

**PHOTOVOLTAIC PROPERTIES OF
BULK-HETEROJUNCTION SOLAR CELL BY
ENHANCING ABSORPTION BAND IN
POLYFULORENE COPOLYMER BLEND.**

By

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**This Work is Dedicated to
Aschalew Ashagre**

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Let us all be blessed. Amen!

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Abstract

In this thesis, the photovoltaic properties of the blended polymer of APFO-G6 have been investigated based on enhancing its absorbance. The structure of the blended polymer was ITO/PEDOT:PSS/D75:APFO-G6:PCBM/Al. The electrical properties were studied using Current Voltage (J-V) characteristics and Impedance spectroscopy (IS) measurement. The optical absorption spectrum was measured using UV/VIS/NIR Spectrometer. The J-V plot shows the structure has photovoltaic properties. The absorption spectrum shows the structure absorbed as needed in the extended visible region of the spectrum. Fill factor and the efficiency was improved due to increment of absorbance. And according to impedance Spectroscopy measurement, the Cole-Cole plot shows the depletion resistance and capacitance depend on the bias voltage.

Chapter 1

Introduction

Natural gas, coal and oil are considered as the main sources of energy for long period in the history of human kind. However because of their limited supply on the planet earth including their impact on environment, we are forced to look for a renewable energy sources such as solar , biomass, wind , Geo-thermal energy and hydropower [1]. They are alternative energy sources for the above conventional energy sources. The main advantages of these energy sources are free of air pollution, sustainability and they are found in abundance.

Solar cell, commonly called photovoltaic, at present is the most important long-durable power supply for satellites and space vehicles, and also as a power supply to electronic equipment such as calculators. It is a pn junction device that converts the light energy from the sun to electrical energy.

A solar cell is to be exposed to polychromatic solar light rather than monochromatic. The sun is treated as a blackbody radiator and has $1.5\text{W}/\text{m}^2$ Air Mass standard. The total amount of irradiated power in the wavelength 300 to 800 nm is $632\text{W}/\text{m}^2$. With our AM 1.5 approximation, and taking a more extended range 300 to 2500 nm , the irradiated power would be $1131\text{ W}/\text{m}^2$.

The solar cell was first developed by Chapin, Fuller, and Pearson in 1954 using a diffused silicon p-n junction. Subsequently, the cadmium sulfide solar cell

was developed by Raynold et al. Nowadays, solar cells have been made in many other semiconducting metals using various device configurations and employing single crystal, and amorphous thin-film structure.

After the discovery of the conductivity of conjugated polymer, Polyacetylene, from insulating through semiconducting to metallic regimes, the researchers shift from inorganic semiconductor to organic semiconductors. Organic semiconductor materials are now in a great research because of their semiconducting properties, diversity, ease of fabrication and potentially low cost in supplying and in fabricating.

Polymers are long chain macromolecules, made of repeating monomeric units, with a large molecular weight $> 10,000$. Polymers (conjugated and non conjugated) are traditionally known for electrically insulating properties. Since the first report of doping the polyacetylene in 1977 ShiroKawa et. al., conjugated polymers (polymers with alternating single and double carbon-carbon bonds) have been studied as electronic materials. They are active materials for thin film transistors (TFT), light emitting devices (LED), photo diodes (PD), photovoltaic (PV), and integrated circuit (IC). In their conducting states, they were used as electrodes [3].

The objective of this experimental research is to study the electrical and photovoltaic characteristics of the blended polymer/fullerene bulk heterojunction solar cells in the form of ITO/PEDOT:PSS/D75:APFO-G6:PCBM/Al sandwiched structures. Where ITO and Al used as electrodes; And to observe photogenerated current and the performance of the device. The I-V characteristic were measured in the dark and under illumination. Using the complex impedance spectroscopy, the complex impedance were also measured. Then the J-V and the cole-cole plot, for impedance were plotted and analyzed.

Chapter 2

Conjugated polymers

2.1 Doped/Undoped Conjugated Polymer

Polymers are long chain macromolecules , made of repeating monomeric units, which have large molecular weight.

The conjugated polymers consist of alternate single and double carbon-carbon bonds [3]. Ideally, these should be infinite, perfectly ordered, linear systems regularly built from repeat units containing π electrons, in such a way that there is no interruption of the conjugation; The π -electron system is extended infinitely along the system. All conjugated polymers (CPs) are semiconductors with wide forbidden gaps, generally , the band gap is of the order of 2eV or more. They become conductors by injection of electron or holes on to the chains, with simultaneous intercalation of compensating ions between the chains. This is the so called doping process.

Undoped polymers are insulators, and have a filled valence band and an empty conduction band separated by a forbidden energy gap. Doping of polymers creates allowed states in the bandgaps through which the charge carriers transit.

Doping is, in principle, reversible and its level can be adjusted continually between 0 and a maximum corresponding to one counter ion for two to a few polymer repeat unit, although there is evidence in some cases of the occurrence of stages, as

in intercalated graphite. This produces a continuous variation of the conductivity between the very small value characteristic of an insulator and 1 to 10^3 S/cm, depending on the material. In the case of I_2 -doped polyacetylene, a value of 10^5 S/cm has been obtained. Usually, the counter ions do not contribute to the (electronic) conduction. More details about doping is given in the next section.

Disorder is a central issue for CPs. Real materials are almost always highly disordered. Accurate description of the structures at all scales and understanding of their influence on the electronic properties have not been achieved.

Many applications have been proposed in the past decade or so. Few require high conductivity; rather, they use semiconducting or modestly doped materials [5].

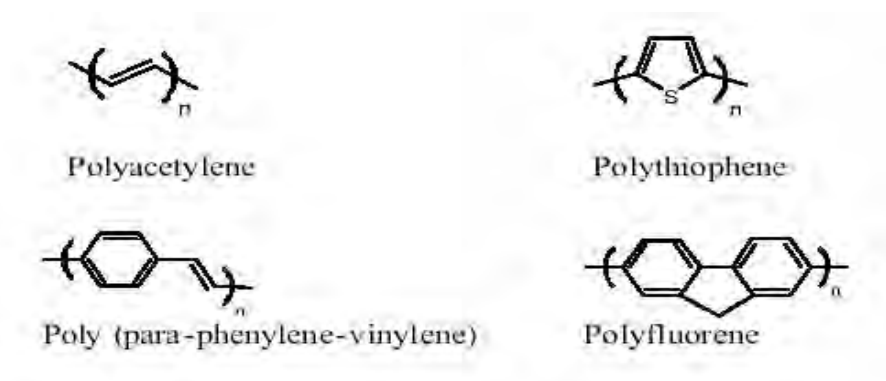


Figure 2.1: Chemical Structure of examples of conjugated polymers

2.2 Quasi-particles/ Excitations /

The alternating CH chain below has a degenerate ground state. But not all CPs have degenerate ground state except for trans-PA, permigranline, and polyheptadiyne(PHT). The actual trans-PA chain has a linear zigzag.

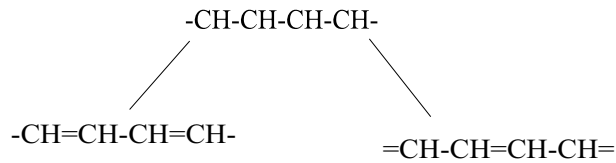


Figure 2.2: Two equivalent ways of introducing bond alternation in a trans-PA chain.

As atoms, ions and molecules are the binding elements of a crystal in the sense of structure, the same is true for CP that it is a building of elementary excitations. some of them are solitons, polarons and bipolarons. The concept of these excitations, i.e quasi-particles are summarized in this section [16].

1. Solitons

In a degenerate ground chain, excitations corresponding to bond alternating defects can exist. This is a domain wall separating two isoenergetic regions with an "opposite" sense of bond alternations. In chemical language, uncharged (i.e undoped) chain is occupied by a single electron that we can think as given by the 2P_z orbital of the C-atom without a double bond on Fig 2.2. This excitation of the chain is a $\text{spin}=\frac{1}{2}$ and charge = 0 state: In other words, a free radical. But its position along the chain is arbitrary; it is a mobile "intrinsic" defect. Because it can move along the chain without distortion, it has become known in the CP literature as a soliton.

The non bonding orbital corresponds to a soliton level at the middle of the forbidden gap. It may contain $n=0$, 1, or 2 electrons; addition or removal of an electron to the neutral $n=1$ state corresponds to a $\pm e$ charged soliton, which now has spin zero.

If electron correlations are neglected, all the levels are isoenergetic and the charged solitons are mobile. Doping is adding an electron or a hole on a CP chain, so if a neutral soliton is present, the added charge will naturally be accommodated on the corresponding midgap state. Pairs of oppositely charged solitons may also be created.



Figure 2.3: A bond alternation defect, shown here localized on a single site, bearing an unpaired electron.

The two main mechanisms of soliton generation, are (a) the intrinsically formed solitons during synthesis or dimerization and (b) doped-induced solitons. And the others are (c) photogeneration and (d) charge injection.

2. Polarons

A single bond alteration defect in a non degenerate ground state CP would have very different consequences: The energies of the two semi-infinite chains on either side of the defect now differ by an amount ΔE per repeat unit, i.e, an infinite amount. In a finite length chain, the defect would move to the end corresponding to the vanishing of the high-energy structure: no soliton can exist, and the radicals that are observed in such CPs must have a different origin.

An electron or a hole injected on such a chain can not then be present as a charged soliton. However, here again the electron-phonon interaction is important. If a charge is put on a true one- dimensional system, it always becomes dressed by a lattice distortion; i.e, it will self-trap and form a polaron.

The polaron, like an ordinary free carrier has charge $\pm e$ and spin $\frac{1}{2}$. Radicals ions of oligomers molecules can be obtained in solution or in the solid state. In polythiophene, the polaron extends over 6 to 10 cycles (i.e 25 to 40 Å).

The polaron extension will often be large. Note that degenerate ground-state chains can sustain a polaron as well, so that one should calculate which kind of excitation is more stable.

3. Bipolaron

Several cases of spin less conductivities have been observed in the doping of non-degenerate ground-state polymers, suggesting that polarons are not the appropriate excitations in these cases. It has been proposed that the pairing of polarons would produce a new species of charge $\pm 2e$ and spin zero. Of course, the energy gained by forming a bipolaron must be large enough to overcome the columbic repulsion between two nearby charges of the same sign and the entropic term.

A non degenerate ground-state chain cannot contain an isolated soliton, but if there are two nearby solitons sandwiching a short segment of the higher-energy geometry a so-called soliton- antisoliton pair- as shown in Fig 2.4a for the case of cis-PA, the excess energy is finite. A bipolaron is then viewed as a doubly ionized soliton-antisoliton pair, such as on Fig 2.4b.

The size of the soliton pair as on Fig 2.4a can be determined by confinement parameter ($\gamma = \frac{\Delta_e}{2\lambda_0\Delta_0}$). If the energy difference ΔE between the two structures increases, the extension of the high-energy one decreases and the pair is "more confined". For vary small γ (i.e $\Delta_e \sim 0$), the soliton pair or the bipolaron will tend to dissociate into independent solitons or polarons.

Contrary to polarons that form "instantaneously" upon injection or photo generation of a charge, bipolarons are not created directly but must form by coupling of preexisting polarons, or possibly by addition of a charge to a preexisting polaron.

Bipolarons are possible excitations of degenerate ground-state chains, so the spinless conductivity of trans-PA could in principle be associated with bipolarons.

4. From insulator and semiconductor to metal(Optical Signature)

Conjugated polymers, in pristine and neutral states, are insulators with wide band gap or semiconductors with narrow band gap. The energy band gap of the semiconducting conjugated polymer is normally in the range from 1 to 4 eV, which is similar to that existing in the common inorganic semiconductor. Conjugated polymers may

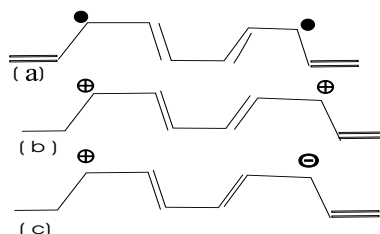


Figure 2.4: Comparison of (a) a pair of solitons (b) a positively charged bipolaron; and (c) an electron-hole pair bound by the lattice relaxation of the chain.

have metallic properties, i.e. high conductivity, after the neutral polymers undergo reduction (n-doping) or oxidation (p-doping) by withdrawing or adding electrons or ions, where a deformation of the main chain is introduced. This is referred to as doping a polymer. A charged polymer molecule, if it creates a degenerate state within the band gap, forms a soliton, such that the conductivity of the polymer is increased. The conductivity of conjugated polymers can cover the range from insulator (10^{-10} S/m) to metal (10^7 S/m). Charged polymer molecules can also generate non-degenerate electronic states in the band gap, forming polarons or bipolarons, such that the optical properties of the polymer are modified. Fig. 2.5 shows the chemical, and electronic structures of a polaron and a bipolaron and their charge and spin.

Charged excitations on the chain also generate new and intense infrared absorption (IRAS lines) which are other manifestations of the strength of the electron-phonon coupling [5,8].

5. Excitons

Another type of quasi particle is the exciton, a neutral excitation well known in semiconductors, where it often dominates the onset of electronic optical absorption. Frenkel excitations, either singlet (spin 0) or triplet (spin 1), are in fact the most important excitations for understanding the electronic properties, the visible and

near -UV absorption to begin with, of crystals of small conjugated molecules such as naphthalene. Again, their existence is a manifestation of electron interactions. It had been shown that the optical properties of PDAs are dominated by a strong excitonic transition to a fairly strongly bound simplest state, 0.5eV below the gap energy.

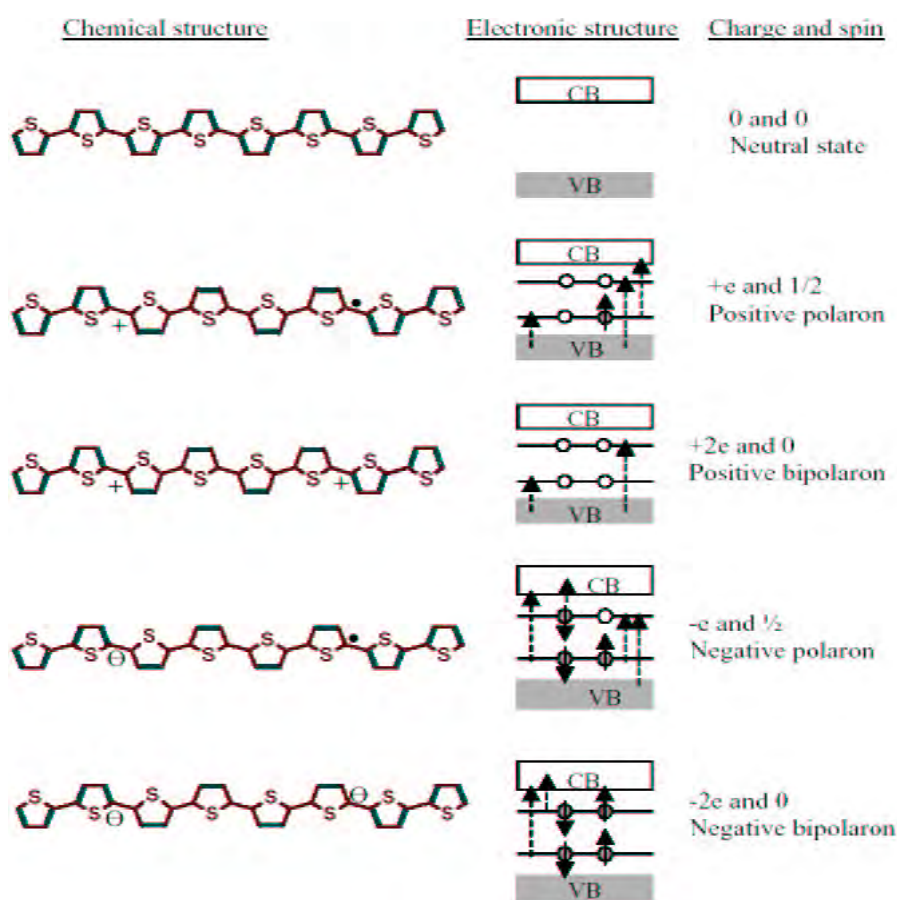


Figure 2.5: Four new levels are introduced in the bandgap as the results of polaron and bipolaron formation. Solid and dash-line arrows represent electron spin and possible transition to/or from the new states, respectively. The charge and spin of the polarons are listed to the right.

One could think of constructing an excitation by coupling two charges of

opposite signs, confining a sequence of the high-energy structure, as on Figure 2.4 c. This would be a neutral excitation of spin 0 or 1. Approximately, Ref. Fig 2.5, its binding energy would be the same as that of the charged bipolaron and independent of its spin, but an independent electron framework does not seem to be a good starting point for studying strongly bound excitons!

In real materials, disorder of any kind localizes the excitations over a limited length on the chain, generating effective "conjugation lengths" so that, for instance, the optical properties are those of a finite, often quite small, molecule. It may well be that excitons are very important in such cases. This has been proposed, for instance, for the substituted PPV and polythiophene.

In conjugated molecular crystals, the triplet exciton energy is always much lower than the singlet one, by up to 1.5 eV. Thus the triplet is the lowest-lying electronic excitation in these systems, but the optical transition between the (singlet) ground state and the triplet is spin forbidden. The unique signature of the triplet is magnetic. Besides, higher-lying triplets exist and the transitions between these and the lowest triplet may be strongly allowed; Intense triplet-triplet absorptions are known in conjugated molecules.

Singlet and triplet excitations are important in at least several CPs is also shown by the occurrence of exciton interactions similar to those well studied in molecular crystals; for instance, singlet-exciton fission has been found in PDAs and triplet-exciton fusion in PPV.

Generally, the picture of CP excitation in terms of excitons is certainly complete than of other quasi particles.

2.3 Doping

Doping is the addition (or withdrawal) of electrons to (or from) the conjugated chains. Doping governs the main properties of CPs, in particular the crossover

from an insulating to a conducting state.

The doping is reversible; the dopant can be removed from the film which returns to its original semiconducting state. That property makes conducting polymers very different from the other organic conductors. Doping is a redox

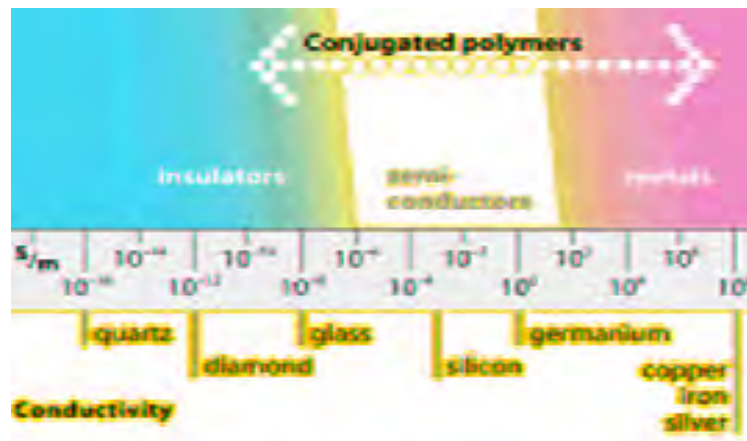
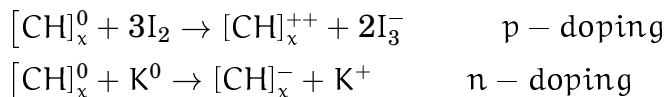


Figure 2.6: conductivity of polymer can be varied over a very broad area, from poor semi-conductors to metallic-level conductivity [25].

reaction that implies electron transfer between a given conjugated chain and surrounding donor or acceptor dopants, which become the counterions. Chemical or electrochemical doping is the most common technique of generating quasi-particles. Polyacetylene, for example, can be oxidized (p-doped) with iodine or reduced (n-doped) with potassium as shown below [16,18].



The electrochemical doping enables continuous and reversible variation of the doping level.

Acceptor and donor doping (known as p-type and n-type doping, after the

nature of the charge carriers on the polymer chains) is a common property among CPs. For instance, polyparaphenylene (PPP), a wide-band gap insulator, can be chemically n-or p-doped to conductivities $\sigma \geq 100\text{S/cm}$.

Generally p-doping in CPs leads to more stable compounds. In the case of n-doping the dopants are alkali metals which are unstable in air atmosphere. Furthermore, oxygen can act as an oxidant and neutralize n-doping. Even p-doping can be unstable in air if the oxidation potential of the polymer is higher.

The role of the counterions is crucial. It has been observed in many cases that the transport and magnetic properties can depend on the nature of the dopant. The counterions create an electrical potential on the chains, which can shift and even modify the relative positions of the polarons and bipolaron levels. They can be a strong source of disorder. It has been shown that the positions of the self-trapped carriers on the chains are determined essentially by the position of these dopants. The counterions weaken the interchain couplings by placing the chains further from each other. It can be envisaged that the electrical charge coming from a counterion is disturbed over two or even several chains, giving rise to a new kind of interchain polaron (or bipolaron) species.

Chapter 3

Organic Solar Cell

The photovoltaic cell is a solid-state device able to convert light into electricity. i.e solar cell and photo detectors convert optical power into electrical power. But LED and laser diodes convert in reverse way.

The characteristics of solar cells are a function of optical energy, which is absorbed in a semiconductor and generates excess electron hole pairs producing photocurrents.

The increasingly recognized need to develop inexpensive and potentially renewable energy sources has caused a tremendous expansion of researcher efforts in photovoltaic. The economic appeal of being able to efficiently convert a free and abundant supply of solar energy directly into electricity is obvious.

The inorganic semiconductor materials Silicon, Gallium arsenide, Sulfide salts of cadmium, and Copper and various alloys of these materials form the basis for the vast majority of research and development work in this area. And the greatest success has been obtained.

During recent years, however, increasing interests has been shown in the application of organic materials in various photovoltaic devices, due to their several features.

They are potentially inexpensive and readily available. The actual fabrication

(processibility) of devices can be rather simple and inexpensive compared with techniques presently used in most inorganic systems. For example, well known spin-coating or dip-coating techniques might be used. Many organic materials can also be used in thin film form; as a result, material costs can be reduced considerably. Organic materials can, in most cases, be easily derivatized; thus, the possibility exists for tailoring specific features such as absorptivity, reflectivity, tensile strength, elasticity, adhesion, resistivity, density, dielectric constant, etc. These ease of preparation, low cost, low weight and flexibility of the devices, make the polymer-based solar cells very attractive, although the power conversion efficiency is not as high as that of silicon-based solar cells (10-20%) [4,7,5,8].

3.1 Basic Working Principles

In organic solar cell, absorption of photons leads to the creation of bound electron hole pairs (excitons) rather than mobile charge pairs (or free charges) [5,6].

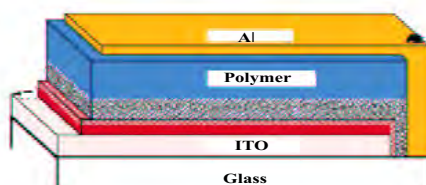


Figure 3.1: Device Structure of a typical organic solar cell

These excitations carrying energy but no net charge may diffuse to dissociation sites where their charges can be separated. The separated charges then need to travel to the respective device electrodes, holes to the anode and electrons to the cathode to provide voltage and be available per injection into an external circuit.

Note that the dissociation into free charge carriers is through the assistance of electric field, bulk trap sites or interface of materials with different electron

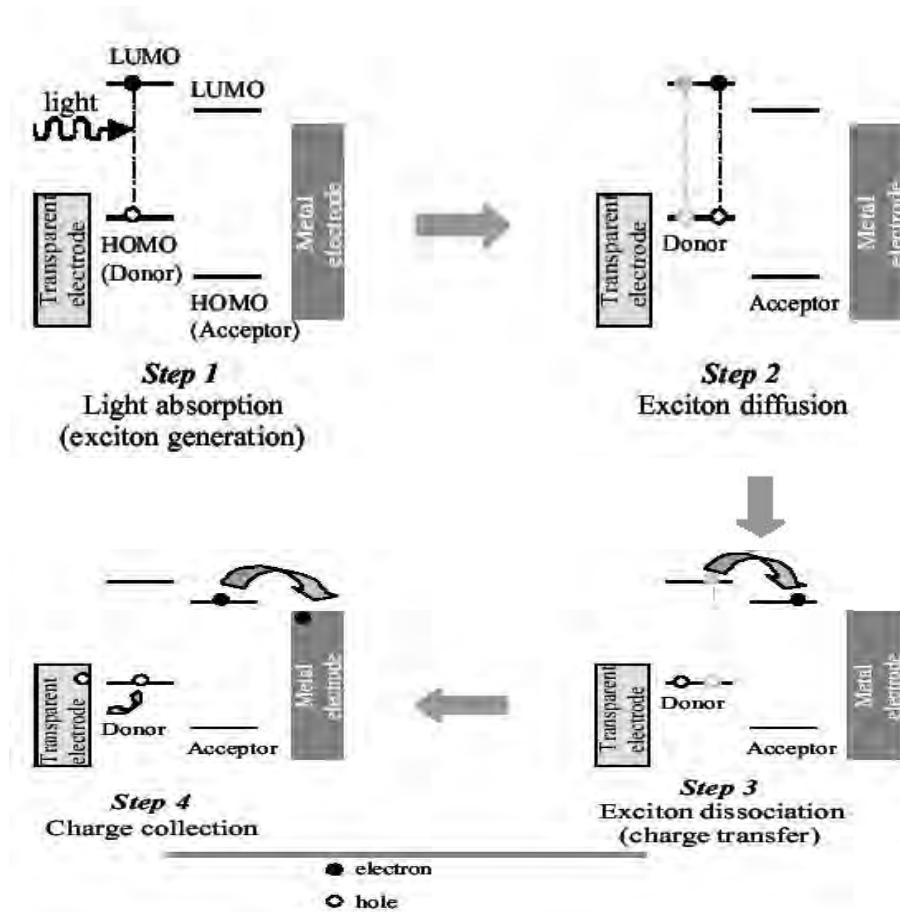


Figure 3.2: The simplified four basic steps of photocurrent generation in BHJ based solar cells.

affinities. The electric field in a solar cell, in its working range, is quite low and doesn't dissociate excitons effectively. The Bulk-Heterojunction (BHJ) active layer which consists of blends of electron donor polymers (D) and electron acceptor polymers (A) is used. This D/A blend composite of nanoscaled heterophases are suitable for efficient exciton dissociation. At D/A interfaces, the driving forces for exciton dissociation and transfer is generated by the electrochemical potential difference between the LUMO of the donor and the LUMO of the acceptor (or in the difference between the electron affinity). Here $\text{LUMO}_{\text{donor}} > \text{LUMO}_{\text{acceptor}}$ [17,8].

Different device designs have been made for efficient photon to charge conversion.

Ideally an electron donor (D) material should be in contact with the electrode material into the higher workfunction (typically ITO) and the electron acceptor material (A) into the lower work function electrode (typically Al). Charge separation occurs at the interface between these two.

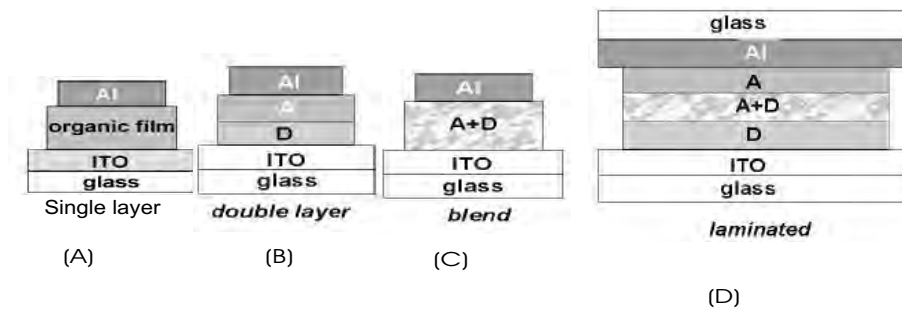


Figure 3.3: Four different types D/A architecture for organic solar cell

Various methods have been utilized for the production of thin films: vacuum sublimation, spin coating, and electro chemical deposition. The optimum film thickness depends on the absorption coefficient of the material, but if the thickness is below the critical value, the risk of short circuits greatly increases. In general, the thickness ranges between 100 and 10,000 Å [6,5].

3.2 Types of Organic Solar Cell and its Development

In 1980, it was proposed that the high local electric field at the heterojunction interface favored the dissociation of excitons that diffuse towards it. This reports of strong photovoltaic effect in a combination of two molecular semiconductors, lead to the efforts to see such kind of effects in a conjugated polymer with the conjugated polymer acting as a donor. Heterojunction is formed between two semiconductors with different band gap energies [4,3].

In these kinds of Donor-Acceptor bilayer, the conjugated polymer is used as

an electron donor and the organic molecule say, C_{60} , as the electron acceptor.

The photogenerated exciton moves towards the donor acceptor interface and dissociates to free charge carriers. The mechanism involved in this process is that the highly electronegative C_{60} dissociates the exciton and accepts an electron. The exciton diffusion length for most conjugated polymer is $\sim 10\text{nm}$. So the thickness of such a device should be small enough to make all the excitons reach the interface and contribute to maximum efficiency.

However, the transport property of C_{60} is poor, which results in low transfer of free charge carriers to the electrode. This increase the probability of recombination. Other than C_{60} , organic molecules and polymers with higher electron affinity were used to make laminated bilayer device. These devices also limited by the efficiency of exciton dissociation.

Even though, these heterojunctions work very well at separating excitons that arrive at the junction, the lifetime of excitons is short, to reach at the junction so that only excitons that are formed within $\sim 10\text{nm}$ of the junction will ever reach it. To avoid this limitation and to optimize exciton dissociation, interpenetrating network concept was introduced.

Inter penetrating-networks of donor and acceptor polymers have been produced. New conjugated polymer species were made that contained electron donating and electron accepting species with these materials, the number of heterojunctions within the polymer blend is greatly increased; and thus enhance the probability that an exciton will encounter a junction be separated.

The photovoltaic efficiency of the device also depends on the absorption of incident photon and transfer of the free charge carriers to the external circuit. Most of the conjugated polymers have a high mobility for holes in the undoped form and hinders the effective transfer of electrons to the electrodes. The interpenetrating networks and heterojunction which are made by molecular solids lack high electrons transfer rates which results in low efficiency and higher recombination rate due to high density of photoinduced free charge carriers. These problems can be solved

by using a polymer which is intrinsically electron transporting and has the energy levels which can form a p-n heterojunction similar to the inorganic one.

In general, there are number of different types of conjugated polymer-based solar cells:

1. Polymer/Polymer blend
2. Polymer/Polymer double layer
3. Polymer/fullerene double layer
4. Polymer/fullerene bulk heterojunction
(polymers blended with soluble fullerene derivatives)
5. Polymer/Inorganic hydride.



Figure 3.4: Schematic view of types of CP solar cells.

Polymer/fullerene bulk heterojunction solar cells are promising because they have considerably high power conversion efficiency and easiest fabrication [3,5,8,17,20].

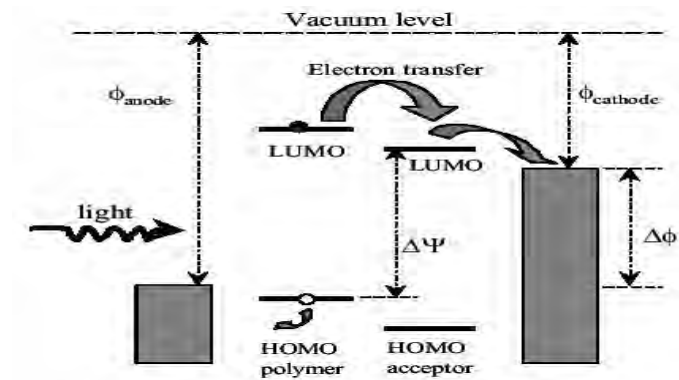


Figure 3.5: charge carrier generation and internal fields of BHJ based solar cell under light.

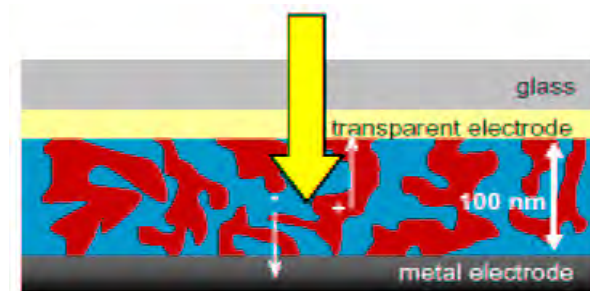


Figure 3.6: A film based on blended D/A bulk heterojunction (BHJ) based solar cell.

3.3 Photovoltaic Parameters

Let V be the voltage drop across a variable load resistance R_L , and I be the current (current density) through it. The photovoltaic cell generates current $I_{ph}(J_L)$, and this photocurrent is partially offset by a diode forward current $I_d(J_D)$. (Dark recombination current density); see figure 3.7a.

This diode is shunted across the generator as shown in figure 3.7b. The total

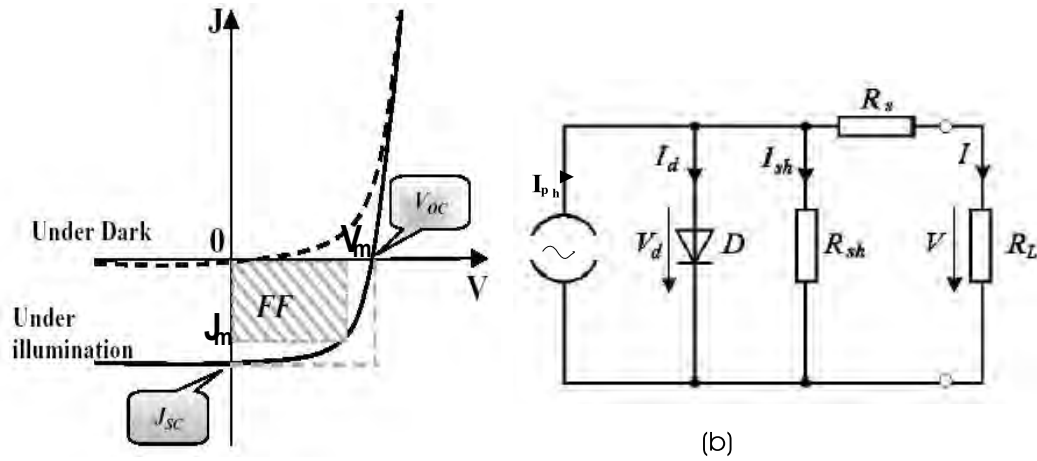


Figure 3.7: (a) Current-voltage characteristics of a typical pn junction or Schottky barrier device in the dark (J_D) and under illumination (J_L). (b) Equivalent circuit of a typical well-behaved solar cell under actual operating conditions.

circuit current I measured at the ammeter is given by

$$I = I_{ph} - I_0 [\exp(eV^*/kT) - 1] - \frac{V_{sh}}{R_{sh}} \quad (3.1)$$

$$\text{Where } V^* = V + IR_s + \left(\frac{R_s}{R_{sh}}\right)V.$$

If $R_{sh} \gg R_s$ (and hopefully this is the case), we ignore the $\frac{V_{sh}}{R_{sh}}$. So the total current becomes

$$I = I_{ph} - I_d = I_0 [\exp(eV^*/kT) - 1] \quad (3.2)$$

It should be noted that even when corrected for R_s and R_{sh} , equation 3.2 fails to agree with observed experiment behavior for voltages $\leq 0.4V$. In case an empirical factor n is used for kT and is replaced by nkT . The larger the value of I_0 (example , $> 10^{-6} - 10^{-5} A/cm^2$), the larger the value of n . Generally , $n \simeq 2$, but for organics , it is usually in the range between 2 - 3.

For (highly resistive) organic materials one should also consider additional alteration of the equivalent circuit of the series resistance part of the above figure 3.7b, where now the photovoltaic cell is considered to be a capacitor in parallel with a variable series resistance, which is a function of both the potential across the cell and the intensity L of the incident light.

So, the J-V characteristic under illumination is given by

$$\mathbf{J} = \mathbf{J}_{ph} - \mathbf{J}_o[\exp(\frac{qV}{nkT}) - 1] \quad (3.3)$$

This is near-ideal situation. It is the net observed equilibrium density, $\mathbf{J} = \mathbf{J}_{ph} - \mathbf{J}_d$ [7]. Important parameters that are used to characterize the properties of a solar cell are briefly discussed below.

a) **Short circuit current ($\mathbf{I}_{sc}$)**

The maximum output current when the load impedance (R_L) is much smaller than the device impedance (R_s). See figure 3.7.

It is the conditions where photocurrent flows under zero applied voltage. It is obtained by substituting $V=0$ into equation 3.3. Ideally, it is equal to the current density, J_{ph} , generated by light.

$$J_{sc} = J_{ph} \quad (3.4)$$

b) **open circuit Voltage (V_{oc})**

The maximum output voltage when the load impedance (R_L) is much greater than the device impedance (R_s) see fig 3.7.

It is the condition where photovoltage is generated but no photo current flows through the circuit. The open circuit voltage is obtained by setting $J = 0$ into equation 3.3. i.e under open circuit condition, R_L approaches to infinity so that the net current is zero and the photo current is just balanced by the injected current. (i.e the net current becomes zero). So, we have

$$J = 0 = J_{ph} - J_o[\exp(\frac{qV_{oc}}{nkT}) - 1], \quad (3.5)$$

which implies

$$V_{oc} = \frac{nkT}{q} \ln(1 + \frac{J_{ph}}{J_o}) \quad (3.6)$$

With increasing applied forward bias, the electric field-induced current (injection current) competes with the photo-induced current and at a certain applied voltage, the two current cancel each other. This voltage is V_{oc} . The band gap between the LUMO of the electron accepting molecule and the HOMO of the electron-donating polymer has a major effect on V_{oc} .

The difference between HOMO and LUMO level (the bandgap) can be seen as a theoretical upper limit for V_{oc} . Many organic solar cells that a higher workfunction difference of the electrodes ΔW_f can also increase V_{oc} . This is explained by assuming that ΔW_f introduces a "built-in-field" across the thin semiconducting layer that helps to extract the photoexcited charge carriers. So the upper limit for V_{oc} is the band gap for single layer whereas ΔW_f of the electrodes or the band gap- which is higher- for donor/acceptor cell. Note that losses occur due to radiative recombination. Lower I_o due to the frequently low non-radiative recombination, favors high V_{oc} .

C) Maximum output power(P_{max})

The maximum output power delivered to the load, and is simply calculated by

$$P_{max} = I_m V_m \quad (3.7)$$

where I_m , V_m are the current and voltage at the maximum output power.

The output power IV of the device for an ideal generator (constant-current-generator) is

$$P_{\max} = I_m V_m = I_{sc} V_{oc}. \quad (\text{an ideal case}) \quad (3.8)$$

For non ideal generators (generator of constant internal resistance), the maximum output power can be calculated by

$$\frac{dP}{dV} = 0, \quad (3.9)$$

i.e the current and voltage, which deliver the maximum power to the load can be found by derivative of power to the applied voltage equal to zero.

$$P = I_{\text{net}} V = (I_{ph} - I_o [\exp(\frac{eV_m}{nkT}) - 1])V, \quad |I = I_{\text{net}}| \quad 3.9b$$

$$\frac{dP}{dV} = 0 = I_{ph} - I_o [\exp(\frac{eV_m}{nkT}) - 1] - I_o V_m (\frac{e}{nkT}) \exp(\frac{eV_m}{nkT}), \quad 3.9c$$

where, V_m is the voltage which produces maximum output power. So we get

$$[1 + (\frac{e}{nkT})V_m] \exp(\frac{eV_m}{nkT}) = 1 + \frac{I_{ph}}{I_o}. \quad 3.9d$$

The value of V_m can be determined by trial and error from the I-V curve of the cell under illumination. (See fig 3.7a) . Therefore, the maximum rectangular area that can be enclosed by I-V curve under illumination gives the maximum output power of the typical solar cell.

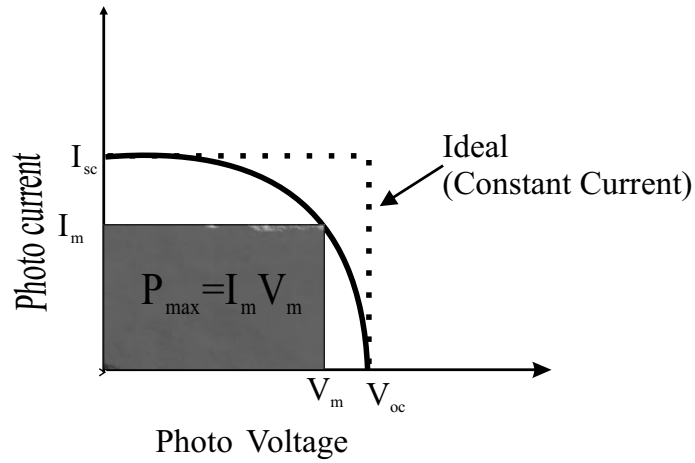


Figure 3.8: Output current-Voltage (I-V) curve for a typical photovoltaic device

Fig 3.8 is the 3rd quadrant in figure 3.7a. The solid curve above shows most photovoltaic devices are generators of variable current.

d) **Fill Factor (FF)**

It is the quality of the solar cell as a power source, and is defined as the ratio between the maximum power delivered to an external circuit and the potential power, and reflects the charge transport properties in the diode.

$$FF = \frac{P_{max}}{I_{sc} V_{oc}} = \frac{I_m V_m}{I_{sc} V_{oc}}. \quad (3.10)$$

For an ideal generator $FF = 1$, but practically <1 .

For inorganic solar cell, it is typically between 0.7 and 0.8. For undoped organic semiconductors, it assumes values less than 0.7.

For most organic materials, high-bulk resistivities, large trap densities, non ideal contacts, recombination, short diffusion lengths, etc, result in field-dependent and space-charge-limited effects that cause the photovoltage and photocurrent outputs to be load-dependent (or load-limited).

FF can also be determined easily by considering the ratio of the largest rectangular area that can be drawn under the out put photo-I-V curve (maximum output power) to the area defined by $V_{oc}I_{sc}$ in the I-V curve.

Ideally ,the FF is the function of V_{oc} , and is given by an empirical expression as

$$FF = \frac{V_{oc} - \ln(V_{oc} + 0.72)}{V_{oc} + 1}, \quad (3.11)$$

Where $V_{oc} = V_{oc}/\frac{kT}{q}$ is the normalized voltage.

e) **Power Conversion Efficiency (η)**

Photovoltaic devices should be used for the direct conversion of sunlight to electricity. Power conversion efficiency (η) is the ratio of the maximum power output P_m from the cell to the incident power P_{in} on the same device of area A. This ratio of input light power to the output electric power of the device can be determined by J-V characteristic, and written as

$$\eta = \frac{P_{out}}{P_{in}} = \frac{I_m V_m}{P_{in}}, \quad \text{or} \quad \eta = \frac{J_{sc} V_{oc} FF}{P'_{in}}, \quad (3.12)$$

where P'_{in} is the intensity of the light incident on the cell. It is the power density of incident light in unit Watt/m².

In general, the conversion efficiency of a solar cell in percentage is given by

$$\eta(\%) = \left(\frac{I_{sc} V_{oc}}{P_{in}} \right) FF \times 100\%.$$

Sometimes the use of the power conversion efficiency of the barrier region is preferable,

and is defined as

$$\eta' = \frac{I_{sc} V_{oc} FF}{P_T},$$

where P_T is the transmitted light power through the metal electrode [6,7,5,8,12,15,17].

f) The Incident Photons to Current Conversion Efficiency

It gives us information on the spectral coverage and efficiency of the device to convert monochromatic light into electrons. The short-circuit current generated at every wavelength defines the spectral response SR of the solar cell, which is defined as

$$SR = \frac{J_{sc}}{P_{in}}.$$

Where J_{sc} is the photogenerated short-circuit current at a specific incident wavelength λ and P_{in} is the incident monochromatic photon flux.

The IPCE is also known as the external quantum efficiency (EQE). It can be determined by measuring the photo-induced current of a solar cell under illumination from an incident monochromatic light under short circuit conditions. EQE can be derived from the spectral responded SR considering that the energy of a photon $E_p = \frac{hc}{\lambda}$ with h being plank's constant, c is the speed of light and q the elementary charge. Therefore,

$$EQE(\lambda) = \frac{hc}{q} \frac{J_{sc}}{P_{in}\lambda}$$

or

$$IPCE(\lambda) = EQE(\lambda) = 1240 \frac{J_{sc}}{P_{in}\lambda}$$

The EQE gives higher values for short wavelengths. Since the output current is determined by the number of electrons that can be "pumped" in to the CB

regardless of their energy, the EQE represents a true measure for the photon to current conversion efficiency [5,7,17,8]

3.4 Material and Performance

For the design of solar cell, it is important to know whether a specific material combination is likely to lead charge transfer, exciton splitting etc, so that the choice of material and the desired efficiency can be achieved.

3.4.1 Polymers

Some of the relevant properties of organic photovoltaic materials are donor/acceptor properties, band gaps, solubility, photoluminescence etc. Most organic semiconductors behave more like electron donors. Materials with higher band gaps tends to show stronger photoluminescence. Moreover, the presence of impurities or structural defects usually leads to energy levels within the band gaps. Let us briefly discuss properties of some of the materials which are used in PV cell design.

APFO and PCBM

APFO (**A**lternating **P**oly **F**lu**O**rene) family of copolymers are based on a fluorene monomer combined with donor acceptor-donor (D-A-D) co-monomers and designed to have a low band gap and form birefringent liquid crystalline phases. These copolymers have been used to construct efficient solar cells. Some of these copolymers have broad absorption band that extends into the red and near infrared solar spectrum. The low band gap APFOs have been used to construct solar cells that generate photocurrent in the near infrared region.

Hole transport in APFOs is field and temperature dependent, which is a typical features of hopping transport. Accumulation of charges in a bulk of a polymer film creates a field that reduces current flow. The net effect is the transition of constant mobility to field dependent mobility of the Poole-Frenkel type.

As far as transport concerned, well-mixed D/A materials create well-behaved transport percolation paths. For various types of polymer/PCBM BHJ films hole

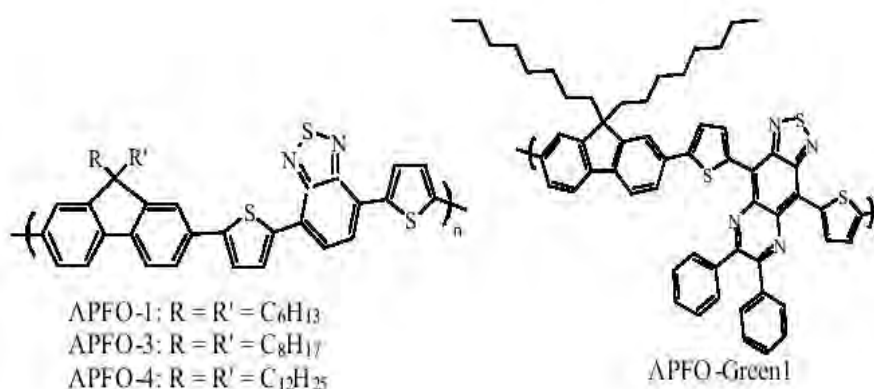


Figure 3.9: The chemical structure of low band gap Poly Fluorene copolymers (APFOs)

mobility in the blend phase has substantial increase over values measured in pure polymer films. Thin hole mobility is, enhanced in the presence of high concentration PCBM in the blend. This can be exemplified based on the work of C.M Bjorström et al. The segregated PCBM promotes hole conduction resulting into increased hole

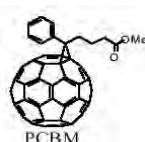


Figure 3.10: The chemical structure of PCBM

collection efficiency and the overall solar cell power conversion efficiency. Note that different acceptors obviously provides different exciton dissociation energy and charge transport profiles. The knowledge of charge transport in solar cell materials is quite beneficial in order to select the appropriate polymer-molecule combinations that provides excellent charge generation and collection efficiencies

[17].

PEDOT:PSS is a commercially available polymer and is Poly (3,4 ethylenedioxy thiophene) (PEDOT) Doped with poly (Styrenesulphonate)(PSS). It is water soluble, and it has high conductivity, high visible light transmittivity and excellent stability. Once a film is formed, it is highly conducting transparent, mechanically durable and insoluble in any common solvent.

PDOT:PSS can be considered as one of the electrodes (anode) if its sheet resistance

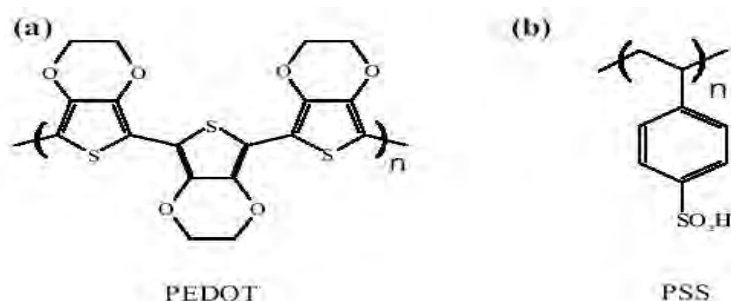


Figure 3.11: The chemical structure of PEDOT:PSS

is reduced and its conductivity is enhanced by doping or other means. To find an organic material that serves as an electron-conducting layer (Cathode) is the most difficult step. However the VPP-PEDOT is as a potential candidate for a cathode in photovoltaic devices. It has a low work function ($4.3 \pm 0.1\text{eV}$) which is close to that of most low workfunction metal such as aluminium and silver. Note that the work function of PEDOT:PSS is 5.1 eV.

Other important soluble or transparent conductors used as electrode materials for organic solar cells are PANI, ITO, TO and FTO.

3.4.2 Electrode Materials

The workfunction and absorption properties of electrodes have a clear effect on the performance of organic solar cells. The workfunction of the electrode materials

determines together with the LUMO/HOMO and Fermi level of the semiconductor whether the electrode forms an ohmic or a blocking contact for the respective charge carrier (holes in VB, electrons in CB). Moreover, a large difference in work function of the electrode materials can increase the V_{oc} considerably.

Common electrode materials for the electron collecting contact (low workfunction required) of organic solar cells are Al, Ca, In, Ag whereas for the hole collecting contact high workfunction materials like gold (Au) and palladium (Pd) are preferred.

For both solar cells and LEDs one contact has to be at least partly transparent. Au is not much thicker than about 15-20nm compared to about 50-100 nm which are typical values for non transport contact.

We note that the sheet resistance of such a thin layer can be considerably increased compared to a 50 to 100 nm thick layer and possibly add to the series resistor of the cell significantly. Also the optical properties change considerably in the thickness range from 10 - 20nm so that devices with slightly different thickness may not be immediately comparable. For these reason so called conducting glasses are often used.

ITO

Indium Tin oxide (ITO) which is a degenerated semiconductor comprising a mixture of In_2O_3 (90%) and SnO_2 (10%) with a band gap of 3.7eV and a Fermi level between 4.5 to 4.9 eV is widely used. ITO covered quartz substrates are commercially available since they are widely used as conducting glasses in the liquid crystal screen industry.

ITO can be used as antireflection layer as active semiconductor. The surface can be modified via plasma etching or the semiconducting molecules can even be chemically attached to it.

Generally , ITO and other conducting glasses like Indium oxides, Tin oxide, doped Zinc oxides are highly transparent and highly conducting degenerate semiconductors with a work function of up to $\sim 5.1\text{eV}$.

Practice confirms that organic devices using **Au** and **Ca** instead of **ITO** and **Al** show indeed considerably higher open circuit voltages and often also higher photocurrents and EQE values. However, because of the lower W_f of Ca compared to Al, Ca is more prone to oxidation than Al. Gold electrodes are expensive and have to be very thin to become transparent and are more difficult to pattern via etching. For the above reasons Al and ITO electrodes are actually more suitable, reliable for research devices since they can be reproduced easier [3,6,17,21].

Other Electrodes

The sample prepared may be in the form of a fiber, film, single crystal, block, or compacted disk of powdered material. Each presents its own peculiar problems. To ensure that the observed behavior is characteristic of the material, cross-checking experiments are required using different electrodes. Some of the most commonly used electrode materials are listed below with their properties and methods.

- Hg - Liquid metal, not recommended ; easily oxidized, toxic vapors.
- Al - Vacuum deposited; may oxidize.
- Ag - Vacuum deposited, silver paint, silver epoxy cement; may react with some substrates; may diffuse into sample.
- Au - Vacuum deposited, paint, paste; inert and not oxidized
- NeSa - A semitransparent conductive tin oxide coating often applied to quartz or glass for contact electrodes; for photoconduction experiments.
- Hg, In, Sn, Pb - Low-melting metals used alone or as alloy; easily oxidized; vapors may be toxic.

So formation of the electrode is of paramount importance. In laying down the conductive material, the surface shouldn't be chemically changed and there should be no gaps between the electrode and sample. Vacuum deposition of a metal

such as, Al, or Au is commonly employed. The use of conductive paints is acceptable, provided that the solvent does not affect the substrate to be studied. Foils have also been employed but may create interfacial voids. For experiments involving light, one electrode must be semitransparent. Frequently, NeSa glass has been used for the semitransparent electrode, as have been thin layers of gold or grids of metal (evaporated or embedded).

Photoinjection experiments use layers of an established photoconducting material, example selenium. The electrode should be Ohmic, that is, it should not perturb the potential distribution across the sample by injecting charge carriers or by creating potential barriers at the surface. It is also advisable to use guard-ring electrodes in order to minimize surface leakage currents [7].

3.5 Loss Mechanisms

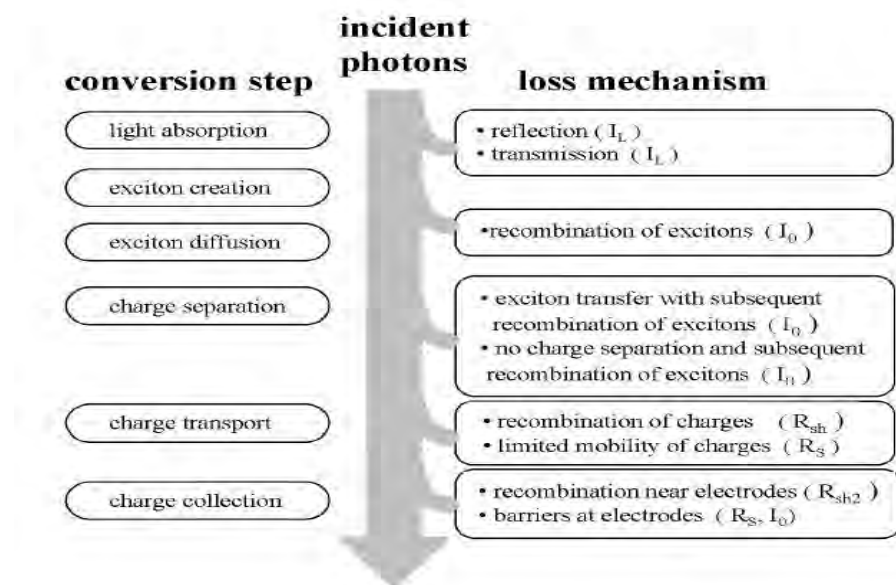


Figure 3.12: Specific conversion steps and loss mechanisms in an organic cell

Optical Absorption

The photon may be absorbed or propagates through the semiconductor depending on the photon energy ($h\nu$) and on band gap E_g .

When $h\nu > E_g$, the photon energy is absorbed in a semiconductor, there by creating electron hole pairs. Excess energy may give the electrons or holes additional kinetic energy, which will be dissipated as heat in the semiconductor. And when $h\nu < E_g$, the photons are not readily absorbed, so the light is transmitted through the material and the semiconductor appears to be transparent. The intensity of photon flux decreases exponentially with distance through semiconductor material. This is given mathematically as

$$I_\nu(x) = I_{\nu 0} e^{-\alpha x}$$

Where, I_ν is the intensity of the photon flux. It's unit is Watt/cm^2 and α is the absorption coefficient. α increases very rapidly for $h\nu > E_g$ and very small for $h\nu < E_g$.

There are several possible photon-semiconductor interaction mechanisms. photons can interact with semiconductor lattice, so that photon energy converts to heat; impurity atoms, i.e. either donor or acceptors; defects; and with valence electrons. When photon interact or collide with valence electrons, electrons elevates to conduction band then electron-hole is generated, and then creates excess carrier concentration.

Now, it is better to comment each steps involved in the generation of photocurrent and its loss mechanisms in an organic solar cell.

1. Absorption of photons. In most organic device only a small portion of the incident light is absorbed for the following reasons:
 - The semiconductor bandgap is too high. A bandgap of 1.1eV (1100nm) is required to absorb 77% of the solar radiation on earth whereas the

majority of semiconducting polymers have bandgaps higher than 2.0eV (600nm) limiting the possible absorption to about 30%.

- The organic layer is too thin. The typically low charge carrier and exciton mobilities require layer thickness in the order of 100nm. Fortunately the absorption coefficient of organic materials is generally much higher than in e.g. Si so that only about 100nm are necessary to absorb between 60 and 90% if a reflective back contact is used. . Reflection losses are probably significant but little investigated in these materials. Systematic measurements of photovoltaic materials are desired to provide knowledge of their impact on absorption losses. Anti-reflection coatings as used in inorganic devices may then prove useful once other losses such as recombination become less dominant.

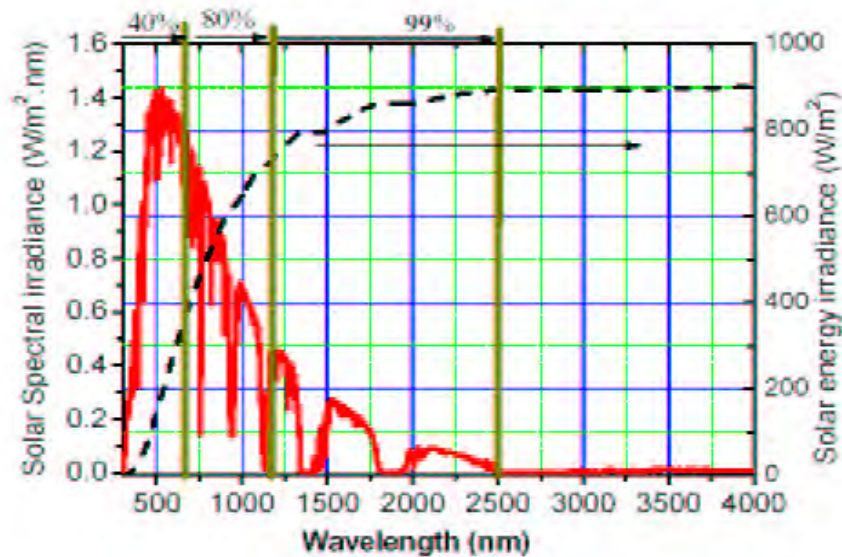


Figure 3.13: Solar spectrum irradiation (solid line) and solar energy irradiation distribution (dash line) as a function of wave length. The total poer density of irradiance calculated from the spectrum is 90 mW/cm²[8].

2. Exciton diffusion. Ideally, all photoexcited excitons should reach a dissociation site. Since such a site may be at the other end of the semi-conductor, their diffusion length should be at least equal the required layer thickness (for sufficient absorption) - otherwise they recombine and photons were wasted. Exciton diffusion ranges in polymers and pigments are typically around 10nm. However, some pigments like perylenes are believed to have exciton diffusion lengths of several 100nm.
3. Charge separation. Charge separation is known to occur at organic semiconductor/metal interfaces, impurities (e.g. oxygen) or between materials with sufficiently different electron affinities (EA) and ionisation potentials (IP). In the latter one material can then act as electron acceptor (A) while the other keeps the positive charge and is referred to as electron donor (D) - since it did actually donate the electron to A. If the difference in IP and EA is not sufficient, the exciton may just hop onto the material with the lower bandgap without splitting up its charges. Eventually it will recombine without contributing charges to the photocurrent.
4. Charge transport. The transport of charges is affected by recombination during the journey to the electrodes - particularly if the same material serves as transport medium for both electrons and holes. Also, interaction with atoms or other charges may slow down the travel speed and thereby limit the current.
5. Charge collection. In order to enter an electrode material with a relatively low workfunction (e.g. Al, Ca) the charges often have to overcome the potential barrier of a thin oxide layer. In addition, the metal may have formed a blocking contact with the semiconductor so that they can not immediately reach the metal.

We note that both exciton and charge transport in organic materials usually require

hopping from molecule to molecule. Thus, close packing of the molecules is assumed to decrease width of the intermolecular barriers and a flat molecular structure should generally lead to better transport properties than bulky 3 dimensional molecules. we note that dense packing also favors a higher absorption coefficient[4,6,7].

3.6 Summary of Desirable Photovoltaic Materials Properties

It is important to summaries some of the more important properties to look for in potentially efficient organic photovoltaic materials. This desirable properties are:

- High quantum efficiency for charge generation (in particular, by visible light)
- High absorption coefficient over as broad a region of photon energies as possible (match the solar spectral radiance if possible)
- Ready availability from cheap, nontoxic materials.
- Good electronic transport properties such as high mobility and low bulk resistivity.
- Low dark conductivity in device configuration.
- Ready film-forming capability and easy device fabrication
- Good performance at high intensities (100-130 mW/cm²)
- Long-term and chemical stability [7].

Chapter 4

Metal Semiconductor Contact (MCP)

4.1 Ohmic and Schottky Contact in MCP contact

The physics of conjugated polymer/metal junction (i.e Metal CP interfaces) formation is essentially the same as inorganic semiconductor/metal surface barrier devices.

An electronic device has at least two contacts. First, let us consider a single one; therefore, it is assumed that the bulk conductivity of the material and the distance between contacts are large enough, so that over most of that distance the material's energy levels are not influenced by the contacts. This is not true in the case of space-charge-limited currents, especially in double injection, a situation that may occur in conjugated polymer LEDs [16,5].

When metal is making contact with a semiconductor, the Fermi levels (E_F) in the two materials must be coincident at thermal equilibrium. Consider Fig 4.1, in the ideal metal and n-type semiconductor, in the absence of surface states before contact, the Fermi level in the semiconductor was above that in the metal. In order for the Fermi level to become a constant through the system in thermal equilibrium, electrons from the semiconductor flow into the lower energy states

in the metal i.e. the Fermi level on both sides line up. The fermi level of the semiconductor is lowered by an amount equal to the difference between the two work functions. In this case, positively charged donor atoms remain in the semiconductor creating a space charge region.

The work function (ϕ) is the energy difference between the vacuum level and the Fermi level ($E_{va} - E_f$). The electron affinity (χ) the energy needed to add an electron to the material. It is measured from the bottom of the conduction band E_c to the vacuum level ($E_c - E_{va}$). Ionization Potential (I_p) of the material, the energy needed to remove an electron from the material ,is ($E_v - E_{vac}$) . The parameter ϕ_{Bn} is the barrier height of the semiconductor contact, the potential barrier seen by electrons in the metal trying to move into the semiconductor. This barrier is the Schottky barrier and ideally given by,

$$\phi_{Bn} = \phi_m - \chi.$$

On the semiconductor side, V_{bi} is the built-in potential barrier. And is given by

$$V_{bi} = \phi_{Bn} - \phi_n.$$

For the forward bias where a positive voltage is applied to the metal with respect to the semiconductor then the barrier V_{bi} is reduced. Since the barrier has been reduced, electrons can more easily flow from Semiconductor into the metal. For reverse bias, where a positive voltage is applied to the semiconductor, the barrier height increases [2,4].

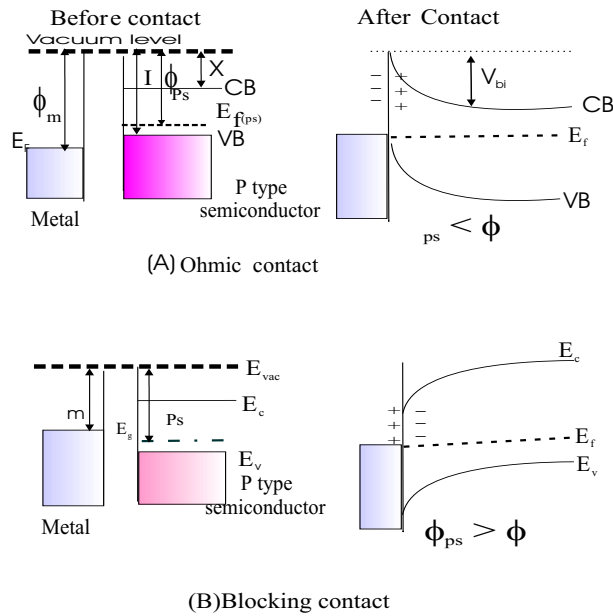


Figure 4.1: Ohmic contact and Schottky barrier contact between a metal M and a p-type semiconductor. VB, Valence band, CB, conduction band, ϕ , χ , E_f and I are energies.

The work function ϕ_m is known approximately and varies from $\approx 2.15\text{eV}$ (for Cesium) to $\approx 5.7\text{eV}$ (for platinum or rhenium). These values can be greatly affected by surface contamination in real metal-Conjugated polymer contact.

On the CP side, the situation at the interface and the spatial variation of the energy-level positions away from the contact depend on two parameters: the Fermi level position ϕ_p and the energy of either the top of the valence band I (the ionization potential) for the holes, or the bottom of the conduction band χ (the electron affinity) for the electrons, with the relation $I = \chi + E_g$, where E_g is the forbidden gap width. In CPs as in semiconductors, ϕ is not an intrinsic property of the material. It depends on the nature and concentration of the gap states.

An ohmic contact defined as a contact whose impedance is negligible compared to the total impedance of the device, and which does not affect the bulk carrier

concentrations far into the semiconductor. In some cases, this is equivalent to saying that it can furnish any required current of the carriers for which it is ohmic, and does not prevent carriers from leaving the material. The words Ohmic contact are usually used in that sense, meaning, in the case of insulators, injecting contacts, (i.e., contacts capable of providing space-charge-limited currents under any circumstance.

Ohmic contacts such as shown in fig 4.1a for holes (the majority carriers in CPs) require $I - \phi_m$ to be as small as possible, or even negative. For $I \approx 5.1 \pm 0.3 \text{ eV}$, this can be achieved with several metals, such as gold. i.e. for a high work function metal like gold and a p-type semiconducting polymer interface, the barrier is so low that charge carriers (holes) can readily pass across the junction. The contact is ohmic. see fig 4.1a. The corresponding condition for electrons is $\phi_m - \chi$ as small as possible or even negative, and this conditions is met by highly reactive metals only. Obtaining electron injecting contacts on CPs will therefore be difficult. This is not a problem for FETS, which with CPs work exclusively with the majority carriers, holes; but it is a problem for LEDs, whose operation requires injection of both types of carriers.

Ohmic type of contact can be created when the work functions of both metal and the semiconductor are nearly the same. In this case no potential barrier is created at the contact interface [5,16,18]. Generally, high doping concentration, low barrier height, or both must be used to obtain low values of contact resistance R_c . And these are exactly the approaches used for all ohmic contact [2].

Schottky Barrier

If $I - \phi_m$ or $\phi_m - \chi$ is large, bands on the semiconductor side are strongly bent so as to form a barrier, as shown in figure 4.1 b. This is known as a schottky barrier. In the region adjacent to the interface within the semiconductor, the valence-band edge is moved farther from the fermi level, so the free carrier density is very much decreased; this is called the depletion region. Two important parameters

in describing a Schottky barrier are the thickness λ of the depletion region and the barrier height, which is (for holes) $\phi_{ps} = I - \phi_m$ on the metal side and $V_D = \phi_m - \phi_p$ on the CP side when no external potential V_B is applied to the barrier. V_D is known as the diffusion potential. Both depend on the density of acceptors N_a or trap states in the material. Some fundamental relations are

$$V_D = \frac{N_a e \lambda_o^2}{2 \epsilon \epsilon_o}. \quad (4.1)$$

which at $V_B = 0$ relates the barrier thickness λ_o to the barrier height; but the coulombic screening length in the CP (Debye length) is

$$\lambda_D^2 = \frac{kT}{e} \frac{\epsilon \epsilon_o}{e N_a} \quad (4.2)$$

so,

$$\frac{2V_D}{\frac{kT}{e}} = \left(\frac{\lambda_o}{\lambda_D} \right)^2 \quad (4.3)$$

upon application of a voltage V_B to the barrier, its thickness and shape change and a current flows. For instance, the barrier width is now λ_B , given approximately by a relation similar to Equation 4.1.

$$\lambda_B^2 = \frac{2 \epsilon \epsilon_o (V_D + V_B)}{N_a} = \frac{2 \epsilon \epsilon_o V_B}{N_a} + \lambda_o^2 \quad (4.4)$$

The measurement of the impedance $Z(\omega)$, especially that of the barrier capacitance C_B , given by,

$$C_B^{-2} = \left(\frac{\lambda_B}{\epsilon \epsilon_o} \right)^2 = \frac{2}{\epsilon \epsilon_o e N_a} (V_D + V_B) \quad (4.5)$$

provides a way of proving that a Schottky barrier is present and of determining N_a and V_D .

In practice, the device follows the Schottky barrier behavior given by the equation.

$$J = J_{\text{sat}} \exp\left(\frac{-eV_B}{nkT}\right) \quad (4.6)$$

where,

$$J_{\text{sat}} = A^* T^2 \exp\left(\frac{-e\phi}{kT}\right)$$

Here the current may flow over or through the barrier by a variety of processes (i.e., by thermionic emission or, if it is narrow enough, by tunnelling).

These two factors, interface layers and interface state, i.e electronic states localized at the interface, may greatly modify the properties of the contact. For instance, let us return to the problem of forming an ohmic contact for electrons on to a CP. In fact, the majority of actual ohmic contact Semiconductors do not work. They depend on the presence of a thin highly doped semiconductor layer adjacent to the metal. The width of the depletion region in the Schottky barrier thus formed is then so small (equation 4.1) that injection occurs by field emission. Such a process could in principle be used in CPs, for electron injecting metals such as K are also n-dopants of all CPs. But, this would require that we get ride of most, if not all of the oxide at the interface. Example of the difficulty of forming such an injecting Ca contact on PPV is given.

The presence of a thin insulating layer made of a wide-bandgap material such as an oxide between the metal and the semiconductor is actually the most common situation. For instance, an Al_2O_3 layer will grow very rapidly on Al to a thickness of $\simeq 25\text{\AA}$ except in ultra high vacuum(UHV). This is likely to be very common with CPs. This layer will influence the situation in several ways. First

there is a potential drop in the insulator, which will be large since its conductivity is negligible compared to that of the Semiconductor. Consequently, the zero-bias barrier height (the difference between the top of the valence band at the CP-insulator interface and the metal Fermi level) will be lowered. Second, the insulator bandgap is large, so the layer is a high barrier for both carriers. Current can flow through the insulator by tunnelling only, but if the barrier is thin enough, say $\approx 20\text{\AA}$, the metal and the semiconductor levels will be well coupled, and the current can be high. Under bias, the barrier height is a function of voltage, changing the slope of the $J(V)$ dependence, hence introducing non ideality [5].

4.2 Interpretation of I-V curve

The properties of the thin film is characterized based on the I-V curve it shows. This curve can be analyzed by interpreting qualitatively or/and analytically. These methods of interpretation were shown below in brief.

4.2.1 Qualitative Interpretation

The interpretation of the I-V curve lies in the heart of the general relation known as thermionic emission/diffusion equation. If the device forms a depletion region at the metal/semiconductor interface such that it yields a rectifying current-voltage characteristics, then the current density and the voltage have an exponential relation given by.

$$J = J_0 \left[\exp\left(\frac{qV}{nKT}\right) - 1 \right] \quad (4.7)$$

Where J = the total current per unit area,

J_0 = the reverse saturation current.

Here we consider three cases. Case1: When the reverse saturation J_0 is very

small compared with the current density J (i.e., $J \gg J_0$), the contact will effectively block current flow for the reverse bias and exponentially increasing current occur in the opposite polarity called the forward bias. Better rectification properties may be obtained for decreasing values of the reverse saturation current density J_0 . Rectifying contacts are desirable for photovoltaic cells, photo detectors, Field Effect Transistor(FET), chemical sensors and numerous other semiconductor devices. This phenomenon occurs when electropositive (low work function) metals are in contact with p-type semiconductors. Case2: When J_0 is very large compared with the current density J (i.e., $J \ll J_0$), in this case the junction will readily pass current for both signs of the applied voltage. And the above equation 4.7 can be expanded and approximated to give

$$V \approx \left(\frac{nkT}{qJ_0} \right) J$$

This equation is Ohm's law. In such a case the I-V curve becomes linear(Ohmic) and symmetric. Ohmic contacts are necessary to avoid resistance losses for almost all types of semiconductor structures. Case3: If the current density is intermediate between the two limits (i.e., $J \gg J_0$ nor $J \ll J_0$), then the I-V curve becomes non-ohmic and non-rectifying. It is symmetric and non linear. This is the case where there is a thin insulating layer formed at the interface because Aluminium (the electrode) was exposed to air before the formation of the junction.

Generally, all measurements of current-voltage characteristics may involve more than one type of charge transport mechanisms such as tunnelling, generation-recombination , and leakage current. The semi-log plot of the I-V curve is evidence for this argument. It has several slopes each linear region corresponding to one type of charge transfer mechanism. Probably, the strongest current limitation arises from the series resistance which indicates the electrical transport that is dominated by space charge limited current (SCLC). In such a case, no Schottky

Process	Voltage and Temperature Dependence
Schottky emission	$\sim T^2 \exp(+a\sqrt{V}/T - q\phi_B/kT)$
Frankel-Poole emission	$\sim V \exp(+2a\sqrt{V}/T - q\phi_B/kT)$
Tunnel(or field emission)	$\sim V^2 \exp(-b/V)$
Space-Charge-Limited	$\sim V^2$
Ohmic	$\sim V \exp(-C/T)$
Ionic Conduction	$\sim \frac{V}{T} \exp(-d'/T)$

Table 4.1: Basic conduction processes in insulators. b , c , d are constants independent of V and T .

barrier is formed. The I-V curves become non-linear and Symmetrical [9,16]. In dealing MIS (Metal-Insulator-Semiconductor) diode, the summary of the basic conduction process in insulators are tabulated in table 4.1 and itemized accordingly. And note that an ideal MIS diode the conductance of the insulating film is assumed to be zero.

Thermionic emission process across the metal-insulator interface or the insulator-semiconductor interface are responsible for carrier transport. The Frenkel-Poole emission is due to field-enhanced thermal excitation of trapped electrons into the conduction band. For trap states with columbic potentials, the expression is virtually identical to that of the Schottky emission. The tunnelling emission is caused by field ionization of trapped electrons into the conduction band or by electrons tunnelling from the metal Fermi energy into the insulator conduction band. The tunneling emission has the strongest dependence on the applied voltage but is essentially independent of the temperature.

The space charge limited current results from a carrier injected into the insulator, where no compensating charge is present. The current for the unipolar trap-free case is proportional to the square of the applied voltage. For ohmic, at low voltage and high temperature, current is carried by thermally excited electrons hopping from one isolated state to the next. This mechanism yields an ohmic characteristic exponentially dependent on temperature. Ionic conduction is similar

to a diffusion process. Generally, the DC ionic conductivity decreases during the time the electric field is applied, because ions can not be readily injected into or extracted from the insulator. After an initial current flow, positive and negative space charges will build up near the metal-insulator and the semiconductor-insulator interfaces, causing a distortion of the potential distribution. When the applied field is removed, large internal fields remain which cause some, but not all, ions to flow back toward their equilibrium position; hysteresis effects result.

For a given insulator, each conduction process may dominate in certain temperature and voltage ranges. The processes are also not exactly independent of one another and should be carefully examined. For example, for the large space-charge effect, the tunnelling characteristic is found to be very similar to the Schottky-type emission [2,18,17].

In polymer solar cell, all these charge transport mechanisms can be reveals typically by three main transport features. The Ohmic region, injected limited region, and the space charge limited region (see figure 4.2).

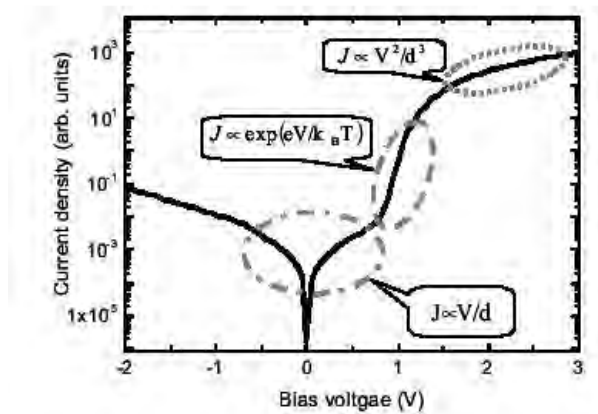


Figure 4.2: Some Various features of a typical IV characteristics of a polymer based diode under forward bias condition. the ohmic region ($J \sim \frac{V}{d}$), injection-limited region ($J \sim \exp(eV/k_B T)$), and the space charge limited region ($J \sim \frac{V^2}{d^3}$).

Here, J is current density, V is potential, d is film thickness, T is temperature, k_B is the Boltzmann constant and e is the elementary charge [17].

4.2.2 Analytic Interpretation

a) Reverse Saturation Current Density (J_0)

As discussed above, the reverse saturation current density J_0 that we found in the dark I-V curve, determine whether the junction acts as a rectifier, an ohmic contact, or a mixture of these limiting cases.

Experimentally, J_0 is obtained by extrapolating the linear part of the plot of $\ln J$ versus V and taking the intercept with the J -axis. This extrapolated value of current density at zero voltage is the saturation current J_0 . Or theoretically, the above equation 4.7, for $V \gg \frac{3kT}{q}$ can be expressed as

$$J \simeq J_0 \exp\left(\frac{qV}{nkT}\right), \quad \text{for } V \gg \frac{kT}{q} \quad (4.8)$$

so that substituting $V = 0$, we can find J_0 [16,2].

b) The Barrier height (ϕ_b)

For inorganic Semiconductor/Metal contacts, an explicit relationship between the barrier height ϕ_b and J_0 can be obtained from thermionic diffusion theory as

$$J_0 = A^{**} T^2 \left[\exp\left(\frac{-q\phi_b}{kT}\right) \right] \quad (4.9)$$

where A^{**} is Richardson constant. Since J_0 is already known from extrapolating the curve, then the value of ϕ_b is calculated using equation (4.9)

Note that the exponential term represents the Boltzman factor relating fraction of the charges in the metal or semiconductor (at zero bias) which will overcome the barrier. The modified Richardson constant, A^{**} , expresses the number of electrons at the semiconductor/metal interface, which may be injected into the metal. A^{**}

also takes into account the effective density of states in the conduction band, the effective mass of the electrons in the semiconductor, phonon scattering, and quantum mechanical reflection at the semiconductor/metal interface. A^{**} is typically between 10 and 100 $\text{A}/\text{cm}^2\text{k}^2$.

For organic semiconductor Schottky diodes the modified Richardson constant is assumed to be that of a free electron, namely $A^* = 120\text{A}/\text{cm}^2\text{k}^2$.

Low barrier height leading to large J_0 so that ohmic contact is formed. This occurs for contacts between low work function metals and n-type semiconductors; or contacts between high work function metals and p-type semiconductors.

High barrier height contacts leading to low J_0 obtained from junction between high work function metals and n-type semiconductors or from low work function metals and p-type (organic) semiconductors.

c) The Ideality Factor (n)

Using the above equation 4.8, the ideality factor defined as

$$n \equiv \frac{q}{kT} \frac{1}{\partial(\ln J)/\partial V} \quad (4.10)$$

Here, we note that first we determine the slope of semi-log of J versus the voltage curve. The ideality factor (n) is very close to unity at low doping and high temperatures. However, it can depart substantially large from unity when the doping is increased or the temperature is lowered.

The interpretation of n values in forward bias:

- $n=1$, the schottky barrier is ideal. And closing to unity indicates diffusion dominates, for a large forward bias voltage.
- $n \geq 2$, a midgap recombination of electrons and holes occur. i.e recombination dominates for low forward bias voltage
- $1 < n < 2$, there is a transition region [16,2].

d) Rectification Ratio(γ)

A rectifier is a p-n junction diode that is specifically designed to rectify alternating current, i.e to give a very low resistance to current flow in one direction and a very high resistance in the other direction. The forward and reverse resistances of a rectifier can be easily derived from the current-voltage relationship of a practical diode.

$$I = I_s(e^{qV/nkT} - 1) \quad (4.11)$$

The forward Dc (or static) resistance R_F and small-signal (or dynamic) resistance r_F are obtainable from the above equation as

$$R_F \equiv \frac{V_F}{I_F} (\simeq \frac{V_F}{I_s} e^{-qV_F/nkT} \quad , \text{ for, } \quad V \geq \frac{3kT}{q}) \quad (4.12)$$

$$r_F = \frac{\partial V_F}{\partial I_F} = \frac{nkT}{qI_F} \quad 4.12b$$

The reverse DC resistance R_R and small-signal resistance r_R are given by

$$R_R \equiv \frac{V_R}{I_R} (\simeq \frac{V_R}{I_s} \quad , \text{ for, } \quad |V_R| \geq \frac{3kT}{q}) \quad (4.13)$$

$$r_R = \frac{\partial V_R}{\partial I_R} = \frac{nkT}{qI_s} e^{q|V_R|/kT} \quad 4.13b$$

comparing Eqns 4.12's and 4.13's shows that the Dc rectification ratio $\frac{R_R}{R_F}$ varies with $\exp(\frac{qV_F}{nkT})$, while the Ac rectification ratio $\frac{r_R}{r_F}$ varies with $\frac{I_F}{I_s \exp(-q|V_R|/kT)}$

Experimentally, we can simply take the ratio of forward current density J_+

and the reverse current density J_- at a given higher bias voltage.

$$\gamma = \left(\frac{J_+}{J_-} \right)_V \quad (4.14)$$

Usually, obtained by taking the two extreme bias voltage ($\pm 3V$ or $\pm 2V$) from $\log J$ - V curve [2,12].

Finally, note that other parameters that we find from I-V curve under illumination (J_{sc} , V_{oc} , FF , η , P_m , EQE) are well discussed earlier so that it can be referred from section 3.2.

4.3 Impedance Spectroscopy Analysis and The Model Circuit

Impedance spectroscopy (IS) is a powerful method of characterizing many of the electrical properties of interfaces of various substances with electronically conducting materials. It may be used to investigate the dynamics of bounded or mobile charges in the bulk or interfacial regions of any kind of solid or liquid material that conducts electronically (electrons and/or holes), ionically or mixed electronic-ionic conductors, and even insulators (dielectric).

An impedance spectroscopy measurement shows the existence of two capacitances, one of the depletion region and the other of the thin insulating layer formed in the sample diode.

The complex impedance Z (real and imaginary components) is directly measured as a function of frequency and applied bias voltage to the device under test (DUT). Using this, one can find the resistance (R) and the capacitance (C) of the junction formed by two electronically conducting materials.

This complex impedance ($Z = Z_r + jZ_i$) may be plotted in a complex plane with their real parts along the x-axis and the imaginary parts along the y-axis.

This plot is called the Cole-Cole plot.

Theoretically a Cole-Cole plot is a semicircle with its center, the 'zero-frequency' and the 'infinite frequency' intercepts lie on the Z_{real} axis. For actual measurement, the zero-frequency intercept is obtained by extrapolation. The diameter of the semicircle corresponds to resistance (R).

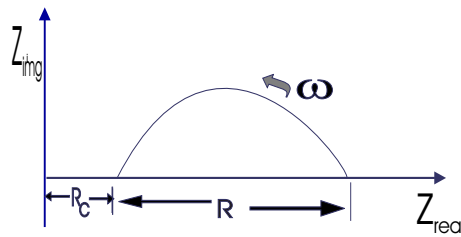


Figure 4.3: Idealized Cole-Cole plot.

Real part of the impedance related to the electronic conductivity of the polymer. R_c is the series contact resistance accounts for the conduction along the evaporated metal electrode. It is the high frequency intercept on the Z_{real} -axis.

In IS measurements, diodes are commonly analyzed using electrical equivalent circuit. The parallel RC circuit is an equivalent circuit model for a junction between a metal and a semiconductor in which the depletion region accounts for the observed capacitance and resistance.

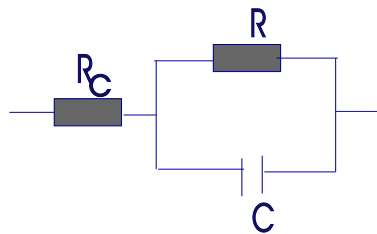


Figure 4.4: An equivalent circuit as modelled from fig 4.3

The total impedance Z of this model, the equivalent circuit, is given by:

$$Z = R_c + \frac{R}{1 + j\omega RC} \quad (4.15)$$

If there is no contact resistance, equation (4.15) becomes $Z = R/(1 + j\omega RC)$. Rationalizing and rearranging terms results

$$Z = \frac{R}{1 + \omega^2 R^2 C^2} - \frac{jR^2 \omega C}{1 + R^2 \omega^2 C^2} \quad (4.16)$$

Where the first term on the right is the real part and the second term is the imaginary of the impedance. Taking the derivative of the imaginary part as.

$$Z_i = \frac{-R^2 \omega C}{1 + R^2 \omega^2 C^2} \quad (4.17)$$

$$\frac{dZ_i}{d\omega} = \frac{-CR^2(1 - R^2 \omega^2 C^2)}{(1 + R^2 \omega^2 C^2)^2} \quad (4.18)$$

This equates zero when $\omega = \frac{1}{RC}$. substituting this value on equation 4.17 we get

$$-Z_{i\max} = \frac{R}{2} \quad (4.19)$$

This equation helps to calculate the unknown resistance directly from $Z_{i\max}$.

The capacitance (C) is calculated from the relation of constant phase element (CPE) whose impedance depends on frequency according to the expression

$$-(Z)'_{Im} = \frac{1}{\omega C} \quad (4.20)$$

Where $\omega = 2\pi f$ is the angular frequency.

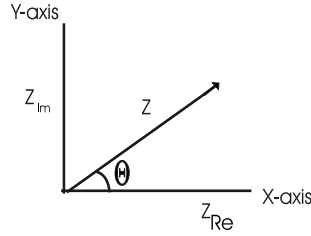


Figure 4.5: Impedance in a rectangular and circular coordinates system.

Thus, knowing the value of $-Z_i$ and the frequency f at which this impedance yields the time constant $\tau = 1$ i.e., where the phase angle $\theta = 45^\circ$ and $-Z_i$ has a maximum value, the geometric capacitance C is obtained.

Here, it may be meaningful to express the impedance in terms of the phase angle θ . From the above expression, in equn (4.15),

$$Z = \frac{R}{1 + j\omega RC} \quad (4.21)$$

The component becomes,

$$Z_{Re} = \frac{R}{1 + \omega^2 \tau^2}, \quad Z_{Im} = \frac{R\omega\tau}{1 + \omega^2 \tau^2} \quad (4.22)$$

where $\tau = RC$.

substituting $\omega\tau = \tan(\theta)$ yields:

$$Z_{Re} = R \cos^2(\theta) \quad \text{and,} \quad Z_{Im} = R \sin \theta \cos \theta \quad (4.23)$$

or

$$Z_{\text{Re}} = R \frac{1 + \cos(2\theta)}{2}, \text{ and, } Z_{\text{Im}} = R \frac{\sin 2\theta}{2}$$

So, the maximum value of Z_{Im} is attained for $2\theta = 90^\circ$, in which case $Z_{\text{Im}} = \frac{R}{2}$ and $\omega\tau = 1$.

Many reports reveal the formation of an interfacial insulating thin layer between conjugated polymers doped with large anions and reactive metals. For this MIS device, Metal/doped polymer contacts, another model equivalent circuit is required. This model can be obtained by considering two parallel RC circuits, R_1 and C_1 represent this layer, while R_2 and C_2 stand for the depletion region.

The corresponding impedance will be

$$Z = R_C + \frac{R_1}{1 + j\omega R_1 C_1} + \frac{R_2}{1 + j\omega R_2 C_2}. \quad (4.24)$$

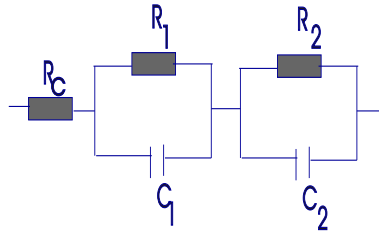
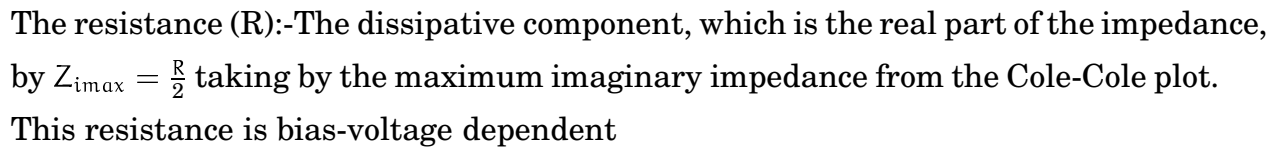


Figure 4.6: An equivalent RC circuit of metal-insulator-semiconductor (MIS) device.

The complex impedance plot of such a device consists of two semicircles as Fig.4.7.

To summarize all points, for the interface formed by Metal-polymer contact: Contact resistance (R_C)- which is a constant at all bias voltage can be obtained by extrapolating the Cole-Cole plot to the intercept at Z_{Re} -axis. Note that this need to be comparable with the inverse of the slope of the J-V curve at zero voltage:



Capacitance (C)- this storage component calculated from $Z'_{lm} = 1/\omega C$ where $\omega = 2\pi f$ [16,9,15,12,10].

Chapter 5

Experimental

5.1 Sample preparation

Two types of samples are prepared; one is to perform the absorption spectrum and determine the band gap of the polymers. The second one is to characterize the photovoltaic properties of the active layer made from conjugated polymer. The first sample is prepared by spin coating from the solution of pure D75:APFO-G6 on transparent glass substrate while D75:APFO-G6:PCBM blend on ITO coated and cleaned glass.

First the solution was prepared using chloroform solvent at (1:1:4) weight ratio of D75,APFO-G6, PCBM at concentration 10 mg/ml. Then the photovoltaic device of bulk heterojunction solar cell (i.e thin film)was fabricated as follows.

The ITO coated glass was cut into the desired size of the cell - usually with the area $1.5 \times 2.0 \text{ cm}^2$. Two-third of the ITO glass was covered by the photoresist and exposed partially to the solution of Hydrochloric acid $\text{HCl}:\text{HNO}_3:\text{H}_2\text{O}$. The etched part is used for Aluminium contact. The surface was then washed with detergent and then the photoresist was removed and cleaned with acetone and distilled water respectively. The ITO-glass substrate was lastly cleaned by ethanol and distilled water.

PEDOT:PSS was spincoated on the dried partially ITO coated-glass at a speed rate of 3000rpm. The PEDOT:PSS is used here to facilitate the hole transport. Before spin coating, the solution should be warmed up so that uniform thickness can be obtained. Since the PEDOT:PSS is water soluble, distilled water is used to remove the PEDOT:PSS partially from the bare glass. The solution of the mixture of polymers (D75:APFO-G6:PCBM) was then spincoated at spin rate of 1000 rpm. Various spin rates are used to get the desired thickness. The higher the rotational speed (rpm) the thinner the film would be. For electrical contact, the polymer should be removed from the bare glass part and from the edge of the ITO-glass part using chloroform. The Aluminium electrode was deposited using vacuum depositor, partially on polymers-blend and partially on the glass substrate. This was done to avoid the possible damage of Aluminium during electrical contact. Finally, the device would have a Al/D75:APFO-G6:PCBM/PEDOT:PSS/ITO active layer. See fig (5.1)

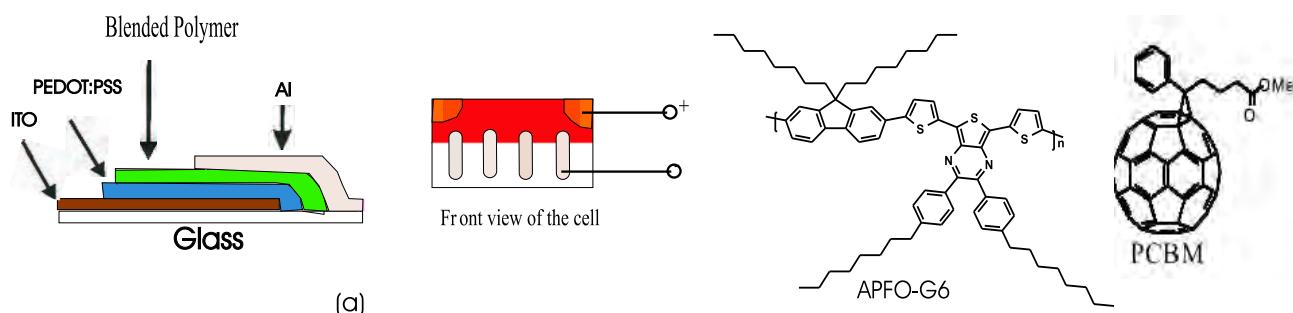


Figure 5.1: (a)Al/D75:APFO-G6:PCBM/PEDOT:PSS/ITO sandwich structure. (b)The chemical structure of APFO-G6 and PCBM

5.2 Absorption Spectrum Measurement

The solution of pure APFO-G6 and blended polymers: D75+APFO-G6, D75+APFO-G6+PCBM were prepared on transparent glasses. The weight ratio of the blended polymers were 1:1 and 1:1:4 respectively, with the concentration 10mg/ml. These three solutions spin coated with 1000rpm on separate pure glass substrates. They were well cleaned with Acetone, ethanol and distilled water successfully. The optical absorbance for each sample were then measured by perkin Elmer λ 19 UV/vis/Nir spectrometer. The scanning wavelength range used for the measurement was from 400 to 900 nm. Finally the absorption spectrum was obtained and analyzed.

5.3 Current-Voltage Measurement

The current-Voltage (I-V) characteristic both under dark and under illumination were measured by using HP4140B PA meter/DC Voltage source. The meter was interfaced with HP test fixture where the sample is kept in the dark. A linear sweep voltage applied was from -3V to 3V at the step of 0.05V for dark measurements.

Under illumination, the applied voltage was from -2V to 2V at the step of 0.05V. In this photovoltaic measurements, the sample was illuminated from ITO side using white light at the intensity 1900 Lux at the position of the sample. The collected data was then plotted and analyzed.

5.4 Complex Impedance Measurement

Complex impedance spectroscopy of the diode was measured as a function of frequency and applied bias voltage using an HP4192A LF impedance Analyzer together with an HP16047A-test fixture. The data were taken in the frequency range from 0.5kHz to 50kHz in 1kHz interval for a given bias voltage. The bias voltage used were from -2V to 2V in the step of 1V. For every applied bias voltage a sinusoidally

oscillating voltage of $V_{\text{rms}} = 50\text{mV}$ was used. Then the data was analyzed by the Cole-Cole plot.

Chapter 6

Results and Discussion

6.1 Absorption spectrum

The optical absorption of the blended polymer APFO-G6 in the fig 6.1 shows that it absorbs electromagnetic radiation in the visible range. Plot 1 , which is of D75+APFO-G6, rises at a wave length $\lambda = 800\text{nm}$. Using the energy relation,

$$E_g = \frac{hc}{\lambda}$$

the energy band gap E_g can be determined. The constant values are planck's constant $h=4.135 * 10^{-15}\text{eV-s}$, speed of light $C=3 * 10^8\text{m/s}^2$ and the wavelength from the figure 6.1a is $\lambda = 800\text{nm}$. Therefore, the energy gap calculated was $E_g = 1.55 \text{ eV}$. This values indicates D75+APFO-G6 has a semiconductor properties as it's band gap lies between 1.5 and 3.0 eV.

Figure 6(b) shows the absorbance is enhanced when the polymer is blended with PCBM. As we observe, the absorbance of plot 3 increases at low value length range due to the increment of concentration of the PCBM.

This increament of absorbance favoures high generation of photo-current so does the efficiency.

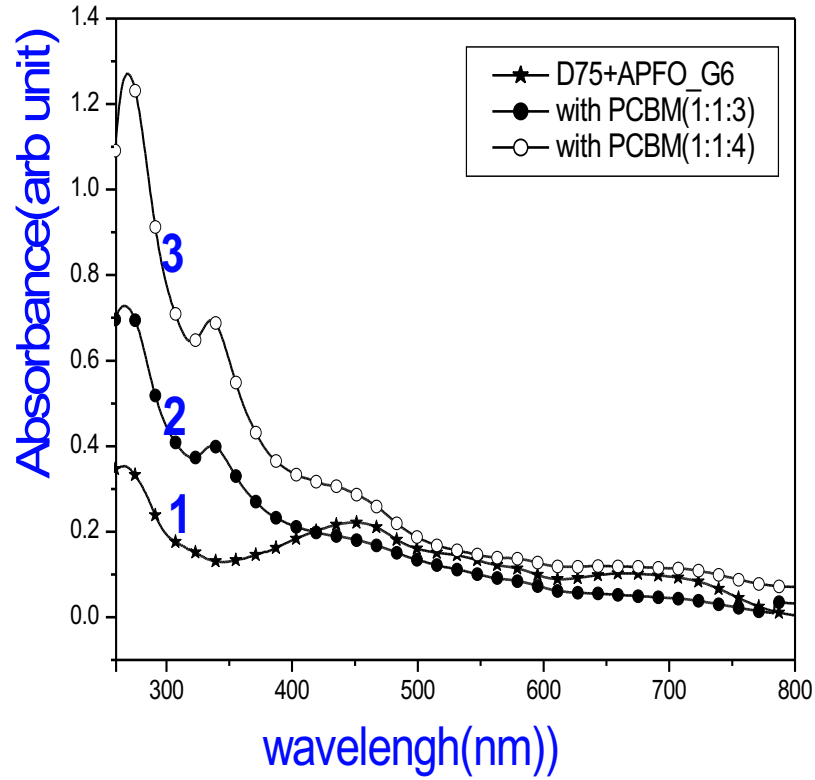


Figure 6.1: Absorption spectrum for D75+APFO-G6+PCBM

6.2 Current Density-Voltage (J-V) Characteristics

6.2.1 Dark J-V Characteristics

From the current voltage characteristics(see fig 6.2), we observe that the forward current is exponentially increased. This is an indication of the diode characteristic. Analytically the rectification ratio was obtained from equation (4.14),

$$\gamma = \left(\frac{J_+}{J_-} \right)_{\pm 3V}$$

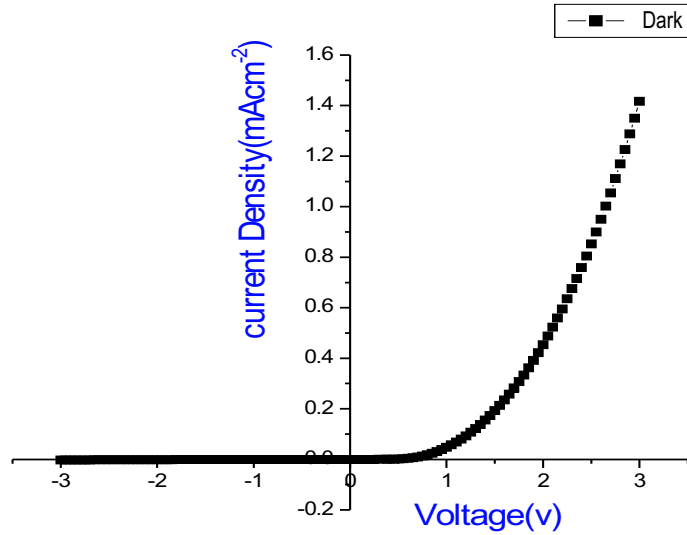


Figure 6.2: Current density-voltage characteristics under dark for D75/APFO-Green6/PCBM device structure.

where for a +3V the forward current density $J_+ = 1.41666 \text{ mA/cm}^2$, and the reverse current density at -3V is $J_- = 0.00220 \text{ mA/cm}^2$. Therefore, the rectification ratio obtained was $\gamma = 643.03$. The diode is regarded as well rectified.

In the semilog plot Fig 6.4, it is observed that the forward current is exponentially increasing in the small applied voltage region, which is between 0.2V and 0.55V. This exponential dependence in this region can be attributed to the formation of a depletion region between the aluminium and the active layer. This exponential increment indicates that the diode is Schottky diode, and is governed by diode equation.

It can also be observed from the figure that, for higher forward voltage $V > 0.55\text{V}$, the increment is too slow. A huge amount of charges are injected into the device and the growth of current becomes limited by the over all amount of space charges loaded into organic film. This limitation of the flow of charges is due to the electron-electron interaction. This limitation for transporting all charge due to the bulk resistance expressed as Ohmic loss of the diode.

By plotting a semilog $\ln J$ versus V using the experimental data (see Fig 6.4) for higher voltage $\frac{qV}{nkT} > 1$, i.e., in the range between 0.2 V and 0.55V, and extrapolating backward this linear curve to the intercept where $V=0$, the saturation current J_0 is obtained from the vertical axis.

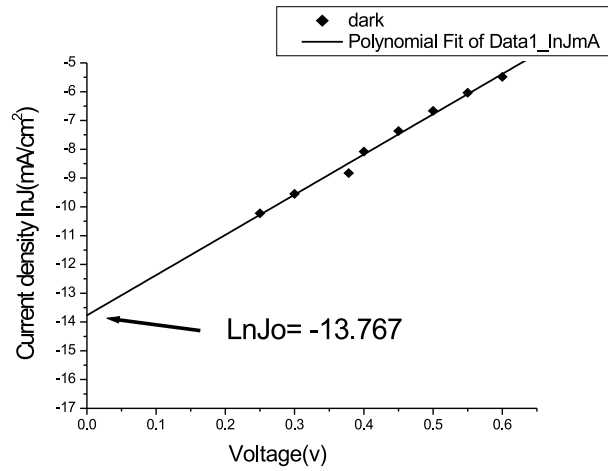


Figure 6.3: Extrapolating the injected limited region of the semi log J-V plot to find the saturated current J_0 .

So, the J_0 obtained was $1.0496 \times 10^{-6} \text{ mA/cm}^2$. Once the value of J_0 was obtained, the barrier height ϕ_b is calculated using equation(4.9) as;

$$\phi = \left(\frac{kT}{q} \right) \ln \left(\frac{A^{**} T^2}{J_0} \right)$$

The barrier height is found to be $\phi_b = 0.95 \text{ eV}$. The ideality factor n is obtained from the slope of the plot $\ln J$ versus V through the relation given by equation (4.10) as,

$$n \equiv \left(\frac{q}{kT} \right) \frac{\partial V}{\partial (\ln J)}$$

The value of the ideality factor is found to be $n=2.76$. This value is different

from unity and is $n \geq 2$. It indicates that there is recombination of electrons and holes.

To summarize the above points, the J-V characteristic were studied applying thermionic emission theory. For small bias voltage the condition were only Ohmic i.e ($J \sim \frac{V}{d}$), and for the intermediate bias region, the condition were governed by injected-limited. i.e the depletion resistance was too low and the current flow increased high with the relation ($J \sim \exp(\frac{eV}{nkT})$, $n = 2.76$). For high bias region, the condition were dominated by space charge limited current and ohmic loss. i.e ($J = \frac{V^2}{d^2}$).

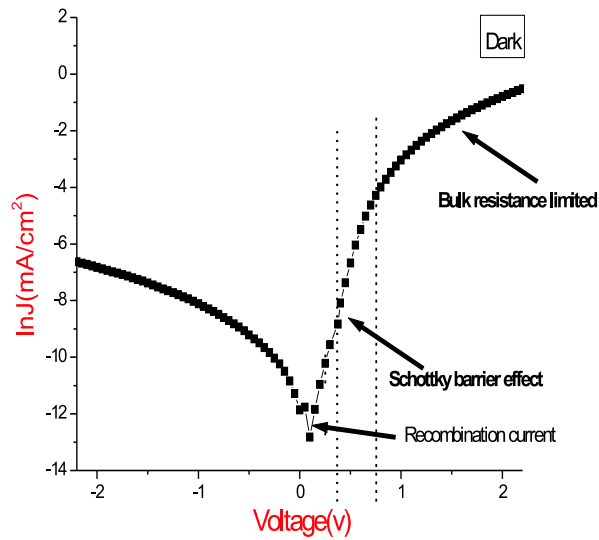


Figure 6.4: Semi-log plot of J-V characteristics under dark for D75/APFO-Green6/PCBM structure .

The overall parameters for the J-V curve under dark can be tabulated as follows.

parameters	J_o (mA/cm ²)	ϕ_b (eV)	γ	n
Value	1.0496×10^{-6}	0.95	642.5	2.76

Table 6.1: The summary of the photovoltaic parameters under dark

6.2.2 Photocurrent Density-Voltage (J_{ph} -V) Characteristics

In organic cells, however, the steps involved in the generation of photocurrents are (1) light absorption, (2) exciton creation, (3) exciton diffusion, (4) field-assisted carrier separation in the bulk or at the interface, (5) carrier transport, and (6) carrier delivery to external circuit that yield current. Figure 6.5 shows the photocurrent produced for a given intensity.

The J-V characteristics of this device under white light illumination (which is $9.5 \frac{mW}{cm^2}$) from the ITO side is given in Fig 6.5. According to the curve, the device shows photovoltaic behavior.

The intensity of light is measured at the sample position in the texture box. It is 1900lux. Using conversion factor where

$$1\text{Lux} = 5 \times 10^{-6} \text{W/cm}^2$$

We got 9.5mW/cm^2 . This is the intensity (input power per unit area) delivered to the device. The effective area of the device was $A_e = 0.042 \text{cm}^2$.

The short-circuit current and the open-circuit voltage of the cell ,from fig 6.5, are $J_{sc} = 0.076 \text{mA/cm}^2$ and $V_{oc} = 0.55 \text{V}$ respectively. The fill factor obtained was $FF=0.377$ and the power conversion efficiency calculated is found to be $\eta = 0.157\%$.

All parameters that we found under illumination in I-V curve are smmarized in table 6.2

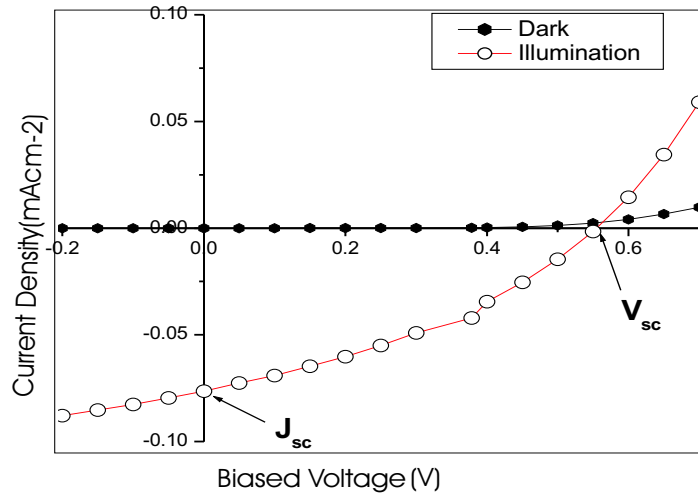


Figure 6.5: Photocurrent density-Voltage characteristic for D75/APFO-Green6/PCBM structure at the intensity $P_{in} = 9.5 \frac{mw}{cm^2}$.

parameters	$J_{sc} (mA/cm^2)$	$V_{oc} (V)$	FF	η
Value	0.076	0.55	0.377	0.157

Table 6.2: Extracted parameters in J-V characteristic under illumination.

The open circuit voltage **V_{oc}** obtained was comparable with the theory. Theoretically, the upper limit of V_{oc} for Donor/Acceptor cell is below the difference of the work function of the electrodes (in this case, $\phi_{Al} = 4.3eV$, $\phi_{ITO} = 4.9eV$), which is 0.6eV. It is also expected that V_{oc} should be bellow the difference of LUMO of the acceptor and HOMOs of the donors in addition to the differences of each LUMOs and at each HOMOs of the blended polymer. [i.e., $V_{oc} \leq |LUMO_A - HOMO_D| + \Delta LUMO + \Delta HOMO$ ($HOMO_{APFO-6} = 5.3eV$, $LUMO_{PCBM} \simeq 4eV$)]. Therefore, the $V_{oc} = 4.9eV - 4.3eV = 0.6eV$. Which is very close to the measured data 0.55 V. It is very good agreement with the theory. But, the small change is observed due to the insulating layer formed between metal and semiconductor contact and secondly

due to the charges in the localized state that weaken the electric field in the band gap.

The short-circuit current J_{sc} obtained here is $0.076 \frac{mA}{cm^2}$, which is small compared with the previous reported work (note: current reported by WMammo , $J_{sc} = 3.4 mA/cm^2$ [23], and Tesfaye.M $J_{sc} = 0.314 mA/cm^2$ [22]). Some of the factors for this small current are (i) there might be small photoinduced generation of excitons (electron hole pairs) due to small input intensity used (ii) the second factor is dissociation rate. Even though the dissociation rate in BHJ films is better due to the inter penetrating network, the driving force that need to dissociate the excitons at a site might not be enough to harvest more charges, (iii) the third factor is the mobility of free charge carriers. If one considers the generation rate and dissociation rate are sufficient, in most conjugated polymers the mobility is too slow (typically 10^{-3} to $10^{-6} cm^2/Vs$). Mostly the conjugated polymers have a high mobility for holes (in the undoped form) but it hinders the effective transfer of electrons to the electrodes. The inter penetrating networks and heterojunction lack high electron transfer rates which results in low efficiency and higher recombination rate due to high density of photo induce free charge carriers. In short, the photo generated charge carrier disappear because of recombination process. (iv) Traps, impurities, and disorder are also limits for the production of photo current.

The fill factor **FF** , which is an important parameter that determines the quality of the solar cell as a power source, is calculated by taking the ratio of the maximum out put power delivered to external circuit and the product of the short circuit current density J_{sc} and open circuit voltage V_{oc} (Refer figure 3.7a, 3.8, 6.4). from equn (3.10) as,

$$FF = \frac{P_{max}}{I_{sc} V_{oc}} = \frac{I_m V_m}{I_{sc} V_{oc}}$$

And taking the largest possible area as P_{max} (where $J_m = 0.042 mA$, $V_m = 0.378$,from the data) and the other experimental value $J_{sc} = 0.076 mA/cm^2$, $V_{oc} =$

0.56V, the value obtained was $FF=0.377$. It is above the minimum value which is 0.25 [7]. The obtained value indicates that the charge transport property of the material was good but all dissociated free charges were still unable to reach to the electrodes. This is because of bulk resistivities, large trap densities, poor contacts, short diffusion length, and the intrinsic nature of electron transfer rate of the material. These factors led to the field dependent and SCL effects. So, FF is also affected by series resistance. In short, it is load-dependent. This low transfer of free charge carriers to the electrode is mainly solved by using high electron affinity polymers. The power conversion efficiency η was calculated from equation (3.12) as

$$\eta(\%) = \frac{J_{sc} V_{oc}}{P_{in}} FF \times 100\%$$

From the measured data $J_{sc} = 0.076 \frac{mA}{cm^2}$, $V_{oc} = 0.55V$, $FF = 0.377$ and $P_{in} = 9.5 \frac{mW}{cm^2}$. The efficiency obtained was $\eta = 0.157$. This small value is due to less current production and less photon conversion factor. However, it is better result compare to the previous reported work (Tesfaye.M: $\eta = 0.107$ [22]) as it was desired to.

6.3 Cole-Cole Plot

The result of the impedance measurements as a function of frequency and applied voltage is given in Fig 6.6. The impedance Z_{real} , Z_{img} were recorded at a test frequency between (0.5kHz and 40.5 kHz) at a range of different biased voltages. All of the measurements at different biased voltages showed a single semicircle. The semicircles are displaced from the Z_{real} axis. This displacement is a series resistance R_c with a value $\sim 115\Omega$ (See fig 6.6).

From figure 6.6, one observes that the semicircles are bias dependent. The bulk resistance (**R**) is the diameters of these semicircles and corresponds to the resistance of the depletion region. Once **f** is known, **C** can be calculated from the

relation $Z_{\text{img}} = (\omega C)^{-1}$ where $\omega = 2\pi f$. This figure indicates that there is a unique **R** and **C** for each bias voltage V_b (See also table 6.3). So , **R** and **C** are bias voltage dependent.

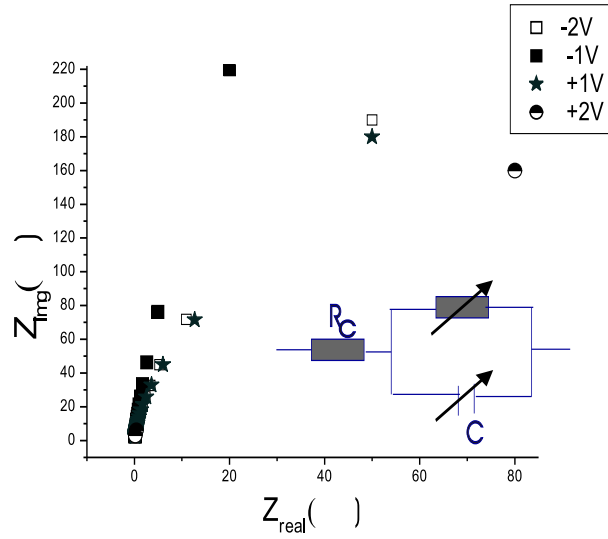


Figure 6.6: The complex impedance spectroscopy of the device shown in the figure 5.1 where Z is the impedance.

The values derived from the Cole-Cole plot is summarized in Table 6.3. The

parameters	$-V_b$	$R_c(\Omega)$	$R(k\Omega)$	$C(nF/cm^2)$
Value	-2	115	380	1.67
	-1	115	461	1.37
	1	115	359	1.77
	2	115	335	1.89

Table 6.3: Extracted parameters in the impedance measurement.

table confirm that the series resistance is constant while the bulk resistance and the capacitance of depletion region vary due to bias voltage, as expected.

The bulk resistance (R), decreases as the magnitude of the bias voltage increases, either for forward case or reverse case. At the forward bias the peak voltage +2V has low resistance and the lower intervals (-1V, 1V) has high resistances.

This is consistent with the dark J-V curve as shown in the figure 6.2. This figure shows high current was obtained for the peak voltage +2V and a few current is for -1 to 1Volt or consider the slope of the figure 6.2 in the given intervals. This slope is obtained as

$$R_{+2} = \left(\frac{\partial I}{\partial V} \right)^{-1} \bigg|_{+2} = 4.39$$

$$R_{[-1,1]} = \left(\frac{\partial I}{\partial V} \right)^{-1} \bigg|_{[-1,1]} = \infty$$

This slope results confirm the higher the resistance for lower intervals and less resistance at higher voltage +2V. One can also analyze figure 6.4 in the same fashion for this consistency.

The contact resistance R_c , is the conduction of the electrodes (Al) contact. It was almost constant as we see in table 6.3 and figure 6.6, too.

The contact resistance is, of course, large. This can be minimized either by increasing doping concentration or using low barrier height or both, according to Ohmic contact theory. For depletion resistance R , the same reasons can be coted from previous discussion why J_{sc} was too small, as they have ohmic relation.

Chapter 7

Conclusion

The photovoltaic properties of the Schottky diode of the device structure of Al/D75:APFO-G6:PCBM/PEDOT:PSS/ITO bulk hetero junction solar cell have been investigated.

The photovoltaic measurements show that the device has a photovoltaic property converting light energy to electrical energy. The short circuit current density and the open circuit voltage of the cell found to be $J_{sc} = 0.076 \text{ mA/cm}^2$ and $V_{oc} = 0.55 \text{ V}$, under illumination of intensity 9.5 mW/cm^2 . The small value of the current is due to the small generation of excitons, recombination, poor dissociation rate, poor mobility and the availability of some trap sites in the active area. The open circuit voltage V_{oc} was found as it was expected. The fill-factor and the efficiency obtained are **0.377** and **0.157**, respectively. These better results obtained by increasing the absorbance of the blended polymer.

The Cole-Cole plot shows single semicircles for each bias voltage. This shows the impedance characteristics of the device under test. In general, all parameters of impedance are depends on the bias voltage. The plot also shows as the bias voltage increases, the bulk resistance of the depletion region decreases. This is evident on the J-V curve, too. Further studies should be done to improve the device

performance by blending polyfluorene(APFO-Green6) with better and appropriate acceptor polymer in order to get high absorbance,high mobility rate, and high dissociation rate. So that high efficiency can be achieved.

Appendix

constants

- $K(\frac{eV}{k}) = 8.62 \exp(-05)$
- $K(\frac{1}{k}) = 1.38 \exp(-23)$
- $KT(eV) = 0.0259$
- $K(\frac{A}{Cm^2K^2}) = 1.38 \exp(-23)$
- $A(\frac{1}{k}) = 120$
- $T(k) = 300$
- $A * T^2 = 1.08 * 10^7 \frac{A}{Cm^2}$
- $\frac{KT}{q} = 0.0259V[4]$

Table A1

	Φ	E_F	HOMO	LUMO	E_g	Other properties
PEDOT:PSS	52				37	
ITO	49					
AF60G6			-53	-35	1.8	
PCBM				-4		$\mu_e=2 \times 10^7 m^2/Vs$
Al	43					

[*]

* = Collected

Table 7.1: some parameters of photovoltaic materials (in eV)

Table A2

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA
Li	Be											B	C	N	O
2.9	4.98											4.45	5.0	-	-
Na	Mg											Al	Si	P	S
2.75	3.66											4.28	4.85	-	-
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
2.30	2.87	3.5	4.33	4.3	4.5	4.1	4.5	5.0	5.15	4.65	4.33	4.2	5.0	3.75	5.9
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
2.16	2.59	3.1	4.05	4.3	4.6	-	4.71	4.98	5.12	4.26	4.22	4.12	4.42	4.55	4.95
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
2.14	2.7	3.5	3.9	4.25	4.55	4.96	4.83	5.27	5.65	5.1	4.49	3.84	4.25	4.22	-
Fr	Ra	Ac	Th	Pa	U										
-	-	-	3.4	-	3.63										
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
			2.9	-	3.2	-	2.7	2.5	3.1	3.0	-	-	-	-	-

[6,11]

Table 7.2: work function of the elements in poly-crystalline form. unit=eV.

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DECLARATION

I the under signed declare that the thesis is my original work, has not been presented for a degree in any other university and that all sources of material used for the thesis have been duly acknowledged.

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Signature: _____

This Thesis has been submitted for examination with my approval as university advisor.

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Signature: _____