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Effect of Thickness and Composition Ratio of Poly(3-Hexylthiophene) and [6,6]-Phenyl C60-Butyric Acid Methyl Ester Thin Film on Optical Absorption for Organic Solar Cell Fabrication

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Abstract: A Blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C60-butyric acid methyl ester (PCBM), a fullerene derivate based donor-acceptor copolymer, is one of the widely used organic solar cell materials for photon-electron conversion. Thin films were developed, characterized, and optimized for optical absorbance. Absorption spectra were measured using a UV-VIS spectrophotometer. In this work, the effects of composition ratios of P3HT:PC_{60}BM and various thicknesses was studied in ambient conditions. The P3HT:PC_{61}BM thin film was deposited in two different composition ratio (1:1 and 1:3) and fabricated at seven different thicknesses of 20 nm, 30 nm, 35 nm, 87 nm, 98 nm, 115 nm, and 146 nm corresponding to spin coating speeds of 4000rpm, 3000rpm, 2000rpm, 1500rpm, 1250rpm, 1000rpm, and 750rpm, respectively. P3HT:PC_{60}BM thin film composition ratio of 1:1 with thickness of 87nm shows relatively better photon absorption optical parameter than P3HT:PC_{60}BM composition ratio of 1:3. P3HT: PC_{61}BM solution coated at a spin speed of 1500 rpm shows a better absorption of photon energy. The results showed that the optimum thickness of the thin film is 87 nm at composition ratio of 1:1. Energy band gap values of composition ratio of 1:3 is observed to decreases with increase in spin- speed from 3.9 eV to 3.7 eV. The results can be used as a guideline for improving the design and fabrication of active layer of organic solar cells.

Keywords: Optical Transmittance, Reflectance, Absorbance, Organic Thin Film, P3HT, PCBM Blend, Bandgap Energy

1. Introduction

The demand for clean energy sources has increased, leading to a rapid growth in the field of research and development of solar energy. Solar cells are devices which convert the light into electrical energy [1]. Solar cells can be fabricated using organic, inorganic or hybrid materials and are divided into three different generations [2]. The First generation consists of crystalline semiconductor wafers with a thickness of 200-300 µm. The Second-generation solar cells are based on thin film technology having thickness, usually in the range of 1-2 µm. Third generation solar cells are under research process, to increase the efficiency. Third generation solar cells, instead of expensive semiconductors, usually employ solution-processed materials such as polymers, nanoparticles and additives which make them easier to manufacture using cheap methods and processes [3]. In the field of polymer-based photovoltaic cells, blend of poly(3-hexylthiophene) (P3HT), a polymer, and [6,6]-phenyl C61-butyric acid methyl ester (PCBM), a fullerene derivate based donor-acceptor copolymer, is one of the most-studied active materials organic solar cell materials for photon-electron conversion [4-15] Organic polymers such as P3HT:PCBM blends have wider band gaps than natural semiconductors [16-17]. This paper studied the effects of composition ratios of P3HT:PC_{61}BM on photo-absorption optical properties under various thicknesses in ambient conditions for photoactive layer device. Very limited research efforts have so far been dedicated to this topic. Most research effort has been focused on the efficiency improvement and analyses of film morphological behavior.

2. Materials and Methods

To study the effect of varying the thickness and composition ratio of Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C60-butyric acid methyl ester (PCBM) thin film on optical absorption: A precursors for active layer organic solar cell fabrication. Thin film of P3HT:PCBM was deposited on cleaned glass substrate using the materials itemized below.

2.1. Materials

[6,6]-phenyl C_{61} butyric acid methyl ester (PCBM), with >99.5% purity, product of Nederlands was obtained from Sigma – Aldrich. Poly (3-hexylthiopene-2,5-diyl) regioregular (P3HT) product of USA, was supplied by Sigma – Aldrich.

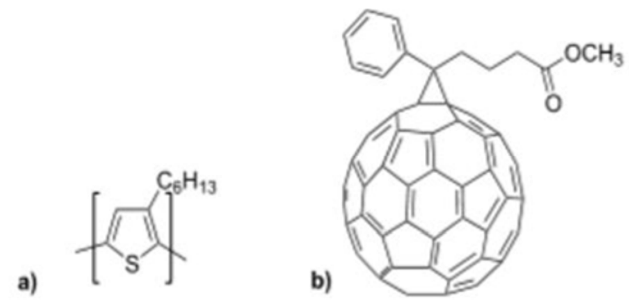

Figure 1. Structure of (a) P3HT and (b) PCBM Beilstein J. Nanotechnol. (2018, 9, 1108–1115).

2.2. Methods: The Following Experimental Procedures Were Carried Out

2.2.1. Substrate Preparation

Clean rectangular glass slides of dimension 25.4 mm by 76.2mm were used as substrates. The glass substrates were washed with detergent solution for 10 to 15 minutes in ultrasonic sonicator and rinsed in distilled water for 15 minutes at 30 ^{0}C. The substrate was cleaned with Isopropanol alcohol [IPA] in ultrasonic bath for 15 minutes at 30 ^{0}C and dried in a stream of nitrogen gas (N_2).

2.2.2. Preparation of P3HT, PCBM and P3HT:PCBM Blend Solutions

1ml of chloroform solvent was added into 15mg of poly (3-hexylthiophene) (P3HT) and to 15mg of [6,6] phenyl C-butyric acid methyl ester (PCBM) all from Sigma Aldrich to form P3HT and PC_{60}BM solutions separately. The two solutions then underwent ageing process by using magnetic stirrer for 3 hours without heat to allow the organic materials mixture to fully dilute into the solvent. Composite solutions were prepared by mixing P3HT solution with PC_{60}BM solution in composition ratios of 1:1 and 1:3 respectively. The solutions were stirred for another 3 hours using magnetic stirrer for homogeneous mixture. The solutions were thoroughly completely covered from light ray using an aluminum foil to avoid degradation of the materials.

2.2.3. P3HT:PC_{60}BM Thin Film Fabrication

Spin- coater Model WS-650MZ-23NPP was used for deposition of solution on substrate. P3HT:PCBM solution of composition ratios of (1:1, 1:3) were spin-coated onto cleaned glass substrate respectively at spin speed of 4000 revolutions per minute (rpm), 3000rpm, 2000rpm, 1500rpm, 1250rpm, 1000rpm, and 750rpm, respectively for all films. P3HT:PC_{61}BM thin film was deposited in two different composition ratio (1:1 and 1:3) and fabricated at seven different thicknesses of 20 nm, 30 nm, 35 nm, 87 nm, 98 nm, 115 nm, and 146 nm corresponding to spin coating speeds of 4000 rpm, 3000 rpm, 2000 rpm, 1500 rpm, 1250 rpm, 1000 rpm, and 750 rpm, respectively.

2.2.4. P3HT:PCBM Thin Film Optical Properties Characterization

Transmittance and Reflectance of P3HT:PCBM thin film was measured by an optical spectrophotometer (UV-VIS Avantes, Avalight-DH-5BAL). Absorption spectra was calculated using equation (1).

$$\text{Absorbance} = 2\text{-log10} \ (^0/_0T) \tag{1}$$

Where $^0/_0T$ is percentage transmittance

Results from the UV-VIS spectra helped to map the optical absorption and transmittance characteristics of the materials which included the percentage absorption and the wavelength position. Refractive index of P3HT:PCBM thin film was calculated using equation (2) [18].

$$\text{Refractive index (n)} = [\ 1+ (R)^{0.5} / \ 1-(R)^{0.5}] \tag{2}$$

Reflectance R values was obtained from UV-VIS spectrophotometer measurement. The variation of refractive index with wavelength is shown in figure 8 and 9.

According to Tauc (1970) [19] the dependence of the absorption coefficient α on the photon energy hν for near-edge optical absorption in semiconductors takes the form equation (3).

$$(\alpha h\nu)^{1/m} = k(h\nu - E_g) \tag{3}$$

where E_g is the optical band gap, k is a constant and m=1/2 for an allowed direct energy gap and m=3/2 for a forbidden direct energy gap. In order to determine the optical band gap of a semiconductor thin film, taking m=1/2, $(\alpha h\nu)^2$ must be plotted versus hν using the data obtained from the optical absorption spectra. The direct bandgap of the semiconductor thin film is obtained by extrapolating the linear part to the zero of the ordinate. The absorption coefficient of thin film is calculated from equation (4) [20].

$$\alpha = 2.303(A/t) \tag{4}$$

Where, A is absorbance and t is the thickness

$$\text{Band Gap Energy (E)} = hc/\lambda \quad (5)$$

Where h = planks constant =6.626 x 10^{-34} joules sec. C= speed of light =3.0 x 10^{8} meter/sec. where 1ev =1.6 x 10^{-19} joules (conversion factor). For calculation of the optical band gap of films, the curve of $(\alpha h\upsilon)^2$ vs. hυ was plotted. The energy band gap was obtained from straight line plot of $(\alpha h\upsilon)^2$ versus hυ by extrapolating of the line to base line in Figure 10 and figure 11.

3. Results and Discussion

Results from the UV-VIS spectra helped to map the optical transmittance, reflectance, and absorption characteristics of the materials which included the percentage absorption and the wavelength position.

3.1. Optical Transmittance

Figure 2 shows the graph of transmittance versus wavelength of composition ratio 1:1 at different spin speeds. Deposition at 3000 rpm has two peaks one at 350nm corresponding to 48% and at 600 nm corresponding to 92%. Figure 3 depicts composition ratio 1:3 which has its peaks at 350 nm, 40% and 500 nm with spin speed at 3000 rpm.

3.2. Optical Reflectance

Figure 4 shows the graph of reflectance against wavelength of composition ratio 1:1 spin coating done at 1000 rpm has the highest reflectance followed by the one done at 750 rpm. Figure 5 of reflectance versus wavelength graph at composition ratio 1:3 shows that deposition done at 4000 rpm has the highest reflectance.

3.3. Optical Absorbance

Figure 6 shows the optical absorption spectra of P3HT:PC_{60}BM thin films with composition ratio 1:1 and fabricated in seven different thicknesses, the one fabricated at 87nm produce the highest optical absorption in the wavelength range 400 to 600 nm with peak at 500nm. Figure 7 shows the optical absorption properties of P3HT:PC_{60}BM thin films in composition ratio of 1:3, the highest absorption occurs in the wavelength range 400 to 510 nm having peak at 470nm in the visible wavelength band with 87nm (1500 rpm) thickness.

3.4. Refractive Index

Refractive index of P3HT:PCBM thin film was calculated. The variation of refractive index with wavelength is shown in figure 8 and 9. Deposition done at spin speed 4000 rpm in figure 9 has the highest refractive index.

3.5. Optical Band Gap Energy

The energy band gap was obtained from straight line plot of $(\alpha h\upsilon)^2$ versus hυ by extrapolating of the line to base line in Figure 10 and figure 11, the curve of $(\alpha h\upsilon)^2$ vs. hυ. The Optical energy band gap values were evaluated by plot of $(\alpha h\nu)^2$ versus hυ. Band gap value of composition ratio 1:1 at spin speed 3000 rpm (30 nm) is 3.85 eV in figure 10. While the band gap values of composition ratio of 1:3 is observed to decreases with increase in spin- speed from 3.9 eV to 3.7 eV in figure 11.

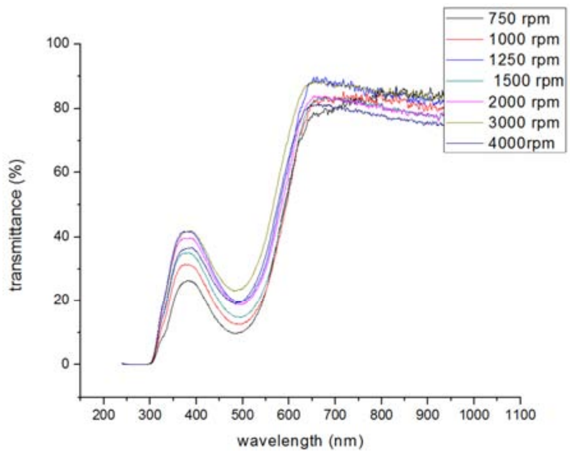

Figure 2. *Transmittance spectrum of P3HT:PC_{60}BM (1:1) thin films at different thicknesses of deposition.*

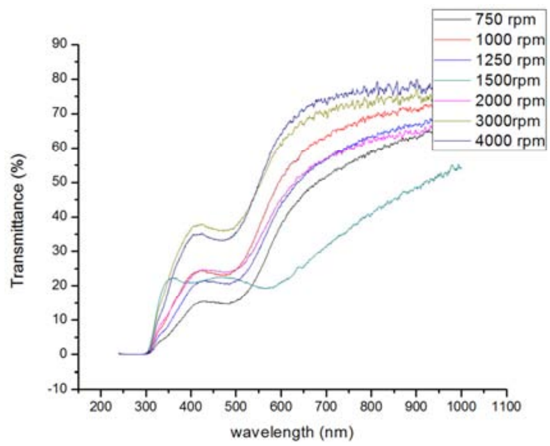

Figure 3. *Transmittance spectrum of P3HT:PC_{60}BM (1:3) thin films at different thicknesses of deposition.*

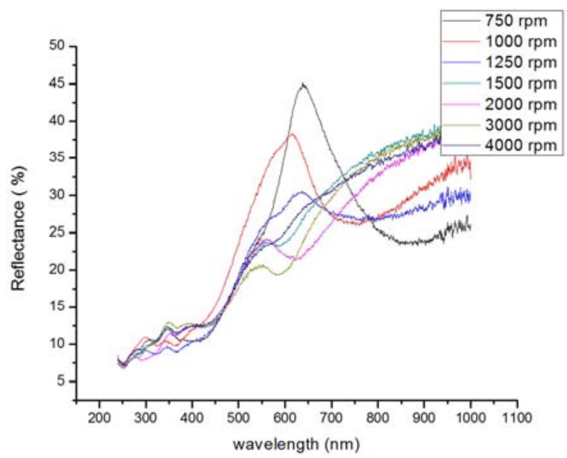

Figure 4. *Reflectance spectrum of P3HT:PC_{60}BM (1:1) thin films at different thicknesses of deposition.*

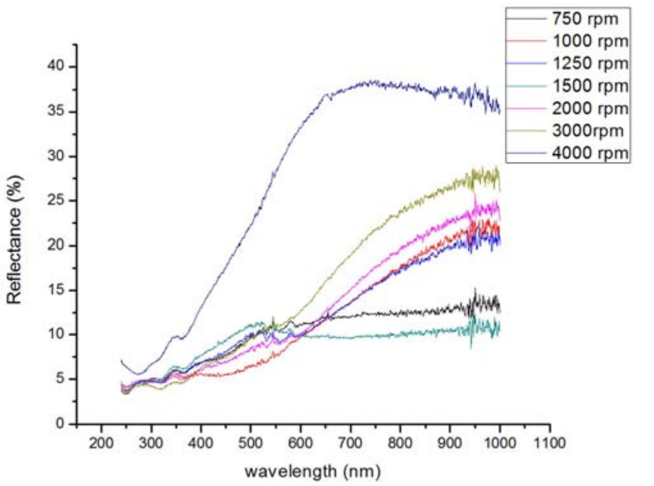

Figure 5. *Reflectance spectrum of P3HT:PC$_{60}$BM (1:3) thin films at different thicknesses of deposition.*

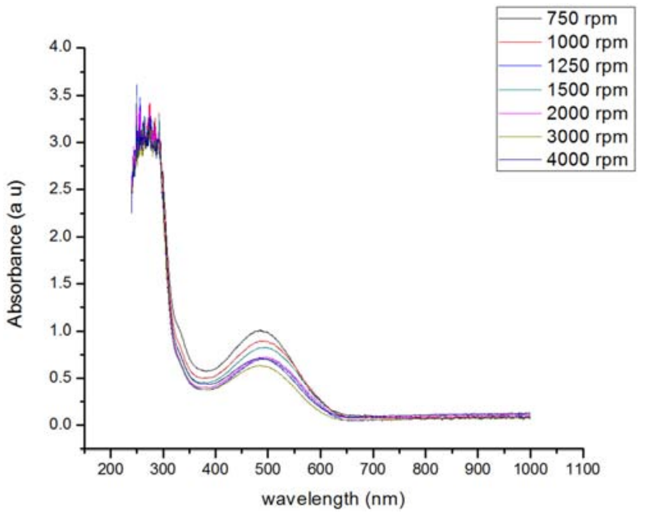

Figure 6. *Absorption spectrum of P3HT:PC$_{60}$BM (1:1) thin films at different thicknesses of deposition.*

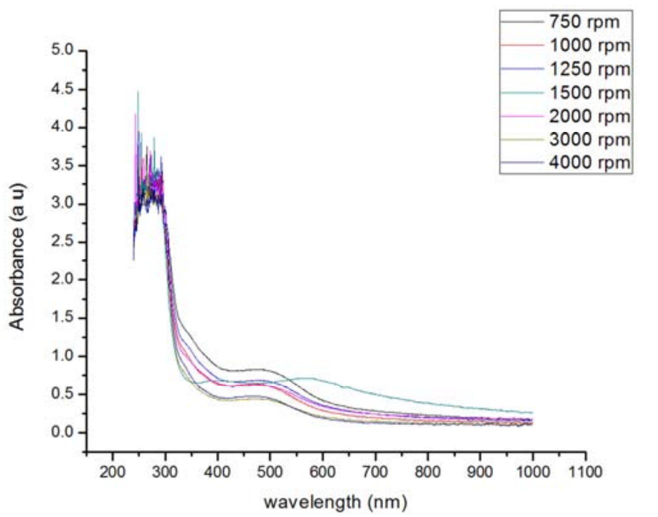

Figure 7. *Absorption spectrum of P3HT:PC$_{60}$BM (1:3) thin films at different thicknesses of deposition.*

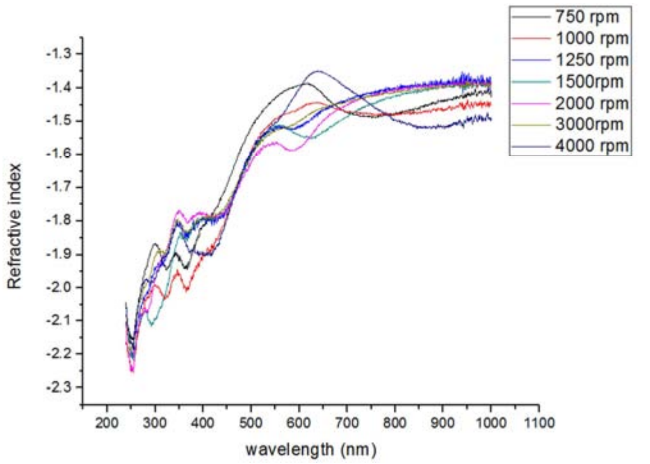

Figure 8. *Refractive index versus wavelength graph of P3HT:PC60BM (1:1) thin films at different thicknesses of deposition.*

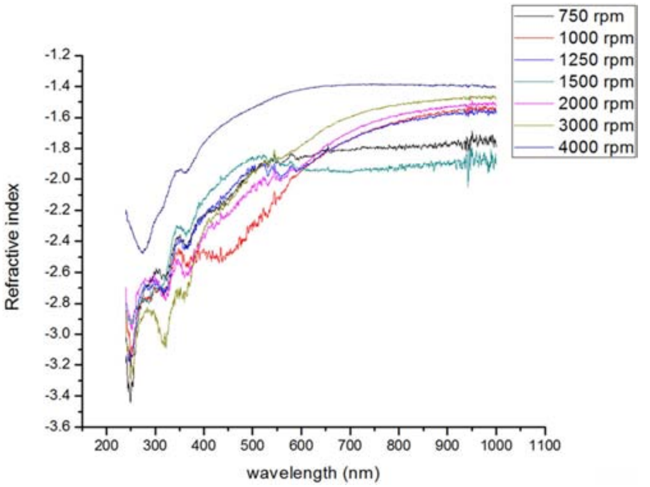

Figure 9. *Refractive index versus wavelength graph of P3HT:PC$_{60}$BM (1:3) thin films at different thicknesses of deposition.*

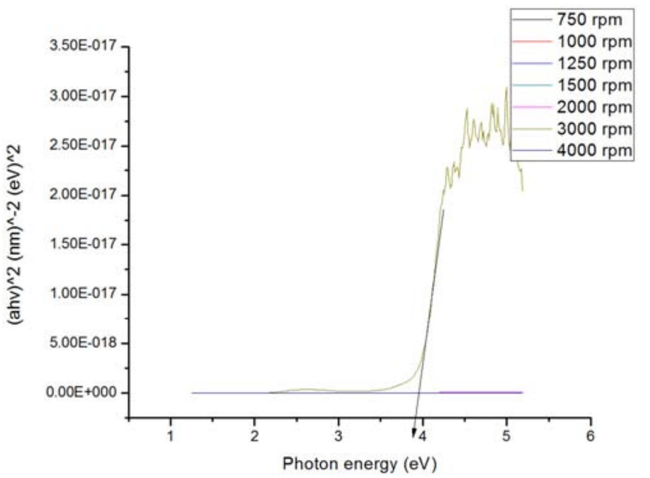

Figure 10. *Plot of $(\alpha hv)^2$ versus hv for P3HT:PC$_{60}$BM (1:1) thin films at different thicknesses of deposition.*

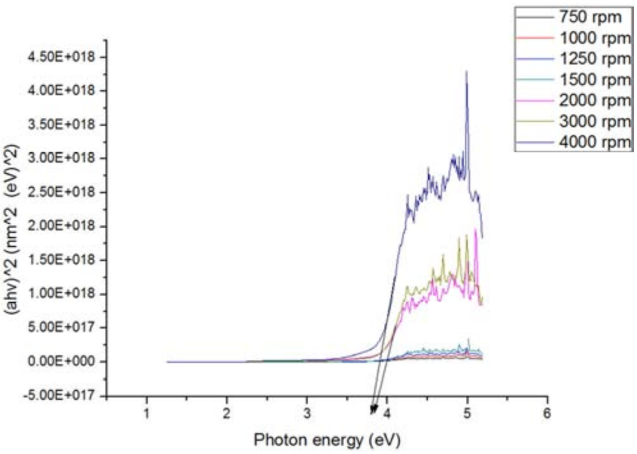

Figure 11. *Plot of* $(\alpha h\nu)^2$ *versus hv for P3HT:PC*$_{60}$*BM (1:3) thin films at different thicknesses of deposition.*

5. Conclusion

This work presented an in-depth study of the effect of Varying the Thickness and composition ratio of Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C60-butyric acid methyl ester (PCBM) Thin Film on optical absorption spectroscopy. We have investigated thin films of P3HT:PCBM blends deposited by spin-coating. Thin film of P3HT:PCBM as the photoactive layer have been optimized. The highest measured optical absorption is 1.0 a u at thin film thickness of 87nm (1500 rpm) corresponding to 500nm in the visible wavelength band. P3HT:PCBM blend ratio of 1:1 produce the highest optical absorption than composition ratio of 1:3. Thin film deposited at 1500 rpm corresponding to thickness of 87nm produce the best photo absorption. The refractive indices were calculated, for composition ratio 1:3 deposited at 4000 rpm exhibited highest refractive index in the visible range of wavelength spectrum. The Optical energy band gap values were evaluated by plot of $(\alpha h\nu)^2$ versus hυ. Band gap value of composition ratio 1:1 at spin speed 3000 rpm (30 nm) is 3.85 eV. While the band gap values of composition ratio of 1:3 is observed to decreases with increase in spin- speed from 3.9 eV to 3.7 eV. As the thickness decreases the band gap energy decreases. The results can be used as a guideline for improving the design and fabrication of active layer of organic solar cells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this article.

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