CHAPTER V

EFFECT OF THERMAL ANNEALING ON P3HT:PCBM BLEND MORPHOLOGY AND USE OF TITANIUM SUB-OXIDE AS INTERLAYER
Summary

In this chapter, results of the study, regarding P3HT:PCBM blend morphology control by thermal annealing has been discussed. The effect of annealing the blend films at various temperatures for short time as well as for longer duration, on both nanometer scale and micrometer scale morphology has been studied. Blend films have been characterized by UV-visible absorption spectroscopy, static PL spectroscopy, optical microscopy, atomic force microscopy, and low angle X-ray diffraction. We show that the morphology at the micrometer scale affects the morphology at the nanometer scale. The effect of using a titanium sub-oxide layer between the P3HT:PCBM blend and Al electrode has also been discussed. Effect of the quality of interface between the photoactive layer and the TiO₉ layer has been explained. The titanium sub-oxide film has been characterized by UV-visible absorption spectroscopy and X-ray photoelectron spectroscopy. With the help of J-V characteristics under illumination and in dark, we show that the interface between photoactive layer and the titanium sub-oxide layer improves, upon thermal annealing below a particular temperature.
V-1: INTRODUCTION

In addition to various other methods, the nano-morphology of photoactive blend layer in PSC’s is mainly controlled by thermal annealing [1-3]. In spite of the fact that there are numerous studies on thermal annealing of the blend films, more study is needed to understand the proper phenomenon through which the morphology changes in the polymer: modified fullerene blend films. Also the use of an electron conducting and hole blocking layer between the photoactive layer and the top Al electrode has been studied [4-5]. However, effect of the quality of interface between photoactive blend layer and the titanium sub-oxide (TiOₓ) layer on device performance needs further attention.

V-2: LITERATURE REVIEW

In P3HT:PCBM solar cells, the crystallization and de-mixing induced by thermal annealing controls the nanoscale organization of P3HT and PCBM in the photoactive layer [6]. Both, P3HT and PCBM components should have a large interfacial area for efficient charge generation and attain crystalline order that improves charge transport. M. Campoy Quiles and others [1] performed in-situ study regarding the morphology evolution in P3HT:PCBM blend films upon thermal annealing. They found that, P3HT crystallization and PCBM diffusion are strongly co-related, and also these phenomena can be semi-independent in given scenarios. They showed that initial efficiency improvement upon thermal annealing, was due to P3HT crystallization, and PCBM diffusion, while further improvement upon heating for longer times was due to PCBM diffusion only, as P3HT crystallization was complete upon annealing for 5 minutes. Modification in absorption spectra of P3HT:PCBM blend films were studied by V. Shrotriya et al. [7]. The P3HT absorption spectra modification was attributed to the lowering of the inter-chain interaction due to the presence of PCBM molecules, and a non-photo induced charge transfer between P3HT and PCBM in solid state. Karagianidis et al. [8] studied the effect of thermal annealing on the nano-mechanical properties and structure of P3HT:PCBM thin films. They found that an increase in the thermal annealing temperature causes an increase in the size of PCBM crystallites, and enhanced crystallinity of the two phases. Jo et al. [9] studied the time dependent morphology evolution by thermal and solvent annealing processes. A detail thermal annealing study of the blend films is also performed by P. E. Hopkinson et al. [3]. Formation of interconnecting channels of the two
phases is important for proper device performance [9-11]. Park et al. studied the effect of the solubility of annealing solvents on the performance of P3HT:PCBM solar cells [12]. Kim et al. [13] also reported enhanced efficiency of bulk heterojunction OSC’s using blend films of regioregular P3HT and PCBM by thermal annealing process. They concluded that irrespective of the solvent used, the highest efficiency was obtained by thermal annealing at 140\textdegree{}C.

Pearson et al. [14] demonstrated that an improvement in device efficiency occurs once the P3HT:PCBM blend film was heated above the upper apparent glass transition temperature of the blend. If annealing is performed above the optimum temperature, excessive phase-separation and a partial reduction in film optical density leads to a general decrease in device efficiency. Treat et al. used a combination of in situ current–voltage measurements and grazing-incidence wide-angle X-ray scattering experiments at elevated temperature to correlate the changes in photoconversion efficiency to the changes in the molecular ordering of P3HT:PCBM bulk heterojunction active layer [15].

Insertion of titanium sub-oxide (TiO\textsubscript{x}, where x < 2) layer between the Al electrode and the photo-active layer in OSC was studied by Hayakawa et al. [16]. They found that the TiO\textsubscript{x} layer not only serves as a hole blocking layer but also prevents contact between Al and the active layer. Heeger et al. studied the use of TiO\textsubscript{x} layer as an optical spacer in P3HT:PCBM solar cells [17-19]. Gilot et al. have used thin ZnO film as an optical spacer for P3HT:PCBM solar cell to improve the device efficiency [20]. Sariciftci et al. [21] inserted a thin LiF layer between organic layers and Al electrode to improve the device performance. Li et al. [22] demonstrated enhanced efficiency of polymer-modified fullerene, bulk heterojunction solar cells with insertion of thin CdS layer near the Al electrode.

V-3: CHALLENGES, OPEN AREAS FOR STUDY, AND OBJECTIVES OF PRESENT WORK

In spite of the fact that numerous studies have been contributed to thermal annealing the photoactive layer in polymer solar cells, a comprehensive study regarding the effect of short time and long time thermal annealing on the nanoscale as well as the microscale morphology is lacking. Also a study regarding the effect of the quality of interface
between the photoactive layer and the TiO$_x$ layer is lacking. On the basis of above discussion the following studies have been presented in this chapter.

1) The effect of short time and long time annealing on the nanometer scale as well as on the tens of micrometer scale morphology has been studied.

2) The effect of the quality of interface between the photoactive layer and the TiO$_x$ layer has been studied.

V-4: EXPERIMENTAL DETAILS

V-4.1: P3HT:PCBM BLEND FILM PREPARATION

The P3HT:PCBM blend films were prepared by spin coating a solution containing P3HT and PCBM in chlorobenzene at a concentration of 15 mg P3HT plus 15 mg PCBM per ml of chlorobenzene. The solution was kept for stirring in dark for 15 hours. After stirring, the solution was filtered through a 0.2 μm filter. By rotating at a particular speed 100 nm films were obtained on glass substrates. To anneal these films, substrates coated with the blend films were place on a pre-heated hot plate for the required time. Annealing was performed in air.

V-4.2: TiO$_x$ SYNTHESIS

The TiO$_x$ material was prepared by mixing titanium isopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$], 2-methoxyethanol [CH$_3$OCH$_2$CH$_2$OH] and ethanolamine [H$_2$NCH$_2$CH$_2$OH] under dry nitrogen flow, following a sol-gel procedure [23]. Experimental arrangement is shown in figure 1.

![Figure 1: Schematic drawing of the sol-gel processing apparatus employed for the preparation of TiO$_x$.](image)

Nitrogen gas (99.999 %) was purged through one of the necks of a three necked flask. The outlet for N$_2$ gas was through the 2$^{nd}$ neck while the chemicals were introduced
through the 3rd neck. The necks were fitted with air tight cocks. The whole sol-gel process was performed under flowing nitrogen. Initially 10 ml titanium isopropoxide [Ti(OCH(CH₃)₂)₄] was introduced in the flask. Thereafter, 40 mL of 2-methoxyethanol (CH₃OCH₂H₂OH), was injected under vigorous stirring, followed by 4 ml ethanolamine (H₂NCH₂CH₂OH) into the tree-necked flask. The flask was fitted with a water condenser. The entire procedure was carried out at room temperature. After one hour stirring at room temperature, the mixed solution was heated at 80°C for an hour (using a silicone oil bath), followed by heating to 120°C for one hour. Following this procedure, the solution transformed to a low density Gel with dark wine color. As a final step after cooling to room temperature, a particular quantity of ethanol was injected to extract the final TiOₓ product.

V-4.3: DEVICE FABRICATION

The photoactive layer (P3HT:PCBM blend) was spin coated by using a solution containing P3HT and PCBM in chlorobenzene at a concentration of 15 mg P3HT plus 15 mg PCBM per ml of chlorobenzene. This solution was kept for stirring in dark, for 15 hours before filtering with 0.2 μm filter. Active layers of thickness ∼ 100 nm were coated by spin casting the solution at the particular rpm. The films were then baked for 10 minutes before deposition of 100 nm Al layer by thermal evaporation. For the device with TiOₓ layer, the TiOₓ precursor solution was further diluted before spin coated at 2000 rpm to produce a 5 nm film. Finally ∼ 100 nm Al layer was deposited by thermal evaporation. More detail of device fabrication is given in chapter II.

V-5: RESULTS AND DISCUSSION

V-5.1: BLEND FILM ANNEALING STUDY

Figure 2 show the UV-Visible absorption spectra of the as coated P3HT:PCBM blend films and after annealing at various temperatures for different times. Peak corresponding to P3HT absorption, in the as coated film appears at ∼ 483 nm. Upon annealing the film at 80°C, for 5 minutes, absorption maxima red-shifts to ∼ 512 nm, and further to ∼ 515 nm when heated for 2 hours. Such a shift in absorption spectra implies a larger proportion of the longer conjugation length polymer chain, or a longer average conjugation length of the polymer chain [24-26]. However, the absorption peak for pristine P3HT is usually obtained at 520 nm. This shows that annealing at 80°C for the mentioned time is not
sufficient to completely transform the disordered P3HT chains into completely ordered one.

Figure 5.2: UV-Visible absorption spectra of the P3HT:PCBM blend films annealed at various temperatures and for various times

In addition to this, the shoulder peaks at \( \sim 550 \) nm and \( \sim 610 \) nm becomes more prominent upon annealing, which indicates a homogeneous electronic \( \pi-\pi^* \) transition due to a less wide distribution of conjugation lengths. Increase in the shoulder absorption
intensity at \( \sim 610 \text{ nm} \) implies improved regioregularity and hence the local order or the crystallinity of the polymer. Upon increasing the annealing temperature absorption intensity increase further, with additional red-shift in the absorption peak. This is as a result of enhanced local order and conjugation length of the polymer chains. Upon heating at \( 160^\circ \text{C} \) the absorption peak shifts to 518 nm, and the shoulder peaks become more prominent which implies an enhanced P3HT conjugation length and crystallinity. In addition to the changes in P3HT absorption, the PCBM absorption spectra, also shows few changes, upon annealing at \( 140^\circ \text{C} \) for 10 minutes or longer times and at higher temperature. Upon annealing at \( 140^\circ \text{C} \) for more than 10 minutes the PCBM absorption intensity decreases. Upon heating at \( 160^\circ \text{C} \) for 2 hours marked decrease in the PCBM absorption was observed.

To investigate the effect of annealing the blend films on the micrometer scale morphology, optical microscope images were recorded (See figure 3).

**Figure 3:** Optical microscope images of the surface of spin coated blend films, heated at different temperatures and for different times (Scale: 100 \( \mu \text{m} \times 100 \mu \text{m} \))
It can be observed that upon heating at higher temperatures, larger PCBM aggregates (dark dots) were observed. Size of these aggregates increases upon heating for longer times. In the films annealed at 140°C for 30 minute, and at 160°C for 5 minute, certain regions with greater density of the PCBM aggregates was observed, compared to other regions. Colour contrast around these regions of high PCBM aggregate density implies that the aggregates were formed due to the nucleation of PCBM spread around the aggregates. Such observation has earlier been reported [1, 27].

In general, temperature is related to the diffusion coefficients ($D$) of the materials according to [28],

\[ D = D_0 \exp \left( - \frac{Q_d}{RT} \right) \]  

Where $D_0$, $Q_d$, $R$, and $T$ are the temperature independent pre-exponential, the activation energy of diffusion, the gas constant, and absolute temperature respectively. This shows that the diffusion coefficient is a strong function of temperature. Therefore by heating at higher temperatures, large PCBM aggregates are formed, due to the enhanced diffusion coefficient of PCBM molecules.

To investigate the effect of annealing on the charge transfer between the P3HT and PCBM, static PL spectra were recorded and are shown in figure 5.4. The PL spectra were normalized to absorption intensity. It can be observed that in films annealed at 80°C the PL emission intensity decreases. After heating for 30 minutes at this temperature, prominent decrease in PL intensity was observed. However after heating for 2 hours the PL intensity rises, but still is less than that of the as prepared films. This decrease in PL intensity can be due to [29],

\begin{itemize}
  \item [$a)$] Increase in the crystallinity of polymer, as the excitons can now easily diffuse to the interface, and
  \item [$b)$] Diffusion of PCBM into the P3HT chains, which will increase the charge transfer.
\end{itemize}

Absorption spectra have already shown that upon annealing for 5 minutes at 80°C, P3HT crystallinity increases. However upon increasing the annealing time to 30 minutes, increase in polymer crystallinity was less compared to that for 5 minutes (0.33 % increase in absorption peak intensity). At the same time the decrease in PL peak intensity after annealing for 30 minutes was 58.32 % compared to that of 5 minutes annealing. This change indicates that the first reason is not the only factor affecting the PL quenching. We conclude that, PL quenching is also affected by the diffusion of PCBM into the P3HT.
Chapter-V: Effect of Thermal Annealing on chains. This observation is in accordance with Ostwald ripening [30-32]. This phenomenon causes the dissolution of small crystals over time and redeposit into larger crystals. Small particles have a larger surface energy and hence higher total Gibbs energy, than larger particles, giving rise to their dissolution. This dissolution causes decrease in the PL intensity initially. Upon heating for longer durations these particles starts aggregating. This then causes the PL intensity to rise.

![Photoluminescence spectra of the P3HT: PCBM blend films annealed at various temperatures and for various times](image)

Figure 4: Photoluminescence spectra of the P3HT: PCBM blend films annealed at various temperatures and for various times
Upon heating at 140°C for 5 minutes, the PL intensity is less than the as deposited film. However upon increasing the annealing time to 10 minutes the PL intensity becomes greater than the as coated film. Optical microscope images have shown larger PCBM aggregates, suggesting the re-deposition of the smaller particles to form larger aggregates. With increase in annealing time the aggregate size increases further. Due to the increase in PCBM aggregate size, it can be expected that PCBM content would decrease in the bulk of the blend film, as most of the PCBM is in aggregated form. Depletion of PCBM from the bulk resulted in the enhancement of PL intensity in the films heated for longer durations. In the films heated at higher temperatures for longer duration (10 min. or more at 140°C, and 5 min. or more at 160°C) PCBM absorption intensity decreases, which is again an indication of PCBM depletion from the bulk of the material.

To study the effect of annealing on the nanoscale morphology, AFM images were recorded. Figure 5 show the AFM images of the as coated films and that of annealed films. Image contrast was adjusted to equalize the negative and positive phase by using WSxM 5.0 Develop 2.1 software [33].

Figure 5: Atomic force microscopy images of the P3HT:PCBM blend films annealed at various temperatures for 10 minutes and at 140 °C for different times
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Lesser contrast in the P3HT and PCBM phases in the films annealed at 120°C and 140°C for 10 minutes indicates that PCBM has diffused in the P3HT regions. This is in support to the PL studies where PL quenching was found upon heating. However, the contrast in the film heated at 140°C is larger compared to that heated at 120°C. This indicates the formation of purer phases upon increasing the heating temperature. Upon annealing at 140°C, interconnecting channels are formed. At lower temperatures such channels were not observed. The interconnecting channels are helpful to enhance the charge transport once they are generated at the interface. After heating at 160°C for 10 minutes, the contrast increased further (greater than the as coated film). However it can be seen that the bulk is depleted of PCBM, probably due to the fact that, larger aggregates were formed at the micrometer scale (optical microscope images).

AFM images of the films heated at 140°C, for 5 minutes, 10 minutes, 30 minutes and 120 minutes are also shown in figure 5. It can be seen that the phase separation between the two components increases upon increasing the heating time. Upon heating for 30 minutes, larger PCBM aggregates can be seen. Correlating the optical microscope images and the AFM images it becomes clear that upon heating at 140°C for 30 minutes, larger PCBM aggregates are formed both at the nanoscale as well as at tens of micrometer scale. However upon heating for 120 minutes, larger PCBM aggregates disappeared from the nanometer scale and size of aggregates increased at the micrometer scale. Figure 6 shows the histogram of the number of events measured for a particular phase in the AFM images.

![Figure 6: Plots of the number of events measured for a particular phase in the AFM images](image-url)
It can be observed that in the as deposited film more events are at higher phase compared to the annealed films. Number of events observed for smaller phase is lesser in the as deposited films, compared to the annealed films. This is again an indication of the fact that upon thermal annealing even at 140°C for 10 minutes purer phases compared to the as deposited film are not formed. However more crystalline P3HT phases are obtained on annealing. This shows that obtained increase in P3HT crystallinity upon thermal annealing is not due to the diffusion of PCBM molecules out of the polymer. It is possible that P3HT may crystallize by local reordering of the chains rather than PCBM diffusion. Upon annealing at 160°C, for 10 minutes, however more number of events having negative phases is observed. This is an indication of the formation of purer phases. Optical microscope images have shown the formation of larger aggregates at the micrometer scale. This shows that the purer phases are formed because, at such high temperature the formation of aggregates dominates compared to their dissolution. Also the occurrence of more number of events having negative phase shows that upon thermal annealing at 160°C for 10 minutes P3HT phase has segregated at the surface, or there is lack of PCBM phase. Comparing this with the optical microscope images it can be inferred that the lack of PCBM in the bulk is due to the fact that it has moved towards larger aggregates. The increase in the quality of crystalline P3HT phase upon annealing was confirmed by small angle x-ray diffraction experiments.

Figure 7: Small angle X-ray diffraction pattern of P3HT blend films

Figure 7 show the x-ray diffraction pattern of as coated blend film and that of annealed blends at various temperatures for 10 minutes. Intensity increase at ∼ 5° value of 2θ,
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confirms the increase in crystalline P3HT with annealing temperature [34, 35]. At annealing temperature of 140°C, the peak appears at 5.3° compared to 5.0° for as coated film. This shows a decrease in d-spacing of the P3HT corresponding to head to tail order. Also the sharp peak upon heating at 140°C indicates highly homogeneous d-spacing in the film. Peak at ~ 22°, was not observed by annealing at 140°C for 10 minutes.

Above discussion show that, during the initial period of annealing, PCBM diffuses into the polymer phase. Simultaneously increase in P3HT crystallinity and enhanced local order of polymer chains was observed. Thus, enhanced P3HT crystallinity is not due to the diffusion of PCBM out of the P3HT chains as mentioned in few earlier studies [36]. Upon annealing, the P3HT chains reorganize and crystallize. From the present data we cannot infer whether reorganization of P3HT and diffusion of PCBM are dependent processes. However, it is clear that P3HT crystallization can take place independent of whether PCBM diffuses out of the P3HT phase or dissolute into the chains. Also maximum P3HT crystallization takes place during the first 5 minutes of heating. Upon heating for longer time increase in P3HT crystallinity is less, when PCBM was found to diffuse out of the P3HT chains. This again confirms the fact that P3HT crystallization may take place independently whether PCBM diffuses in or out of P3HT, and occurs mainly due to local re-ordering of the polymer chains.

V-5.2 TiOx CHARACTERIZATION AND EFFECT OF BLEND:TiOx INTERFACE ON DEVICE PERFORMANCE

Figure 8 show the absorption spectra of the TiOx film prepared on glass substrates.

**Figure 8:** UV-Visible absorption spectra of TiOx film. Inset show the (a) stored TiOx precursor solution (b) dilute solution used for coating, and (c) solution after leaving in air for 2 hours.
The absorption edge of the materials is \(~ 335 \text{ nm},\) corresponding to \(~ 3.7 \text{ eV}\) energy. This matches with the earlier reported value \([23]\). Inset shows the photograph of the TiO\(_x\) solution (a) stored after synthesis, (b) diluted solution used for deposition, and (c) after leaving the solution (b) opens for 2 hours in air. After leaving the solution in air, white aggregates are formed due to the formation of Ti-O linkages. Figure 9 show the Ti 2p and O 1s core level X-ray photoelectron spectra of TiO\(_x\) film. The Ti 2p\(_{3/2}\) spectra could be resolved into three components at binding energies 457.6, 459.7, and 461.8 eV. A similar spectrum has been earlier obtained by Pan et al. \([37]\) for oxygen deficient TiO\(_2\) films. The component at 459.7 eV is attributed to TiO\(_2\) while that at 457.6 eV is due to Ti\(_2\)O\(_3\). This confirms the existence of oxygen deficient Ti species. The O 1s peak was resolved into three components at 531.2, 533.3 and 533.6 eV. The component at 531.2 eV is attributed to the Ti-O bonds. Other two contributions are attributed to Ti-O-H, Ti-O-C, or H\(_2\)O originating from adsorption from the surface of sample or due to residuals from the precursor solution \([38, 39]\).

Figure 9: Ti 2p and O 1s XPS spectra of TiO\(_x\). Deconvoluted peaks are also shown for the reference.

Figure 10 show the J-V characteristics of the devices prepared with TiO\(_x\) layer and without TiO\(_x\) layer. Devices 1 to 6 were heated at 140\(^\circ\)C, for 8 minutes immediately after coating the P3HT:PCBM blend. Thereafter, the TiO\(_x\) layer was coated. After coating the TiO\(_x\) layer, device 1 was not heated, while device 2, 3, 4, 5 were heated at 100\(^\circ\)C, 120\(^\circ\)C, 140\(^\circ\)C and 160\(^\circ\)C respectively for 8 minutes each. Device 6 was not coated with the TiO\(_x\) layer. Device 7 and 8 were heated at 140\(^\circ\)C for 8 minutes, only after coating the TiO\(_x\)
layer. After coating the blend layer in device 7 it was exposed to air for 30 minutes and then the TiO\(_x\) layer were coated, while in device 8 the TiO\(_x\) layer was coated immediately after coating the blend. In the devices 1-5 and device 7-8 the Al layer was coated 30 minutes after the TiO\(_x\) layer was coated.

It can be seen that in all the devices where the active layer was heated in air, the performance is excessively degraded, compared to that annealed after TiO\(_x\) layer deposition. The calculated device parameters are depicted in Table 1. The degradation in device performance can be attributed to the heating of the blend layer in air. Due to the contact of O\(_2\) and moisture with P3HT at elevated temperatures the performance degrades. In devices 2-5 annealing was performed at different temperatures after coating the TiO\(_x\) layer. It was observed that upon annealing and with increase in annealing temperature the device performance improves. When the device is not annealed after TiO\(_x\) layer deposition (device 1), the series resistance is very high compared to that annealed at 140\(^\circ\)C after TiO\(_x\) layer deposition. Such increase in series resistance can be attributed to the resistance of TiO\(_x\) layer as well as to the resistance of the interface between blend and the TiO\(_x\) layer. There are reports where it has been shown that 5 nm thick TiO\(_x\) layers are highly conducting [40].

![Figure 10: J-V characteristics of the devices under 1.5 AM illumination](image)

The series resistance of device is contributed by (a) contacts between different layers, (b) resistance of active layer, and (c) resistance of different layers. The sharp reduction of the series resistance (from 4006 \(\Omega\)-cm\(^2\) to 210 \(\Omega\)-cm\(^2\) after annealing at 140\(^\circ\)C can attributed
to the reduction in resistance across the interface between the TiO\textsubscript{x} and blend layer. It is known that amorphous TiO\textsubscript{x} turns into crystalline form only after heating above 400\textdegree{}C. Much change in the resistivity of TiO\textsubscript{x} layer by heating at 100\textdegree{}C to 160\textdegree{}C is not expected. Resistance of the layers and across the other interfaces is same in all devices. This clearly shows that annealing the device after coating the inorganic TiO\textsubscript{x} layer is essential to improve the contact between the active layer and the TiO\textsubscript{x} layer and reduce the series resistance, and hence improve the device performance. However heating at 160\textdegree{}C after coating the TiO\textsubscript{x} layer again increases the series resistance and the resultant device performance degrades. Optical microscope image have shown cracks in the film heated at 160\textdegree{}C after depositing the TiO\textsubscript{x} layer. Such cracks may be due to the increase in roughness of the film due to the formation of large PCBM aggregates. This, performance degradation can be attributed to the increased PCBM domain size and the cracks formed on the TiO\textsubscript{x}, layer due to the increase in blend layer roughness.

<table>
<thead>
<tr>
<th>Device</th>
<th>Rs ((\Omega\cdot\text{cm}^2))</th>
<th>R\textsubscript{sh} ((\Omega\cdot\text{cm}^2))</th>
<th>J\textsubscript{sc} (mA/cm\textsuperscript{2})</th>
<th>V\textsubscript{oc} (V)</th>
<th>FF</th>
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<td>0.39</td>
<td>0.52</td>
<td>0.13</td>
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<td>0.58</td>
<td>0.54</td>
<td>0.18</td>
<td>0.056</td>
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<td>1.68</td>
<td>0.52</td>
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<tr>
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<td>460</td>
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<td>0.51</td>
<td>0.28</td>
<td>0.451</td>
</tr>
<tr>
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<td>504</td>
<td>1.12</td>
<td>0.58</td>
<td>0.26</td>
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</tr>
<tr>
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<td>0.49</td>
<td>0.30</td>
<td>0.532</td>
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<td>0.59</td>
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</table>

It was also observed that, as a result of heating the devices after coating the TiO\textsubscript{x} layer, shunt resistance was not much affected. However these values are significantly greater than device 6, where the TiO\textsubscript{x} layer was not used. This is a clear indication that the TiO\textsubscript{x} layer serves to increase the shunt resistance by reducing the parallel pathways through which the leakage current flows. When the TiO\textsubscript{x} layer was not used the shunt resistance is only 260 \(\Omega\cdot\text{cm}^2\) compared to 460 \(\Omega\cdot\text{cm}^2\) for the device heated at 140\textdegree{}C after TiO\textsubscript{x} layer deposition. In spite of the above fact, the J\textsubscript{sc} value for device 6 is larger than that of
device 4. The reduction of $J_{sc}$ in device 4 may be due to the fact that it was heated at 140°C for a total of sixteen minutes compared to eight minutes for device 6. It has been shown earlier that heating at 140°C for longer times leads to the formation of larger aggregates of PCBM and thereby increasing the phase separation and film roughness (optical microscopy images). This leads to the loss of generated excitons, and hence reduction in resultant $J_{sc}$.

For the proper collection of electrons at the Al electrode, the interface between organic bulk heterojunction and metal electrode should selectively provide low resistance to electron flow towards the cathode [41]. The overall power conversion efficiency ($\eta$) of the device heated immediately after coating the TiO$_x$ layer is 1.936 % (device 8) compared to 0.532 % without the TiO$_x$ layer. It is worth noting that fill factor (FF) increased markedly from 0.30 to 0.49 by the addition of TiO$_x$ interfacial layer, which must be attributed to the better ohmic contact and suppression of a counter diode at the cathode. Improved ohmic contact at the interface is evident from the low series resistance $R_s$ with the use of TiO$_x$ layer. With the TiO$_x$ layer $R_s$ obtained is 26 $\Omega$-cm$^2$ compared to 115 $\Omega$-cm$^2$ when the TiO$_x$ layer is not used. Upon using the TiO$_x$ layer the hot Al electrode is prevented from diffusing into the active layer during evaporation and offers good contact morphology between the active layer and the Al electrode through TiO$_x$. According to few earlier studies Al-O-C bonds formation takes place between the conducting polymer and Al interface [42, 43]. This highly stable chemical bond originates from the small amount of oxygen in the carbonyl groups in polymer chains. Due to the high reactivity between Al and carbonyl groups such bond formation takes place during thermal evaporation process. The formation of such oxygen bridging complexes and the Ti-O-Al bonds at TiO$_x$/Al interface is expected to increase the interface adhesion. Since TiO$_x$ have much more oxygen compared to active layer more enhanced interface adhesion would be expected between the active layer and Al electrode. This can contribute significantly towards reducing the resistance at the TiO$_x$/Al interface. In device 7 the blend layer was exposed to air for 30 minute. Due to this the active layer comes in contact with O$_2$ and H$_2$O leading to partial degradation of the film surface. Such a surface (also when annealed in air) can act as an additional oxide barrier layer at the interface and contributes towards the series resistance of the device. Due to the oxygen vacancies formed during hydrolysis and condensation, TiO$_x$ can actively scavenge O$_2$ and H$_2$O from
the bulk surface [44]. Therefore, in the device with TiO\textsubscript{x} layer the bulk heterojunction surface was protected from oxygen and moisture in the ambient due to the scavenging of O\textsubscript{2} and H\textsubscript{2}O by TiO\textsubscript{x}. In an ideal bulk heterojunction solar cell, P3HT should be in contact with ITO through PEDOT:PSS and PCBM in contact with metal electrode. However, as already revealed in the AFM images substantial P3HT can also be in contact with Al electrode. The presence of such a large quantity of P3HT at the surface would cause, undesirable contact of P3HT with Al electrode, which in turn leads to hole leakage from P3HT to Al electrode giving rise to a counter diode at the cathode. Such an effect leads to lower shunt resistance $R_{sh}$. The shunt resistance of device with TiO\textsubscript{x} layer increases to 537 $\Omega\text{cm}^2$ (device 8) from 260 $\Omega\text{cm}^2$ (device 6) for device without TiO\textsubscript{x}. The high $R_{sh}$ implies that leakage currents are suppressed by the TiO\textsubscript{x} layer. Undesirable contact of P3HT with the Al electrode would cause dark carrier recombination dominantly at the interface between P3HT and Al, which accounts for a large reverse saturation current $J_{sc}$ [45, 46]. The reverse saturation current in device without TiO\textsubscript{x} layer is 1.5 x 10\textsuperscript{-5} mA/cm\textsuperscript{2} which decreases to 2.5 x 10\textsuperscript{-6} mA/cm\textsuperscript{2} due to the use of additional TiO\textsubscript{x} layer above the bulk heterojunction surface (See figure 11). The TiO\textsubscript{x} layer having high electron mobility cuts off the direct contact between P3HT (having high hole mobility) and Al, which leads to a situation where the Al electrode is in contact with active layer through electron conducting TiO\textsubscript{x}. This morphology is equivalent to segregation of PCBM having high electron mobility, at the Al electrode interface. The use of TiO\textsubscript{x} would therefore lead to increased dark carrier recombination at the P3HT:PCBM interface.

![Figure 11: Dark J-V characteristics of the devices](image-url)
Moreover, due to large energy difference (1.5 eV) between the LUMO of PCBM and HOMO of P3HT compared to the energy difference (0.9 eV) between work function of Al and HOMO of P3HT the probability of recombination at P3HT-PCBM interface is higher (figure 12). Also the highly negative valence band (- 8.0 eV) of the TiO$_x$ layer serves as efficient hole blocking layer, thereby restricting the hole leakage from P3HT to Al electrode. The diffusion of minority charge carriers from the neutral region to the depletion region under reverse bias is restricted by the highly negative valence band of TiO$_x$. The overall result of effects discussed above is responsible for lower $J_{sat}$ with TiO$_x$ layer. The rectification ratio (current ratio measured at +1.2 V versus -1.2 V) of the device with TiO$_x$ is 471, but that without TiO$_x$ is only 80. This again confirms reduced additional leakage pathways with TiO$_x$ layer. This high degree of rectification suggests improved carrier transport in the device by eliminating some of the leakage sources that are often seen in polymer solar cells. FF with TiO$_x$ layer (device 8) is 0.49 while that of without TiO$_x$ is 0.3. Earlier also FF has been related to contact effects [47, 48]. We therefore attribute the improved FF in device with TiO$_x$ to the improved interface between bulk heterojunction layer and Al electrode.

![Energy band diagram showing usual electron and hole paths in the device and recombination paths](image)

In addition to the improved FF by using TiO$_x$ layer the open circuit voltage $V_{oc}$ obtained with TiO$_x$ layer is 0.59 V compared to 0.49 V when TiO$_x$ is not used. This increase in $V_{oc}$ is ascribed to the large reduction in $J_{sat}$ with the additional TiO$_x$ layer. It is well established...
that in devices with low $J_{sat}$ improved open circuit voltages are obtained. Also, the short circuit current density $J_{sc}$ value without TiO$_x$ is 3.62 mA/cm$^2$ which improves to 6.70 mA/cm$^2$ by using the TiO$_x$ layer. The large series resistance in the device without TiO$_x$ layer shows that $J_{sc}$ is less than the light generated current inside the solar cell and accounts for the low measured $J_{sc}$. Due to improvement of the interface between P3HT:PCBM/Al by using TiO$_x$ layer, electron collection at the cathode is enhanced in addition to suppressing the leakage currents. The comparatively high shunt resistance with TiO$_x$ leads to reduced loss of current through shunt path.

**CONCLUSIONS:**

The major conclusions of the present work are,

1) Due to thermal annealing of P3HT:PCBM blends, the PCBM aggregates dissolves initially and later on redeposit to form larger aggregates in accordance with Ostwald ripening.

2) Upon heating at 140°C for 10 minutes or for longer duration, micrometer sized PCBM aggregates are formed at the expense of the PCBM in the bulk. The aggregation process accelerates by increasing the temperature.

3) P3HT crystallization and PCBM aggregation can take place independently.

4) Interface between the photoactive layer and the TiO$_x$ interlayer is important for optimal device performance. Annealing the blend after coating the TiO$_x$ layer improves the interface and hence the device performance.
REFERENCEs:


