Optimizing material properties of bulk-heterojunction polymer films for photovoltaic applications

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ABSTRACT

Bulk-heterojunction photovoltaic devices consisting of poly (3-hexylthiophene) (P3HT) as a donor and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as an acceptor are investigated in this paper. To achieve an efficient photo-induced charge transfer, the following aspects have been studied: (1) Selection of suitable solvent to obtain good morphology of the films and optimal absorption spectrum; (2) Determination of the donor/acceptor composition ratio that yields good film interface and high photon absorption; (3) Thermal annealing process to enhance the photon absorption, improve the short circuit current and the filling factor, and therefore the efficiency of the devices.

Keywords: photovoltaic, solar cell, P3HT, annealing

1. INTRODUCTION

Polymeric solar cells based on conjugated polymer/fullerene to form a donor/acceptor (D/A) bulk heterojunction blend system have been reported recently [1-5], in which power conversion efficiency over 6.5% has been achieved [5]. Previous work on these D/A systems focused on the materials of poly (3-hexylthiophene) (P3HT), poly [2-methoxy, 5 ethyl (2' hexyloxy) paraphenylenevinylene] (MEH-PPV), and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). Compared with other organic donor materials, P3HT possesses some unique characters, such as high degree of crystallinity, high hole mobility in regioregular state (10^{-4} to 10^{-2} cm^2/V s), extended absorption in the red spectra region (up to 650 nm), and environmental stability [6]. PCBM is an acceptor material for photovoltaic cells with favourable characteristics, such as solubility and absorption profiles. The major difference in the functionalities of donor and acceptor is that the acceptor molecules stabilize free electrons. PCBM, a derivative of fullerenes (C_{60}), has a high electron affinity. With the attachment of a long chain on the C_{60} molecules to form a PCBM molecule, the solubility of the fullerenes has been significantly improved. Both pure C_{60} and its simple derivatives absorb at wavelengths shorter than 400 nm [7].

To achieve an efficient photo-induced charge transfer, it is very important to understand the following aspects: (1) Selection of the solvent is the key for obtaining good morphology of the films as well as the efficiency and stability of the photovoltaic devices. Several solvents such as xylene, toluene, chloroform, chlorobenzene and 1, 2 dichlorobenzene were investigated to prepare thin films. (2) The morphology of the films should be of good quality. It should be free from pinholes, kinks, and overlapping of chains. The composition of donor/acceptor thus plays an important role to achieve good device performance. If the concentration of the acceptor is too high, the films will have kinks, overlapping chains, and the photo-induced charge transfer rate will be low, which result in low photon absorption [8]. On the other hand, if the concentration of the acceptor is low, the interface of the organic layer and the electrode will become smooth, and the exciton will not have enough space to diffuse, resulting in low exciton generation efficiency [8]. (3) Thermal annealing was found to be a possible approach to enhance the photon absorbance, improve the short circuit current, fill factor, and therefore the efficiency of the device [9]. To achieve a high efficiency, the optimal annealing conditions of P3HT/PCBM film must be determined. In this study, we will carry out research to address these aspects in order to discover optimal parameters for sample preparation as well as optical constants of thin films for multilayer design and performance improvement. The optimal solvent, composition ratio, and thermal annealing conditions will be

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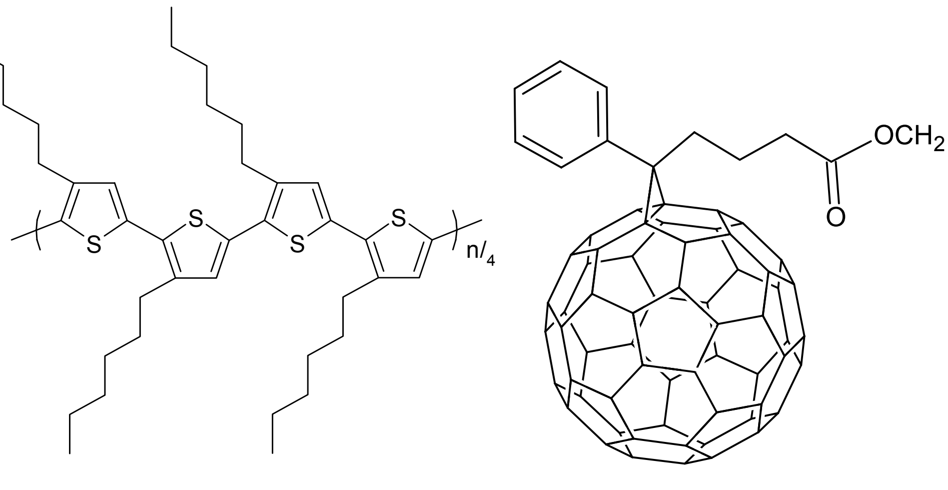
Photonics North 2008, Réal Vallée, Michel Piché, Peter Mascher, Pavel Cheben, Daniel Côté,
Sophie LaRochelle, Henry P. Schriemer, Jacques Albert, Tsuneyuki Ozaki, Eds., Proc. of SPIE
Vol. 7099, 709919, (2008) · 0277-786X/08/$18 · doi: 10.1117/12.806958

revealed through the characterization of the optical properties of thin films, aided by morphology study with atomic force microscopy.

2. EXPERIMENTAL DETAILS

P3HT from American Dye Source, Inc. is used as the donor of the photovoltaic cell due to its unique properties over other polymers [10]. Figure 1 shows the chemical structure of P3HT, which possesses an alkyl chain to achieve high solubility in most common solvents, such as chloroform, chlorobenzene and dichlorobenzene. PCBM from nano-C, Inc. is used as an acceptor in the photovoltaic cells with the molecular structure illustrated in Fig. 1.



P3HT PCBM

Fig. 1. Molecular structures of P3HT and PCBM.

Vacuum evaporation and solution processing techniques are the most commonly used thin film preparation methods in the fabrication of organic solar cells. Since polymers decompose under excess heat, most photovoltaic polymers are solution processed films through spin-coating. During the process of spin-coating, an excess amount of the D/A (Donor/Acceptor) blend solution is dropped on the substrate, which is then rotated at a high speed in order to spread the fluid by centrifugal force. A photo-resist spinner manufactured by Headway Research Inc. was used in our experiment. Solutions of D/A blends can be prepared by dissolving donor and acceptor materials in a common solvent. The blend films in this study were all prepared by spin-coating method. An Ocean Optics USB 2000 ultraviolet-visible spectrophotometer was used to obtain the absorption spectra of thin films. In order to acquire the spectra from the thin films only, the spectrum of the substrate must be measured first and then removed from the spectra obtained from the measurement of the thin film on the substrate. The light source used to measure the absorption spectra was a tungsten halogen lamp (LS-1 Ocean Optics).

3. RESULTS AND DISCUSSION

To prepare a P3HT/PCBM solution of weight-ratio 1:1, P3HT powder was dissolved in chloroform, chlorobenzene or dichlorobenzene to achieve a concentration of 10, 17 and 20 mg/mL respectively. Similarly, PCBM was dissolved in these solvents at the corresponding concentrations, followed by mixing P3HT and PCBM solutions, stirring and heating at 50^{o}C for ~12 hours. Afterwards, the P3HT/PCBM blend solution was spin coated onto the cleaned glass substrates [11]. Figure 2 shows the effect of the different solvents on the UV-Vis absorption spectra for the thin films of P3HT/ PCBM. For the P3HT/ PCBM thin film fabricated from the chloroform, wavelength of the absorption peak (λ_{max}) is at 613.1 nm. For the P3HT/PCBM film fabricated from dichlorobenzene, λ_{max} is 673.8 nm showing a red-shift, and two shoulders at 725.0 and 770.0 nm, respectively. However for the P3HT: PCBM film prepared from the chlorobenzene, a blue shift was found with λ_{max} at 544.9 and 545.3 nm. The change in the peak absorption wavelength in the different solvents may be attributed to an increased interchain interaction among P3HT chains. The redshift in the peak absorption wavelength results in more delocalized conjugated π electrons, the lowering of the band gap between π and π^* and the increase of the optical π-π^* transition [6]. It was reported that the interface between the polymer and the cathode is important to determine the electrical characteristics of the devices [12]. In this case, the morphology of the spin coated polymer film is an important factor to understand the property of the metal-polymer interface. Figure 3 shows AFM images of the surfaces of typical P3HT/PCBM films prepared from different solvents. Root mean square (RMS) roughness is used as a parameter to quantitatively characterize the roughness of the surfaces of the thin films. The values of the RMS roughness were obtained from the AFM software (Quesant). For the P3HT/PCBM film fabricated from chloroform, the surface is smooth with a RMS roughness of 3.3 nm (Fig. 3c), which is similar with the surface roughness of the film prepared from chlorobenzene, i.e., 2.4 nm (Fig. 3a). However, the film fabricated from dichlorobenzene indicates a higher roughness value (10.8 nm) than the cases using other solvents. To take advantage of the merit of large roughness to achieve a high efficiency [6, 8,13], we use dichlorobenzene as the solvent to prepare P3HT/PCBM thin film in this study.

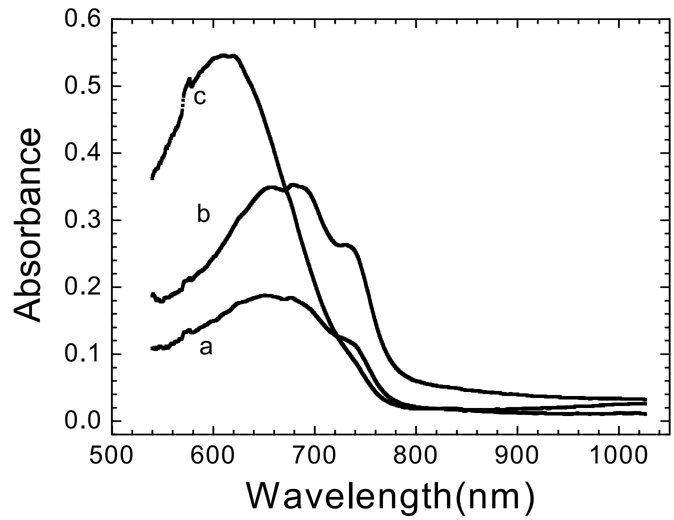
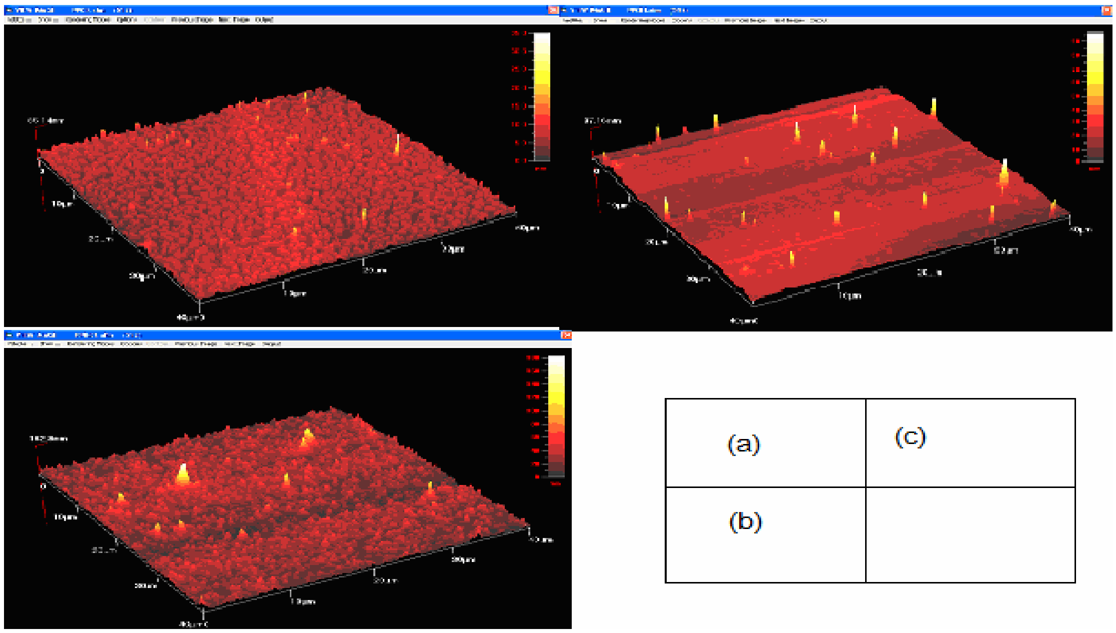


Fig. 2. Absorption spectra of P3HT: PCBM thin films (with PCBM 50 wt %) prepared from (a), chlorobenzene; (b), 1, 2 dichlorobenzene; and (c), chloroform.

After the selection of dichlorobenzene as the suitable solvent, the composition ratio of the donor/acceptor (P3HT/ PCBM) to be dissolved in dichlorobenzene needs to be optimized. The absorption and morphology of the film of pure P3HT and the composition with a ratio varying from 1:1 to 1:3 were studied by the spectrometer and AFM. Figure 4 shows the absorption spectra of the films of P3HT/PCBM with a weight ratio of 1:1, 1:2 and 1:3, respectively. The absorbance of P3HT/PCBM film becomes weak with the addition of PCBM, which is not preferable for a photovoltaic device. For P3HT at 1:2 weight ratio and further the absorbance becomes too weak to have a pronounced absorption peak, which is too weak to collect the photon effectively. The morphology of the thin films of P3HT and P3HT/PCBM at a weight of 1:1, 1:2 and 1:3 has been observed by AFM, as shown in Figure 5. With the increase in the PCBM concentration, the roughness of the film surface was found to increase accordingly except for the case with a ratio of 1:2. Compared with other AFM images (Fig. 5 a, b and d), some giant spikes were found on the surface of the P3HT/PCBM film at the ratio of 1:2, which are believed to be either the grains on the surface or abnormalities of the AFM tip. However, the absorbance of P3HT/PCBM film at a ratio of 1:3 is too low to absorb photons. As a compromise to achieve high device efficiency, P3HT/PCBM film at 1:1 weight ratio will be used in this study to prepare the P3HT/PCBM film from dichlorobenzene.

Figure 6 shows the effect of thermal annealing on the absorption spectra of the thin films of P3HT/PCBM deposited on the glass substrates. A pronounced change after thermal annealing of the films can be found on the absorption spectra.

For the as-deposited film the wavelength of the absorption peak (λ_{max}) is 520.3 nm with one visible shoulder at ~545 nm and the other one at ~594 nm. After annealing at 70°C the λ_{max} is blueshifted to 518.9 nm without any change in the positions of the two shoulders. Further increase of the annealing temperature results in the similar trend in the change of the absorption spectra. For thermal annealing at 150°C, λ_{max} shows a redshift to 516 nm and the positions of the two shoulders at ~545 and ~549 nm become more distinguishable. It is interesting to note that the absorbance of the film increased gradually with the thermal annealing process and the largest increase was found for the annealing at the high temperature of 150°C.



	Chlorobenzene (a)	Dichlorobenzene (b)	Chloroform (c)
RMS roughness	2.4 nm	10.8 nm	3.3 nm

Fig. 3. AFM images (40×40 μm) of the morphology of P3HT/PCBM thin films (with PCBM concentration 50 wt% prepared from different solvents of (a) chlorobenzene, (b) dichlorobenzene and (c) chloroform.

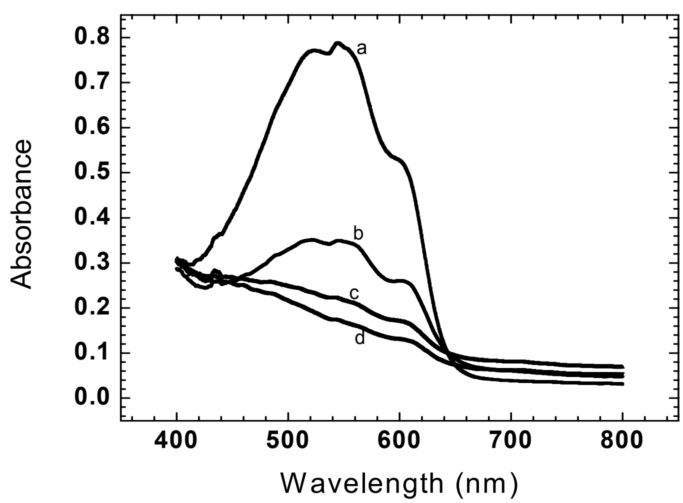
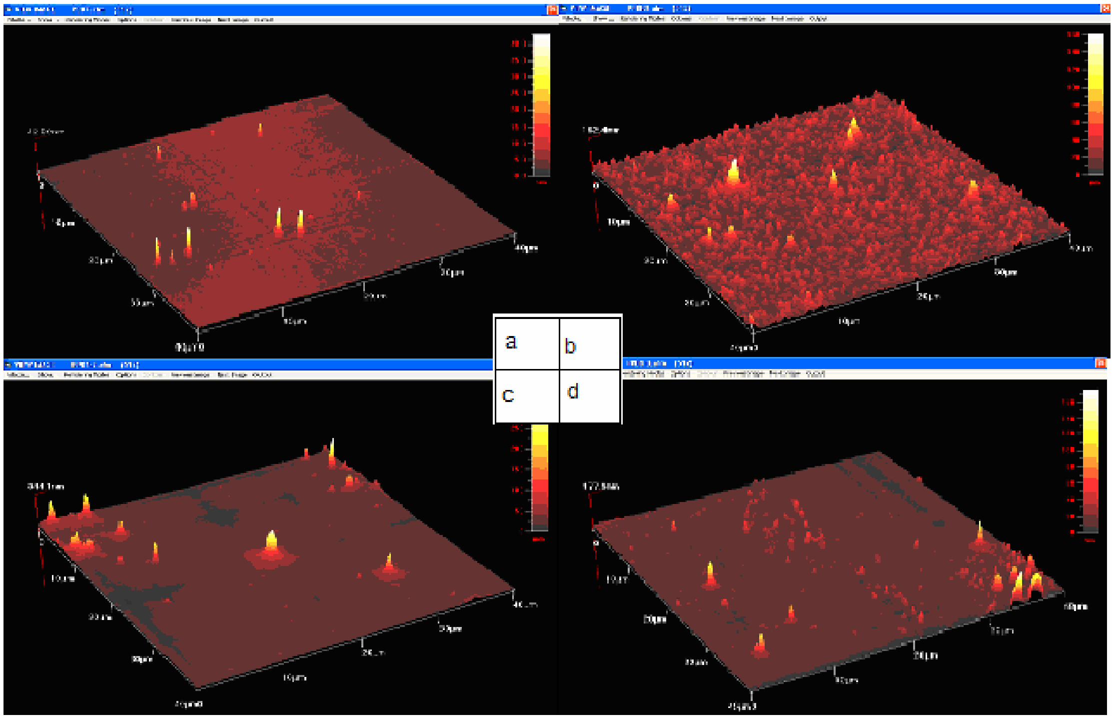


Fig. 4. Absorption spectra of thin films of pure P3HT (a) and P3HT/PCBM prepared from solutions with a weight ratio of (b) 1:1,(c) 1:2, and (d) 1:3, respectively. The concentrations of P3HT in these cases are 16 mg/ml.



	Pure P3HT	P3HT/PCBM at 1:1	P3HT/PCBM at 1:2	P3HT/PCBM at 1:3
RMS roughness	1.1 nm	10.8 nm	12.5 nm	15.7 nm

Fig. 5. AFM images (40×40 μm) of the films of (a) pure P3HT and P3HT/PCBM prepared with a composition ratio of (b) 1:1, (c) 1:2 and (d) 1:3.

The AFM images of the active layer before and after annealing at different temperatures are shown in Fig. 7. The surface of the as-deposited film is smooth with a RMS roughness value of 10.8 nm. However, after undergoing thermal treatments at 70, 110 and 150^{o}C for a duration of 10 minutes separately the roughness becomes 9.4, 22.1 and 4.7 nm, respectively. The surface becomes rougher as the annealing temperature is increased to 70 and 110^{o}C, but not for the case in the further increase up to 150^{o}C. The surface becomes less rough as the annealing temperature is in the range from 110 to 150^{o}C. The morphology of Fig. 7c shows the largest roughness as compared with the annealing at other temperatures. The optimal annealing condition for P3HT/PCBM film is thus 110^{o}C for 10 min.

The refractive index of the films blended with two materials is a complex number with a real part and an imaginary part (extinction coefficient, k), which has been determined by ellipsometry. The absorption coefficient α will be derived from the relationship between the absorption coefficient and the extinction coefficient [11], i.e.,

$$\alpha = -\frac{\mathrm{In}\left(\frac{I_0}{I_t}\right)}{t} \qquad (1)$$

where I_o is the intensity of the incident light source; I_t is the intensity of the light after passing through the film, and t is the thickness of the film.

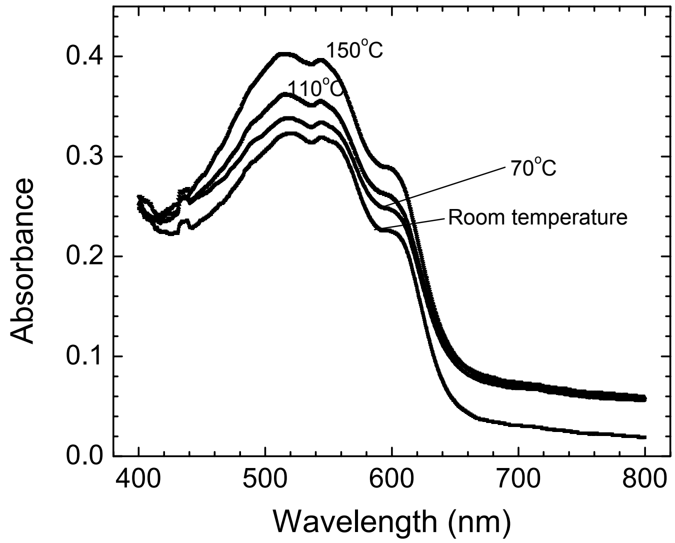


Fig. 6. Absorption spectra of the P3HT/PCBM thin film before and after annealing at different temperatures. The annealing time is 10 min for all films.

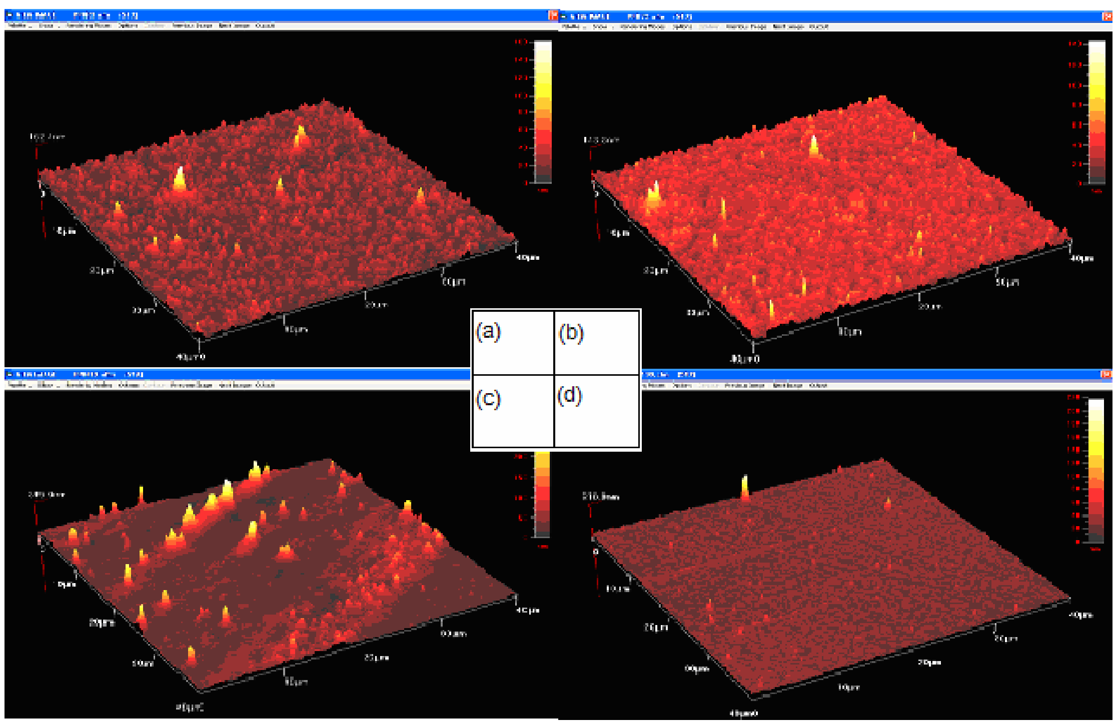


	Fig.7(a)	Fig.7(b)	Fig.7(c)	Fig.7(d)
RMS roughness	10.8 nm	9.4 nm	22.1 nm	4.7 nm

Fig. 7. AFM images (40×40 μm) of P3HT: PCBM (1:1 wt%) thin film before (a) and after annealing at (b) 70°C, (c) 110°C and (d) 150°C for 10 min.

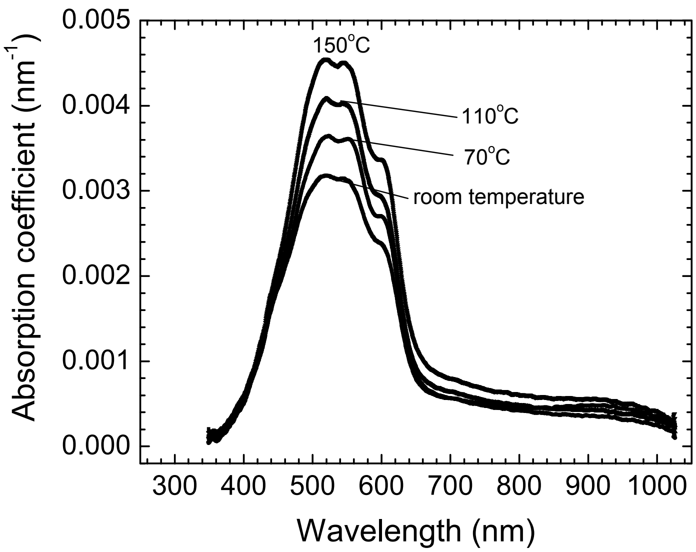


Fig. 8. Absorption coefficients of the P3HT/PCBM thin films annealed at different temperatures

Table 1. Optical constants of the P3HT/PCBM blend thin films annealed at different temperatures.

	Refractive index n	Extinction coefficient k	Thickness (nm)	Absorption coefficient at 632.8 nm (nm^{-1})	Absorption coefficient at 632.8 nm from Fig. 8 (nm^{-1})
P3HT/PCBM film (as-deposited)	2.0583	0.0082	175.6	1.5083×10^{-4}	1.258×10^{-4}
P3HT/PCBM annealed at 70°C	3.1580	0.0083	181.2	1.6482×10^{-4}	1.361×10^{-4}
P3HT/PCBM annealed at 110°C	2.1534	0.0041	174.5	8.1421×10^{-5}	1.483×10^{-4}
P3HT/PCBM annealed at 150°C	3.1015	0.0125	162.1	2.4823×10^{-4}	1.776×10^{-4}

The absorption coefficients of the P3HT/PCBM films derived from Eqn. (1) and annealed at different temperatures are shown in Fig. 8. It can be found that, the absorption coefficient of the P3HT/PCBM film increases with the increase in the annealing temperature. The annealing temperature slightly changes the wavelength of the maximum absorption coefficient: i.e. 519.3 nm for the as-deposited film, and 523.6, 521.1, and 518.6 nm for the films annealed at 70, 110 and 150°C, respectively.

The optical constants of the P3HT/PCBM films annealed at different temperatures are given in Table 1. It can be found that the refractive index of the as-deposited P3HT/PCBM film is N=2.0583+0.0082i. The thickness of the films is 175.6 nm. The table shows the absorption coefficients of the P3HT/PCBM film at 632.8 nm, which were obtained from two independent methods: one from the absorption spectra in Fig. 8, and the other one from the extinction coefficient measured by ellipsometry. The discrepancy ranges from 16-42%. For the ellipsometric measurement, since the film thickness and the complex refractive index are obtained from the regression performed on the initial parameters input by the user, the accuracy of the initial values will significantly influence the accuracy of the final results. On the other hand, the areas to be measured by both methods were not necessarily the same, which also contributed to the discrepancy. Nevertheless, the results obtained from these two independent methods do agree with each other.

3. SUMMARY

In this paper, important factors for improving the performance of donor-acceptor bulk-heterojunction photovoltaic cells have been investigated, which include identification of optimal solvent to dissolve organic materials and composition of the blend, optimization of thermal annealing parameters, and measurement of optical constants of thin films. From the AFM images of the thin film of P3HT/PCBM prepared from chloroform, chlorobenzene and dichlorobenzene, P3HT/PCBM film prepared from dichlorobenzene shows a rough surface morphology. Spectroscopic study also indicates that the films prepared from dichlorobenzene possess larger absorption. Dichlorobenzene was thus identified as the optimal solvent for P3HT/PCBM blend. Morphology of P3HT/PCBM films with composition ratios of 1:1, 1:2 and 1:3 observed by AFM shows that the roughness of the film surface increases with the increases in PCBM concentration, however, the absorption in the thin film is significantly quenched as the PCBM concentration increases. As a result, the optimal D/A composition ratio for P3HT/PCBM film is 1:1. The annealing effects of the photovoltaic films based on P3HT/PCBM thin film have been optimized. From the morphology study by AFM, the surfaces of P3HT/PCBM films have been found to become rougher as compared with the film treated at 70^{o}C and 150^{o}C. Absorption spectra of the P3HT/PCBM film annealed at different temperatures reveals that the absorbance of the film increases as the annealing temperature increases. Thus, the best annealing condition for the P3HT/PCBM films are thermal treatment at 110^{o}C for 10 minutes. The optical constant of the P3HT/PCBM films has been measured by ellipsometry. The complex refractive index of the P3HT:PCBM (1:1) films is 2.55+0.0084i. The absorption coefficients obtained from UV-Visible spectrometer agrees with the results obtained from ellipsometry. The absorption coefficients of the P3HT/PCBM films increase as the annealing temperature increases. The information on the optical constants of the photovoltaic films is very important for multilayer design and device optimization.

ACKNOWLEDGMENT

The authors thank Natural Science and Engineering Research Council of Canada (NSERC) for the grant support. One of the authors (Q. Chen) thanks Canada Research Chairs Program, Canada Foundation for Innovation, the Province of Newfoundland and Labrador, and Memorial University of Newfoundland on the support of research infrastructure.

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