Polymeric Solar Cells: Basics And Methods To Improve Morphology Of Spin Coated Films

Adhirath S. Wagh
Final Year B.Tech
Department of Polymer
Engineering and
Technology

ABSTRACT

The following review paper contains the basic principle behind working of the solar cell. The present day PSC are made of electron donating (conjugated polymer) and electron accepting molecules(usually fullerene and its derivatives). The concept of the bulk heterojunction has resulted into great improvement in the efficiency of the PSC. In order to control the morphology and to improve the efficiency of the PSC processes like thermal annealing, solvent annealing and choice different solvents are being adopted by researchers. The reasearch carried out by Yang and D Chirvase are described in this paper.

1. INTRODUCTION

There has been a tremendous increase in the demand for energy in the last 30 or 40 years. In the year 2008 the worlwide energy consumption was around 15TW [1] and it will rise approximately to 30TW in the year 2050 [2]. The rapidly increasing energy demand and population has widened the gap between the supply and demand of energy. Use of the fossil fuels for energy production is posing a threat to the envronment and also they are becoming less day by day. The requirement of a clean and cheap energy resource is necessary. Sun is the biggest source of energy to the earth. The first efficient solar cell was reported at the Bells Lab in 1954 and from the mid 1960's to the mid of 1980's there was focus on improving the efficiency to produce more power. Crystalline silicon is used in 90% of the photovoltaics used today. The other materials used are cadmium telluride (CdTe), copper indium gallium arsenide(CIGS), etc. However only about 0.1% of the total electricity generated in the world is supplied from PV installations. The primary reasons are the high cost of raw materials and processing, and the difficulty in fabrication an installation of the PV systems. Today, solar cells based on organic molecules and polymers are considered as a promising alternatives to the inorganic counterparts. Some of the advantages of the organic organic PV's are the low fabrication cost of the large area devices, loe specific weight, mechanical flexibity and easy tunability of chemical peoprties of the organic molecules. Inspite of these advantages the polymer solar cells (PSC) aren't commercial yet due to there low efficiencies. PSC's having efficiences 4-5% have been reported. It is widely believed that the effciency barrier of 10% is to be crossed for commercialisation of PSC's. [M.C. Scharber, 2006].

2. WHAT ARE POLYMER SOLAR CELLS?

A polymeric solar cell is a device using a conjugated polymer (electron donating component) and/or a acceptor molecule as the photoactive layer of the cell. The active componenets are solution processible, and can be spin coated, printed, roll to roll printing or vacuum evaporated on a glass or a plastic substrate precoated with a transperent elctrode, usually ITO (indium tin oxide). The four basic steps in the working of the polymer solar cell are:

- Absorption of light
- Charge transfer and separation of the opposite charges
- Charge transport

- Charge collection. [Rene Janssen]

2.1 Device architectuures

2.1.1 Single layer Devices

The simplest used organic semiconductor device is the metal–insulator-metal (MIM) tunnel diode with metal electrodes of asymmetrical workfunction. Under forward bias, holes from the high workfunction metal and electrons from the low workfunction metal are injected into a thin film of a single-component organic semiconductor. Because of the asymmetry of the work function of the cathode and the anode, forward bias currents for a single carrier type material are orders of magnitude larger than reverse bias currents at low voltages. Improvement was reported for the devices using a Schottky contact that forms between the conjugated polymer and the metal electrode. [C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, 2001]. However, only photoexcitations generated close to the depletion region W of the Schottky contact may lead to separated charge carriers as a result of the limited exciton diffusion length. Therefore, only a small region denoted as the active zone contributes to photocurrent generation, as illustrated in Fig. 1. [Harald Hoppe, N. Serdar Sariciftci, 2007]

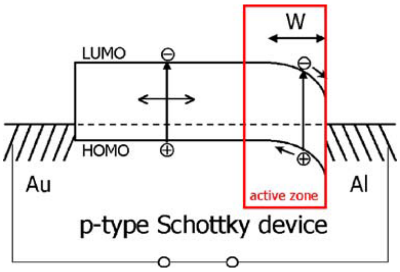
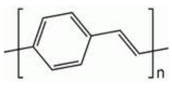


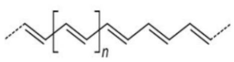
Fig. 1. The active zone for the single layer device [Harald Hoppe, N. Serdar Sariciftci, 2007]

2.2.2 Bilayer devices

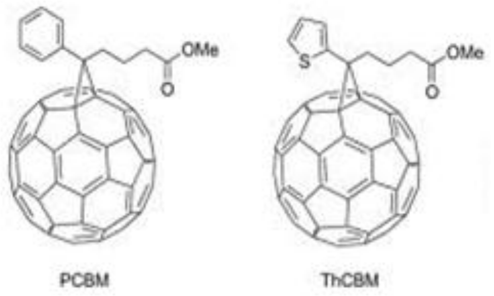
These devices use the concept of donor and acceptor molecules. When light is incident on the PSC, it results in the formation of excitons (Coloumbically bound electron hole pair). In a two layer device these excitons can be generated in either layer. These excitons can diffuse towards the interface where they dissociate into free electron and free hole. The dissociation is said to be efficient at the interface because of the materials have different electron affinities and ionization potentials, where electron is accepted by the material having the more electron affinity and the hole by the material with a low ionization potential. However the exciton diffusion lengths happen to be at least 10 times (5 to 20nm) smaller than the optical absorption depth, thus limiting the efficiency of charge collection [J.J.M. Halls, C.A. Walsh, 1995]. Different types of donors and acceptors are shown in Fig. 2. Inorganic semiconductors generally have a high dielectric constant and a low exciton binding energy (for GaAs the exciton binding energy is 4 meV). Hence, the thermal energy at room temperature (kBT = 0.025 eV) is sufficient to dissociate the exciton created by absorption of a photon into a positive and negative charge carrier. The formed electrons and holes are easily transported as a result of the high mobility of the charge carriers and the internal field of the p-n junction. Organic materials have a lower dielectric constant and the exciton binding energy is larger than for inorganic semiconductors [Rene Janssen].

When the donor molecule absorbs light, an electron in the HOMO is excited and is transferred to the LUMO of the acceptor molecule.





poly(p-phenelynevinylene)
polyacetylene



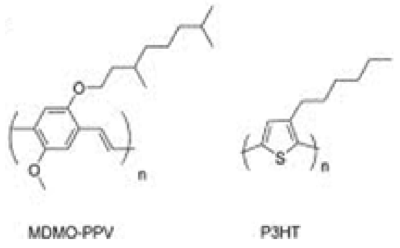


Fig. 2. Structures of electron acceptors (PCBM, ThCBM) and electron donors (Polyacetylene, PPV, P3HT, MDMO-PPV)

As mentioned above the driving force for the electron transfer is the difference in the ionization potential of the donor and the electron affinity of the acceptor, minus the Coloumb correlations. As a result of photoinduced charge transfer the, positively charged hole remains on the donor and the acceptor gets a unit negative charge. This photoinduced charge transfer between conjugated polymers as donor and fullerenes as acceptor takes place within less than 50 fs. Since all competing processes like photoluminescence (~ns) and back transfer and thus recombination of the charge (~μs) take place on a much larger timescale, the charge separation process is highly efficient and metastable [Harald Hoppe, N. Serdar Sariciftci, 2007]. This process is as shown in the Fig. 3.

[Rene Janssen].

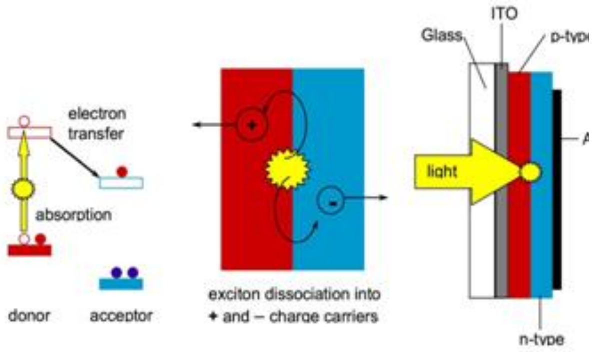


Fig. 3. Schematic diagram of working of PSC

After the separation of the charges it is necessary to transport the charges to the electrodes. Thus there is requirement of percolation path. In bilayer devices, charge carriers can be dissociated at the donor-acceptor material heterojunction. Only excitons generated within diffusion distance to the interface can contribute to the photocurrent. The donor carries the holes whereas the acceptor carries the electrons. However there are great chances of recombination of charges and thus a decrease in the efficiency of the PSC.

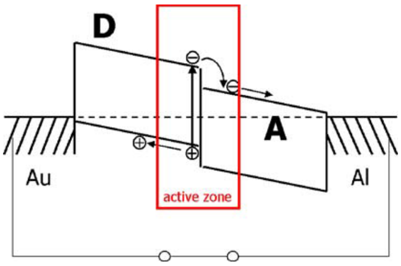


Fig. 4 active zone for the bilayer device

2.2.3 Bulk heterojunction device (BHJ)

The improvement in the transport of the separated charges to the respective electrodes was reported for bulk heterojunction devices. In the BHJ the donor and the acceptor molecules are intimately blended, so that the excitons do not need to travel much to reach to the heterojunctions. Thus this decreases the probability of the recombination and in turn improving the efficiency of the cell. Conseqeuntly the BHJ concept led to the improvement in the photocurrent and there are reports of upto 5% power conversion efficiencies with these type of cells [Harald Hoppe, N. Serdar Sariciftci, 2007]. The following digram (Fig. 5)[Rene Janssen] will give the idea of the BHJ.

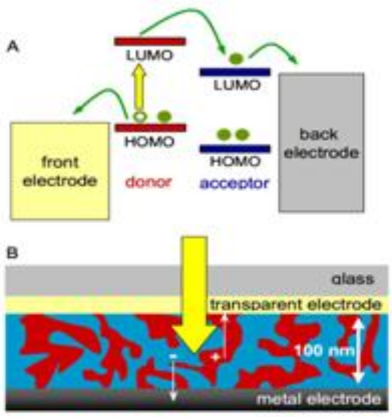


Fig. 5 Bulk heterojunction

Along with the efficient charge separation, this type of morphology also leads to the formation of good percolation paths for the electrons and the holes to travel to the respective electrodes. Since the polymer solar cells are solution processed, mostly spin coated, the morphology of the BHJ strongly depends on the type of solvent and the acceptor-donor combination used.

We will be focusing on comparing the morphologies reported for different solvents like xylene, o-dichlorobenzene (o-DCB), chlorobenzene,THF mainly for P3HT/PCBM and MEH-PPV/ buckminsterfullerene(C_{60}) systems. We will also lookat the ways of improving the nanomorphology of the same.

3. MEH-PPV/C60: Morphology dependence on solvent and the C60 composition

It has recently been elucidated that the conformation of polymer chains can be controlled by the selection of the organic solvents, by the concentration of the polymer solution, and by the rotational speed of the spin-casting process. The resulting polymer morphology in the thin film plays an important role in controlling both the material and the device characteristics, such as the absorption and emission spectra, the device turn-on voltage, and the energy barrier height between the polymer/metal interfaces. Yang et *al* studied the morphology of the MEH-PPV/C60 system using THF(non aromatic solvent) and xylene and o-DCB (aromatic solvents). He has, for pure MEH-PPV device reported that the device made with THF always has a smaller photocurrent than the device made with a similar film thickness but processed with xylene. On blending with the C60, the photocurrent of the composite increases rapidly. Also with the change in the concentration of the C60 component the photocurrent of the device increases (refer Fig.6). This enhanced photo response was attributed to the effective separation of the charge carriers by photoinduced charge transfer process. [Jie Liu, Yijian Shi, and Yang Yang, 2001].

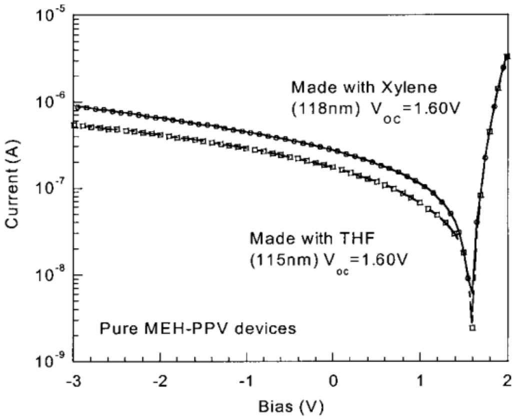


Fig. 6 (a)

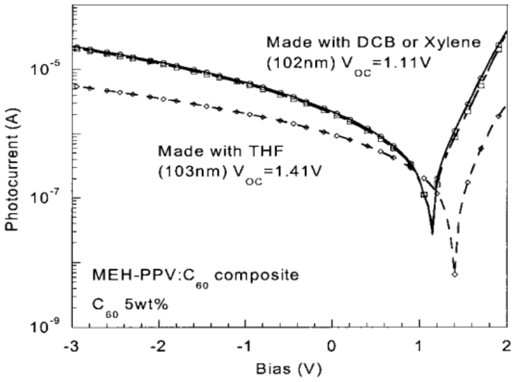


Fig. 6 (b)

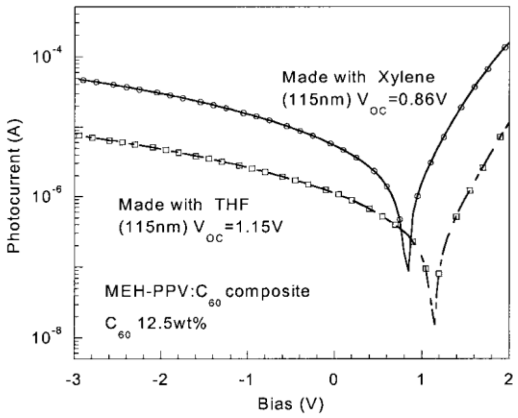


Fig. 6 (c)

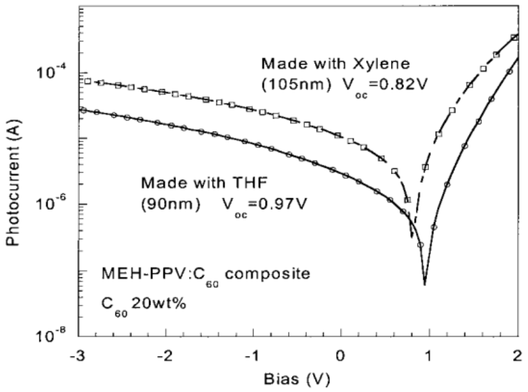


Fig. 6 (d)

Fig. 6 Graphs for MEH-PPV/C60 system with different solvents and different concentrations of C60

The above graphs were reported by Yang and associates.

Solvation-induced morphology results into different arrangements of polymer chains. For aromatic solvents, such as xylene, the solvent molecules preferentially solvate the p-electron conjugated segments and result in a conformation that has better $\pi - \pi$ stacking and subsequently better electrical conduction. On the other hand, non-aromatic solvents, such as THF, preferentially solvate the non-conjugated segments of the polymer and result in a polymer conformation with a lower electrical conductivity [Y. Shi, J. Liu, Y. Yang, 2000], [J. Liu, Y, Shi, L. Ma, Y. Yang, 2001].

Yang et al suggested that due to the solvation effect, a photovoltaic device made from an MEH-PPV:C60 composite using xylene or DCB should have a better (more direct) contact between the p-electron conjugated segments of the polymer and the C60 molecules. When using THF, the possibility of direct contact between the conjugated segments of MEH-PPV and the C60 molecules is dramatically reduced by the presence of non-conductive side-chain groups between them. Since the side-chain groups have a dimension of several angstroms, which is comparable to the diffusion length of the charge carriers, it is most likely that both the intrinsic forward transfer process and the charge diffusion process are hindered in films fabricated with THF or chloroform. The incorporation of C60 into MEH-PPV can lower the open-circuit voltage in comparison to the pure MEH-PPV device because part of the available difference in potential energy is taken up internally during the CT within the MEH-PPV and C60 composite. [Jie Liu, Yijian Shi, and Yang Yang, 2001].

The following are AFM of MEH-PPV/C60 system, taken from [Jie Liu, Yijian Shi, and Yang Yang, 2001].

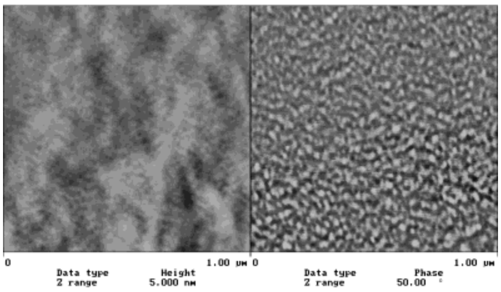


Fig. 7 (a)

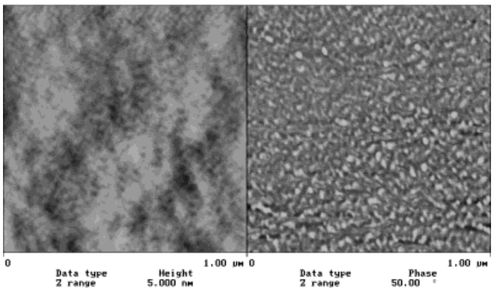


Fig. 7 (b)

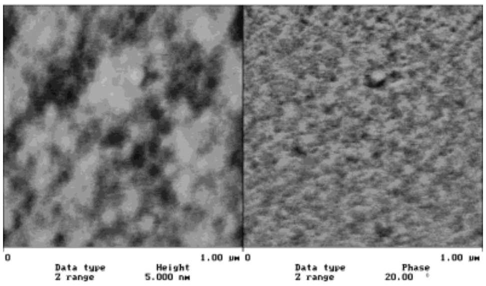


Fig. 7 (c)

Fig. 7 AFM of MEH-PPV/C60(20 wt%) with (a) Xylene, (b) o-DCB, (c) THF

4. Thermal annealing of P3HT:PCBM system

The process of thermal annealing has been demonstrated to considerably increase the efficiency of P3HT based light emitting diodes and solar cells. As a result of heating, the morphological structure of the organic active layer can be improved by reducing the free volume and the density of defects at the interface during evaporation of the solvent and by enhancing interchain interactions. In a bilayer structure, interdiffusion between the donor and the acceptor was observed. In this way, the acceptor molecule may enter the exciton diffusion radius of the polymer, resulting in a highly efficient charge separation. Thermal annealing of polymer–polymer donor–acceptor blends with subsequent exposure to solvent vapour led to a significant increase of thecharge carrier photogeneration efficiency [D Chirvase, J Parisi, J C Hummelen and V Dyakonov, 2004].

4.1. Improvement in absorption

As a result of enhanced P3HT crystallization upon thermal annealing, the P3HT absorption shows significant improvement. The effect of thermal annealing on polymer crystallization is discussed in the following section. Fig. 8 shows the UV-Vis absorption spectra obtained for P3HT : PCBM thin films (thickness 80 nm; PCBM conc. = 50 wt%) before and after annealing at different temperatures (70, 110, 130 and 150 uC for

10 min).45 The absorption enhancement seems to saturate at 110 uC after which increasing the annealing temperature has no positive effect on absorbance [Gang Li, Vishal Shrotriya, Yan Yao, Jinsong Huanga and Yang Yang, 2007]

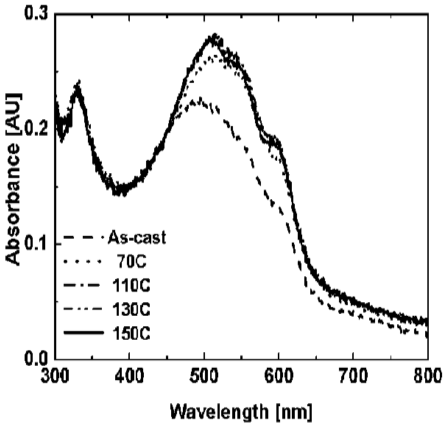
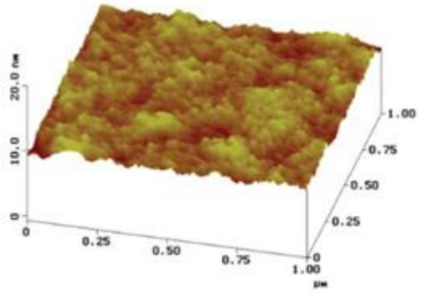


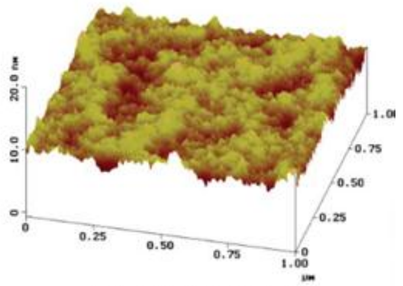
Fig. 8 UV-Vis absorption spectra obtained for P3HT : PCBM thin films (80 nm, with PCBM conc. = 50 wt%) before and after annealing at different temperatures.

4.2 Changes in Morphology

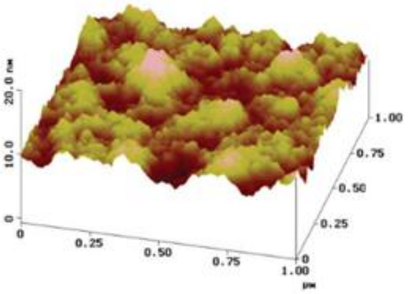
The BHJ structure basically consists of 3-D interpenetrating networks of donor and acceptor materials. The morphology of the polymer blend layer and the metal/polymer interface properties play important roles in determining device performance. The surface of the as-cast film is very smooth with rms roughness (drms) of 0.377 nm. After undergoing thermal treatment the drms first increases up to 110 C and then decreases. The film texture also changes after annealing. The film annealed at 110 C shows a much coarser texture with broad hill-like features compared to the other films. Higher film roughness gives higher device efficiency. However, the surface area of the roughest film is only about 0.1% more than that of a completely flat surface. Therefore the increased surface roughness probably does not play any direct role in efficiency improvement. Instead, higher surface roughness is more likely a signature of annealing enhanced ordered structure formation in the polymer film. Higher absorption and increase in the charge carrier mobility due to ordering are the most likely reasons for efficiency enhancement. (fig .9)



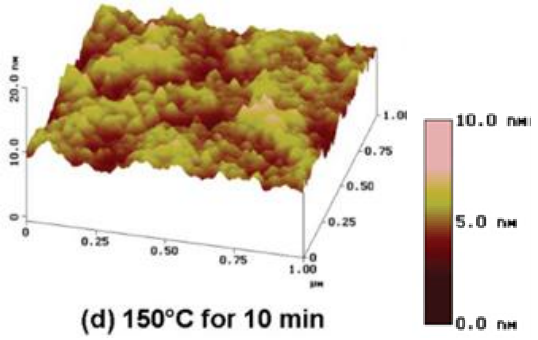
(a) As-cast



(b) 70°C for 10 min



(c) 110°C for 10 min



(d) 150°C for 10 min

Fig. 9 AFM height images of the P3HT : PCBM surface (a) before annealing, and after annealing at (b) 70 ^{0}C, (c) 110 ^{0}C, and (d) 150 ^{0}C for 10 min

5. Solvent annealing of P3HT/PCBM system

Instead of recovering the RR-P3HT crystallinity (ordering) which is lost during the fast solvent removing (fast spin-coating) process, this approach aims at maintaining the polymer ordering during the film formation stage. Reducing the solvent removal speed, results in self-organization in polymer chains by controlling the active polymer layer growth rate from solution to the solid state. The intrinsic polymer selforganization capability gives higher absorption, higher carrier mobility, and balanced carrier transport.

5.1 *Effect on absorption spectrum* [Gang Li, Vishal Shrotriya, Yan Yao, Jinsong Huanga and Yang Yang, 2007]

The absorption in the red region for the slow-grown film is significantly stronger compared to that of the fast-grown film. The three vibronic absorption features are the most prominent reported in the literature, indicating strong interchain–interlayer interactions of RR-P3HT chains, as well as well-maintained polymer ordering in the blend films. After annealing at 110 uC for 20 min, the absorbance of the fast-grown film shows a significant increase and the vibronic features become clearer, indicating a partial recovery of ordering. For the slow-grown film, the absorption spectra show no significant differences before and after thermal annealing.

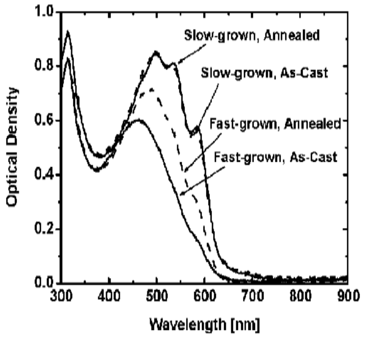
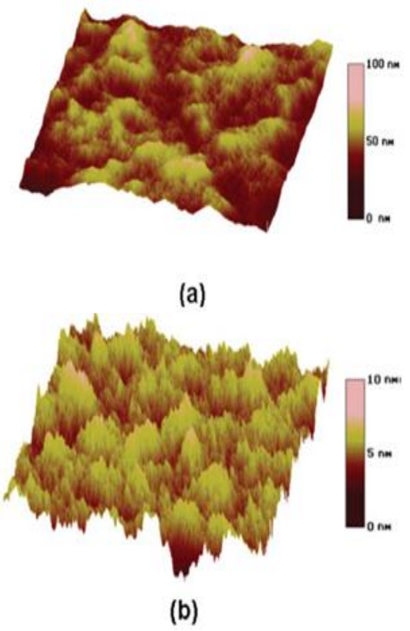


Fig. 10 UV-Vis absorption spectra for slow- and fast-grown P3HT:PCBM films, before and after thermal annealing at 110 uC for 20 minutes.

5.2 *Effect on the morphology [*Gang Li, Vishal Shrotriya, Yan Yao, Jinsong Huanga and Yang Yang,2007]

The AFM height and phase images (Fig. 11) show that the slow-grown film (a) has drms 9.5 nm, whereas the fast-grown film (b) has a very smooth surface with drms 0.87 nm. The peak to valley height of the slow grown film is about 100 nm, corresponding to 50% of the mean thickness (210 nm). The phase image of the fast-grown film (d) shows coarse chain-like (fibrillar) features running across the surface. These fibrillar features are assigned to the domains of pure P3HT crystallites. The region between these features is a disorder zone which harbors structural defects like chain ends and folds as wells as tie segments.54 PCBM molecules suppress the formation of P3HT crystallites in the fast-grown films and most of the film consists of mixed domains which are amorphous in nature. For the slow-grown film (c), the crystalline domains of pure P3HT chains are denser. They have a strong tendency to form an interconnecting network and are distributed more uniformly throughout the film. The separation distance between the features is also less, which suggests tighter packing of P3HT crystallites in the slow-grown film. The separation distance between surface features in the slow-grown film (~28 nm) is smaller than that in the fast-grown film (~55 nm). P3HT chains get more time to self-organize into a more ordered structure during very slow growth. As a result, the regions of mixed P3HT/PCBM domains will reduce.



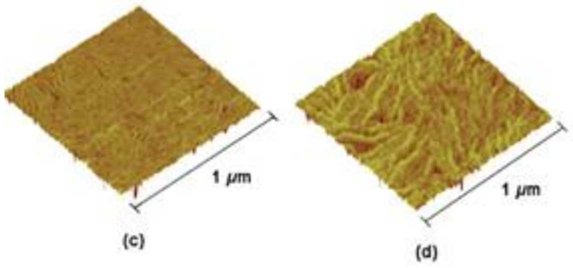


Fig. 11 AFM images for different growth rate of polymer active layer. Height images for (a) slow- and (b) fast-grown films. Phase images for (c) slow- and (d) fast-grown films.

The EQE for the device with a fast-grown film shows a maximum of y19% at a wavelength of 350 nm. On the other hand, for the device with a slow-grown film, the EQE maximum increases by more than three times to y63% at 500 nm (fig. 12).

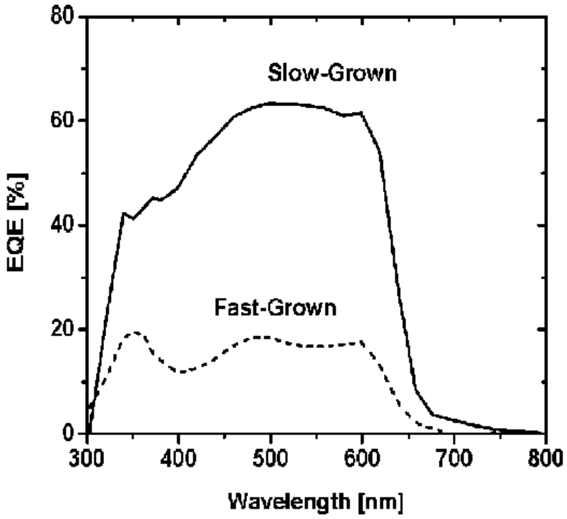


Fig. 12 EQE for P3HT : PCBM solar cells for two types of active layers: slow-grown and fast-grown.

Conclusion

In this paper we have seen the basic working of the solar cell and the various techniques that have a major effect on the morphology of the cell and hence a major effect on the efficiency of the polymeric solar cell.

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