes the transparency of low energy photons of the in sunlight spectrum without absorption which affects the efficiency severely.

Therefore, Electronic devices based on organic semiconductors offer an attractive alternative to conventional inorganic devices due to potentially lower costs, simpler packaging and compatibility with flexible substrates. The need to develop inexpensive renewable energy sources stimulates scientific research for efficient, low-cost photovoltaic devices. The organic, polymer-based photovoltaic elements have introduced at least the potential of obtaining cheap and easy methods to produce energy from light. The possibility of chemically manipulating the material properties of polymers or small organic compounds combined with a variety of easy and cheap processing techniques has made organic-based materials present in almost every aspect of modern society with the advantages organic semiconductors being low cost synthesis, easy manufacture of thin film devices by vacuum evaporation/sublimation or solution cast or printing technology, flexibility etc. ^{[14] [35] [34]}

The most important stimulation is with various research groups in the world trying to improve the efficiency and performance of Organic Solar cells the efficiency of organic solar cells is increasing faster than other types of solar cells. This can be seen in the figure below especially in the years after 2008. ^[14]



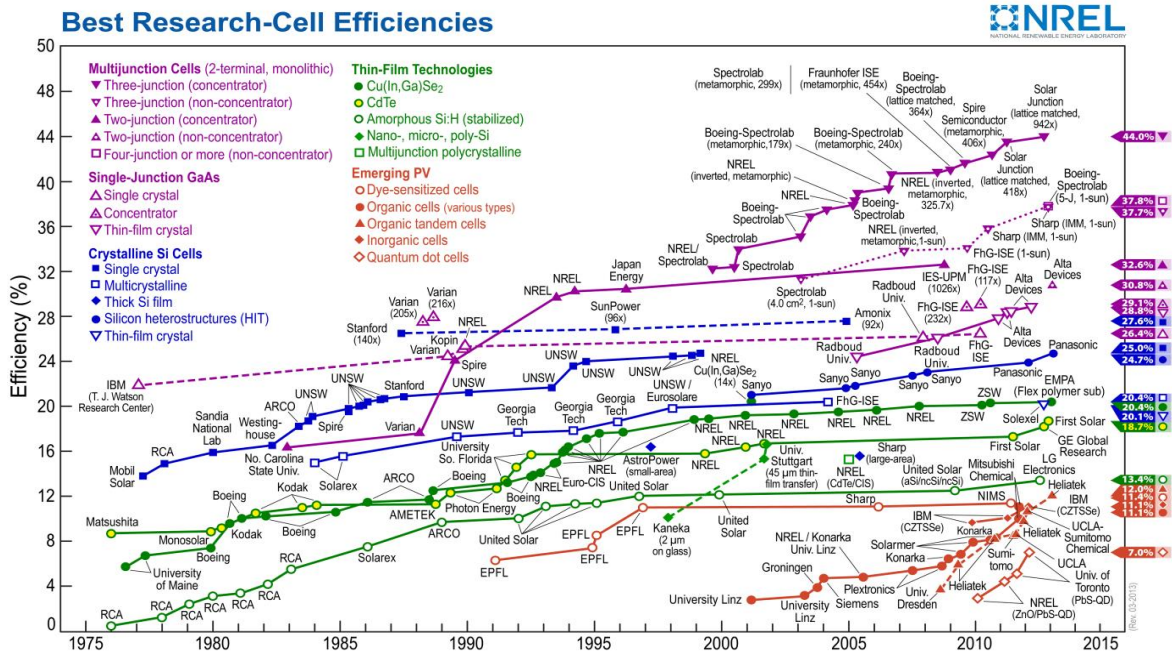


Figure 2: Evolution of efficiency of all types of Solar Cells with the organic solar cells showing increment and others look like they are saturated



2. Organic solar cells

2.1. Basics of Organic Solar Cells

2.1.1. Conjugated Π -bondings systems

Almost all organic compounds are insulators with the exception of some which are semiconductors. The conductivity of these semi-conductive materials lies in the specific arrangements of the valence electrons the atoms involved in the chemical structure of the materials, especially carbon, called conjugation. In the normal hydrocarbon compounds, the valence electrons are bound to each other by a strong SP^3 hybridization where by all of the four valence electrons of the carbon form a sigma bond (σ -bond). The electrons involved in such strong σ -bond have such low mobility that they don't contribute to the electrical conductivity of the organic material. However, in conjugated organic materials, the valence electrons are bound by SP^2 hybridization in which case three of the valence electrons of carbon are bonded by σ -bond and one of the valence electrons of this carbon forms a Π -bond. The pi-bonding is a weak bond compared to the sigma bond. The valence electron that involve in the pi-bonding exists in the p-orbital oriented in the z-axis (called p_z -orbital) perpendicular to the x-y plane where the sigma bond co-exist. ^{[30][27]}

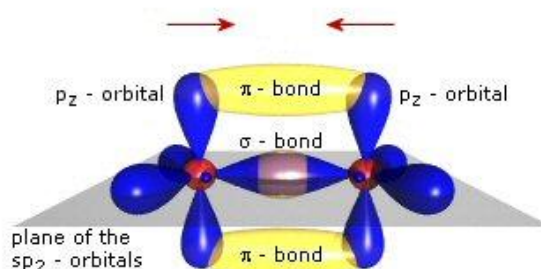


Figure 3: Overlap of Pz Orbitals in SP_2 hybridization that leads to conjugated Π -bonding

The p_z -orbitals of the two carbon atoms can't overlap one on the other to form a strong bond like the sigma bond does. However, they utilize the area above the two atoms in the z-axis as an area overlap as shown in the figure above. For example, for benzene ring, it has 6 carbons each bonded to two carbons in the ring and a hydrogen atom by sigma bond. The electrons in this bond are localized the as bond is very strong. However, the 6 p_z -orbitals of each carbon atom remain perpendicular to the plane of the ring. The electron in the p_z -orbital of carbon number one can make pi-bond either carbon number two or 6. The pi-electrons do not belong to a single bond or atom, but rather to a group of atoms. ^{[29] [27] [35]}



Hence, the electrons in the Π -bond are delocalized that they have better freedom than the localized electrons involved in the sigma bond.

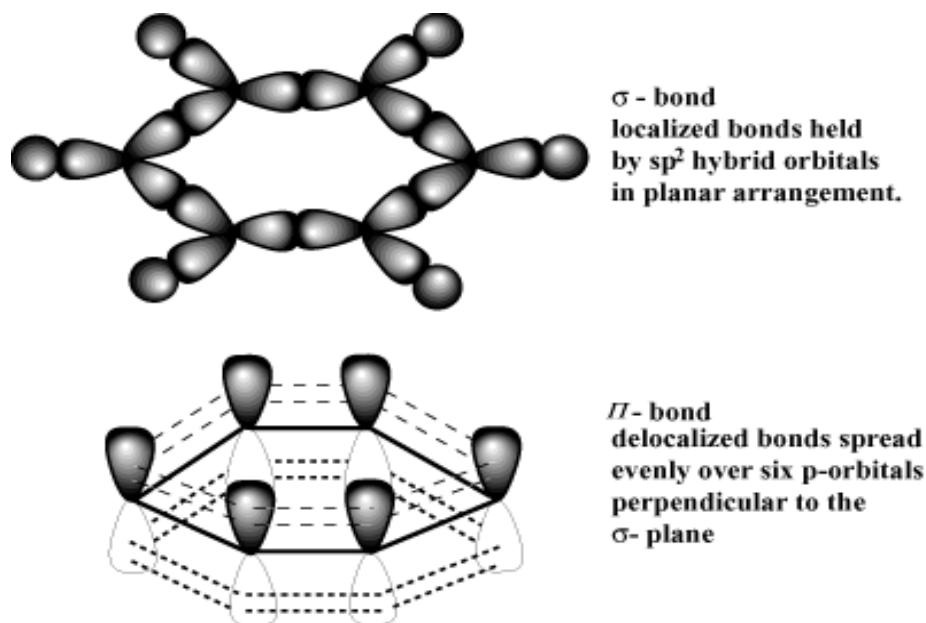


Figure 4: the difference between the localized sigma bond and delocalized pi-bond

In other words, the electrons in the delocalized orbital involved in the pi-bond have higher mobility when modified by doping to add electrons or holes to the material. This doping of the organic material makes it either a P-type or N-type material depending on the material is doped to have more holes or electrons respectively. The doping is very important as it brings the organic material from being almost insulator to a very good semiconductor level. [13] [27]

In general, a conjugated bonding system is a system of connected p-orbitals with delocalized electrons in compounds with alternating single and multiple bonds. If number of the molecules that have conjugated bonding system form a polymer or a big single organic compound, there will be plenty of these delocalized electrons with the help of proper doping bring semiconductivity. When an electron in the conjugated bonding system absorbs a photon of light of the right wavelength, it can be promoted to a higher energy level. This electronic transition is from one conjugated Π -bonding molecular orbital system (Π -MO called HOMO) with an even symmetry to another conjugated Π -bonding molecular orbital system (Π^* -MO called LUMO) with an odd symmetry. When the number of conjugated Π -bonding system low it requires higher energy to transform the electron from its HOMO to LUMO level like photons from ultraviolet region of the spectra (the longer wavelength of the



spectra won't be absorbed). With addition of more double bonds or conjugated π -bonding system, the system absorbs photons of longer wavelength or lower energy. Conjugated π -bonding systems also can accept or lose electrons which are the basics of conductivity which enables many organic compounds accomplish different functions in the living things. For example, Porphyrins have conjugated π -bonding ring systems that appear in many enzymes of biological systems. Porphyrins form different complexes with different atoms like Iron, Magnesium and cobalt to form haemoglobin, chlorophyll and part of vitamin-D. ^[30]
^[29] ^[35]

The influence of the conjugated pi-bonding system on the organic compound as discussed in the previous section is for the relatively higher motilities of the charge carriers. This is because unlike the electrons in the sigma bond, the electrons in the conjugated pi-bond are governed by weak dispersion force. When the molecule gets bigger it gives more freedom for the electron because of the crystal structure is usually formed by Van-der-Waals forces. When the molecule is bigger, there will be much of these pi-bonding interactions; the association of them in a certain area will enable to support the absence of one electron in a certain region by the dispersion forces like London force. Therefore, the π -electrons determine fundamentally the solid properties of the organic semiconductor. More specifically, molecules with conjugated pi-bonding systems ^[35]

are more stable than the un-conjugated ones

have lower HOMO-LUMO gap or band gap and decreases with number of pi-bonding systems

can be shifted from ultraviolet and visible light absorption to longer wave length (i.e. lower energy) spectra

their electrons can be excited and promoted to higher energy level by light

have charge transfer capability to another molecule

All these additional properties obtained by the molecules with conjugated pi-bonding systems are advantages for acquiring higher charge carriers motilities in the molecule. That is exactly what we need in the materials used to make organic solar cells. ^[13] ^[29]

2.1.2. Generation of Electric Current from the Organic solar cells

Generation of electric current from a semiconductor is a collection of many processes that take place within fractions of seconds. This involves the absorption of the sunlight by semiconductor; generation of an electron-hole association called exciton; diffusion of this excitons towards the an interface; separation of the exciton in to its corresponding



components called electrons and holes; diffusion of this charge carriers towards their corresponding electrons to be collected so as to generate electricity. Each process has its own characteristics on how they take place. Therefore, I will discuss each process one by one. ^{[41] [29]}

Absorption of light by semiconductors

When light is irradiated on the surface of an organic semiconductor, its photons would be absorbed by the electrons in the valence band of the molecule that are involved in the conjugated pi-bonding system. These will excite the electron and move it from HOMO energy level towards LUMO level. When the electron i.e. negative charge carrier, is excited to its higher energy level due to the energy absorbed from the photons, it leaves a hole i.e. a positive charge carrier, on the other end. In fact, an electron-hole association called exciton will be created due to the excitement. ^{[29] [14] [27]}

For the photons to be able to create this excitement depends on two factors. These are the different in energy level between the HOMO and LUMO of the molecule called the band gap and the energy content of the photons. If the difference in energy level between the HOMO and LUMO level of the molecule is very high the energy required exciting an electron from the HOMO to LUMO level will be also high. In this case, the photons that will be absorbed will be the ones with short wave length only. Hence, the excitement depends on which part of the spectra the photon is from and the energy level difference. The photons having less energy than the different in energy level between the HOMO and LUMO won't be absorbed. If the different in energy level between the HOMO and LUMO is very high most of the photons having higher wave length will be lost. This will reduce the absorption efficiency of the solar cell. ^{[14] [27]}

Most of the time molecules with higher number of conjugated pi-bonding systems have the advantage of having lowered different in energy level between the HOMO and LUMO. This is because as the molecule gets bigger and having more conjugated pi-bonding system the dispersion forces help to reduce the LUMO level of the molecule so that the electron can be excited by a longer wavelength photons. However, having bigger molecule is a disadvantage as it increases its melting and/or sublimation points which requires a high energy for vacuum deposition of small molecules or affects solubility of polymers for solution based deposition of polymers. Hence, it is a trade-off between lower LUMO level and easy processing. Therefore, searching for the right molecule is important. This requires the knowledge of photochemistry, molecule synthesis and photovoltaic properties of materials. ^{[29] [27]}



Exciton diffusion

This is the second process that takes place in the semiconductor during generation of current while illuminated by sunlight. In this stage the exciton created due to the absorption of proper energy photons. Once the exciton is created, it has to be separated in to its corresponding charge carriers i.e. the electron and the hole. The electron and the hole are bound together by some binding energy designated by E_B in the order of magnitude 0.1eV. The right place for these two charge carriers to separate from each other is the interface between the P-type and N-type material (to be discussed below). There is a potential at this interface that can separate the two charge carriers that is the electron affinity and ionization potential of these materials. For the exciton to separate in to its corresponding charge carriers it has to first diffuse towards this interface.^{[29][14][15]}

The effectiveness of the diffusion depends on many factors with major ones: the diffusion length of the material, L_D , the type of deposition and structure we use for the solar cells and life time of the excitons since they are created.

Every material has its own thickness above which excitons created won't reach to the interface before they lose their energy and the electron goes back to its ground state. This thickness of a material is called diffusion length; L_D . If the created excitons don't reach to the interface, the charge generation will be lost and lowers the performance of the cell. Hence, before we deposit any material for organic solar cell fabrication we need to know the diffusion length so that we don't exceed it. To avoid this disadvantage of low diffusion length we can co-evaporate the two materials i.e. the P-type and N-type materials instead of planar deposition, so that the distance for the exciton to travel long distance and otherwise to lose its energy can be avoided. Well, this also has its own disadvantage as the charge carriers might be trapped; to be discussed later. The main important thing we have to know for the time being is the excitons should diffuse easily, in a short period of time (with in less than nanoseconds) towards the interface travelling as short as possible with in the diffusion length of the material. Otherwise, the energy from the photons utilized for excitation will be lost and the electron will go back to its ground state.^[14]

The P-type and N-type materials, doping and charge separation at the interface

Once the exciton has reached the interface there must be some potential that pulls the components of the exciton i.e. the electron and hole, towards the corresponding directions where they will be conducted in the circuit of the photovoltaic system. Hence, we need to have materials that can attract the electrons and the holes towards corresponding electrodes.



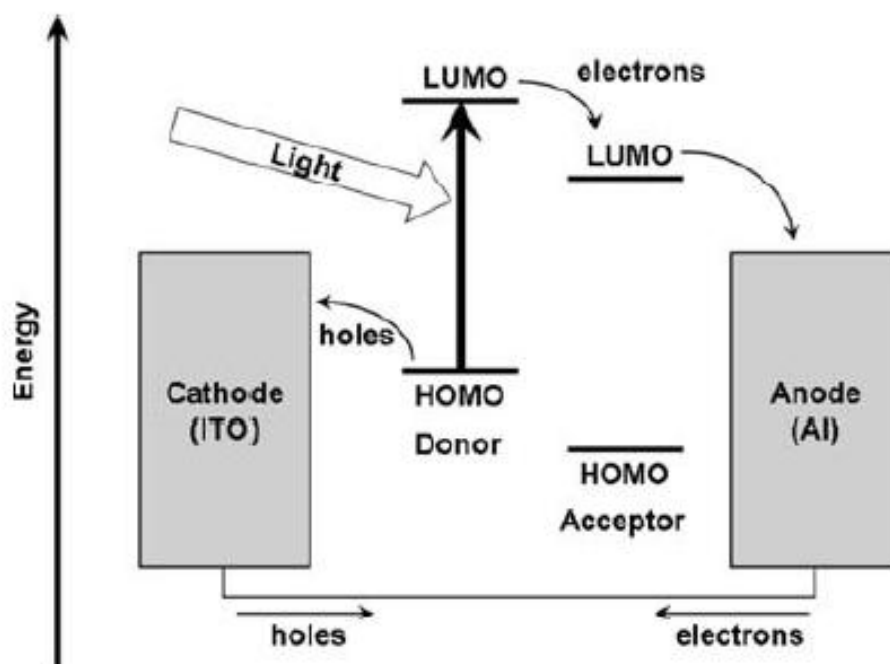


Figure 5: Energy levels of the donor and acceptor materials and charge carrier flow directions

The materials that are capable of attracting the holes i.e. good hole conductors are called the donors. They give the electrons to other materials called acceptors and remain with holes i.e. they pull the holes towards themselves. They are good conductors of holes and they are positively charged because holes are positively charged particles. They are also called the P-type materials with the P designating positive.^[37] They pull the holes towards themselves because they have high ionization potential. Materials with high ionization potential have a tendency to lose electron and become positively charged. On the other side are the materials that pull the electrons towards themselves. These materials are called acceptors because they receive electrons from the donors.^[29] They are good conductors of electrons and remain negatively charged because of the electron. They are called N-type materials the N designating Negative. They have the ability to accept electron because they have high electron affinity. Hence, the potential that separates the exciton in to its corresponding charge carriers is the difference in ionization potential of the P-type material and the electron affinity of the N-type material; and this potential difference between the materials should be greater than the binding energy of the electron with its hole. Once the charge carriers are separated they should diffuse through their corresponding materials to a place where they are collected towards the circuit. These collection areas are the electrodes i.e. the anode and the cathode. The holes diffuse and collected at the anode and the electrons diffuse towards the cathode.^{[30] [29] [27] [33]}



This is a clear indicative that we require to different materials called donor and acceptor to fabricate an organic solar cell. This materials will be deposited in bilayer or bulk form in a way the diffusion length is low enough; the corresponding orientation of these materials is proper for charge carriers diffusion towards their electrodes and the binding energy of the electrons and holes is exceeded by the potential difference between the ionization potential of the donor material and the electron affinity of the acceptor material. This requires again proper synthesis of these materials based on their proper photochemistry and their use in the solar cell fabrication. One of the best methods used in the synthesis of these materials is doping. The main purpose of doping is to contaminate an organic material for our own purpose intentionally so that if it is donor material we want, it will have required ionization energy and if it is acceptor material that we want, it will have proper electron affinity. Doping has also used to improve the difference in energy level of the HOMO and LUMO of a material. Sometimes it is possible to dope a single material differently so as to make it act as either of the materials. It is similar to the situation of haemoglobin and chlorophyll that have the same organic composition with similar structure with the former having iron and the later magnesium in the centre respectively; and haemoglobin is used to transport oxygen in blood and chlorophyll is used to capture photons to produce glucose in leaves of green plants. ^{[30] [14] [33]}

The main purpose of having two different materials is

to create an interface of these to materials so that the excitons that have diffused effectively to the interface will definitely be separated and electrons and holes will be created ^[30]

to that the potential to overcome the binding energy of the electron to its hole comes from the ionization potential and electron affinity of the materials.

to make sure that the charge carriers are conducted towards their corresponding electrodes so easily.

Charge collection

The charge collection process takes place at the electrodes. Before the charge carriers reach the electrodes they should flow through the donors and acceptors. Once the charge carriers are formed, it is the potential difference between the semiconductors and electrodes that derives them towards the electrodes. However, there is one additional layer of material between each semiconductor layer and the electrode layers called electrode interfacial layers. These layers have couples of functions to accomplish and they are also called buffer layers. The one between the donor and the anode is called hole transport layer or electron blocking layer or exciton blocking layer. That means it allows the flow of holes from the donor or P-type material to the anode but blocks the flow of electron and/or exciton in that



direction. Some of the examples to name are molybdenum oxide, MoO_3 , poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) etc.... The one between the acceptor and cathode, on the other hand, is electron transport layer or hole blocking layer or exciton blocking layer. Therefore, it allows the flow of electrons from the acceptor or P-type material towards the cathode but blocks the flow of holes and/or excitons in that direction. Some of the materials that are used as cathode interfacial layer are BCP, pentacene, etc....
[29][15]

These layers, in addition to buffering the transport of charge carriers, they also contribute to the open circuit voltage of the solar cell although they are not for that purpose. If high thickness of these materials is used, they might increase the serious resistance of the solar cell; they might affect the transparency of the layers; or might also contribute to the current of the solar cell helping in the absorption. Sometimes, the energy level of these layers might not be an appreciated one compared to the neighbouring layers which diminishes the open circuit voltage of the solar cell. Hence, proper selection of these interfacial layers and further study on their characteristics is required. [29]

Once the buffered charge carriers pass through the electrode interfacial layers they should be collected efficiently. For this to happen the electrodes at the either end should be highly conductive to electricity so that the charge carriers won't be dissipated and lost. This will reduce the current expected from the solar cell. Hence, the purity of the material used for electrode layer should be high for there will be no receptivity across the electrode. [29]

To summarize, generation of current in a solar cell is a combination of different processes that take place one after the other within fractions of seconds. If all of the processes mentioned above take place effectively the performance of the cell will be very high. [14][45][33] Each of the processes that contribute to the generation of the current from the solar cell depends on many factors:

- The materials constituting to each layers of the solar cells have their own physical and photochemical properties that enable them to give optimum charge carriers under a given condition. Therefore, choosing or synthesising the right material for specific purpose is very important. This requires a knowledge and skill of photochemistry and synthesis of organic materials, specifically organic semiconductors.
- The interaction between one of the material in one layer with another one next to it is very important based on their energy level difference, charge carriers buffering and good conductivity. The energy level of one layer with respect to the one next to it should enhance the effectiveness of pulling charge carriers towards their respective electrodes; otherwise it will diminish the current and the voltage of the solar cell.



- The morphology of the each material deposited determines the effectiveness in the charge transport and separation. The morphology also determines the way on of the material align against the other one during deposition. This will also affect the voltage across the cell. This is because when properly oriented the difference in the HOMO-LUMO energy difference could be reduced. The morphology and orientation of one molecule against another one depends at what rate they are deposited, the temperature of the substrates, the pressure of the evaporation chamber and ratio of amount of one molecule to another one when they are co-evaporated.
- Every semiconductor has its own are of high and low absorption in the spectra. No organic compound yet has high absorption throughout the length of the spectrum. Some absorb well in the range where others don't and sometimes the absorption region of two or more materials may overlap. Sometimes two or more materials are complementary for their respective absorption regions sums up to the whole are of the spectrum or majority of the region of the spectrum. Actually, that is what we require in principle. However, two materials that are complementary in absorption may not have required energy level difference to pull the charge carriers for effective charge separation and collection. This also needs close investigation during synthesis and research to get the right couple for the material in terms of required parameters.
- Diffusion of the exciton; after the absorption of sunlight photons by the photoactive part of the solar cell, towards the interface between the donor and acceptor is also very important to be considered. This is because every material has the maximum thickness called diffusion length beyond which the excitons couldn't manage to reach the interface because of the short life time of the excitons. Therefore the thickness of the material deposited should be within the diffusion length of the material. if the thickness is beyond the diffusion thickness the excitons lose their energy they absorbed from the photon and the electron moves to its ground state.
- If the mobility of the charge carriers in the materials that comprise the photoactive layer is very low, the probability of getting high current from the solar cell is a dream.
- The HOMO-LUMO energy level difference is the one that determines the open circuit voltage of the solar cell. Hence, if difference between the ionization energy of the donor and electron affinity of the acceptor is low the open circuit voltage will be low.

Having these factors taken into consideration and addressed well, one can expect high performance solar cells. To put it mathematically, the efficiency of the cell is:

$$\eta_{\text{cell}} = \eta_{\text{abs}} * \eta_{\text{diff}} * \eta_{\text{char.sep}} * \eta_{\text{char.coll.}}$$



At the end of the day the performance of the cell if the cumulative effectiveness of each process specified above i.e. proper absorption of photons to excitation, exciton diffusion, charge separation and charge carriers effective collection. Hence, optimizing the physical characteristics and looking for the best complementary photoactive materials is very important. ^{[30] [29] [14] [45] [33]}

2.2. Types and Structures of Organic Solar Cells

Organic solar cells, as explained earlier comprise layers of thin layers in the order of less than 100nm. These layers are the anode that collects the holes to send them in to the circuit; the ITO i.e. the indium tin oxide that is a transparent and conductive oxide; the anode interfacial layer or the hole transport layer which also blocks excitons and buffers the charge carriers like electron; the photoactive layer that comprise of the donor and acceptor layers which are involved in the absorption of photons of sunlight to create exciton which ultimately separated in to charge carriers due to the ionization potential and electron affinity of the donor and acceptor materials respectively and put them in to the circuit to generate electricity after collected at the electrodes; the electron transport layer that blocks excitons and holes passing to the cathode; and finally the cathode that collects the electrons to send them to the circuit. ^{[13] [45]}

The main difference between the inorganic and organic solar cells; besides their photoactive materials being inorganic and organic respectively; is that in the inorganic solar cells electricity is generated directly by absorbing the photons in the sunlight i.e. the charge carriers are created directly. However, in the organic solar cells, it is exciton instead of charge carriers that are created directly. ^[45] This exciton is composed of an electron and hole which are bind together by the binding energy. To generate electricity or electric power we need the charge carriers move in opposite direction i.e. the electron to the cathode and the hole to the anode. For this case the electron and the hole has to be separated first. It is the energy difference between the ionization potential of the donor and electron affinity of the acceptor material which is used as a pulling potential to separate these two charge carriers. The separation takes place at the interface between the two photoactive materials as this is area where the required potential difference is realized. It is obvious that this potential should be greater than the binding energy of the exciton. In addition, the inorganic solar cells are based on the elemental state of materials (except the thin film organic solar cells) where as organic photovoltaics deals with long chained and/or pi-conjugated hydrocarbons which are compounds. ^[13]

There are millions of hydrocarbons part of which have semiconducting properties that can be used in the fabrication of solar cells and other related useable things like OLED. These compounds are not made of a single element like silicon alone or a compound made of two



three elements rather they are compounds made of hundreds of elements bonded in the sigma and most importantly in the conjugated pi-bonding. The materials made of these hydrocarbons could be relatively small molecules or large molecules. The number and kind of atoms they comprise, the arrangement of these atoms for the construction of the whole structure; the number and kind of bondings involved in the structure; the crystal packing involved for the material determine the physical, photochemical and chemical properties of the material. These properties determine what kind of processing is convenient; if the energy its energy levels are convenient and which material would be its counterpart; which part of the different layers of the solar cell would be convenient for the material. ^[13]

The energy level of the materials that determine the HOMO-LUMO levels or band gap; the processability and kind of process it follows to deposit it in the fabrication of the organic solar cell are the most important factors determine the destination of a material to be used in certain type of solar cells. To deposit a material in an organic solar cell layer we have two methods: one is through evaporation or sublimation of the material under vacuum and the second one is by dissolving the material with suitable solvent and apply it in layers using spin coating or Doctor Blade's method etc.... To apply the former one the material should be relatively small molecule that can sublime or evaporate at low temperature under vacuum. The later method is for those materials that are relatively very large having high molecular weight which are difficult to be deposited through evaporation either because of their high evaporation or sublimation temperature or because they will be prone to decomposition at higher temperature. For these materials proper thinner is important to dissolve them and deposit them in to layers using the above mentioned coating methods. Most of these materials are polymers and they can be dissolved by small molecules like acetone, iso-propanol or combination of thinners. The third types of materials are those that are used in wide-band gap inorganic semiconductors. In this case, an organic dye adsorbed at the surface of an inorganic wide-band gap semiconductor is used for absorption of light and injection of the photo-excited electron into the conduction band of the semiconductor.

2.2.1.Types of Organic Solar Cells

Based on these variations in the chemical, photochemical and physical properties of the materials we have three different types Organic solar cells. Today three different types of organic solar cells are known: the organic semiconducting material can either be comprised of so-called small molecules (SM solar cells) or polymers (polymer solar cells). The third type of organic solar cells is called dye-sensitised solar cell (or Grätzel cell) and contains a highly porous layer of titanium dioxide as electron transport layer on which dye molecules are adsorbed. Small molecule solar cells are processed in vacuum by physical vapour deposition; whereas polymer solar cells are processed by spin-coating or ink-jet printing (vacuum deposition is still necessary for metal deposition). Grätzel cells are typically



processed by screen-printing of the titanium dioxide with subsequent sintering and drying. The OSOL group at the IAPP concentrates on small molecule solar cells. ^[45]

- **Small Organic Molecule solar cells**

These organic solar cells; as their name indicates are those with their photoactive layer are made of relatively small organic compounds. Since, the molecular weight of these compounds is relatively low and can be evaporated relatively easily at lower temperature; they can be deposited on a substrate by evaporation or sublimation. The evaporation takes place under vacuum. This will enable the components evaporate at relatively easier way and prevent the molecules not to be deteriorated by the oxygen and the water vapour in the atmospheric air. However, the vacuum operation has its own disadvantage of being a little bit costly.

The performance of the solar cells based on Small molecule solar cells is increasing time to time. The research around is going on and the efficiency is increasing at a relatively higher slope with time compared to their inorganic counterparts. Synthesis of new photoactive organic semiconductors that can absorb in a wider range of the spectrum is being going on. The combination of proper donors with proper acceptor that have supplementary range of absorption being part of the good achievements, different structures of the solar cells are on trials to get high efficiency.

- **The polymer based solar cells**

The polymer based solar cells have the same structure with the small molecule organic solar cells except on the process of fabrication. The polymer based organic solar cells are their photoactive layers made of polymeric compounds that have relatively high molecular weight and evaporation or sublimation temperature. Due to their high evaporation temperature it is difficult and costly to deposit them on a substrate through evaporation unlike the small organic molecules. So the most convenient method is to dissolve them in a solvent or thinner and deposit them on the substrate using any of the convenient coating methods the likes of screen printing, doctor blade method, inkjet printing, and spray deposition. Since they have lower chemical activity compared to the small organic molecules they can be processed in the atmospheric air without fearing the deterioration with the oxygen and water vapour of the air. So the deposition is easier as it takes place at atmospheric temperature which is low and no vacuum is necessary which is costly.

- **Dye-Sensitized organic solar cells**

These solar cells are based on the photo-electrochemical systems. They have titanium as cathode and titanium oxide as sandwiching a photoactive part composed of electrolyte,



titanium oxide immersed in the electrolyte and the dye surrounding the titanium oxide. The dye is the photo active part that absorbs photon from the sunlight and excites its electron which flows towards the cathode to be collected to enter the circuit. After finishing its trip in the circuit it comes back to the anode side of the cell and through the electrolyte solution it goes to the dye where it was originated. So they are based on the concepts of batteries although the initiator of the current is absorption of solar energy carrying particles called photons by organic dyes that adds the photovoltaic concept in to scene. They have high efficiency of record 12.3%.

2.2.2. Structure of Organic Solar cells

The structure of an organic solar cell comprises two electrode layers sandwiching the photoactive layer of the solar cell between the each electrode and the corresponding photoactive layer is sandwiched an electrode interfacial layer. The first layer deposited on top of the ITO is the hole transport layer or the anode interfacial layer that blocks excitons and electrons from diffusing towards the anode. On this hole transport layer is deposited the photoactive layer that absorbs the photons of the sunlight and converts the thermal energy stored in the photons in to electric power through photovoltaic effect. On this layer will be deposited the electron transport layer or the cathode interfacial layer. This layer blocks excitons and holes from flowing to the cathode and on top of which is deposited the cathode; which is a metal most of the time Silver or Aluminium, that collects the electrons to lead them towards the circuit. ^[45]

Despite all layers important, the photoactive layer is the most important part of the solar cell without which the concept of organic solar cells can't be realized. The structure and arrangement of the materials in the layer is very important. The photoactive layer can be modified in such a way that it can give a better performance of the cell. The majority of the factors that affect the characteristics of the solar cell reside in this layer. Some of these factors are: the mobility of the charge carriers in the materials that constitute the photoactive layer; the HOMO-LUMO levels or the ionization potential of the donor and the electron affinity of the acceptor; the diffusion length of both the donor and the acceptor and absorption range in the sunlight spectrum. If the mobility of the charge carriers in the materials that comprise the photoactive layer is very low, the probability of getting high current from the solar cell is a dream. The HOMO-LUMO energy level difference is the one that determines the open circuit voltage of the solar cell. Hence, if difference between the ionization energy of the donor and electron affinity of the acceptor is low the open circuit voltage will be low. When thicker layer of the material in the photoactive layer is deposited the excitons after created will recombine that the electron goes to its ground state from excitement which is a loss and deteriorates the performance of the cell. Absorption of each material in the photoactive layer should be high and they should be complementary i.e. one



of the material should absorb high where the other one absorbs low and should cover as much of the solar spectrum as possible.

Optimizing the performance of the solar cell requires optimization of the above factors. To do so is important to modify the photoactive layer of the solar cell. There are some methods of doing so through depositing as donor-acceptor layer, co-evaporation of the two materials, the co-evaporated layer sandwiched between the layers of each materials and making tandems of the each of the cells mentioned before or the combination of them. ^{[45] [27]}

- **the single photoactive layered organic solar cell**

This solar cell is the simplest kind of solar cell with a single material is used as a photoactive material sandwiched between two electrodes as shown in the figure below. When illuminated by sunlight the photons will be absorbed by the photoactive material to excite its electron and create exciton. The potential that separates the excitons in to its corresponding charge carriers is the electric field developed due to the difference in the work function of the electrodes. ^{[45] [27]}

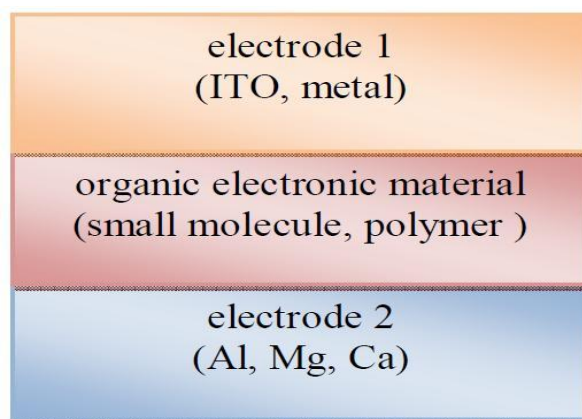


Figure 6: Single Photoactive layered organic Solar Cell where only one layer of semiconductor is deposited sandwiched between the electrodes

However, this electric field is not strong enough to separate much exciton in to electrons and holes that the power generated is low. These days more advanced kinds of these photoactive layer structures are developed and they are much more efficient than the single layer structure.

- **Photoactive Bi-layer or Planar Junction**

The insufficient potential difference to separate the exciton in to its corresponding charge carriers of a single layered photoactive solar cell is improved by the deposition of two complementary organic semiconductors as shown in the figure below [28]. This, as



explained before, is based on the fact that if two materials called donors and accepters are deposited one on top of the other, difference between ionization potential of the donor and the electron affinity of the acceptor is the driving force for the exciton to separate in to electron and hole easily. So in this kind of solar cell, after the anode and its interfacial layer a layer of donor or P-type material is deposited which has a relatively high ionization potential to donate electron and become positively charged itself. Another layer of material that has relatively high electron affinity should be deposited to accept the electron and become negatively charged. [45] [27]

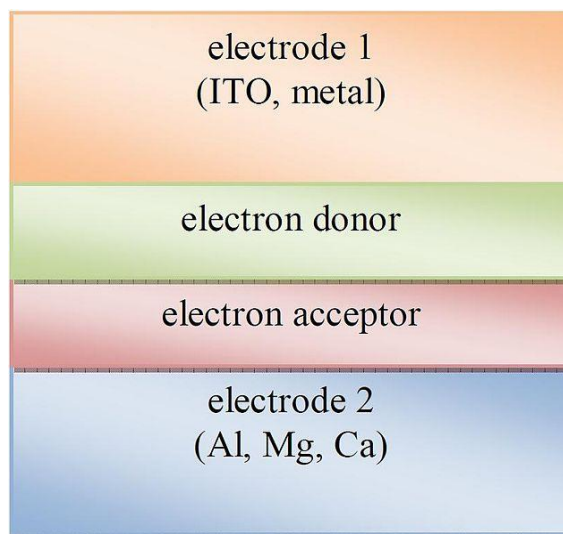


Figure 7: Double layered planar type organic Solar Cell with the Donor and the acceptor material are deposited one on top of the other in thin layer

When illuminated by sunlight, the photon of the sunlight is absorbed by the donors to excite their electron and create exciton which should diffuse towards the donor-accepter interface to ultimately separate into its charge carriers due the difference in the potential of the ionization potential and electron affinity of the donors and accepters respectively. The life time of exciton is very short that the exciton should travel a shorter distance before it reaches the donor-accepter interface. The life time of the exciton is determined by the diffusion length of the material. The diffusion length of the material is the maximum distance that an exciton created in the organic semiconductor should travel before it loses its energy and the electron moves from its excited state to its ground state. If the exciton should travel more than the diffusion distance of the semiconductor it will lose its energy before it reaches the interface where it should be separated. This depends on the thickness of the material deposited. If the thickness of the material deposited is beyond the diffusion length, most of the exciton created will recombine and lose their energy. [15] [45] [18]



Therefore, to get an optimum performance of the solar cell the thickness of each material in the photoactive layer should be its diffusion length. Otherwise, the absorbed photon energy will be lost due to recombination. This is a disadvantage in that with a higher thickness it is possible to absorb much photon than at lower thickness. But with the thickness of the layers increased much beyond the diffusion much of the excitons lose their energy.

This kind of deposition is called planar hetero-junction as the two materials are deposited one on the other one in planar form.

- **Bulk-junction or Co-evaporated photoactive layer**

The third kind of photoactive layer structure is the bulk-junction deposition where the donor and acceptor materials are deposited together as shown in the figure below.

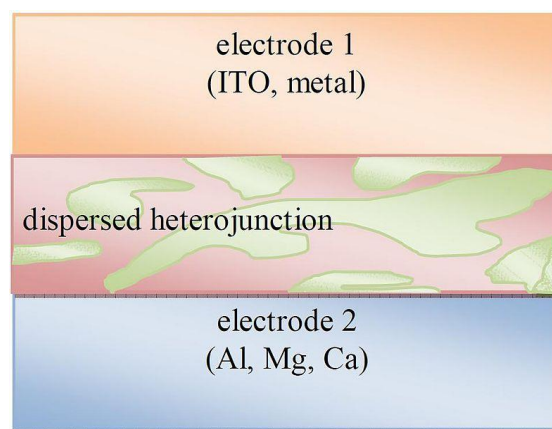


Figure 8: type of solar cell where the photoactive part of the solar cell is obtained by Co-evaporation of the donor and acceptor with certain proportion

This kind of deposition is based on the fact that co-deposition of the two materials increases the intimacy of contact between the two complementary semiconductors. This intimacy of contact has two advantages

- The total area of contact between the two semiconductors is increased. This increased area of contact increases the interface where excitons separate into electrons and donors. Due to this the current generated will increase proportional to the increased area relative to the planar deposition where the area of contact is the rectangular area of contact between the two semiconductors ^{[42] [7]}.
- It reduces the length of through which the exciton should diffuse to reach the interface below the diffusion length of the material. This reduces the probability of recombination of the exciton to render the electron to its ground state.



The deposition can be manipulated in different ways to get high performance cells. These can be done in two ways. One is by varying the proportion of the two materials and the other one is by varying the thickness of the co-evaporated layer. The former one can be done by fixing the rate of deposition in such a way that the ratio will be 1:1 or 1:2 or etc.... these different ratios will give the materials different alignment against themselves. At the end of the day the ratio that favours the best cell performance can be repeated. The later one can be done by varying the thickness of the bulk evaporated layer to look for the optimum. ^{[7] [45]}
[18] [27]

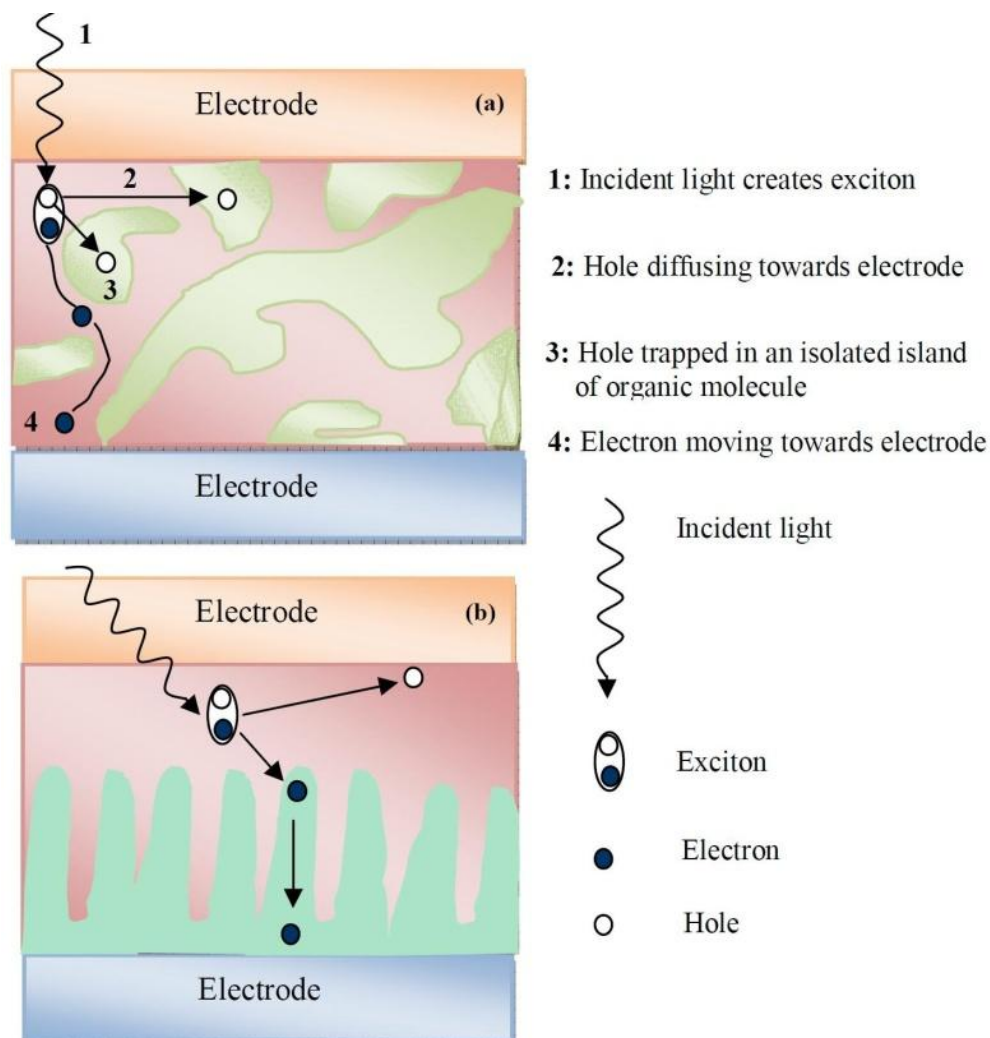


Figure 9: when one of the proactive materials is isolated islanded in the other material the separated charge will not have way out to its corresponding electrode that is a loss

However, co-evaporation has its own disadvantage in that if one of the materials is islanded in the other one with any connection with its parent material the charge carrier won't have way out to go to its corresponding electrode which is a loss. The other disadvantage is the



each material has a high probability of contacting directly with electrode of its opposite side which reduces the open circuit voltage of the solar cell ^{[28][16][18]}.

- **Donor Layer-Co-evaporated layer- acceptor layer (P-i-N)**

This kind of deposition is also called the P-i-N structure with the ‘‘P’’ denoting the donor or P-type layer, the ‘‘N’’ denoting the acceptor of N-type layer and the ‘‘i’’ denoting the intrinsic co-evaporated layer. This type of deposition is to take the advantages and avoid some of the disadvantages of the above depositions. The co-evaporated layer is sandwiched between the donor and the acceptor layers which are within their diffusion lengths. In doing so the direct contact of each material with its opposite electrode is avoided this improves the open circuit voltage. In addition, the two layers of materials added to the co-evaporated layer, as long as they are within their diffusion lengths they can still generate excitons and charge a separation that is additional boost in current generated. Hence, P-i-N deposition boosts both the current and voltage of the solar cell ^{[28][42][16][27]}.

- **Tandem solar cells**

Fabricating tandem solar cells is to improve some of the parameters of the solar cell like. It is done by depositing another layer of solar cell on top of another one to get one of the parameters or both depending on how the cells are connected and what we want to improve. For example, if the solar cells are connected in series, the output open circuit voltage of the solar cell so that the output voltage of the solar cell increases. If the cells are alike, it might double. ^[27]

2.3. Materials Used for Fabrication

For a material to be used in organic solar cell fabrication it has to have certain specific properties required by a solar cell. The simplest criterion if for the material to be either P-type material or N-type material or electrode interfacial layer i.e. the buffering layer or electrode. At least it should have either of these characteristics otherwise it couldn't be used in the fabrication material. On in all the fabrication of efficient solar cells require the integration between photo-chemists, photovoltaic engineer, organic material synthesis experts and solar cell fabrication experts. These people should discuss, share ideas, work together so that the benefits, disadvantages and trade-offs between parameters of the organic solar cell would be optimized. ^{[29][27]}

The most important materials required to fabricate organic solar cell are the semiconductors which when exposed to sun light could generate photocurrent. These materials should be synthesised carefully with excellent purity and combined in thin film layers in a way their difference in energy level leads to effective charge separation and collection. The main



characteristics of these materials are the mobility, the HOMO-LUMO levels, diffusion length, absorption and their physical properties. Some of these materials used in our laboratory during my study are listed in the table below. These characteristics and their physical properties are the results of their chemical composition, chemical structures. These chemical compositions and the chemical structures give rise to certain kind of arrangement of the atoms which lead to specific crystallization. This determines the morphology of the layer of the material when deposited in thin layers. Morphology on the other hand determines how materials align itself with respect to another material deposited next to it. The alignment alleviates some higher potential climbing difficulties of charge carriers. ^{[29] [27]}

The composition also affects their conductivity and the mobility of the charge carriers in the material when exposed to potential difference. In general, all the characteristic of organic semiconductors required for solar cell fabrication are results of the chemical composition, chemical structure and crystallization of the materials. ^{[45] [27]}

Some of these materials used in the lab as donor materials are: or tetra-phenyl di-benzo periflanthene (DBP), Gallium Phthalo-cyanine chloride (GaPcCl), Tin Phthalo-cyanine chloride (SnPcCl), Copper Phthalo-cyanine (CuPc) and Zinc Phthalo-cyanine (ZnPc). Although all of them are donor materials the range in which they absorb and the amount they absorb, their HOMO-LUMO level, with which acceptor they absorb in a complementary manner is very different. This holds true for the acceptors namely: Fullerene C60, fullerene C70. The physical and chemical properties of some of these materials are shown in the table below. ^{[32] [7] [27]}

Table 1: Chemical and Physical properties some of the materials used for the fabrication of Organic Solar Cells

Name of the material	Initial Temperature *	Density [kg/m ³]	Molecular weight [kg/kmol]	Molecular Formula	HOMO level [eV]	LUMO level [eV]
Acceptor Materials						
Fullerene, C60	250-350	1650	720.64	C ₆₀	-6.2	-4.5
Fullerene, C70	300-310	1700	840.75	C ₇₀	-6.2	-4.2
Bathophenanthroline or	95-105	1210	332.39	C ₂₄ H ₁₆ N ₂	-6.4	-2.9



Di-phenyl phenanthroline (Pphen)							
F ₄ TCNQ		1400	276.15	C ₁₂ F ₄ N ₄	-5.8	-3.45	
Donor Materials							
Zinc Phthalocyanine (ZnPc)	280-300	1400	577.19	C ₃₂ H ₁₆ ZnN ₈	-5.2	-3.1	
Pentacene	120-130	1300	278.35	C ₂₂ H ₁₄	-5	-3.5	
Dibenzo tetraphenyl dindeno perylene (DBP)	250-300		804.97	C ₆₄ H ₃₆	-5.5	-3.5	
Tin Phthalocyanine chloride (SnPcCl)			902.37	C ₄₈ H ₂₄ Cl ₂ N ₈ Sn	-5.2		
Copper Phthalocyanine (CuPc)	250-280	1600	576.07	C ₃₂ H ₁₆ CuN ₈	-5.2	-3.5	
Gallium Phthalocyanine chloride (SnPcCl)			617.7	C ₄₈ H ₂₄ Cl ₂ N ₈ Ga	-4.52	-1.54	
Anode Interfacial Layers							
PEDOT:PSS					-5.2	0	
Molybdenum-trioxide,		4690	143.94	MoO ₃	-5.3	-2.0	



Cathode Interfacial Layers						
Bathocupoine or Di-methyl di- phenyl phenanthroline (BCP)	100-120	1170	560.45	$C_{26}H_{20}N_2$	-7.0	-3.5

* Initial Evaporation or sublimation temperature of the material at a pressure of 10^{-6} to 10^{-7} mBar [$^{\circ}C$]

The other materials are those required for some supportive tasks in the generation of the current from the solar cell. These are the electrode interfacial layers and the electrodes themselves.

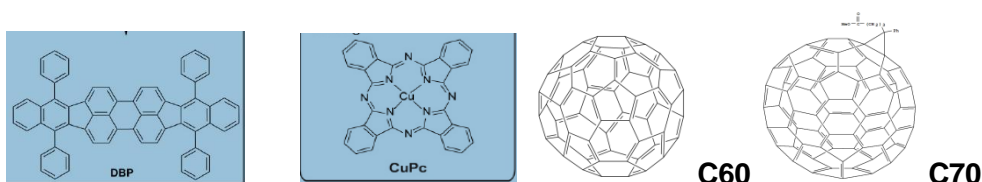


Figure 10: Chemical Structures of some of the Organic semiconductors used in our Lab

As explained before, Materials having a delocalized π electron system can absorb sunlight, create photo-generated charge carriers and transport these charge carriers. Research on organic solar cells generally focuses either on solution processable organic semiconducting molecules/polymers or on vacuum-deposited small-molecular materials. ^{[16] [45] [27]}

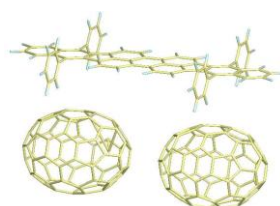


Figure 11: size comparison for DBP and Fullerene

As an example, phthalocyanine and perylene have commonly found applications in thin film organic solar cells. Phthalocyanine is a p-type, hole conducting material that works as electron donor, whereas perylene and its derivatives show an n-type, electron conducting



behaviour and serve as electron-acceptor material. In general, organic semiconductors can be regarded as “intrinsic wide band gap semiconductors” (band gaps above 1.4 eV) down to “insulators” (band gaps above 3 eV) with a negligibly low intrinsic charge carrier density at room temperature in the dark. Chemical, photochemical, or electrochemical doping is used to introduce extrinsic charge carriers into organic semiconductors. For example, photo-induced electron transfer from a donor to an acceptor-type organic semiconductor film introduces free charge carriers (positive charge carriers on the donor layer, i.e. p-type, and negative charge carriers on the acceptor layer, i.e. n-type).^{[29] [45] [27] [33]}

2.4. Characteristics of Organic Solar Cells

Once a solar cell is fabricated it has some special characteristics that it should have to be taken as a good performance cell. This holds true for an organic solar cell. These characteristics can be determined through different measurements that are accomplished on the cell. Before discussing about the measurement techniques we need to know what characteristics a solar cell has. A solar cell is a diode. Hence, the characteristics of a solar cell is that of a diode that to get the equations that govern a solar cell one needs to modify the diode equation to account for the additional features of the solar cell.

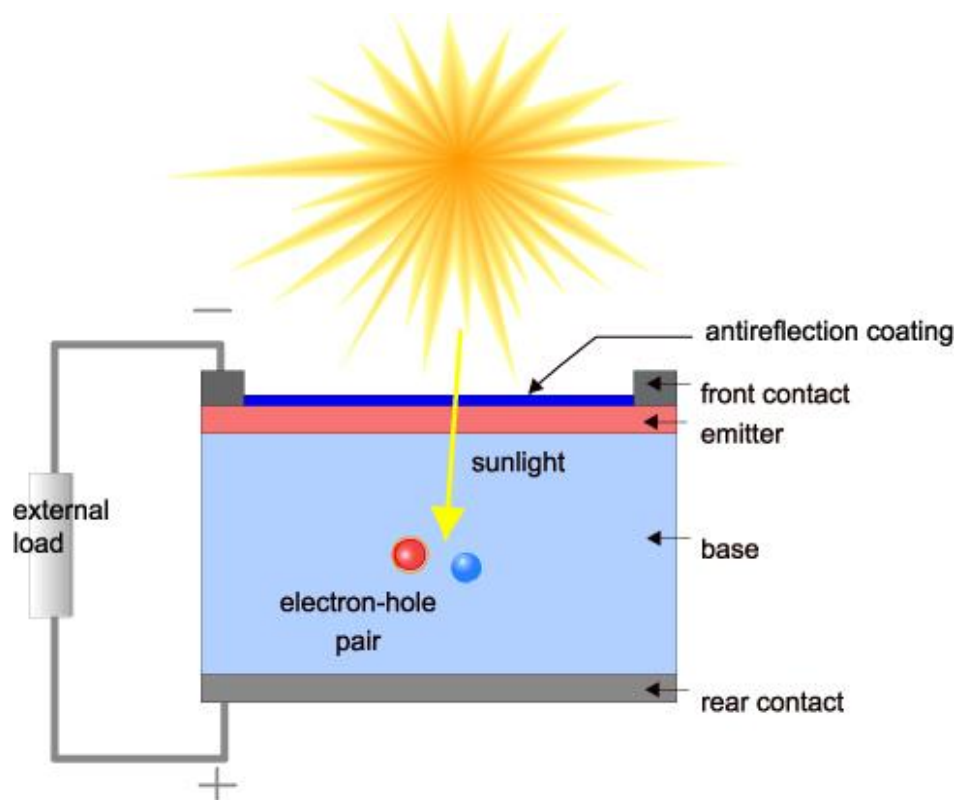


Figure 12: Basic operations that take place in the solar cell to generate power.



The main objective of a solar cell is to generate power through a voltage and current. The basic operation of a solar cell as explained before involves absorption of the photons of sunlight by the photoactive layer of the solar cell which excites the electron to create an exciton; diffusion of the exciton towards the donor-accepter interface; separation of the exciton into its charge carriers called electrons and holes by the difference in ionization energy and electron affinity of the donor and acceptor materials of the photoactive material respectively; flow of the charge carriers towards their corresponding electrodes i.e. electrons to the cathode and holes to the anode to be collected into the circuit. Effective flow of the charge carrier towards its corresponding electrode and its collection into the circuit builds up to the current of the solar cell. The net difference in potential that effect charge separation and drive charge carriers in the circuit is the voltage of the solar cell. If an electronic device can supply current at a certain voltage, it is giving power. This power can do some work if electric load is connected to the circuit. The basic operation is shown in the figure below. ^[29]

A simplified equivalent circuit model of the solar cell is shown in the figure below. One of the basic assumptions of a solar equivalent circuit is that it has much higher parallel resistance, R_{sh} than series resistance R_s which will prevent backflow of the current before it flows through the load.

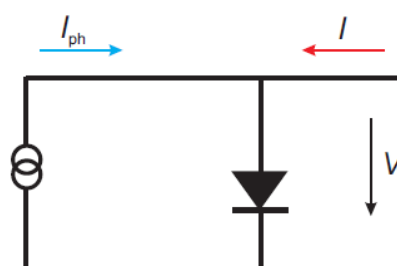


Figure 13: a simplified equivalent circuit model of an ideal diode of the solar cell that doesn't take into account the resistances in the diode

The corresponding ideal equation for the above equivalent circuit; taking the same as the inorganic solar cells although the exact equation for the organic solar cells is not known, is shown below. Although the photocurrent generation in organic solar cells is different from the inorganic solar cells, the inorganic solar cell equation describes it pretty well. This equation is developed assuming that the diode has no parallel and series resistances. ^[30]

$$I = I_{ph} - I_0 \left(e^{\frac{V}{nRT}} - 1 \right)$$



Where:-

- I_o – is the diode saturation current
- n – is the diode ideality factor
- I_o – is the diode saturation current

However, in real case the solar cells have both series and parallel resistances although the parallel resistance is thought to be much higher than the series resistance. Therefore, the above equation is modified to a new one that takes in to account the effect of the two resistances on the current-voltage characteristics of the solar cell.

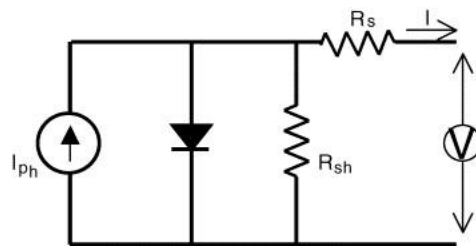


Figure 14: the equivalent circuit for the real diode of the solar cell that takes in to consideration the series and parallel resistances.

$$I = I_{ph} - I_o \left(e^{\frac{V + IR_s}{nkBT}} - 1 \right) - \frac{V + IR_s}{R_{sh}}$$

Where:-

- I_o – is the diode saturation current
- n – is the diode ideality factor
- I_o – is the diode saturation current

Where:-

- I_o – is the diode saturation current
- n – is the diode ideality factor
- I_o – is the diode saturation current
- R_{sh} – the shunt resistance or the parallel resistance
- R_s – the series resistance in the diode of the solar cell



The above equation that accounts all the resistances in the solar cell describes the characteristics of the solar cells and all the characteristic parameters of the solar cell can be determined from this equation.

During measurements only the open circuit voltage, the short circuit current and the fill factor can be known directly. We can get the current-voltage characteristics of the solar cell by measuring a computer integrated solar simulator. The additional measurement of the solar cell that we can get is the quantum efficiency curve. ^[30]

The open Circuit Voltage, V_{oc}

The open circuit voltage is the maximum voltage measured from the terminals of the solar cell when the circuit is open i.e. when there is no current flowing. This voltage is related to the energy offsets between the materials constituting the photoactive part of the solar cell specially the difference in the energy level between the HOMO of the acceptor and the LUMO of the donor. This in other words is directly related to the difference between the ionization energy of the donor and the electron affinity of the acceptor at the interface between the two materials ^[41]. This potential is the one that drives the charge carriers i.e. the electron and hole to separate from each other to be collected at the electrodes.

When the I-V curve is measured with the computer integrated solar simulator without light i.e. in dark it gives a curve that looks like the blue curve in the figure below. It enables one to predict some of the parameters of the solar cell when illuminated. When illuminated, the I-V curve shifts down ward (the red curve in the I-V curve shown below). The open circuit voltage of the solar cell is therefore, the voltage reading when the I-V curve after illumination (the red curve in the I-V curve shown below) crosses the zero current density line i.e. the x-axis. ^[34]

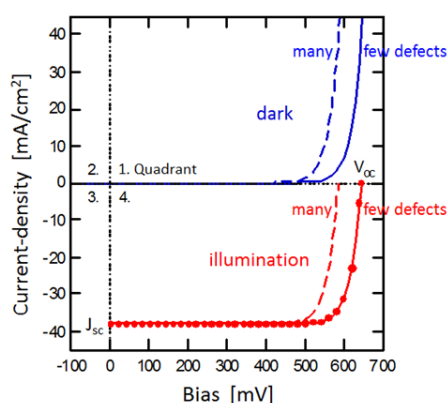


Figure 15: I-V characteristic curve of a solar cell when illuminated and not illuminated



The Short Circuit Current density, J_{sc}

The short circuit current is the maximum amount of current that can be obtained from the solar cell that takes place assuming there is no resistance in the equivalent circuit of the solar cell i.e. when the voltage across the resistor is negligibly small ^[41]. This is the current that is expected to flow through the external circuit towards the external loads if all the charge carriers created in the solar cell reach the electrodes without any problem. However, this is ideal in that the solar cell has resistances, the charge carriers recombine and energy is lost. The short circuit current of the I-V curve can be read from the red curve of the above figure easily. It is the value of the current read when the red curve crosses the y-axis. However, the value that we read from the curve is current density i.e. the current per unit area of the solar cell.

The Maximum Power, P_{max}

Power is defined as the product of the current and voltage of an electric device. The maximum power that can be extracted from the solar cell therefore is the product of the maximum current and maximum voltage that can be obtained from the solar cell ^[41]. The maximum current and maximum voltage of a solar cell is the short circuit current and the open circuit voltage, respectively. This power is the maximum power that can be achieved which is impossible due to some resistances and losses. Mathematically, it can be expressed as follows.

$$P_{max} = V_{oc} I_{sc}$$

This power on the I-V curve is the rectangle tracked by the short circuit current and the open circuit voltage.

The Fill Factor, FF

The power generated from a solar cell is not the maximum power; in fact it is less than the maximum power. This is because the output current and voltage of the solar cell are both less than the short circuit current and open circuit voltage respectively. The current output is less than its maximum counterpart, the short circuit current, because of losses due to recombination, islanding isolations and short diffusion length problems. The potential developed due to the difference between the ionization energy and electron affinity; and the work functions of the electrodes is also deteriorated by some potential losses across the cell.



Therefore, the real power output from the solar cell; as it is the product of the real voltage across the cell and its real current output, is less than the maximum power, P_{max} .

However, any combination of the current and the voltage on the I-V characteristic curve can give the output power, P_{output} . But we want the combination that gives the maximum output power and the point on the I-V curve that belongs to this maximum power is called maximum power point, P_{MPP} . The power out due to different possible combination of the current and the voltage is drawn with the I-V curve as shown in the figure below as a mirror image of the normal I-V curve. As can be seen from the blue curve has a maximum point and this is the maximum power point.

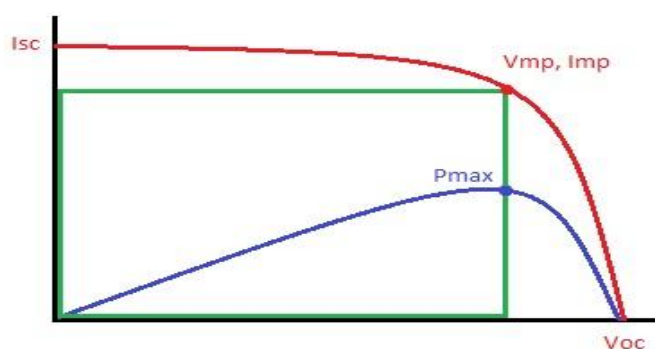


Figure 16: the power curve and the I-V curve in the positive quadrant

The corresponding current and voltage at this point are designated as I_{MP} and V_{MP} to say current at the maximum power point and the voltage at maximum power point. Due to advancement of technology we have instrument that makes sure that we are extracting the power at the maximum power point. This equipment is called maximum power point tracker, MPPT.



Now we have two rectangles in the I-V curve: one that traced by I_{MP} and V_{MP} and that of I_{sc} and V_{oc} .

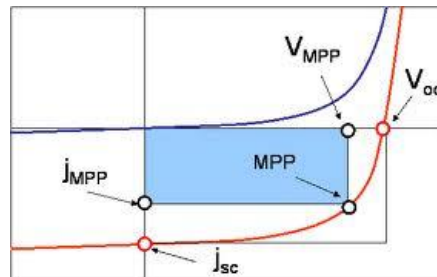


Figure 17: the maximum power point on the I-V curve

The parameter that is used to indicate how far less is the output power from the maximum power is the Fill Factor. The Fill factor is the ratio of the output power to the maximum power. It shows what percentage of the maximum power is extracted from the solar cell. It is also the ratio of the two areas traced by the parameters at the P_{MPP} and P_{max} .^[41]

$$FF = \frac{P_{output}}{P_{max}} = \frac{P_{MPP}}{V_{oc}I_{sc}} = \frac{I_{MP}V_{MP}}{V_{oc}I_{sc}}$$

From this one can see that:

$$P_{output} = FF * P_{max} = I_{MP}V_{MP} = FF * V_{oc}I_{sc}$$

The output power is therefore, a fraction of the maximum power. A solar cell with high fill factor will have higher power extracted from it. Improving the fill factor of a solar cell is one important areas of research.

The shape of the I-V curve and the intercepts give some ideas about the filling factor and other parameters. The two intercepts are very important parameters i.e. the short circuit current and the open circuit voltage. The more the curve is drawn to the left and down the more the cell we will have higher values of these parameters which increases the P_{max} . As the power output is a fraction of this power it may lead to high output power. The shape of the curve between the two intercepts could be different: a nearly right angled, nearly straight



line or in between. When the shape of the curve is nearly right angle the filling factor would be very high. The more the curve tends to be straight line between the two intercepts, the less the fill factor gets.

The efficiency of the Solar Cell

Efficiency of the solar cell is defined as the ratio of the output power of the solar cell and the input power to the solar cell.

$$\eta_{\text{cell}} = \frac{P_{\text{output}}}{P_{\text{input}}}$$

The input power is the solar energy input to the solar cell. This power is given per unit area and it depends on the solar intensity that varies time of the day and time of the year. The standard power density called One Sun is 1000W/m^2 or 100mW/cm^2 and the efficiency of every cell in a laboratory is measured against this standard. The output power can also be found per unit area taking the output current of the solar cell per cross sectional area of the solar cell to get current density, J [mA/cm^2].

Therefore, the efficiency of the solar cell can be rewritten as:

$$\eta_{\text{cell}} = \frac{P_{\text{output}}}{P_{\text{input}}} = \frac{I_{MP}V_{MP}}{100\text{mW/cm}^2}$$

As we can't know the maximum power point of the solar cell before hand, we can't use V_{MP} and I_{MP} in the above equation to determine the power output. The correct way will be to write the equation in terms of fill factor.

$$\eta_{\text{cell}} = \frac{P_{\text{output}}}{P_{\text{input}}} = \frac{FF * V_{oc}I_{sc}}{100\text{mW/cm}^2}$$

The efficiency of the solar cell therefore depends on the effectiveness of all the processes and operation that take place during generation of power from a solar cell. That are; the absorption of the photons of the sunlight to create excitons, diffusion of the exciton towards the donor-accepter interface, separation of the exciton into electron and hole i.e. charge separation, flow of the charge carriers towards their corresponding electrodes and the collection of the charge carriers at the electrodes to flow to external loads to give power.



The series and parallel or shunt resistances of the diode i.e. R_s and R_{sh}

These two parameters of the diode are very important in determining the power and /or the current that goes to the external circuit. Ideally, the shunt resistance is very big and the series resistance is very small that all the current flows to the external circuit. However in the real case, that is not true that some current flows back into the internal circuit and lost through recombination.

Determination of these parameters is very important to see the how significant is the recombination in the solar cells fabricated.

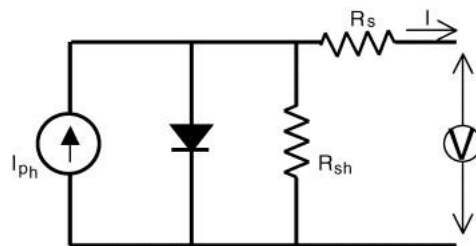


Figure 18: Equivalent circuit of the diode of the solar cell

Looking at the equivalent circuit of the diode of the solar cell; one can see that, when open circuited the current flows across the shunt resistor and when short circuited the current flows through the series resistor ^{[47] [34]}. Mathematically,

$$\frac{1}{R_{sh}} = \left(\frac{dJ}{dV} \right)_{oc} \text{ and}$$

$$\frac{1}{R_s} = \left(\frac{dV}{dJ} \right)_{sc}$$

Where:

$\left(\frac{dV}{dJ} \right)_{oc}$ – is the rate of change of voltage with current density at open circuit point

$\left(\frac{dJ}{dV} \right)_{sc}$ – is the rate of change of current density with voltage at short circuit point



The mobility and life time of the charge carriers

The mobility and life time of the minority carriers is due to the different kinds of bonds that hold the electrons in the molecule with their holes. This depends on the chemical composition and chemical properties of the molecules. These parameters are determined by applying biased voltage across the solar cell without illumination i.e. in dark. This will enable to see how mobile the charge carriers are without applying driving force to create majority carriers by illumination. In the dark applying biased voltage will see the minority carriers mobile. ^[26]

The effective mobility-lifetime of carriers is the sum of the mobility-lifetime of the electrons and mobility-lifetime of the holes. It depends on the difference in the work functions of the ITO (4.5eV) and the electrodes (Al in our case, 4.1eV); the thickness of the photoactive layer and effective collection length of the solar cell. ^{[26][16][15]}

Mathematically; the effective mobility-lifetime of the carriers is given as:

$$\mu\tau_{eff} = \frac{l_{col}L}{V_{dwf}}$$

Where: -

l_{col} – the effective collection length [nm]

L – the thickness of the photoactive layer [nm]

V_{dwf} – the difference in the work functions of the ITO and the electrode [eV]

The V_{dwf} is given by the difference in the work functions of the ITO and the Aluminium electrode as follows

$$V_{dwf} = (V_{wf})_{electrode} - (V_{wf})_{ITO}$$

The effective collection length on the other hand is given by the following equation:



$$l_{col} = \frac{V_c + V_{dwf}}{V_{dwf}} * \frac{L}{2}$$

V_c – is the ratio of the two parameters at the short circuit point of the solar cell.

At the short circuit point, the line tangent to the J-V curve has y-intercept and slope. The ratio of the y-intercept to the slope of the tangent line gives the V_c . In this way the effective mobility-lifetime of the photoactive layer of the solar cell is determined. It is important in the study of the degradation of the solar cells with oxidizing or reducing agents. ^{[26] [34]}



3. Fabrication of Organic Solar Cells

3.1. Substrate Preparation and Cleaning

The so called substrate is a glass on which is deposited an ITO (Indium Tin oxide or Tin-Doped Indium oxide). Indium Tin oxide is the most widely used transparent conducting oxide due to its good transparency of light and conducting ability. It is also easy to deposit it as thin film. The substrate that we use is the one manufacture by Luminescence Technology Corp. which has ITO deposited on Glass with resistance of 15ohm; size 15x15x0.7mm and quality 100pcs. They manufacture it to the quality to be used by qualified personnel for research and development with following specifications.

Product No.	LT-G001	LT-G002	Product No.	LT-Cover
ITO Thickness	: 1200~1600Å	: 3100~3700Å	Size	: 370*470mm or Customize
ITO Resistance	: 9~15 Ω/sq	: 4~6 Ω/sq	Thickness	: 0.7 or 1.1mm
ITO Transparency	: >84% (at 550nm)	: >78% (at 550nm)	Mohs Hardness	: 6.5
Material	: Polished soda lime glass		Thermal Expansion	: 85-90 (10 ⁻⁷ /°C at 20)
Size	: 370*470 mm or Customize		Specific Heat	: 0.19 cal/g°C (at 0)
Glass Thickness	: 0.7 or 1.1mm		Transmittance	: ≥90%
SiO ₂ Thickness	: ≥ 200Å		Resistivity	: 15.3 Log Ω-cm (at 25°C), 7.3 Log Ω-cm (at 250°C)
R _a	: Less than 6nm			
R _{max}	: Less than 35nm			

Figure 19: the specifications of the ITO that we use as a substrate in our lab, (obtained from the website of the ITO manufacture company, Luminescence Technology Corp.)

However, the substrate that we buy may not be clean due to many reasons. These dirt materials have negative impact on the performance of the cell that is going to be fabricated. This is because, the cells we fabricate have layers of different layers of organic materials and electrodes. In other words on top of the ITO we deposit less than hundreds of angstroms (10⁻¹⁰m) of organic materials (P-type and N-type materials) and hundreds of nanometres of contact metal electrodes (Aluminium or Silver). The organic materials or layers deposited before the contact metal electrodes are the ones which receive the sunlight, use the photons in the sunlight to excite their electrons and generate current. They have their own optical transparency and semi-conducting properties so as to allow sunlight to reach the semiconductors or the organic layer and the photons in the sunlight be absorbed by the semiconductors to initiate the electrons excited to generate current. If there



is any kind of impurity on the surface of the glass-ITO substrate, they will either affect the transparency of the substrate. ^{[3] [27] [35]}

Hence, we need to clean the substrate before we carry out the ultimate solar cell fabrication ^[41]. To do that, we put the substrates in acetone for 30minutes under ultrasonic bath. Then, we put the substrates in Iso-propanol for 30minutes under ultrasonic bath. These two solvents will remove all the organic impurities laying on the surface of the substrate. The fact that we put the substrate in Isopropanol after acetone is that the former can be dissolved by the later one. After the ultrasonic bath treatment by the solvents we dry the substrates by Nitrogen to remove the solvents on evaporation. Choosing nitrogen to air for drying is to disallow some particles from air and oxygen in the air which might have some unknown reactions with the surface at higher pressure as nitrogen is inert. ^{[3] [27]}



Figure 20: Photos of UVO cleaner outside and inside hood.

The last stage of the substrate preparation stage is to put them in UV-light in UVO cleaner. The UVO method is a photo-sensitized oxidation process in which the contaminant molecules of photo resists, resins, and human skin oils, cleaning solvent residues, silicone oils, and flux are excited and/or dissociated by the absorption of short-wavelength UV radiation. Therefore, This UV light treatment removes the residue of the Isopropanol and other remaining impurities through the photo-sensitized oxidation process so that the substrates will be free of nearly all potential impurities that affect the properties of the Glass-ITO and ultimately the solar cells. It is important noticing here that, after the substrates are dried to take them to the UV-light treatment we need to cover the substrates otherwise particles will obviously fall on the substrate from the air and our prior ultrasonic bath



cleaning with those solvents will be nonsense. This holds true for taking the substrates from the UV-light treatment to the deposition or solar cell fabrication chambers. UV treatment equipment should be inside hood so that while uncovering the substrates to put them in to or take them away from the UV treatment equipment no particle will fall on the substrates. It is not only doing it inside the hood, but the most important thing is to turn on the hood. This is not only for the sake of the substrates but also for the sake of avoiding suffering ozone as it is produced through the photo-sensitized oxidation process in the UV-treatment equipment or UVO cleaner. If all this is accomplished, the substrate is clean and the performance of the cells that we will get later won't at least be because of substrate preparation. ^[35]

3.2. Deposition and the Glove Box

3.2.1. The Glove Box

The glove box is a sealed box filled with inert Nitrogen in which

- We put the organic and metallic materials required for the fabrication of the solar cell.
- We have the organic deposition chamber and the metallic deposition chamber.
- We open the containers that hold the materials used to fabricate take the amount we needed without fearing the oxidation of the materials due to oxygen or water vapour or contamination due to some particles in the atmosphere entering the container. This can't be done in the open atmosphere.
- We put the solar cells in to characteristics measurement holder before taking them to any of the equipments to measure the characteristics.

All this is to protect the fabrication materials and/or the cells from any deterioration in their chemical composition and contamination with impurities. The ultimate objective is to keep the performance of the cells as high as possible.

As can be seen from the figure above, the glove box is transparent from the front side that one can see anything inside the glove box and manipulate things inside. To do that one has to use the gloves to go inside do whatever he wants inside the glove box. It is equipped with controllers, box light, vacuum pumps, nitrogen vessel, and two chambers for evaporation, doors, annealing heater, nitrogen purifier and other accessories required for fabrication.





Figure 21: The Glove Box of the lab with both the Organic chamber (on the right) and the metallic chamber (on the left) both open inside the glove box.

The inside of the glove box is filled with nitrogen to create inert environment for the fabrication and handling the materials inside. Taking material or anything inside or outside of the glove box should be done carefully as air could enter the globe box and increase the oxygen level. This is done by refilling and evacuation of the door box with nitrogen and vacuum; respectively, at least three times.

3.2.2. Deposition of the organic and metallic layers

To grow films by thermal evaporation, usually a vacuum of $<10^{-5}$ mbar is applied. Thus the mean free path of the evaporated molecule is longer than the distance between the evaporation source and the sample holder. In addition, contaminants like oxygen and water are reduced and can be eliminated further by ultra high vacuum ($<10^{-9}$ mbar) or evaporation inside of a glove box with inert atmosphere. To create interpenetrating donor-acceptor networks or to achieve molecular doping, co-evaporation techniques can be applied. The materials are put in a crucible connected surrounded by electrical heater coil for organic materials or in Tungsten or Tantalum boat that is used as a direct resistor for metallic materials. The cleaned substrate on a shadow mask is put immediately above the boats or crucibles that contain the material to sublime in to gas. When heated the gases go directly upward to the substrate above. Due to the low base pressure of the evaporation chamber (10^{-6} to 10^{-7} for HV and 10^{-8} to 10^{-10} for UHV), the chance of hitting another molecule after evaporation is low, and their mean free path length is longer than the physical dimensions of the evaporation chamber. The transported molecules follow a



straight line until they condense on a surface with temperature below the evaporation temperature. The deposition of these layers is based on the fact that, when vapour forms of materials are in contact with any solid material specially metal they immediately condense and solidify by giving out their latent heat to the solid they are in collide with. Therefore, when the vapour collides with the substrates they condense and on the surface facing down.

The solar cell to be fabricated comprises various layers of different materials one on top of the other. As sublimation needs heating and take place at high temperature, the process takes place in vacuum pressure to fabricate the solar cell at relatively low pressure and temperature. An organic solar cell layers look like as shown in the figure below. For this purposes we have to vacuum chambers that operate in vacuum namely: the organic chamber and the Metal chamber. The organic chamber is the one in which we sublimate the organic materials like the donor or p-type material, the acceptor or N-type material and the Cathode interfacial layers and the anode interfacial layer if it is organic. The Metal chamber on the other hand is in which we sublimate and deposit the metal part of the organic solar cell layers such as the cathode comprising either Silver or Aluminium and the anode interfacial layer if it is molybdenum oxide.



Figure 22: the metal evaporation boats and the substrate holder on top.

The rate of the materials depositing on the surface requires control. This is for various reasons.



The thickness of each layer of material is controlled and specified. This is because thickness of each layer has influence on the performance of the cell. If the thickness of certain organic layer is beyond the diffusion length of the material, exciton recombination will be obvious. Thickness of anode or cathode interfacial layers should also be controlled within specified ranges otherwise they will increase the series resistance of the cell, reduce transparency and lower the performance of the cell. Hence, the rate should be controlled ^[5].

Deposition at higher rate of certain materials like Aluminium or silver on the organic layer will cause short circuiting of the solar cells. This is because, when these materials are deposited on the surface of the organic layer at a higher rate, they will penetrate the organic layer and will form connection with the anode, which of course is short circuiting.

Sometimes, when the rate is higher means the power applied on the sublimates is high and which may reach to the degradation temperature of the materials. This will cause both waste of materials and deterioration of the boats or crucibles due to unwanted decomposing.

Rate of deposition also affects the morphology of the surface ^[7]. Depending on the rate at which deposition takes place on the surface, it will have high or low picks and different arrangements of the one layer on top the other. For example, if the surface of the donor or P-type material has high picks, they will penetrate into the layer of the acceptor or N-type material which increases the intimacy of contact between the two materials and lead to increase of the short circuit current. But this is disadvantageous if the picks penetrate until the cathode that leads to the reduction of the exciton separation probability

To accomplish the objective of rate control we have a controller on which we can read the rate and its deviations and tendencies which will lead us of what action we need to take. This could be by increasing or decreasing the power or the temperature of the evaporation chamber. Depending on the exact growth conditions (the molecular rate hitting the substrate and its temperature being the most important ones), an amorphous or a polycrystalline thin film is created. The evaporation rate (or the flux) is measured with a crystal monitor, based on a built-in quartz crystal oscillator which has the characteristic of changing its frequency of oscillation as its mass changes. When more material is deposited on the quartz crystal, the mass changes, and the change in frequency is monitored.

The low pressure used in this deposition technique leads to a low concentration of unwanted impurities like water vapour and oxygen in the chamber. A second advantage is the high accuracy of the technique: a shutter in the line of evaporation stops the deposition in a fast and controllable way. At the same time, the anisotropic evaporation poses two problems: the uniformity at larger scale is not good, and objects can prevent evaporation on certain parts of the substrate. By rotating the substrate during evaporation and placing the



maximum flux of the evaporated molecules slightly off-centre, a better uniformity is reached and shadow effects are somewhat decreased. The low throughput and the limited size are other disadvantages. Vacuum techniques require load locks to transfer from atmospheric pressure to the very low pressures of HV or UHV.

To see in detail let us see each layer one by one and discuss some basic ideas related to the above ideas.

The ITO:

The first layer is the ITO layer that is transparent to light and conducts electricity. It transmits the light that initiates electron excitement in the organic layer and conducts current (i.e. hole) after the electron is separated from the its corresponding hole. In short it is the anode of the solar cell. As the ITO is deposited by the company we buy from, we don't need to control except cleaning it and preventing it from any scratching.

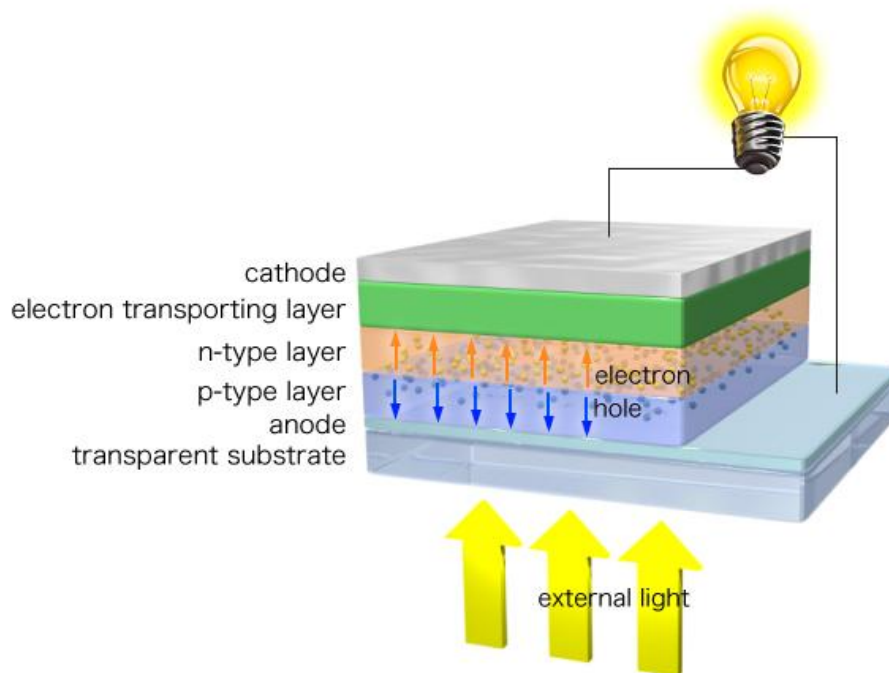


Figure 23: Generation of Electric power from small molecule Organic solar cell comprising all the important layers in it



The Anode interfacial layer:

The layer that is deposited immediately on top of the ITO is the anode interfacial layer called the hole transport layer. Hole transport layers are also known as electron blocking layers. The layer next to the electron blocking or hole transport layer is the P-type or the donor material. This material receives the photons to excite its electron where by the electron goes to the acceptor or N-type material and the hole goes towards the anode ^[42]. Hence, the purpose of the anode interfacial layer is to block electrons from going to the anode and conduct the holes very well towards the anode. In addition to that this anode interfacial layers enhance the fill factor, increase the open circuit voltage and of course the power conversion efficiency of the cell of the solar cell. The material that is used as anode interfacial layer are Molybdenum oxide (MoO_3 ,) and poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) with former one is the one we use in our laboratory often. We deposit Molybdenum oxide in the metal chamber. ^[10]

During deposition, the rate should be kept as low as possible especially during the first 2nm thickness to avoid morphological and unwanted penetration problems. Optimum deposition rate should be kept. The deposition takes place in the metallic deposition chamber as we used to use MoO_3 as anode interfacial layer.

The P-type or Donor and the N-type or Acceptor materials

These two materials are the most important parts of the cell and also called the active layer of the solar cell. As explained previously, this is the layer in which photons of sun light is absorbed to generate electron-hole pair called exciton by exciting the electron from the lower energy to high energy level; the excitons diffuses towards the interface between the P and N-type materials; separate into the corresponding charge carriers called electrons and holes; and generate current. At the interface between the two materials, holes move towards the donor and ultimately towards the anode and the electrons move towards the acceptor and ultimately to the cathode.

The type, thickness and morphology of these materials influence the performance of the cell as they are the main parts of the cells which are capable of generating the current. There are many materials of both kinds. The difference among these materials lies in their characteristic parameters such as absorption in the spectra, band gap which depend on their HOMO and LUMO levels. Some of the materials have lower band gap while having lower range absorption in the spectra and vice versa. Optimizing these characteristics lies in knowing and testing new materials, and combining them with proper counterpart. ^[30]



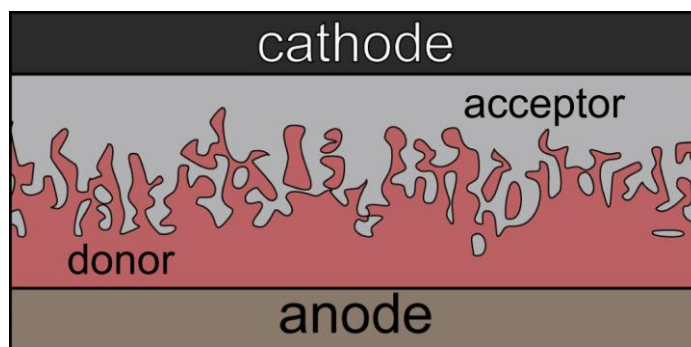


Figure 24: the Bulk-Junction photoactive layer solar cell

To control the morphology of the surfaces of these materials, the rate of deposition optimization is very important. This will enable us to control the compromise between unwanted penetration of the peaks of one material on the other and intimacy of contact. In case of bulk junction solar cells, the arrangement and composition that give the optimum performance should be addressed. ^[16]

The Cathode interfacial layer:

This is the layer that is used as an electron transport layer and hole blocking layer that allows the flow of electrons from the N-type material to the cathode but prevents the flow of holes so that they will only move towards the anode. The material that we use as an electron transport layer is BCP, and we do its deposition in the organic chamber as it is an organic compound. ^[10]

The cathode:

The cathode is the last layer of the organic solar cell, which is made of either Aluminium or Silver. The electrodes are the ones that collect the corresponding charge carriers (electrons and holes). Cathode electrode deposition is the one that needs a lot of attention in terms of high evaporation and deposition rates. This is because they are metals and they will penetrate the organic layer and have contact with the anode side, which ultimately leads to a short circuit. Hence, in the first 2nm of the deposition, the rate is kept below 0.02A/s and between 2nm and 20nm, 0.2A/s, and afterwards we can increase up to 1A/s.

Annealing:

Annealing is a post-production or post-fabrication treatment of the solar cells by heating the cells to certain temperatures for certain seconds. This will enable the layers of the organic solar cells to stabilize in their morphology, physical and chemical structure, and solidification or crystallization of each material. However, the temperature and time to which it should



be annealed should be optimised; otherwise it will affect the performance of the cell. For example, for DBP-Fullerene based solar cells we anneal the cells at 160oC for 30 seconds. [35]

3.3. Factors Affect Effectiveness or Performance of the Solar Cells

The performance of the organic solar cell fabricated depends on many factors that reside on the properties of the materials used to fabricate the solar cell and the conditions during fabrication ^{[6] [43]}. When fabricating a cell one has two take into account of these two things as they determine the efficiency of the solar cell. Some of the properties of the materials used to fabricate the solar cell that should be considered in this case are the absorption of the semiconductor, the HOMO-LUMO level or the Band Gap of the semiconductor, the charge motilities, diffusion length etc.... the fabrication conditions that on the other hand are Temperature of the substrate, rate of deposition, type of structure chosen for the photoactive layer. Discussing each of these factors will give us some insight.

3.3.1. Due to Properties of Materials

Absorption

When light is incident on the surface of a material part of the light will be Absorbed, part of it will be reflected and part of it will be transmitted through the material. The extent of these three processes depends on the optical property of the material. In photovoltaic the main desire is to absorb as much of the photons of the sunlight as possible. The other two i.e. the reflection and transparency of the light are considered as losses. The absorption of the photons of the light depends on the HOMO-LUMO level or the band gap of the semiconductor and the energy content of the photons. The energy content of the photons depends on what wave length it possesses in the spectra. The shorter wavelength photons have higher energy content and vice versa. When light is absorbed by the semiconductor the electron will be excited from its ground state at the HOMO level to its HOMO level. For each semiconductor a specific minimum amount of energy is required to excite an electron to its higher state. That is the Band Gap. Therefore, if the energy contained by the photon absorbed has a higher or equal amount of energy, it will be able to excite the electron otherwise it won't be able to do that. If there is no excitement, no exciton, no charge separation and no power generation.



The absorption of light by semiconductors is described by absorption coefficient or absorption depth. Mathematically:

$$\alpha = \frac{4\pi k}{\lambda}$$

where: – k: – is extinction coefficient

λ: – wavelength of the photon in the spectra

The extinction coefficient is a parameter that indicated the rate at which photons of a certain wavelength disappears due to absorption by the semiconductor. Hence, the unit of absorption coefficient is in form of inverse of unit of length, commonly cm⁻¹. Photons with high energy content i.e. short wave length photons will have high absorption coefficient and vice versa. An absorption depth is another parameter used to indicate absorption of photons. It is the inverse of absorption coefficient and it shows the distance for a certain wavelength photon has to travel before it is absorbed provided that its energy content is greater or equal to the band gap. The photons with high energy content i.e. short wave length photons will have small absorption depth. That is; the shorter the wave length of the photon the shorter it will travel through semiconductor before it is absorbed and vice versa. Shorter wavelength photons will be absorbed near the surface of the semiconductor as soon as they incident while longer ones has to travel to some distances in the layer depending on their energy content. But at certain point of wave length the absorption coefficient goes to very low values like zero. This is the point where the energy content of the photons longer than that wavelength have less than the band gap of the semiconductor. These two parameters can be drawn against wave length and they are mirror images of each other. This can be seen in the figure below.

The HOMO-LUMO level or the Band Gap

To generate power from the organic solar cell, first electron has to be excited from its ground state called HOMO level to its higher energy level called LUMO level to create exciton; then the exciton has to be separated in to charge carriers and finally, the charge carriers have to flow through external circuit. Excitation of the electron and creation of exciton, as explained above, depends on the difference in the energy level between the HOMO and LUMO level of the semiconductor and the wave length of the photons absorbed. The photons which have equal or greater energy than the Band gap will be able to do that. The photons with lower energy than the band gap wont be absorbed rather they will be transmitted through the semiconductor layer. When the band gap gets smaller the



probability of photons from whole range of the spectrum to be absorbed will increase. Practically, the band gap of organic semiconductors is higher than of the inorganic ones. This shows that choosing two semiconductors that can absorb in different part of the spectrum and cover as much of the whole range of the spectrum as possible in a complementary way is important.

The other very important potential worth mentioning is the difference in the ionization potential of the donor and the electron affinity of the acceptor. As mentioned above this is the potential that pulls the charge carriers apart and drive them into the circuit. This potential is proportional to the difference in the energy level of the LUMO of the donor and the HOMO of the acceptor. This potential part of it will be used to overcome the binding energy of the charge carriers in the exciton and part of it is used to overcome the potentials across the resistances inside the solar cell. The rest is the voltage output of the solar cell. Hence, the more it gets bigger than the binding energy the more will be the output voltage.

Charge mobility

Due to the different kinds of bondings that exist in the structure of the organic semiconductors the charge carriers like electrons are hardly free to move like in the metals ^[32]. The concentration of these charge carriers is very low. There is a process called doping that makes semiconductors have higher concentration of charge carriers that are free and mobile. Doping violates the balance of the concentration of one of the charge carriers. The impurity that is put into the semiconductor is a material or molecule that either has some free electrons that are free and mobile to be lost whenever there is a condition allows the molecule become stable than it is right now by giving its electron or needs to accept some electrons from another molecule or material to become stable. The ones that have a tendency to lose their electron to become stable will remain positively charged and are good for hole transport while the others with a tendency to gain electron become negatively charged and will be good for electron transport. The positive ones are the P-type or donor materials and the negative ones are the N-types or accepters. Once the semiconductors are doped with proper molecule the corresponding charge carriers will be mobile that electron in these materials can be excited by photons to jump the band gap. This will lead to high current generation. ^[41]

Diffusion Length

Once the photon is absorbed and exciton is created the exciton has to separate in to the electron and holes i.e. the charge carriers. For charge separation takes place there must be some force or potential difference. This is because the electron and hole of an exciton are bound to each other by a relatively strong energy called binding energy. Therefore, there



must be something that attracts and pulls the electron towards itself and there must be another thing that is capable of attracting and pulling the whole to itself.^[41]

In chemistry, it is known that certain materials have a tendency to lose their electrons and become positively charged and others have a tendency to attract and add electrons to add it in to their orbital and become negatively charged. The ones with a tendency to become positively charged is because of their high ionization energy and those with a tendency to get electron and become negatively charged is because they have high electron affinity. This is exactly what happens in the organic semiconductors. There are semiconductors called P-type materials composed of atoms or molecules that have a tendency to lose electron and N-type materials composed of atoms or molecules that have tendency to get electron. When these materials are close to each other in certain conditions and when there is exciton around their interface, the N-type material will attract the electron and the P-type material attracts the hole. The energy by which the N-type material pulls the electron i.e. the electron affinity and the P-type material pulls the holes i.e. the ionization potential will be applied in opposite direction but for one mission called charge separation. These two potentials sum up and lead to separation of the two charge carriers. However, if this summation of two potentials can't exceed the binding energy of the exciton there will be no charge separation. The most important thing worth mentioning here is there must be an interface between the two materials and the exciton must be at the interface for charge separation to happen.^[15]

However, in real situation the photon is absorbed in the whole part of the semiconductor which could be at the interface or at different distances from the interface. Hence, once exciton is created it has to move to the interface between the two materials where it will be separated in to charge carriers. But the excitons once created will stay for short period of time fractions of microseconds. They lose their energy that they received from photons and the electron goes to its ground state^[5]. This depends on the distance they travel before they reach the interface and varies from one material to another material. Every material has a minimum distance for an exciton to travel before it loses its energy. This minimum distance is called Diffusion Length. If the thickness of the material deposited is thicker, the excitons created far distance away from the interface will lose their energy if created at a distance beyond the diffusion length. This will harm the current generated severely.

3.3.2. Due to Fabrication

Rate of the deposition and Temperature of the substrate

Performance of a solar cell is obtained by complex relationships between the many physical, chemical and photonic properties of the different layers deposited specially the photoactive layer. Rate of deposition determines two properties: the morphology and



penetration of one of the material into the other layer. Morphology is one of the factors that allow easy charge transfer and increment of intimacy of contact between two layers. For example, when there are lots of picks on the surface of one of the materials it penetrates in to the other layer next to it. This increases intimacy of contact i.e. surface area of contact between the two materials. This will lead to higher probability of charge transfers between two layers and reduces probably the diffusion length to some extent. The height and number of picks that certain surfaces possess depends on the rate of deposition and the temperature of the substrates.

However, sometimes having high rate of deposition is a disadvantage for some reasons. Some of these are:

- At high rate, the picks of the surface roughhouses of one of the photoactive materials could be longer than the thickness of the other active layer and in contact with the electrode or electrode interfacial layer of the other side. This may lead to a loss as the charge carried can recombine.
- At higher rate small amount of one the photoactive materials will penetrate in to the bulk of another layer and trapped in the bulk. The charge carrier obtained in this trapped or islanded part can't have a contact with its electrode that it can't add to the current.
- If the material that penetrates in to the other part and in contact with the electrode or electrode interfacial layer is a metal the solar cell will short circuit.

Therefore, rate of deposition should be optimized. Temperature of the substrates has effect on the morphology of the surface of the layers.

Type of deposition of the photoactive layer

As discussed before, there are three types of depositions of the photoactive layer of the solar cells. They have their own advantages and disadvantages. The results obtained from experiments presented later.

Purity of the Materials

Purity of the materials used to make a solar cell is very important to the extent of 99.99%. Otherwise, study of certain material and optimizing for higher performance is fake idea. Impurities deteriorate the performance of a solar cell by affecting the mobility of charge carriers, band gap, absorption and other important parameters of the semiconductors. They also give some abnormal figures in the performance of the solar cell. Post fabrication pollution of the materials can be prevented through using clean spoons for material loading



and unloading in the heating boats and the material containers respectively. In addition opening the material containers only in the glove box and avoid to do it in the open air is very important. This is because; water vapour, oxygen and particles in the air are potential pollutants. ^{[35] [41]}

Cleaning of the Substrates

If any kind of dirt material fall on the surface of the substrates pre fabrication or on the cells post fabrication or during the intermediate processes, it alters the incident light intensity through either absorption or reflecting the light or transition of the light. This alters the performance of the cell directly or indirectly. Therefore, the cleaning of the substrate before fabrication and taking care during fabrication in avoiding impurities from falling on the substrate is very important. The pre fabrication cleaning as discussed in the previous chapter include ultrasonic bath in acetone and iso-propanol and treating by UV-light. ^{[35] [41]}



4. Characterization of Organic Solar Cells

Once the organic solar cells are fabricated we need to check the performance of the cell. The basic characteristics of the solar cell are the open circuit voltage, the short circuit current, the fill factor and the efficiency of the solar cell. To determine these characteristic parameters of the solar cell we need to carry out different kinds of measurements. Manipulation of the graphs or tables obtained from these measurements will enable to infer about the characteristics of the solar cell. The cells, after deposition will be put in measuring holder. Through this holder we can take them to the measuring instruments. Some of the measuring instruments that we used are the computer integrated solar simulator, the External Quantum Efficiency measuring instrument, Atomic force Measurement, absorption measuring device and Vim measuring instrument.



Figure 25: Solar Cells holding device for measuring the characteristics of the solar cells

These instruments are used to measure different kinds of parameters from substrates. The results obtained from the measurement is manipulated in either table or graph form and /or used to derive another parameters used to tell about the performance of the cell.

4.1. I-V Curve

The I-V curve is the most important characteristics curve of a solar cell through which the most important characteristics of the solar cell can be determined. A solar cell is a diode and has its own current-Voltage relationship. It is this relationship in the form of graph called I-V curve. The instrument called solar simulator integrated with computer (shown in the figure below) applies various biased voltages across the solar cell and measures the corresponding current. The curve generated plotting the current versus the voltage will give



as the I-V curve. There are two I-V curves that are generated: one is with illumination and the other one is in dark. The measurement in the dark gives zero current for almost all the biased voltage applied across the cell and the curve stays in the second quadrant. This is because; the solar cells are not illuminated meaning there is no photon that excite the electrons and generate electrons. If the cells are ok, the curve will look like the normal diode characteristics curve. The dark measurement will tell us if the cells are proper or not.

The measurement under illumination i.e. with the lump of the solar simulator on gives another characteristic curve with curve shifted down towards the fourth quadrant crossing both the positive x-axis and the negative y-axis to give two very important parameters: the x-intercept is the open circuit voltage and the y-intercept is the short circuit current. These two parameters of the curve their product gives the maximum power of the solar cell only fraction of which can be extracted. The fraction extracted is determined by the fill factor of the cell which depends on the resistances in the diode of the solar cell. Although the maximum output power can be traced by MPPT, it is the fill factor that determines the fraction extracted. One can see if the fill factor of the cell is high or low by looking at the shape of the I-V curve. If its shape is closer to right angle it will have high fill factor but if it is more of straight line between the x-axis and the y-axis, it has low fill factor.

There is a standard testing condition at which a solar cell should be characterised to compare all the performance of solar cells fabricated at different part of the world. The standard testing conditions for solar cells is at temperature of 25°C and 100mW/cm² of light intensity. The solar simulator can generate 100mW/cm² of light and it is called ONE SUN.

4.2. Quantum Efficiency (QE) Measurements

Quantum efficiency is the ratio of the number of charge carriers collected at the electrodes to that of the number of photons incident on the surface of the solar cell at a given wavelength. In other words, quantum efficiency is a parameter used to show the percentage of the photons converted to electric current. If all of the charge carriers are collected at a certain wave length the quantum efficiency is unity and but if no charge carriers are collected, the quantum efficiency is zero. If the band gap of the semiconductor is greater than the energy content of the photons at specific wavelength, there will be no charge carriers generated and the quantum efficiency will be zero. Sometimes, even when the band gap is less than the energy content of the photons for specific wavelength, the quantum efficiency can be lower than unity. This is because of the relative ineffectiveness all the processes that occur between photon absorption and charge collection. When a solar cell is illuminated part of the light will be reflected, part of it transmitted and the rest will be used in



the generation of charge carriers if the energy content of the photons at specific wavelength surpass the energy gap. ^[32]

There are two kinds of quantum efficiencies measurements in the laboratory: the internal and external quantum efficiency. The external quantum efficiency (EQE) is the quantum efficiency taken with inclusion of the effect of transmittance and reflectance of the solar cell. The quantum efficiency measurement carried out after the reflection and transmittance of the solar cell omitted is the internal quantum efficiency (IQE). The IQE only considers the photons that have the potential to be absorbed neither the reflected ones nor the transmitted ones. In this case less number of photons are considered so the IQE will be higher than the EQE.

The EQE curve is generated by measuring the EQE in percentage against the wave length. The shape of this curve depends on the Absorption of the solar cell along the spectra. It depends on the absorption of the two photoactive materials. The picks and valleys of the EQE curve the follows picks and valleys of the absorption curve of both photoactive materials in a complimentary manner as shown in the figure below.

The EQE is carried out by a standard EQE measurement instrument that emits light chopped from red to violet in the spectrum. This instrument is integrated with computer that measures the EQE in percentage for each wave length in the spectrum. The chopping of the light can be set in to the system. Most of the time, we have been chopping the light each 10nm.

Integration of the quantum efficiency throughout the whole range of the spectrum gives the short circuit current.

4.3. Variable Illumination Intensity Measurement (VIM)

Another important measurement worth carried out is the Variable intensity measurement. This measurement is about generating different I-V curves at different intensity of light as shown in the figures below. These curves will enable one to determine certain additional parameters of the solar cell: different resistances from slopes of curves; some typical voltage and current. Mathematics and the characteristic current-voltage relationship are the most important tools to determine these different parameters.

Varying the intensity of light and measuring the I-V curve give rise to various I-V curves that have varying open circuit voltage, short circuit current and fill factor. In general, it is found that short circuit current increases linearly with intensity of light while open circuit voltage increases logarithmically. The slop of the line for intensity of light against open circuit voltage indicates the type of recombination that take place in the solar cell. Fill factor



decreases with increasing intensity of light which is attributed to the high series resistance [19].

The other important use of carrying out Variable Illumination Intensity Measurement is to see the evolution of degradation of the solar cell with time. As described before, oxygen and water vapour are the most dangerous enemies of the active layer of the organic solar cell as they react with it and change its photochemistry. These two molecules can reach the photoactive layer of the solar cell either during fabrication when the oxygen level in the glove box increases or through the top cover of the holder after fabrication as it is not completely sealed. When deteriorated by these molecules some of the diode parameters of the solar cell change to give less performance of the cells. The deterioration of the solar cell can be revealed by increment of the series resistance of the diode; the decrease in the effective mobility-life ($\mu\tau$) time of the solar cell [20].

So to see the degradation of the solar cell with these two molecules we carried out numbers of series Variable Illumination Intensity Measurements on a single set of solar cells at 5hours time interval.

4.4. Absorption

Every material has its own property towards light when light is incident on the surface of the material. Part of the light will be reflected; part of it will be transmits through the material; and the rest will be absorbed. When we come to semiconductors, when a layer of a semiconductor is illuminated the light will experience all of them at the same time although the extent of each varies. The extent of these three mechanisms depends on the type of material and the thickness of material deposited.

The desire of photovoltaic energy generation is for most of the light is absorbed by the semiconductor and the photons are used to excite electron in the semiconductor for further charge separation and transport to generate power. Negligible reflection and transmittance of light is the ideal scenario. There are mechanisms like antireflection coatings and texturing of the surface that are used to reduce the reflection of light.

However, absorption of light by a material mainly depends on two basic properties of the material. The first one if the HOMO-LUMO energy level difference of a semiconductor. This energy difference decides the photons to be absorbed by the semiconductor as explained earlier. If the energy content of a photon is greater than this energy level difference of the semiconductor, the light will be absorbed otherwise it won't be absorbed. That is photons with shorter wavelength will be absorbed. This is depends on the chemical composition and chemical structure of the material. The second one is the thickness of the semiconductor deposited. Thicker layers absorb higher photons than thinner ones due to increment in the



probability of absorption of lower energy content photons. Shorter wavelength photons; as they have higher energy content are absorbed faster as soon as they reach the surface of the semiconductor. The longer wavelength photons will wait for their turn accordingly to be absorbed throughout the thickness of the layer. However, in the fabrication of solar cells we can't deposit longer thickness of semiconductors as there is trade-off between the diffusion length and absorption. Depositing beyond the diffusion length is a waste of material.

Absorption of a photoactive material is measured using a spectrophotometer that can be made to measure both absorption and transmittance independently.

5. Experimental

5.1. Effect of Thickness of Bulk-Junction layer on Performance of Small Organic Solar Cells made of DBP: C70 (1:1 rate ratio)

Thickness of the photoactive material is one of the factors that affect the performance. For bilayer photoactive solar cells it is important in relation to the diffusion length. Having their diffusion length low having higher thickness of these materials won't lead to higher performance as the excitons will be recombining before they reach the donor-accepter interface for charge separation. However, for the bulk-Junction photoactive solar cells this problem is avoided by co-evaporation of the two materials constituting the photoactive layer. As demonstrated in the previous section results, increasing the intimacy of contact that leads to shorter distance for excitons to diffuse and higher probability of charge separation.

Demonstration of the effect of the thickness of the photoactive layer of the solar cell on the performance of solar cell is important to optimize the thickness. It will be helpful to see whether increasing thickness indefinitely will lead to high performance or if there is a trade of among performance parameters.

To demonstrate we co-evaporated DBP and C70 with the following structure:

ITO/ MoO₃, 3nm/ DBP: C70 (1:1 rate ratio) 30-100nm/ BCP, 8nm/ Al, 75-150nm

Results and Discussions

The results for this comparison can be demonstrated by evolution of the different performance parameters of the solar cells with the thickness. This can be demonstrated by the J-V curve; the absorption curves and EQE curves of each solar cell. Another way is to



show the tendency of each performance parameters of the solar cells with thickness. Both methods are shown below.

I-V Curves of different thickness Bulk junction Photoactive layers

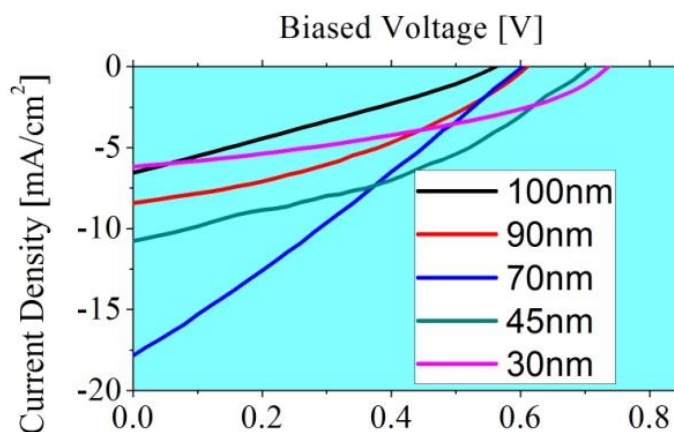


Figure 26: J-V curves of Bulk-Junction solar cells composed of different thicknesses of DBP: C70 (1:1 rate ratio) photoactive layer

The performance parameters of each solar cell are extracted from the results of the above J-V curves of each solar cell. [Figure-26](#) shows that short circuit current of solar cell with 70nm photoactive layer is very high compared to others while that of the 100nm and 30nm have the least. In case of open circuit voltage, solar cell with 30nm photoactive layer has the highest while solar cell with 100nm photoactive layer has the least. The other performance parameter that one can dare to say is the fill factor of the solar cell with 30nm photoactive layer is high as the shape of the curve is more towards right angle.

To see the tendency of each performance parameter with thickness of the photoactive layer it is important to have their curves against the thickness independently. This is shown below.



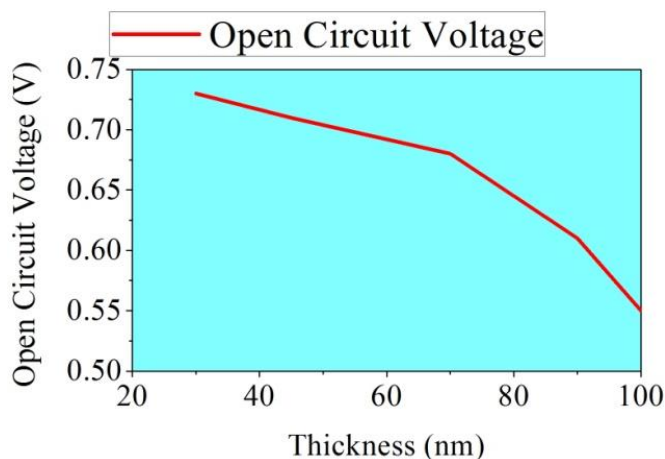


Figure 27: The tendency of Open Circuit Voltage with the thickness of the Photoactive layer of a solar cell composed of DBP: C70 (1:1 rate ratio)

Voltage across a solar cell is developed because of the difference in the energy levels of the donor and acceptor material (i.e. HOMO level of the donor which is related to its ionization energy and LUMO level of the acceptor which is related to its electron affinity) and the effective energy reductions at the electrodes. These two characteristics are constant as long as the same electrode materials and photoactive materials are used. The most important factor that affects the open circuit voltage of the solar cell in this case is therefore; the density of state of the materials that comprise the photoactive layer. The density of state of a materials; if higher; increases the open circuit voltage. With the thickness of the photoactive material increasing, the density of states of the materials is sure to increase. This will reduce the open circuit voltage of the solar cell. *Figure-27* reveals the same fact in that the open circuit voltage of the solar cells decreases with thickness of the bulk-junction photoactive layer.



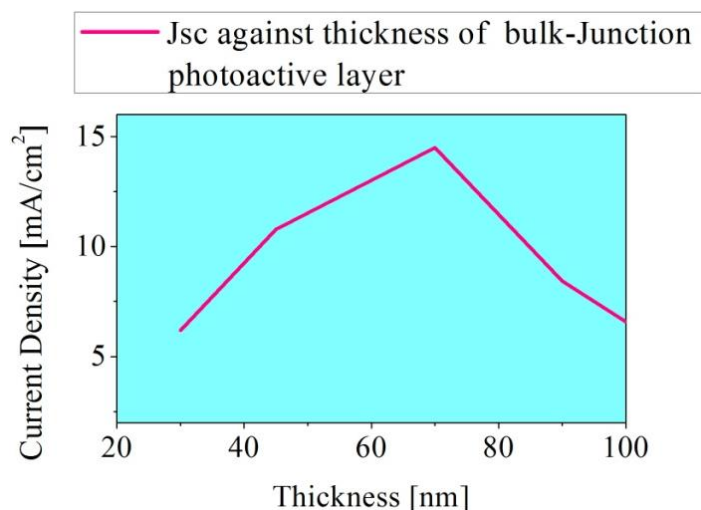


Figure 28: The tendency of Short Circuit Current with the thickness of the Photoactive layer of a solar cell composed of DBP: C70 (1:1 rate ratio)

Short circuit current has optimum value at around 70nm thickness of the photoactive layer of the bulk-junction solar cell having nearly 15mA/cm² Short circuit current density. Up to this 70nm, Short circuit current has been increasing; then it starts to decline with thickness of the bulk-junction photoactive layer. In general, there are two things associated to bulk-junction photoactive layer: one is increasing intimacy of contact between the donor and acceptor materials in the photoactive layer of the solar cell. This shortens the distance that an exciton to diffuse before it reaches the donor-accepter interface for charge separations. This means it increases the probability of charge separation ultimately leading to high quantum efficiency. The second one is isolation of part of one of the photoactive material by the other one. This prevents direct contact of one of the photoactive material with its corresponding cathode in which case separated charge carriers blocked from flowing into the outside circuit. This is a big loss that leads to recombination of the charge carriers.

Therefore from [Figure-28](#) one can easily see that up to a thickness of around 70nm thickness of the bulk-junction photoactive layer short circuit current increases with thickness. This shows that at lower thickness of the bulk-junction photoactive layer increment of intimacy of contact dominates recombination of the charge carriers. The recombination of the charge carriers starts to dominate the effect of the intimacy of contact between the donor and acceptor at thickness greater than 70nm.



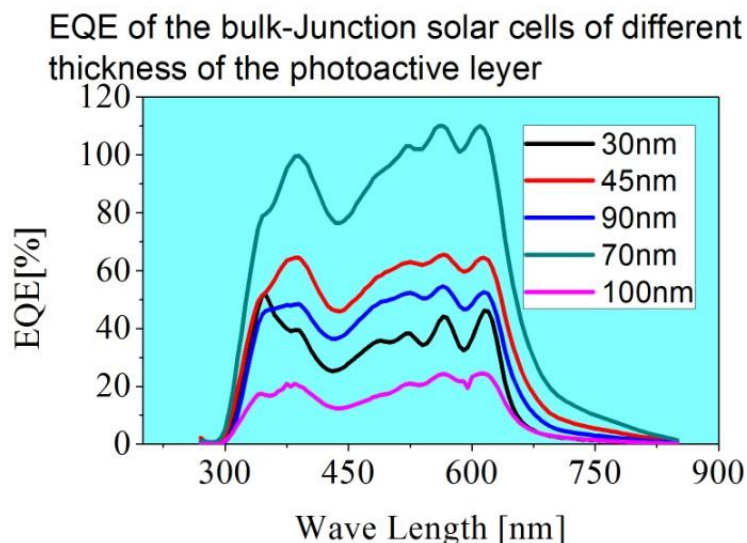


Figure 29: External Quantum Efficiency (EQE) curves of Bulk-Junction solar cells composed of different thicknesses of DBP: C70 (1:1 rate ratio) photoactive layer

The External Quantum Efficiency (EQE) is another way of showing the lowness or highness of short circuit current. [Figure-29](#) demonstrates the External Quantum Efficiency (EQE) of the solar cells composed of different thicknesses of the bulk-junction photoactive layer. The solar cell that has the highest area under its External Quantum Efficiency (EQE) curve has highest short circuit current. The solar cell that has the lowest area under its External Quantum Efficiency (EQE) curve has least short circuit current. The area under the green curve in [Figure-29](#) is relatively much higher than the other curves. This belongs to the solar cell with 70nm bulk-junction photoactive layer that has nearly 15mA/cm² short circuit current. The areas under the black and pink curves in [Figure-29](#) are relatively much lower than the other curves. They belong to the solar cell with 100nm and 30nm bulk-junction photoactive layer that have around 6mA/cm² short circuit current.



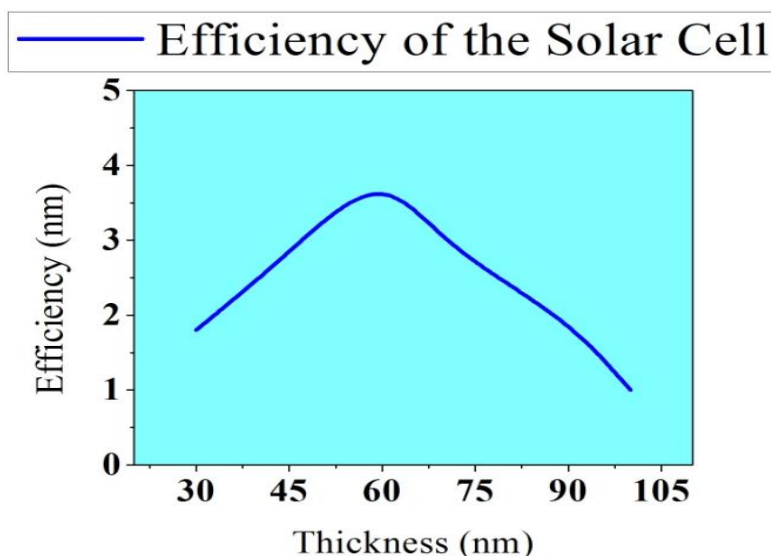


Figure 30: The tendency of Efficiency of the solar cells with the thickness of the Photoactive layer of solar cell composed of DBP: C70 (1:1 rate ratio)

The efficiency of a solar cell is the result of the combinations of the performance parameters like fill factor, short circuit current and the open circuit voltage. The tendency of the efficiency of the solar cells with the thickness of the bulk-junction photoactive layer is shown below in the [Figure-30](#) above. The tendency of the efficiency of the solar cell gives optimum value at a thickness of around 60nm. The figure also reveals that the efficiency curve shows similar declining tendencies away from the 60nm thickness in both directions.

5.2. Performance comparison of the Bi-layer and bulk-Junction (1:1 rate ratio) solar cells made of DBP: C70

As has been explained, the photoactive part of the solar cell can be modified in structure during fabrication so that the performance of the solar cell could be optimized. This can be done in two ways: one is Bi-layer and the other is bulk-junction. The bi-layer solar cell is the one in which the acceptor layer is deposited on top of the donor layer. Each semiconductor is deposited with in its diffusion length thickness to optimize the performance. The second one is bulk-junction where we evaporate the two materials at the same time to make co-evaporation. This can be done in various ways: the donor and acceptor can be co-evaporated at the same rate so that the proportion will be 1:1 or they could also be co-evaporated at different rate ratios. The first case could be optimized by varying the thickness deposited. For the second case for certain thickness the ratio of the two materials can be optimized.



To see the effect on some of the parameters like fill factor, Short circuit current and Open circuit voltage we did various fabrications with bi-layer and co-evaporated depositions.

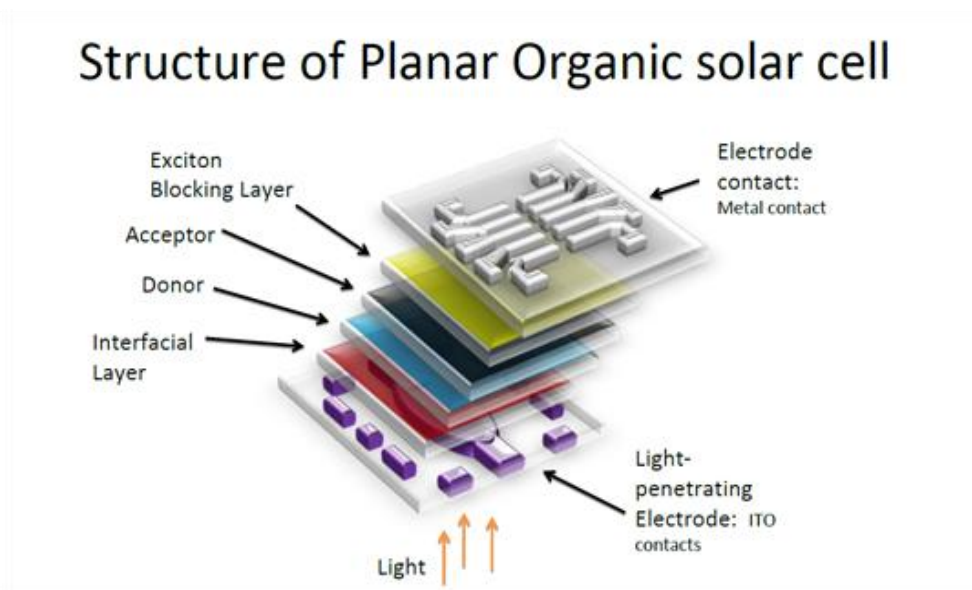


Figure 31: Structure of Bi-layer photoactive solar cell

The solar cells that we fabricated were their layers in the following sequences. The first layer deposited on top of the ITO is Molybdenum trioxide (MoO_3); the cathode interfacial layer. This is the layer also called the hole transport layer blocks electron and excitons from flowing towards the anode which is a loss. The thickness of this layer is optimized to be 3nm. The second layer on top of the Molybdenum trioxide (MoO_3) layer is the photoactive layer composed of the donor and acceptor. It could be a bi-layer or bulk-junction. If it is a bi-layer, the donor should be deposited on top of the Molybdenum trioxide (MoO_3) before the acceptor. This is because the donor should be towards the anode side and the acceptor should be on the cathode side. The next layer after the photoactive side is the cathode interfacial layer also called electron transport layer. It blocks holes and excitons and its thickness is optimized to be 8nm. The last layer is therefore the cathode layer which we use is Aluminum and the thickness ranges from 75nm to 150nm. The thickness of the electrode doesn't affect the performance if it covers the organic layer.

The two structures therefore are:

Bi-layer: ITO/ MoO_3 , 3nm/ DBP, 10-20nm/ C70, 30-40nm/ BCP, 8nm/Al, 75-150nm

Bulk-junction: ITO/ MoO_3 , 3nm/ DBP: C70 (1:1 rate ratio) 40-70/ BCP, 8nm/ Al, 75-150nm



The results for this case is demonstrated using the I-V curve of the solar cell where one can see the fill factor, the open circuit voltage and the short circuit voltage of the solar cell. External quantum efficiency measurement is also used to show the percentage of number charges collected at the electrodes per number of photons contained by the light incident on the surface. The integration of the area under the EQE curve throughout the whole energy content of the photons in the spectrum gives the short circuit current.

Results and Discussions

The structures of the solar cells used for this comparison are as follows:

Bi-layer: ITO/ MoO₃, 3nm/ DBP, 10/ C70, 40nm/ BCP, 8nm/Al, 75-150nm

Bulk-junction: ITO/ MoO₃, 3nm/ DBP: C70 (1:1 rate ratio) 50nm/ BCP, 8nm/ Al, 75-150nm

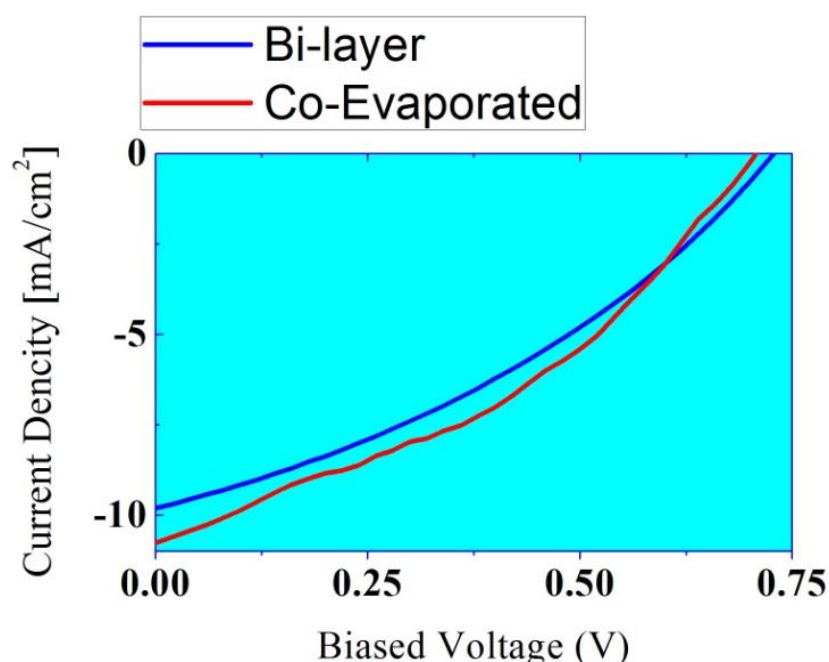


Figure 32: I-V Curves of the Bi-layered and Bulk-Junction solar cells having same thickness of 50nm

The above figure is the J-V curve generated from the results of the measurement of the Bi-layered and Bulk-Junction solar cell that have 50nm thickness the photoactive layer made of DBP and C70. One can easily see from the figure that the Bi-layer has superior fill factor and open circuit voltage over the bulk-junction photoactive layer. However, the Bulk-junction



solar cell has much higher short circuit current. The same result is summarised in the table below.

Table 2: Comparison of the parameters of the Bi-layer and Bulk-Junction Solar Cells having a thickness of 50nm of DBP and C70

Name of Parameter	Value	
	Bi-layer	Bulk-junction
Active layer structure		
Open circuit Voltage, Voc [V]	0.73	0.70
Short circuit Current Density, Jsc [mA/cm ²]	- 9.5	- 12.78
Fill Factor	36%	31%
Efficiency	2.51%	2.82%

The External Quantum Efficiency (EQE) of the two structures is also shown in the figure below. The External Quantum Efficiency (EQE) result is one way of showing the short circuit current as integration of the area under the curve throughout the wavelength leads to short circuit current. So it is easy to see from figure-33 that the area under the red curve is much bigger than that of blue curve.

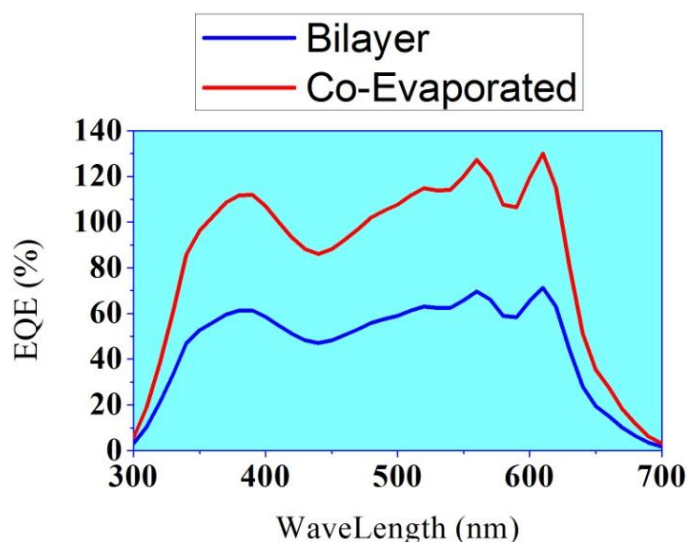


Figure 33: External Quantum Efficiency (EQE) Curves of the Bi-layered and Bulk-Junction solar cells having same thickness, 50nm



The short circuit current of the Bulk-Junction is higher because of the fact that the intimacy of contact between the donor and acceptor material is very high. The intimacy of contact between the donor and acceptor material in the bi-layer case is restricted only to the surface area of the solar cell marked by the interface between these materials. However, in the case of the Bulk-junction layers, the contact between the donor and acceptor is assured the total volume of the photoactive layer. This volume is composed of the surface area of the solar cell multiplied by the thickness of the photoactive layer. With high intimacy of contact the excitons are expected to diffuse shorter distance towards the donor-accepter interface. This increases the probability of charge separation of the exciton in to electrons and holes.

However, increasing the intimacy of contact between the donor and acceptor is not a guarantee to generate high current output to the outside circuit. This is because co-evaporation has a trade off between increasing the short circuit current and decreasing the fill factor. During co-evaporation for bulk-junction layer some materials could be islanded by the opposite counterpart. Once separated at the donor-accepter interface, charge carriers have to flow towards their corresponding electrodes. For this to happen the donor material must have contact with the anode and the acceptor material must be in contact with the cathode. If one of the materials is isolated and has no contact with its corresponding electrode, charge separation in the isolated material won't create current instead, the charge carriers recombine with in their life time. The accumulation of these charges at the donor-accepter interface develops resistance to the flow current. This effect is reflected by the decrease in the fill factor that can be seen the summarised table above.

Voltage across a solar cell is developed because of the difference in the energy levels of the donor and acceptor material (i.e. HOMO level of the donor which is related to its ionization energy and LUMO level of the acceptor which is related to its electron affinity) and the effective energy reductions at the electrodes. These two characteristics are constant as long as the same electrode materials and photoactive materials are used. The difference in open circuit voltage of the solar cells resides in the difference in the density of state of the Bi-Layer and Bulk-junction photoactive layers. The density of state of a materials; if higher; increases the open circuit voltage which is the reality fact for the bi-layer materials. Both the above summarised table and [Figure-30](#) reveal the same fact in that the Bi-layer solar cells have higher open circuit voltage.

5.3. Degradation of Small Organic solar Cell whose active layer is made of DBP: C70 (1:1 rate ratio)

As explained before the semiconductor materials are very sensitive to oxygen and water that they lose their properties if they are in contact with these molecules. The holder of the solar cells during measurement is not completely sealed that it allows some air to inter and



reach the photoactive layer of the solar cells. Hence, the solar cells have to be characterized as soon as possible after they are fabricated. The degradation of the solar cells can be determined by carrying out Variable Illumination Intensity Measurement (VIM). Through Variable Intensity Measurement one can know the different parameters like the resistances of the diodes i.e. the series and parallel resistances and resistances at the short circuit point and open circuit point. If the solar cells are left for some longer time they degrade with oxygen and water. So when Variable Intensity Measurement is carried out every some time gap, these parameters will vary and lead to lower performance of the solar cell. For example, if the series resistance increases, the open circuit voltage of the solar cell will be lower than the one that the solar cell had originally.

Results and Discussions

Reaction of the photoactive material of the solar cell alters their photo-chemical and physical properties. This on the other hand changes the performance of the solar cell through its performance parameters and other photochemical properties. The effect of this reaction on the performance parameters and the photochemical properties of the photoactive layer of the solar cell are illustrated in the figures below.

Figure-34 below indicates that all performance parameters of the solar cell decrease with time. The graph

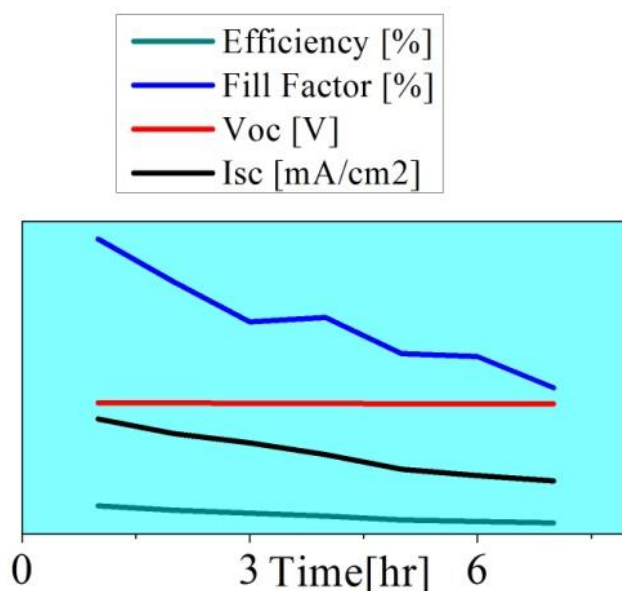


Figure 34: The tendencies of the performance parameters of the Small Molecule Organic solar cells with time due to degradation of the photoactive layer of the solar cell by



These parameters' tendency with time is summarised in the table below. The first row performance parameter values are the ones obtained during the measurement immediately after fabrication. Except the open circuit voltage values; which shows slow reduction in degradation time, all the other parameters show drastic decline in their value. The decline in the values of efficiency and short circuit current is higher compared to the other parameters. It indicates that degradation due to reaction of the photoactive layer with oxygen has more influence on the short circuit current than the open circuit voltage. The reduction in the efficiency of the solar cell due to degradation is much more influenced by the degradation in the short circuit current of the solar cells. This dominance of degradation of short circuit current on efficiency of the solar cell than the other parameters like open circuit voltage is indicative of which properties of the photoactive part are affected by degradation agents.

The open circuit voltage of a solar cell is due to combinations of the effects of

- The difference in HOMO energy level of the donor and the LUMO energy level of the acceptor. They are due to the ionization energy of the donor material and the electron affinity of the donor material. They mainly depend on the type of material used as doping material. Material doped with material having high ionization energy will tend to lose electron and become positively charged. Hence the material will be P-type or donor as it donates electron. Material doped with material having high electron affinity will tend to gain electron and become negatively charged. Hence the material will be N-type or acceptor as it receives electron.
- The effective energy reductions at the electrodes. This depends on the electrode materials mainly; in our case, is Aluminium.
- The Densities of state of the photoactive materials.

The fact that the open circuit voltage degrades very slowly with time indicates that reaction of oxygen and water with the photoactive materials affects very little of their HOMO-LUMO levels and density of states.

Thus the degradation agents mainly are in positions to deteriorate other photochemical properties of the photoactive material. These properties should reside in the diode of the solar cell.



Table 3: Summary of the evolution of performance parameters of the Small Molecule Organic solar cells with time due to degradation of the photoactive layer of the solar cell by oxygen and water vapour from air

Time [hr]	Jsc [mA/cm ²]	Voc [V]	FF [%]	η [%]
0	6.19	0.75	39.0	1.76
1	2.57857	0.75656	32.54889	0.63498
2	2.25121	0.75553	31.58145	0.53716
3	2.04507	0.74364	30.68457	0.46665
4	1.77854	0.73723	30.7845	0.40364
5	1.4471	0.73142	29.97722	0.31729
6	1.30919	0.72582	29.91601	0.28427
7	1.18547	0.72907	29.2127	0.25248

The main photochemical and electrical properties of the solar cell that reside in the diode are the resistances of the diode and the effective mobility-lifetime of the charge carriers. These three parameters are factors for the current output to the outside circuit. The mobility-lifetime of the solar cell is most important factor that determines how the free charge carriers are handled in the chemical structures of the photoactive materials. If the bonds associated with these free charge carriers are very strong the mobility is very restricted. Even if they are allowed to be mobile it will be for short periods of time. This affects the current output of the solar cell to the outside circuit severely. The other parameters that affect the current output are the series and parallel or shunt resistance of the diode of the solar cell. Ideally the series resistance is very small and the parallel resistance is very high so that more current flows to the external circuit. If there is any mechanism that alters and increases the series resistance will reduce the current output.



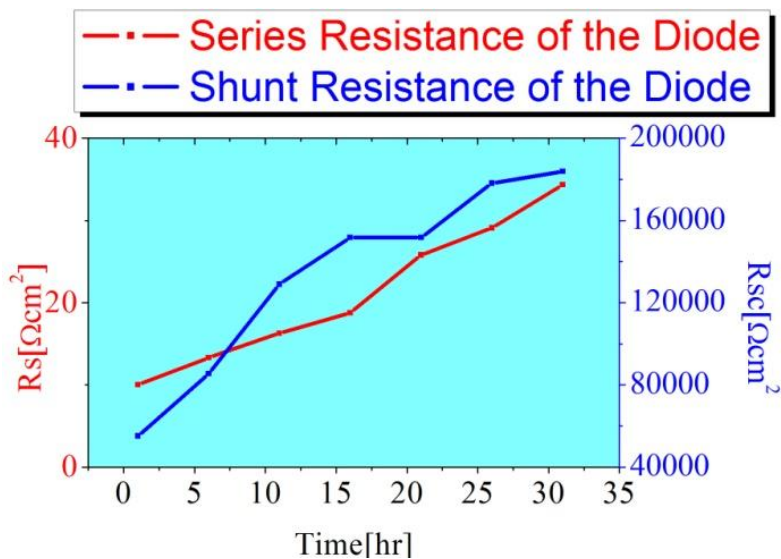


Figure 35: The tendencies of the series and parallel or shunt resistances of the diode of the Small Molecule Organic solar cells with time due to degradation of the photoactive layer of the solar cell by oxygen and water vapour from air

The above figure shows that both the series and parallel resistances of the diode increase with time. The increment of the parallel or shunt resistance is not that bad as it restricts the flow of current back to the inside circuit of the diode while favouring the flow of current to the external circuit. However, small increment of the series resistance is more pronounced than that of the shunt resistance that leads to loss current.

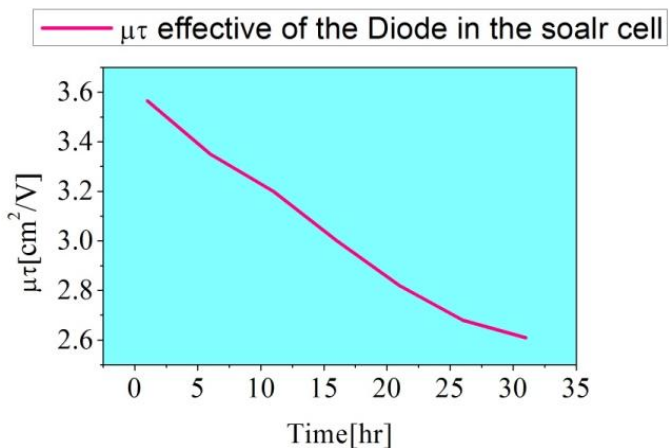


Figure 36: The tendencies of the effective mobility-life time ($\mu\tau_{\text{eff}}$) of the Small Molecule Organic solar cells with time due to degradation of the photoactive layer of the solar cell by oxygen and water vapour from air



The above [figure-36](#) shows continuous decline of the mobility and life time of the charge carriers with time. The mobility-lifetime of the solar cell is most important factor that determines how the free charge carriers are handled in the chemical structures of the photoactive materials. If the bonds associated with these free charge carriers are very strong the mobility is very restricted. Even if they are allowed to be mobile it will be for short periods of time. This affects the current output of the solar cell to the outside circuit severely. Thus degradation agents severely damage the mobility and lifetime of the charge carriers by reacting with the photoactive layer of the organic solar cells.



6. Conclusions

The reduction in open circuit voltage of Bulk-junction photoactive layer solar cells resides in variation of the density of state of the material with its thickness. At lower thickness of the bulk-junction photoactive layer increment of intimacy of contact dominates recombination of the charge carriers. The recombination of the charge carriers starts to dominate the effect of the intimacy of contact between the donor and acceptor at thickness greater than 70nm.

Comparing the performance parameters of Bi-layered and bulk junction photoactive layers of the thickness indicate that Bi-Layers have better fill factor and open circuit voltages than their bulk-junction counter parts. However, the bulk-junction solar cells have high short circuit voltage. This is basic indicative that combining both types of structures in one solar cell can help increasing the performance of the solar cells. That is; sandwiching the bulk-junction layer between the pure layers of the photoactive layers. Increasing the intimacy of contact between the donor and acceptor is not a guarantee to generate high current output to the outside circuit. This is because co-evaporation has a trade off between increasing the short circuit current and decreasing the fill factor. The difference in open circuit voltage of the solar cells resides in the difference in the density of state of the Bi-Layer and Bulk-junction photoactive layers.

Oxygen and water vapour from air are the most dangerous agents that lead to the degradation of the performance of the solar cell. Thus measuring as soon as possible after fabrication is important to obtain the real performance of the solar cell. This is because oxygen and water leak in to the holder to reach the solar cells. The degradations were very severe as demonstrated by the figures in five hours that it is an indicative of a very effective encapsulation is important. Otherwise life time of the solar panels would be very small. If the degradation of the photoactive layer is this fast, service life of the solar panels for years is unthinkable.



7. Recommendations

The fabrication of efficient solar cells requires the integration between photo-chemists, photovoltaic engineer, organic material synthesis experts and solar cell fabrication experts. These people should discuss, share ideas, work together so that the benefits, disadvantages and trade-offs between parameters of the organic solar cell would be optimized. Hence, Centre for Research in Nano-Engineering, CRNE-UPC should find ways to integrate these intellectuals together for the better benefit of the institution.



8. Future works

8.1. Laboratory Works

The trend of the performance parameters of a solar cell made of DBP: C70 bulk junction with time was demonstrated. However, the rate ratio of the two materials during co-evaporation was 1:1. However this is not enough as varying the rate ratio may lead to high performance. The figure below shows the size comparison of one DBP structure with fullerene. It indicates that one DBP structure is bigger than two fullerene structures. This may be indicative to try 1:2, 1:3 ... rate ratios.

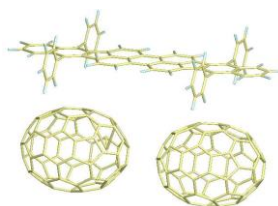


Figure 37: size comparison of one DBP and two C70 molecules

The P-I-N structure is the one that shares the advantages of bi-layer and bulk-junction photoactive layers. Optimization of the thicknesses of the different layers of the photoactive part is important.

8.2. Business opportunities

It is obvious now that, the increased need for more energy each year in the countries of the world and the problem associated with increased price of the natural oil; gas and coal have brought call for alternative and sustainable energy sources. The hydropower, wind power, solar thermal power, Biofuels and photovoltaic system power are the most important ones with hydro being the one exploited better both in terms of time and relative capacity. The geothermal and tidal energy are on their infant stage of utilization. The world has to use these renewable energy sources as much as possible to sustainably and in environmentally friendly way. Lots of researches are taking place to get the most out of these renewable energy recourses.

Among these renewable resources solar power released by the sun towards the earth is the most abundant one. As explained well before, the power that comes every hour to the earth on average could cover the total yearly energy requirement of the world. This is huge potential. Capturing even a very small fraction of this natural power is remarkable input to the world energy requirement. Scientists are trying their best and improving effective



mechanisms to extract this solar power. One of the mechanisms is the solar thermal method; in which the heat energy contained by the sun is transferred between thermal fluids in heat receivers and heat exchangers to finally get it pressurized so as to drive a turbine to generate electricity; or to use the hot fluid; if it is water; for some domestic applications. The second one is to capture the solar power and directly convert it in to electricity using the advantage of photovoltaic effect. Both of them have their own optimization constraints.

The silicon based solar cells are in their infant stage to the grid parity because the cost of the whole photovoltaic system and the production cost of the silicon solar cells to panels. They are to grid parity in some countries as mentioned before. The organic solar cells are the promising photovoltaic systems in the near future. The main problems with organic photovoltaic cells are their low efficiency and degradation on air. Both of these are under scrutiny research and improvement. Cost analysis shows that with about half efficiency as that of the silicon solar cell, the organic solar cells can be economical than the inorganic ones. In Germany a solar cell of 12 percent efficiency is patented with undisclosed photoactive material. Encapsulation mechanisms are under study to deal with the degradation problem. ^{[11][12]}

Despite these two problems organic solar cells have much better advantages compared to the inorganic ones. Organic solar cells can be coloured or transparent as they can be fabricated from wide variety of organic semiconductors. Every organic semiconductor has its own colour and they are many in numbers. Organic semiconductors due to their elastic property give rise to flexible layers which can be deposited on various shaped substrate where the flat type silicon solar cells are unable to be applied. Organic semiconductors have also low density that they are very light. Even if they density is high them thickness of material deposited as a layer in hundreds of micrometers which avoids high material cost, waste and unnecessary weight. The other important property is that organic semiconductors can capture light and generate electricity even in cloudy days. All this properties force one to think if solar cells can be used elsewhere the silicon solar cells haven't been used conventionally. There are areas where systems don't need high efficiency but invite one of the above properties with open arms.

- The fact that they can be colour and/or transparent means they can be used in areas where certain colour is important. These days colour is playing important role in inspiring children for success in their future, psychological treatment of patients and motivating sport athletes. In addition to that some medical systems and sporting parties are in desire of knowing the well being of their patients or athletes during the games or certain conditions where they can't be near them. Therefore the colourfulness and energy generating property can be used. This will enable us to build house or buildings their wall or windows on which organic solar cell is



integrated. The clothing of people, athletes can be deposited with organic solar cells to generate power for self phones and other small important electronic appliances.

- The flexibility of the organic solar cells is another very important input for the above applications. For example, clothing is not rigid.
- Being light organic solar cells can be welcomed almost everywhere low weight is required. Obviously almost everything used by human being is needed to be light weighted. Especially in areas where there is some kind of mobility and low stress is desired this organic solar cells are ideal.
- Organic solar cells have also a capacity to generate power even at low intensity of light. In this case a calculator other small appliances can be powered by organic solar cell at intensity as low as the room. ^[32]
- The economic aspect of organic solar cells is supported by the fact that small amount of material is required for fabrication. This reduces the material cost although organic compounds in general are cheaper than inorganic compounds. The second one is the production cost. Organic solar cells harvest the energy used for their production in a few weeks of operation- faster than any other solar technology.

All these may lead to a new set of application dimension for organic solar cells in addition to their conventional power generation. It is time to think of putting solar cells at home and big buildings in the roof, windows, wall etc ...; in the cars and other vehicles we drive; on the cloths we put on; in agricultural areas; for health centres and sports. They could be big reliefs for military applications where there is no power. This may lead to an era of smart appliances like that of smart phones. The total electric power demand by a certain system can be reduced by making some of the appliances used by the system be self sufficient so that they don't require plugging to the mains either at all or at least not so frequently. Organic solar cells will create unprecedented opportunities thanks to their unique properties. A new breakthrough in solar technology means portable electronic devices such as e-book readers could soon be re-charged on the move in low light levels and partial shading. It is possible to create an organic solar cell that generates a sufficiently high voltage to recharge a lithium-ion battery directly, without the need to connect multiple individual cells in series.

The compatibility of OPVs with a wide range of substrates, including plastics and metals, means that new power applications can be addressed which are not easily met by existing first and second generation PV technologies. OPVs will therefore accelerate market penetration of PV technology as well as enabling new manufacturing and business opportunities.



Acknowledgements

I want to say thank you to KIC-InnoEnergy, Instituto Superior Tecnico (IST), Universitat Polytechnica de Catalunya (UPC) and Centre for Research in Nano-Engineering, CRNE-UPC for giving me the chance to learn renewable energy and for feeding me with knowledge and skills. I also want to thank the staff members of these institutions who organize and facilitate the KIC-InnoEnergy programs timely and patiently.

My special thank goes to Ass. Prof. Enrique Velo; the co-ordinator of the KIC-InnoEnergy program, for his timely important arrangements and his patience.

Professor José Santos-Victor; the KIC-InnoEnergy program at IST, who helped and took care of the first panicking year of our first year at IST.

Graca Pereira, the most helpful person in my first year starting from applying visa for Portugal in my country to the end of the year. I want to thank her a lot she was in every step of our progress and problem solving in situations where things look panicking.

Prof.. Ramon Alcubilla; responsible for clean room and director of the Centre for Nano-engineering the UPC CRnE, who guided me to visit the clean room and CRnE to inspire me for this research.

The very friendly supervisor of my thesis who allowed me to work with him for my thesis internship is Joaquim Puigdollers Gonzalez; I thank you very much Professor.

The organic Group in box-8 of Centre for Research in Nano-Engineering, CRNE –UPC comprising lovely, friendly, eager to help, free to discuss and share ideas with and clever persons like Sergi Galindo Lorente, Mehrad Ahmadpour, Guillermo Gerling, Sitty Winny Maulidiani adya; the diversified group, was fantastic. Thank you very much for being part of the group and make me feel like family.



References

Papers

- [1] EFFECT OF ITO SURFACE TREATMENT ON ORGANIC SOLAR CELLS, Jiyoun Seol, Matthew L. Monroe, Timothy J. Anderson², Md. Azizul Hasnain¹, and Chinho Park,
- [2] Conjugated Polymer-Based Organic Solar Cells, Serap Guñnes,* Helmut Neugebauer, and Niyazi Serdar Sariciftci, 2007.
- [3] Effect of synthetic accessibility on the commercial viability of organic photovoltaics; Timothy P. Osedach, Trisha L. Andrew and Vladimir Bulovi; Energy & Environmental Science; 2013
- [4] Anode Interfacial Tuning via Electron-Blocking/Hole-Transport Layers and Indium Tin Oxide Surface Treatment in Bulk-Heterojunction Organic Photovoltaic Cells; Alexander W. Hains, Jun Liu, Alex B. F. Martinson, Michael Irwin, Tobin J. Marks; 28 DEC 2009
- [5] Effect of thickness on the absorption spectra of GaPcCl, SnPcO and AlPcOH thin films; SUSAN MATHEW, C. S. MENON, C. SUDARSANAKUMAR; School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam; 2008
- [6] Transparent and near-infrared organic photovoltaic solar cells for window and energy-scavenging applications; Richard R. Lunt and Vladimir Bulovic; 2011
- [7] A hybrid planar-mixed tetraphenyldibenzoperiflanthene/C70 photovoltaic Cell; Xin Xiao, Jeremy D. Zimmerman, Brian E. Lassiter, Kevin J. Bergemann, and Stephen R. Forrest; 2012.
- [8] Dual roles of MoO₃-doped pentacene thin films as hole-extraction and multicharge-separation functions in pentacene/C60 heterojunction organic solar cells; Yan-Hui Lou, Mei-Feng Xu, Zhao-Kui Wang, Shigeki Naka, Hiroyuki Okada et al.; 2013
- [9] Business, market and intellectual property analysis of polymer solar cells Torben D.Nielsen, Craig Cruickshank, Søren Foged, Jesper Thorsen, Frederik C.Krebs; Solar Energy Materials & Solar Cells; 2010
- [10] Effect of synthetic accessibility on the commercial viability of organic photovoltaics; Timothy P. Osedach, Trisha L. Andrew and Vladimir Bulovi; Energy & Environmental Science; 2013



- [11] Conjugated Polymer-Based Organic Solar Cells; Serap Guñnes, Helmut Neugebauer, and Niyazi Serdar Sariciftci; Linz Institute of Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University of Linz, Austria; 2006
- [12] Efficiency of Bulk-Hetero-junction Organic Solar Cells; M.C. Scharber N.S. Sariciftci; Austria; 2013
- [13] Strategies for Increasing the Efficiency of Hetero-junction Organic Solar Cells: Material Selection and Device Architecture; PAUL HEREMANS, DAVID CHEYNS, AND BARRY P. RAND Leuven, Belgium; 2009
- [14] Highly efficient organic p-i-n photovoltaic cells based on tetraphenyldibenzoperiflanthene and fullerene C70; Zhongqiang Wang, Daisuke Yokoyama, Xiao-Feng Wang, Ziruo Hong, Yang Yang, and Junji Kido; Energy & Environmental Science; 2013; doi:10.1039/C2EE22952H
- [15] Organic solar cells: An overview focusing on active layer morphology; Travis L. Benanti and D. Venkataraman; 2006.
- [16] Multijunction organic photovoltaics with a broad spectral response; Jill A. Macko, Richard R. Lunt, Timothy P. Osedach, Patrick R. Brown, Miles C. Barr, Karen K. Gleason and Vladimir Bulovic; 2012
- [17] Charge carrier losses of organic solar cells based on Subphthalocyanine/C60 heterojunction; Yue Zang, Junsheng Yuo, Jiang Huang, Yadong Jiang; China; 2010
- [18] Kinetics of light induced defect creation in organic solar cells; R. A. Street and D. M. Davies; Palo Alto Research Center, Palo Alto, California, USA; 2013
- [19] Modelling the low-voltage regime of organic diodes: Origin of the ideality factor; Chang Hyun Kim, Omid Yaghmazadeh, Yvan Bonnassieux, and Gilles Horowitz; Journal of Applied Physics; 2011
- [20] Origin of the dark-current ideality factor in polymer: fullerene bulk hetero-junction solar cells; G. A. H. Wetzelaer, M. Kuik, M. Lenes, and P. W. M. Blom; APPLIED PHYSICS LETTERS; 2011
- [21] The role of the buffer layer in the light of a new equivalent circuit for amorphous silicon solar cells; J. Merten, C. Voz, A. Munoz, J.M. Asensi, J. Andreu; Universitat de Barcelona, Barcelona, Spain; 1999
- [22] Analysis of the dynamic short-circuit resistance in organic bulk-heterojunction solar cells: relation to the charge carrier collection efficiency; C. Voz, J. Puigdollers1, J.M. Asensi, S. Galindo, S. Cheylan, R. Pacios, P. Ortega, R. Alcubilla;
- [23] Charge carrier losses of organic solar cells based on Subphthalocyanine/C60 heterojunction; Yue Zang, Junsheng Yu, Jiang Huang, Yadong Jiang; University of Electronic Science and Technology of China (UESTC); China;
- [24] Charge carrier mobility and lifetime of organic bulk hetero-junctions analyzed by impedance spectroscopy; Germà Garcia-Belmonte, Antoni Munar, Eva M. Barea, Juan Bisquert, Irati Ugarte, Roberto Pacios; Organic Electronics 9 (2008) 847–851, Spain



Thesis

- [25] New Material Concepts for Organic Solar Cells; Jan Meiÿ; Dresden; 2010
- [26] DEVICE PHYSICS AND ARCHITECTURES OF ORGANIC BILAYER PHOTOVOLTAIC CELLS; David CHEYNS; 2008
- [27] Studies on Organic Solar Cells Composed of Fullerenes and Zinc-Phthalocyanines; Steffen Pfützner; Dresden; 2011
- [28] Organic solar cells: Correlation between molecular structure, morphology and device performance; Ingmar Bruder; Max-Planck-Institut für Festkörperforschung; 2010
- [29] Studies on Organic Solar Cells Composed of Fullerenes and Zinc-Phthalocyanines; Steffen Pfützner; Dresden; 2011.
- [30] Fullerene based Organic Solar Cells; Lăcrămioara Mihaela Popescu; 2008
- [31] Novel dopants for n-type doping of electron transport materials: cationic dyes and their bases; Dipl.-Chem. Fenghong Li; January 2005
- [32] [34]. Numerical simulation and optimisation of organic light emitting diodes and photovoltaic cells; Fryderyk Kozłowski; Dresden; 2005
- [33] [35]. THIN FILM SOLAR CELLS GROWN BY ORGANIC VAPOR PHASE DEPOSITION; FAN YANG; 2008
- [34] [36]. Organic Solar Cells Performances Improvement Induced by Interface Buffer Layers; J. C. Bernède, A. Godoy, L. Cattin¹, F. R. Diaz, M. Morsli¹ and M. A. del Valle; France

Reports

- [35] Review of Organic solar cells: An overview focusing on active layer morphology; Travis L. Benanti & D. Venkataraman; Department of Chemistry, University of Massachusetts; 2005.
- [36] European consortium highlights competitiveness of Solar Photovoltaics (PV) in 11 EU countries; PV Parity report on 26 November 2010.
- [37] European consortium highlights competitiveness of Solar Photovoltaics (PV) in 11 EU countries, PV Parity report on 26 November 2012.
- [38] Effect of post production Treatment on plastic solar cells; Franz Padinger, Roman S. Ritbberger, and Niazi S. Sariciftci; January 2003.



- [39] [41]. PHYSICS AND ENGINEERING OF ORGANIC SOLAR CELLS; William J. Potscavage, Jr.; Georgia Institute of Technology; May, 2011
- [40] Fabrication and characterization of small molecule organic solar cells; Sergi Galindo Lorente; 2013

Supplementary

- [41] High Photoelectric Conversion Efficiency of Metal Phthalo-cyanine/Fullerene Hetero-junction Photovoltaic Device; Chi-Feng Lin, Mi Zhang, Shun-Wei Liu, Tien-Lung Chiu, and Jiun-Haw Lee; International Journal of Molecular Sciences; 201; ISSN 1422-0067
- [42] Effect of Synthetic Accessibility on the Commercial Viability of Organic Photovoltaics; Timothy P. Osedacha, Trisha L. Andrewb, Vladimir Bulovi c; 2013
- [43] Organic solar cells: An overview; Harald Hoppe and Niyazi Serdar Sariciftci; Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University; Linz, Austri; 2004
- [44] Organic Solar Cells Performances Improvement Induced by Interface Buffer Layers; J. C. Bern de, A. Godoy, L. Cattin, F. R. Diaz, M. Morsli and M. A. Del Valle;
- [45] Analysis of the dynamic short-circuit resistance in organic bulk-heterojunction solar cells: relation to the charge carrier collection efficiency C. Voz, J. Puigdollers, J.M. Asensi, S. Galindo¹, S. Cheylan, R. Pacios, P. Ortega, R. Alcobilla;
- [46] High Photoelectric Conversion Efficiency of Metal Phthalo-cyanine/Fullerene Hetero-junction Photovoltaic Device; Chi-Feng Lin, Mi Zhang, Shun-Wei Liu, Tien-Lung Chiu, and Jiun-Haw Lee; International Journal of Molecular Sciences; 2011
- [47] AMORPHOUS SILICON SOLAR CELLS OBTAINED BY HOT-WIRE CHEMICAL VAPOUR DEPOSITION; David Soler i Vilamitjana; Barcelona; 2004
- [48] Ideal diode equation for organic hetero-junctions (Derivation and application); N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski, and S. R. Forrest; 2010

