Summary

In the beginning of this chapter, present global energy scenario and the potential of solar energy has been discussed in brief. To understand the reasons for the low contribution of solar photovoltaic for electricity production compared to its traditional fossil fuel counterpart, different generations of solar cells have been discussed, and their merits and demerits have been given. Maximum efficiencies obtained in various kinds of solar cells have been tabulated. Thereafter, basic differences between the traditional crystalline silicon cells and the emerging OPV cells have been discussed to understand, the requirements of OPV for enhancing the efficiency. The construction and working principle of OPV have been discussed in detail, to understand the fabrication requirements of OPV. Thereafter, motivation of polymer based solar cells has been given, and the advantages of OPV cells have been discussed. Finally aims and objectives of the thesis have been discussed, along with the brief results.
I-1: GLOBAL ENERGY SCENARIO AND POTENTIAL OF SOLAR ENERGY
The present global energy consumption has exceeded, 15 trillion watts (15 TW) mark, which is expected to increase by 50% up to 2030 [1, 2]. About 86% of this energy comes from fossil fuels. The continued use of fossil fuels have produced harmful effects, such as pollution that threatens human health and has increased greenhouse gases associated with global warming [3]. Moreover, the reserves of fossil fuels are progressively decreasing [4]. Prompt global action to solve the energy crisis is therefore needed.

To pursue such an action, we are urged to save energy and to use energy in more efficient ways. In addition, we are also forced to find alternative energy sources, the most convenient of which is solar energy for several reasons. The earth receives an inexhaustible power flow from the sun: 120,000 TW of electromagnetic radiation [1-2]. It is a quantity of energy far exceeding human needs. Covering 0.16% of the land on Earth with 10% efficient solar-conversion systems would provide 20 TW of power, nearly twice the world’s consumption rate of fossil energy, and the equivalent of 20,000 nuclear fission plants of 1 GW each.

Inspite of the immense potential of solar energy, photovoltaic (PV) provides only 0.01% of the world’s electricity generated [4]. To understand the reason of low contribution of photovoltaic, the different generations of solar cells and the advantages/disadvantages are discussed.

I-2: DIFFERENT SOLAR CELL TECHNOLOGIES
It is true that PV is becoming a part of solution to the growing energy challenge and an essential component of future global energy production. Solar cells are usually divided into three main categories called generations [5-10]. The first generation contains solar cells that are relatively expensive to produce, and have a high efficiency. The second generation contains types of solar cells that have a lower efficiency, but are cheaper to produce, such that the cost per watt is lower than in first generation cells. The term third generation is used about cells that are generally newer compared to other two generations. Most technologies in this generation are not yet commercial, but there is a lot of research going on in this area. The goal is to make third generation solar cells cheap to produce. Different generations of PV technologies, their cost effectiveness and efficiency limits are shown in figure 1.
I-2.1: FIRST GENERATION CELLS

First generation cells are made of single crystal silicon wafers (c-Si). A low band gap of 1.11 eV for silicon provides broad spectral absorption range. Laboratory scale cells have already achieved 25% efficiency. The greatest disadvantage of such cells is the expensive and energy intensive manufacturing technology which increases the generated power cost to ~4 $/W.

I-2.2: SECOND GENERATION CELLS

Second Generation solar cells are based on the use of thin-film deposits of semiconductors like amorphous silicon (a-Si), polycrystalline silicon (p-Si), cadmium telluride (CdTe), copper indium gallium diselenide (CIGS) etc. Use of thin-films reduces the mass of required material for cell design, which contributes greatly to reduced costs for thin film solar cells. Several second generation technologies/semiconductor materials are currently under investigation for mass production. For a given power rating, they do perform better at low light levels than crystalline panels. The greatest disadvantage of a-Si panels is that they are much less efficient per unit area (~10%) and are generally not suitable for roof installations. You would typically need nearly double the panel area for the same power output. Long term stability of amorphous silicon cells is also a matter of concern. Polycrystalline Si consists, solely of crystalline silicon grains (1mm), separated by grain boundaries and has low band gap ~ 1.1 eV. Charge carrier mobility in p-Si is one order of magnitude higher than a-Si, and shows greater stability under electric field and light-induced stress. Maximum efficiency of p-Si cells is ~20 %. However p-Si cells can be fragile and the cost is still high for widespread use. CdTe has band gap ~ 1.58 eV and laboratory scale efficiency of ~18 % has already been achieved. However an issue with
CdTe cells is the use and recycling of the extremely toxic metal cadmium, one of the six most toxic materials banned by European Union's RoHS (Restriction of Hazardous Substances) regulation. According to this, CdTe solar panel is not in RoHS compliance. CIGS alloy has efficiency ~20%, but it is worth noting that CIGS cells have complex heterojunction model, and difficult to prepare.

1.2.3: THIRD GENERATION CELLS

The third generation comprises of two categories viz. IIIa and IIIb. Category IIIa consists of novel approaches that strive to very high efficiencies. The IIIa technologies have theoretical maximum efficiencies well above the 31% limit (Shockley-Queisser limit) for single-junction devices. Hence, these high efficiency cells can afford higher costs and still show a favorable cost/watt balance. In the second type of third-generation device (IIIb), the goal is exactly opposite. A low cost/watt balance would be achieved via moderate efficiencies (15–20%), but at very low cost. This will require inexpensive semiconductor materials, packaging solutions, production processes (low-temperature atmospheric routes), high fabrication throughput, low investment into the production facility and a production-on-demand scenario. In figure 2, best laboratory efficiencies obtained for various materials and technologies has been illustrated.

Figure 2: Best research-cell efficiencies (source: http://www.nrel.gov/ncpv/)

The development in different PV technologies was possible only through sincere and aggressive efforts both at research and manufacturing technology levels. Table 1 show
some of the confirmed terrestrial cell and submodule efficiencies measured under global AM1.5 spectrum [10].

### Table 1: Confirmed terrestrial cell and submodule efficiencies [10]

<table>
<thead>
<tr>
<th>Classification</th>
<th>PCE (%)</th>
<th>Area (cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (crystalline)</td>
<td>25.0±0.5</td>
<td>4.00</td>
<td>0.706</td>
<td>42.7</td>
<td>82.8</td>
<td>11</td>
</tr>
<tr>
<td>Si (multicrystalline)</td>
<td>20.4±0.5</td>
<td>1.002</td>
<td>0.664</td>
<td>38.0</td>
<td>80.9</td>
<td>12</td>
</tr>
<tr>
<td>Si (thin film transfer)</td>
<td>20.1±0.4</td>
<td>242.6</td>
<td>0.682</td>
<td>38.14</td>
<td>77.4</td>
<td>13</td>
</tr>
<tr>
<td>Si (thin film submodule)</td>
<td>10.5±0.3</td>
<td>i94.0</td>
<td>0.492</td>
<td>29.7</td>
<td>72.1</td>
<td>14</td>
</tr>
<tr>
<td><strong>III–V Cells</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs (thin film)</td>
<td>28.8±0.9</td>
<td>0.992</td>
<td>1.122</td>
<td>29.68</td>
<td>86.5</td>
<td>15</td>
</tr>
<tr>
<td>GaAs (multicrystalline)</td>
<td>18.4±0.5</td>
<td>4.011</td>
<td>0.994</td>
<td>23.2</td>
<td>79.7</td>
<td>16</td>
</tr>
<tr>
<td>InP (crystalline)</td>
<td>22.1±0.7</td>
<td>4.02</td>
<td>0.878</td>
<td>29.5</td>
<td>85.4</td>
<td>17</td>
</tr>
<tr>
<td><strong>Thin Film Chalcogenide</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIGS (cell)</td>
<td>19.6±0.6</td>
<td>0.996</td>
<td>0.713</td>
<td>34.8</td>
<td>79.2</td>
<td>18</td>
</tr>
<tr>
<td>CIGS (submodule)</td>
<td>17.4±0.5</td>
<td>15.993</td>
<td>0.6815</td>
<td>33.84</td>
<td>75.5</td>
<td>19</td>
</tr>
<tr>
<td>CdTe (cell)</td>
<td>18.3±0.5</td>
<td>1.005</td>
<td>0.857</td>
<td>26.95</td>
<td>77.0</td>
<td>20</td>
</tr>
<tr>
<td><strong>Amorphous/Nanocrystalline Si</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (amorphous)</td>
<td>10.1±0.3</td>
<td>1.036</td>
<td>0.886</td>
<td>16.75</td>
<td>67.8</td>
<td>21</td>
</tr>
<tr>
<td>Si (nanocrystalline)</td>
<td>10.1±0.2</td>
<td>1.199</td>
<td>0.539</td>
<td>24.4</td>
<td>76.6</td>
<td>22</td>
</tr>
<tr>
<td><strong>Photochemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dye sensitized</td>
<td>11.9±0.4</td>
<td>1.005</td>
<td>0.744</td>
<td>22.47</td>
<td>71.2</td>
<td>23</td>
</tr>
<tr>
<td>Dye sensitized (submodule)</td>
<td>9.9±0.4</td>
<td>17.11</td>
<td>0.719</td>
<td>19.4</td>
<td>71.4</td>
<td>24</td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic thin-film</td>
<td>10.7±0.3</td>
<td>1.013</td>
<td>0.872</td>
<td>17.75</td>
<td>68.9</td>
<td>25</td>
</tr>
<tr>
<td>Organic (submodule)</td>
<td>6.8±0.2</td>
<td>395.9</td>
<td>0.798</td>
<td>13.50</td>
<td>62.8</td>
<td>26</td>
</tr>
</tbody>
</table>

Several promising technologies for these third-generation low-cost PVs are currently available and grouped under the appellation organic PVs (OPVs). They all have in common that at least one of the key functionalities for PV energy conversion is handled by organic semiconductor or conductor. Dye sensitized solar cells have achieved ~12% efficiency. However, in the last 15 years no significant increase in efficiency has been achieved. Moreover sealing of liquid electrode is still a challenge. Many small molecule organic materials CuPc, ZnPc etc. are also in contention to meet the future energy demands.
Use of conjugated polymers as the donor material is another emerging technology where steady increase in efficiency has been achieved in the last decade. Recently over 10% efficiency has been achieved by using a low band-gap polymer as donor and fullerene derivative as acceptor material. Due to the inherent differences in materials properties of polymer and their inorganic counterpart, the device structure of polymer solar cell (PSC) is significantly different than that of conventional silicon solar cells. It is therefore, necessary to understand the differences between the materials properties and the resultant changes required in polymer based solar cells.

I-3: CRYSTALLINE SILICON CELL VERSUS POLYMER BASED SOLAR CELLS

A solar cell converts photon energy into electrical power, and delivers to a load. A typical solar cell is commonly composed of a photoactive layer in the form of p-n junction sandwiched between two electrodes of differing work functions resulting in an internal electric field (figure 3) [27-28]. Inorganic semiconductors have low absorption coefficient and therefore photoactive layer of several micrometer thickness is required to absorb the solar radiation. Fortunately due to the high electron and hole mobility (typically in silicon $\mu_e = 1400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $\mu_h = 450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), few micrometer thick photoactive layer does not burden the charge transport in silicon solar cells [29]. Due to the high mobility the separated charges are able to reach their respective electrodes. In a crystalline inorganic semiconductor, with a 3-dimensional crystal lattice, the individual highest occupied molecular orbitals (HOMO’s) and lowest unoccupied molecular orbitals (LUMO’s) form a conduction band (CB) and a valence band (VB) respectively throughout the material. However in organic semiconductors the intermolecular forces are too weak to form 3-dimensional crystal lattices. Consequently the molecular LUMO’s and HOMO’s does not interact strongly enough to form a CB and VB. Thus charge transport proceeds by hopping between localized states, rather than transport within a band [27, 30-31]. This means that charge carrier mobility in organic and polymeric semiconductors are generally low compared to the inorganic semiconductors. The charge carrier mobility in organic semiconductors is several orders of magnitude less than those found in crystalline inorganic semiconductors. The hole and electron mobility in P3HT:PCBM blends are between $10^{-2}$-$10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [32-33]. The low mobility limits the feasible thicknesses of the photoactive layer to few hundred nanometers. Fortunately, most organic semiconductors
used in solar cells are very strong absorbers in the visible regime, as a result of which ~300 nm thick poly(3-hexylthiophene) (P3HT) layer is sufficient to absorb the solar radiation effectively [34-35].

The charge separation is more difficult in organic semiconductors due to the low dielectric constant. The exciton binding energy in polymer P3HT is 200-500 meV, which is roughly one order of magnitude greater than that in silicon [27, 29]. Due to the low exciton binding energy in silicon the exciton disassociates into electron and hole at room temperature (thermal energy at room temperature is ~26 meV), while in P3HT the thermal energy is not sufficient for exciton disassociation [29]. Due to the high exciton binding energy in P3HT the generated exciton diffuses up to its diffusion length (exciton diffusion length in P3HT is 10 nm) and finally lost by recombining through radiative or non-radiative pathways [36]. Since the exciton diffusion length in P3HT is ~10 nm, it is necessary that the donor-acceptor interface appears after every ~20 nm distance [36-37]. Even after charge separation at the interface the electron hole pair may remain bounded by coulomb attraction and can recombine if not separated.

I-4: CONSTRUCTION AND WORKING OF POLYMER SOLAR CELLS

Based on above discussion the ideal bulk-heterojunction photoactive layer morphology is shown in figure 4 [27, 37]. Typical organic solar cell structure in bi-layer as well as bulk-hetero-junction form using P3HT as the donor and PCBM as acceptor is shown in figure 5.
In the bilayer form, donor and acceptor are coated as different layers while in bulk heterojunction form, the donor and acceptor are thoroughly mixed before coating.

In spite of the fact that the ideal bulk-heterojunction morphology is difficult to obtain in practice, it has been shown that experimentally obtained morphologies can obtain device efficiency very close to that of ideal structure. The photoactive layer is sandwitched between two electrodes. The hole collecting electrode used is generally ITO (Indium Tin Oxide) and electron collecting electrode is aluminum. A 30-40 nm PEDOT: PSS (polyethylene dioxythiophene-polystyrene sulfonate) is coated on ITO coated glass substrates. PEDOT: PSS act as an exciton blocking layer, and also smoothes the rough ITO surface which critically decides the PSC performance. It is a doped conducting polymer which raises the work function of the ITO electrode in order to accept the holes. Also, indium was found to diffuse into the organic layer, which acts as trapping site for charge carriers. The diffusion of oxygen and indium into the organic layer is also minimized by using the hole conducting PEDOT: PSS layer [38-40]. Photoactive layer of appropriate thickness is then coated over the PEDOT: PSS layer. The top electrode (generally Al is used) is then coated by thermal evaporation technique. The same layer structure may be deposited on a transparent flexible substrate such as polyethylene terephthalate (PET) instead of glass. A similar structure with inverted polarity such as Glass/ITO/ Metal oxide/ photoactive blend layer/ PEDOT: PSS/ Ag are also being widely studied, mainly for the reason that no evaporated metal layers are required. This reduces the additional vacuum processing, and eventually the cost. In general, for a successful organic photovoltaic cell
four important processes have to be optimized to obtain a high conversion efficiency of solar energy into electrical energy [41-45]:

ABSORPTION OF LIGHT
A material with a band gap of 1.1 eV (1100 nm) and sufficient absorption coefficient is capable of absorbing 77% of the solar irradiation falling on the earth surface. However, the majority of semiconducting polymers have band gaps ~2 eV (620 nm), which limits the possible harvesting of solar photons to about 30%. Fortunately, the absorption coefficients of organic materials are as high as $10^5$ cm$^{-1}$, and therefore ~300 nm P3HT:PCBM blend layer thickness (with a back reflective contact) is enough to absorb most of the photons. When light reaches the photoactive layer of device through the ITO electrode (figure 5 and 6), the conjugated polymer absorbs photons with energy higher than its band-gap, and excitons (bound couples of electrons and holes) are produced. In organic materials, the band gap is referred as the difference between the LUMO and HOMO. Extra energy of photon would be wasted in the form of heat. In addition to having a small band gap an efficient solar cell should have a wide absorption spectrum to create as many pairs as possible. However, low band-gap of the active material will have some bearing on the open circuit voltage. Semiconducting polymers have a large absorption coefficient and therefore a thin active layer is required for effective absorption. In general thicker active layer would burden the charge transport and nearly 100 nm photoactive layers gives maximum efficiency.

FREE CHARGE CARRIER GENERATION AND SEPARATION OF OPPOSITE CHARGES
Upon light absorption in the polymer (donor), electrons jump to the LUMO level leaving a hole in the HOMO level (figure 6). Such an electron hole pair is still bounded together due to the coulomb attraction, known as singlet exciton. The excited electron has generally very short lifetime and they can go back to the ground state through luminescence or
photon emission. Therefore, luminescence is a loss mechanism in photovoltaic cells. In P3HT the thermal energy is not sufficient for exciton disassociation (thermal energy is ~26 meV, while exciton binding energy in P3HT is 200-500 meV). If these excitons are not disassociated, they diffuse up to its diffusion length, and finally lost by recombining through radiative or non-radiative pathways. In such materials charge separation can be achieved at the interface between the donor and acceptor material if the difference between the ionization potential of donor and the electron affinity of the acceptor is larger than the exciton binding energy.

Due to difference in LUMO levels (500 meV) of P3HT and PCBM, a high electric field of the order of ~10^6–10^7 V/m is created at the interface and therefore the generated excitons are separated at the donor-acceptor interface. Since the exciton diffusion length in P3HT is ~10 nm, it is therefore necessary that the donor-acceptor interface appears after every 20 nm distance. However, due to the short exciton diffusion length compared to the photoactive layer thickness, interfacial area and thus the exciton dissociation efficiency are limited in bilayer OSC. Higher interfacial areas and thus improved exciton dissociation efficiencies can be achieved in bulk heterojunctions where both the electron donor and electron acceptor are blended together before spin coating. Generally, either two conjugated polymers as donor and acceptor or one conjugated polymer as donor and other non-polymeric material like fullerene derivative, non-fullerene based oligomers, inorganic nanoparticles etc. are used as acceptor. Since the entropy of mixing for the polymers is generally low, solid polymer blends tend to phase-separate and form a
distributed bulk heterojunction. If the phase separation is 20 nm the generated excitons will find donor-acceptor interface at every 10 nm, thus minimizing the loss due to recombination.

**CHARGE TRANSPORT**

In bulk heterojunction solar cell, the electron donor and acceptor are mixed in the solution before spin coating. Percolating pathways for the hole and electron transporting phase connecting to proper electrodes is needed so that the separated charge carriers can reach their corresponding electrodes. The separated electrons and holes are transported along the acceptor and donor networks towards the metal electrodes due to the induced electric field arising from the different work functions of the two electrodes. Thus with increasing thickness the induced electric field between the two electrodes decreases, which in turn burdens the charge transport. Also such percolating channels should have enhanced and comparable mobility. A large difference in charge mobility between the two blend components results in space charge limited current (SCLC) effect.

**CHARGE COLLECTION**

The transported charges are then collected by the electrodes to form photocurrent and photo-voltage. For effective collection of charges at the electrode both the phases in the blend should be connected to proper electrodes in order to form ohmic contacts, in addition to being non-reactive with the adjacent layers. Also the electrode energy levels should match properly with the organic materials used for effective extraction of the charges. A transparent conducting electrode is required as the anode and proper reflective electrode is required as cathode.

**I-5: POLYMER BASED SOLAR CELLS CATEGORIES AND INVESTIGATED MATERIALS**

The solar cell based on organic materials can be categorized into various groups based on the material used in a cell. These are, small molecule based solar cells; polymer: polymer cells; polymer: fullerene derivative cells; polymer: non-fullerene based oligomer cells; polymer: inorganic nanoparticle cells etc. Few of the better performing device structures and parameters for the devices containing polymer as donor are tabulated in table 2. It can be seen that 10.3% efficiency has already been obtained by using polymer as donor. In the present work, a polymer is used as donor and fullerene derivative and TiO\textsubscript{2} nanoparticles are used as acceptor.
Table 2: Device structure and parameter of best performing OPV cells

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF%</th>
<th>PCE%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PEDOT:PSS/PCPDTBT:PCBM/LiF/Al</td>
<td>0.7538</td>
<td>17.46</td>
<td>69.99</td>
<td>9.214</td>
<td>46</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/PCPDTBT:CdSe/LiF/Al</td>
<td>0.674</td>
<td>9.015</td>
<td>51.47</td>
<td>3.13</td>
<td>47</td>
</tr>
<tr>
<td>Al/Si/SiNRs/Spiro-OMeTAD/PH500/Ag-grid</td>
<td>0.54</td>
<td>30.9</td>
<td>58.8</td>
<td>10.3</td>
<td>48</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/Si nanowire/Ti/Ag</td>
<td>0.532</td>
<td>24.24</td>
<td>65.1</td>
<td>8.40</td>
<td>49</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT-CdS/BCP/Mg/Ag</td>
<td>1.1</td>
<td>10.9</td>
<td>35.0</td>
<td>4.1</td>
<td>50</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>0.63</td>
<td>9.5</td>
<td>68</td>
<td>5.0</td>
<td>35</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/PTB7:PCBM/Al</td>
<td>0.74</td>
<td>14.5</td>
<td>0.69</td>
<td>7.4</td>
<td>51</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM (1:0.8)/Al</td>
<td>0.63</td>
<td>9.5</td>
<td>0.68</td>
<td>5.0</td>
<td>35</td>
</tr>
</tbody>
</table>

There are a number of polymers used as donor and fullerene derivatives used as acceptor materials and are currently under investigation. Few of them are listed below in figure 7. MEH-PPV and MDMO-PPV are comparatively older polymers while P3HT, PCPDTBT, PTBT etc. are newer ones. The material under investigation in the present thesis is P3HT. It has a bandgap of 1.9 eV and a maximum PCE of 5.0% have been achieved by blending it with fullerene derivative PCBM. There are many report of P3HT solar cells blended with other acceptor polymers and inorganic nanoparticles also.

![Figure 7: Several solution processible conjugated polymers and fullerene derivatives used in organic solar cells. Upper row: the p-type hole-conducting donor polymers P3HT, MDMO-PPV, MEH-PPV, PCPDTBT, lower row: the fullerene derivatives PCBM with different substitution levels.](image-url)
Chapter-I: General Introduction

PCPDTBT, Lower row: the electron-conducting acceptor fullerene derivatives, [61] PCBM, [71] PCBM, and [84] PCBM

I-6: MOTIVATION FOR POLYMER BASED SOLAR CELL

After the major breakthrough in solar cell performance in 1986 when Tang et al. discovered that much higher efficiencies can be attained when an electron donor and an electron acceptor are brought together in one cell, the first polymer/C-60 based cell was developed in 1993 by Sariciftci et al. [52-53]. In 2005 efficiency over 5% was reported by Heeger et al. [35]. Recently, over 10% efficiency has been reported for polymer based solar cells [48]. It is clear that polymer based solar cells have developed from an inefficient light-harvesting device with almost no lifetime to a device that may be introduced to the commercial market within a few years. Polymer based bulk-heterojunction solar cell have attracted considerable attention due to their unique advantages [54-57]. Few of them are mentioned below.

a) Low-cost materials;

b) Easy manufacture of devices, due to simple solution processibility at low temperature without vacuum;

c) High absorption coefficient of organic materials;

d) Large area coating potential;

e) Environment friendliness;

f) The potential to be manufactured in a roll to roll continuous printing process;

g) Light weight, and flexibility;

h) The possibility of chemically manipulating the material properties of polymers.

Inspite of the advantages of the PSC there are a number of challenges for industrial production [58-60]. Few of them are listed below.

a) Narrow absorption band of polymers;

b) Low dielectric constant;

c) Large exciton binding energy;

d) Low charge carrier mobility;

e) Relatively unstable compared to their inorganic counterpart

f) Sensitive to photochemical degradation;

g) Polymers decompose under excessive heat and have too large molar mass for evaporation;

h) Challenge to control the nanoscale morphology etc.
Because of above limitations, efficiency of polymer based solar cell is limited to around 10%. In the present work, we have mainly concentrated on the morphology control of bulk-heterojunction. The commonly coating techniques used to deposit the photoactive layers are spin-coating, doctor blading, screen printing, inkjet printing etc. Vacuum evaporation technique is mostly used to coat the top electrode [58-60].

I-7: OPEN AREAS FOR INVESTIGATION, AIMS AND OUTLINE OF THE THESIS

From the above discussion it is clear that developing new methods to control nanoscale morphology of bulk-heterojunction and better understanding of the morphology evolution thereof are the few key steps to designing structures in order to enhance the performance of polymer based solar cells. We have therefore concentrated towards developing new methods for controlling the morphology of the bulk-heterojunction and in understanding the basic process leading to a particular phase separation in order to prepare tailor made morphology.

The first part of Chapter II aims to give a brief insight into the important characteristics solar cell parameters and links between them. In the present work, spin coating technique has been used for active layer deposition while top electrode is deposited by thermal evaporation deposition method. Details of the methods have been discussed. In the second part, different characterization techniques used for the studies have been discussed. In the end methodology for device fabrication has been given. The subsequent three chapters’ deals with morphology control of bulk-heterojunction through different methods. Each of them begins with a survey of characteristic parameters of already reported devices and pointing out specific advantages and encountered problems. In chapter III results of the study to control P3HT:PCBM morphology by controlling the ambient during spin coating has been given. Details of the modeling study to explain the PCBM aggregation in the blend films during spin coating has been discussed. In chapter IV, P3HT:TiO₂ morphology control using mixed solvents has been discussed. In addition, morphology control of the blends by thermal annealing and using multiple coatings has also been discussed. Nanocrystalline TiO₂ was synthesized by combustion method. Results have been discussed in this chapter. In chapter V, P3HT:PCBM morphology control by thermal annealing has been discussed. Also, the effect of using a titanium sub-
oxide layer between the P3HT:PCBM blend and Al electrode to enhance the quality of interface has been discussed. The following findings may be of particular interest.

We have shown that the solvent evaporation rate and hence the nano-scale morphology of P3HT:PCBM blend films can be finely controlled by controlling the ambient during spin coating, in order to improve the solar cell performance. Modeling results supported by the experimental evidences show that the phase separation in P3HT:PCBM blend is due to diffusion of PCBM (initiated due to the finite solubility limit of PCBM in the solvent) towards a nucleation site in the drying film during spin coating.

We have shown why specific mixed solvent composition leads to appropriate film formation of composite (polymer: inorganic nanoparticle) during spin coating by using mixed solvents. For the formation of finely intermixed blend films, good solvents used for both the solute components must maintain a constant ratio throughout the drying process. If the content of any one solvent decreases in the course of film solidification, larger aggregates of individual phases are obtained. By knowing the evaporation rates of the component solvents and their Hansen solubility parameters, exact quantities of mixed solvents for appropriate film formation can be predicted through simulation.

We have shown that due to thermal annealing of P3HT:PCBM blends, formation of pure phases of the component takes place. We have shown that effect of thermal annealing on PCBM aggregation is in accordance with Ostwald ripening, which causes the dissolution of smaller particles over time and redeposit into larger crystals. Upon thermal annealing interconnecting channels of each phase are formed. Upon annealing for longer periods large aggregates of PCBM are formed, at the micrometer scale, the dimension of which increases with annealing temperature and time. Using a thin titanium sub-oxide layer between P3HT:PCBM active layer and Al electrode leads to the improvement in device performance due to the formation of low ohmic and highly charge selective contact. Interface between the photoactive layer and titanium sub-oxide layer is important for device performance. Annealing can improve the interface.
REFERENCES:


Chapter-I: General Introduction


