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Effects of Thermal Annealing on Optical Properties of Poly (3-Hexyithiophene): [6,6]-Phenyl C_{6o}-Butyric Acid Methyl Ester Blend Thin Film

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Abstract: Organic solar cells (OSCs) have gained much attention in the field of organic electronics since it has advantage of physical light weight, easy to fabricate, consumed less production cost, and could be produced in large scale for energy harvesting applications. These types of electronics are promising devices that can be used to tackle today's energy issue. Bulk hetero junction organic thin film was deposited using spin-coating method. The material used for the deposition of the thin film is the combination of poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{60}-butyric acid methyl ester ($PC_{60}BM$) that form the interconnection of donor/acceptor component. Deposition was done by spin coating P3HT: $PC_{60}BM$ onto glass substrate in order to form 100nm P3HT: $PC_{60}BM$ active layer. Thermal annealing at three different temperatures was carried out on the samples deposited. The optical characterization of the thin film was investigated using UV-VIS spectrophotometer. The thin film based on P3HT: $PC_{60}BM$ blend film was deposited and annealed at 120°C, 130°C, and 140°C temperature, respectively. The result shows that the film annealed at 140°C has the highest absorption peak at 520nm wavelength in the visible region followed by annealing done at 130°C. This shows that thermal treatment may improve the stability/efficiency of P3HT: $PC_{60}BM$ thin film.

Keywords: Organic Thin Film, Annealing, Blend, P3HT, PCBM, Optical Properties

1. Introduction

Solar energy is a renewable energy source from the sunlight, and has attracted much attention in recent years as one of the most promising ways to tackle today's energy crises because it is renewable and eco-friendly. Efforts to improve the performance of solar cells which convert this abundant energy to electricity had been intensified lately. Organic solar cells (OSCs) have received much attention since it has advantage of physical light weight, easy to fabricate, consumed less production cost, and could be produced in large scale [1-3]. Amongst the popular material used for the fabrication of OSCs is the combination of P3HT and $PC_{60}BM$ that form the interconnection of donor/acceptor components so-called bulk heterojunction. This blend system has been widely used for the study of OSCs and it has been reported to have efficiency increase upon the thermal annealing [4-8]. Great number researches have been carried out on annealing treatment of P3HT:PCBM as an organic system for OSCs applications [9-12]. Annealing is a heat treatment, involves heating a material to above its critical temperature, maintain a suitable temperature and then cooling. It can induce ductility, soften material, relieve internal stresses, refine structure by making it homogeneous and improve cold working properties The thermal treatment has been proven to increase the crystallinity of polymer material performance. Polymer material can be deposited and fabricated at low temperature by spin-coating and printing methods [13-15]. The purpose of the present work is to deposit and characterize bulk heterojunction polymer using a spin-coating method. This research is aimed to investigating the optical wavelength absorption spectra of P3HT: $PC_{60}BM$ film. To study the effect of thermal treatment on P3HT: $PC_{60}BM$ thin film wavelength absorption spectra through three different annealing temperatures and characterized by UV spectrophotometer for UV/Visible/NIR characterization.

2. Materials and Methods

2.1. Materials.

The materials used during the research are P3HT, $PC_{60}BM$ which were supplied by Sigma – Aldrich, glass slides and Syringe.

2.2. Methods

2.2.1. Active Layer Sample Solution Preparation

1ml dichlorobenzene (DCB) 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 PC60BM solutions separately as reported by [16]. The two solutions then underwent ageing process by using magnetic stirrer for 2 hours without heat to allow organic materials mixture to fully diluted into solvent and was filtered using PTFE filter. The solutions were then mixed in the appropriate volume ratio and stirred for 2 hours using magnetic stirrer for homogeneous mixture. This helps organic materials to fully dilute. The mixed solution was completely covered from ray of light using an aluminum foil to avoid degradation of the active components.

2.2.2. Substrate Preparation

Clean rectangular glass slides from sigma – Aldrich were used as substrates. The substrates were washed with detergent solution for 10 to 15 minutes and ultrasonically rinsed in water bath distilled water for 15 minutes at 30°C. The substrates were also cleaned with Isopropanol acid [IPA] in ultrasonic bath for 15 minutes at 30°C and was blown-dried in Nitrogen environment.

2.2.3. Deposition of P3HT: PCBM on the Substrate Using Spin - Coater

To coat substrate with active layer, place cleaned substrate on the stub of the spin- coater, set the program, dispense liquid, run the program that is drop solution of P3HT: $PC_{60}BM$ onto substrate, wait for several moments to enable solution to seep, then spin- coat by adopting 2-step setting 500rpm for 30 seconds and 3500rpm for 60 seconds. The system rotates first at low speed to spread the liquid then at high speed to dry. This technique is cheaper and easier to use, it allows for uniform deposition unto flat substrate. The desired thickness of organic layer is between 85nm to 100nm to avoid any exciton recombination. 100nm thickness for P3HT: $PC_{60}BM$ film was chosen. Samples deposited were annealed at different temperatures of 120 – 140°C for 30 minutes at step size of 10°C then apply slow cooling at room temperature and one sample was untreated.

2.2.4. Optical Characterization

Optical characterization of both treated and untreated samples were performed using UV-Vis spectrophotometer under ambient condition model All samples were characterized to determine the optical spectrum for different annealing temperatures.

Mathematically A+R+T=1, A is the absorbance, R is the reflectance and T is the transmittance. To convert between the absorbance and transmittance, use the equation below,

$$\text{Absorbance (A)} = 2 - \log_{10}(\%T)).$$

Absorbance is the portion of light that gets absorbed by the samples. If no light is absorbed, it will have zero absorbance and 100% transmittance.

3. Results and Discussion

In figure 1 the un-annealed sample has its peak at wavelength of 401.152nm corresponding to 88.200% transmittance value. The sample 2 annealed at 120°C has its peak at 518.365nm (wavelength) in visible spectrum corresponding to 57.4385% transmittance as shown in Figure 2. At 130°C annealing there are two transmittance peaks, the first at 389.894nm (wavelength) corresponding to 41.1109% transmittance in UV spectrum and 699.912nm in visible spectrum corresponding to 51.2808% transmittance in Figure 3. The last sample annealed at 140°C has two peak transmittance, one at 395.821nm corresponding to 29.6920% transmittance and the other peak at 712.534nm (wavelength) in (NIR) near infrared ray spectrum corresponding to 45.9157% transmittance as shown in Figure 4. We can deduce from figure 4 that annealed P3HT: $PC_{60}BM$ thin film at 140°C has the highest absorption of light. Figure 5 – Figure 8 showed the reflectance of the samples under different annealing temperatures. In figure 9, the transmittance of the samples was shown and the un-annealed sample exhibits highest value of transmittance followed by samples annealed at 120°C, 130°C and 140°C respectively. This shows that the sample annealed at 140°C could absorb light from the sun as an active material than every other samples as shown in figure 10. The wavelength absorption spectra of blend P3HT: $PC_{60}BM$ thin film annealed at three different temperatures is as shown in Figure 10. At 140°C the highest absorption peak was observed at 520nm in the visible region. At 130°C the absorption peak was at 519nm in the visible spectrum. At 120°C and un-annealed the absorption was minimal. The visible region lies between the infrared and ultraviolet regions and has wavelengths of 400-700 nm. It shows that absorption of the samples (un-annealed to 140°C) blue- shifted as was reported by [17].

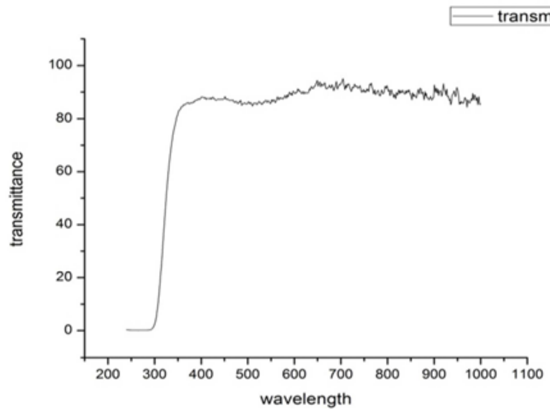

Figure 1. *Un-annealed P3HT: $PC_{60}BM$ film Transmittance.*

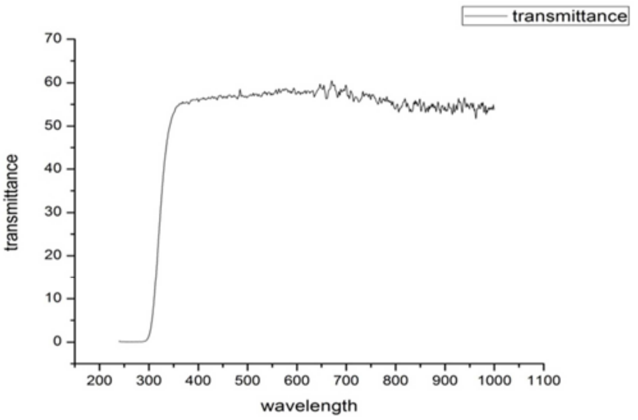

Figure 2. *Annealed P3HT: PC60BM film at 120°C.*

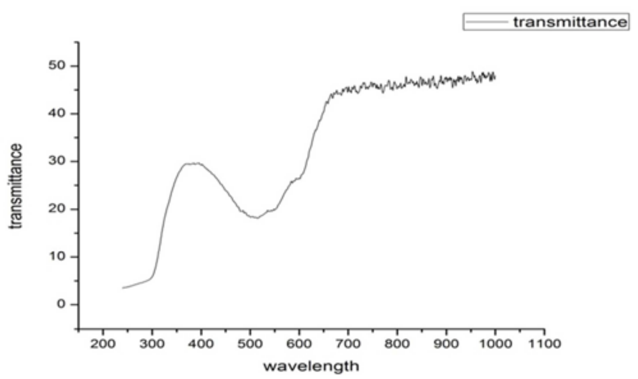

Figure 3. *Annealed P3HT: $PC_{60}BM$ film at 130°C.*

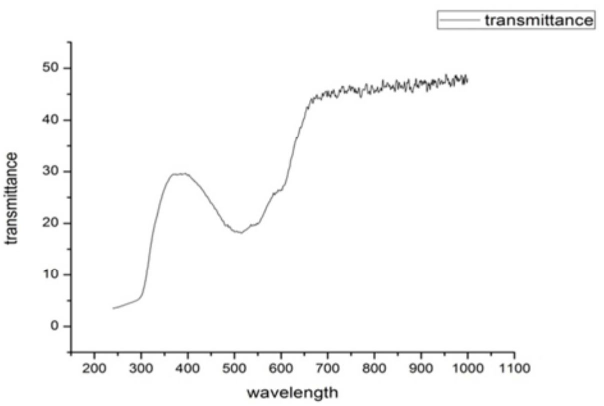

Figure 4. *Annealed P3HT: $PC_{60}BM$ film at 140°C.*

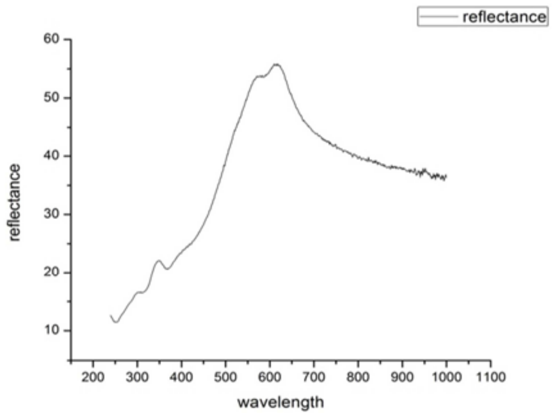

Figure 5. *Un-annealed P3HT: PC60BM film reflectance.*

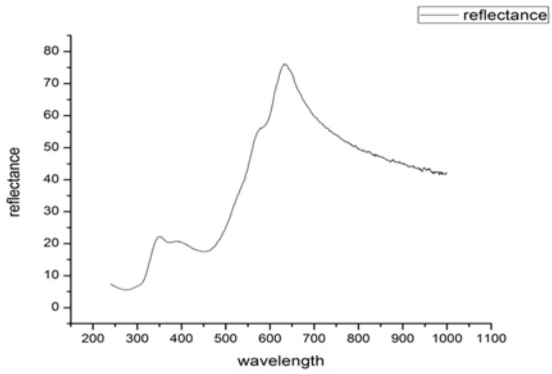

Figure 6. *Annealed P3HT: $PC_{60}BM$ film at 120°C.*

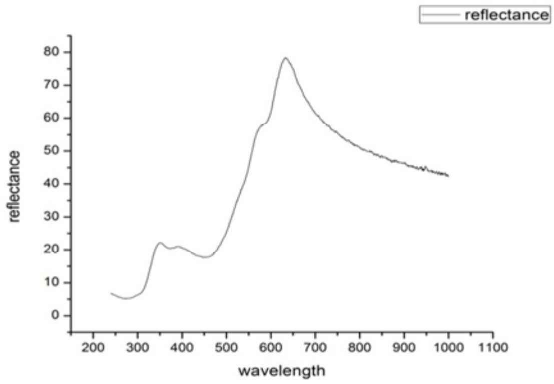

Figure 7. *Annealed P3HT: $PC_{60}BM$ film at 130°C.*

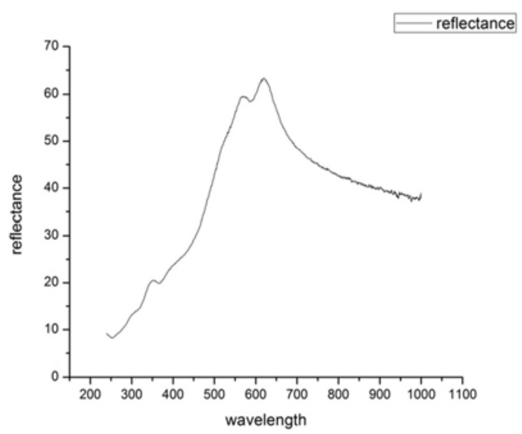

Figure 8. *Annealed P3HT: $PC_{60}BM$ film at 140°C.*

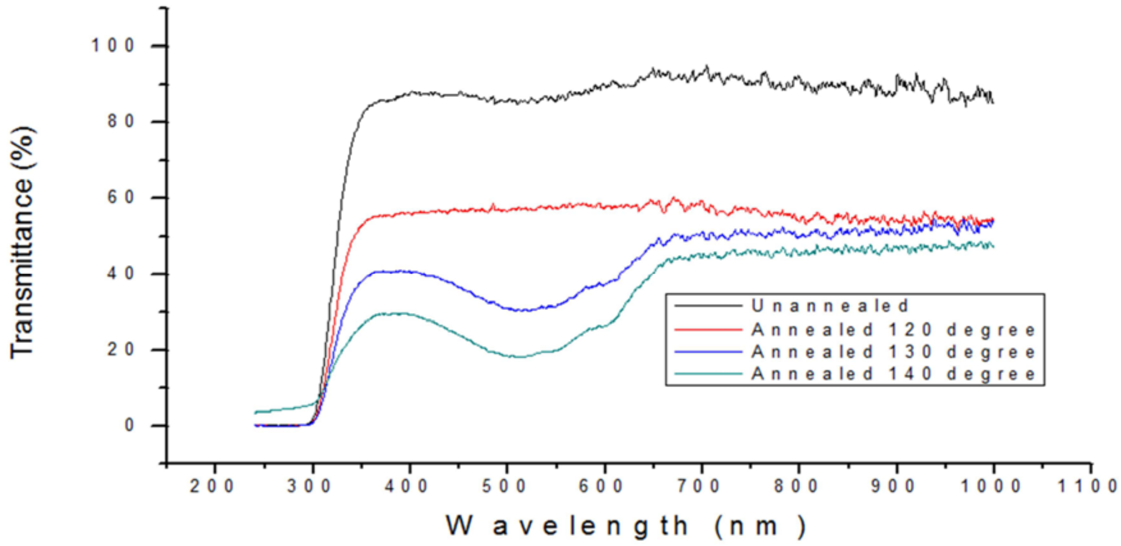

Figure 9. *Transmittance versus wavelength graph.*

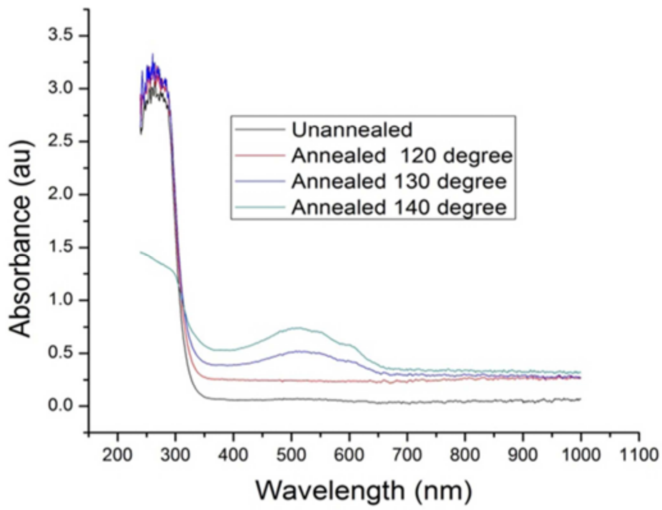

Figure 10. *Absorbance of P3HT: $PC_{60}BM$ thin film.*

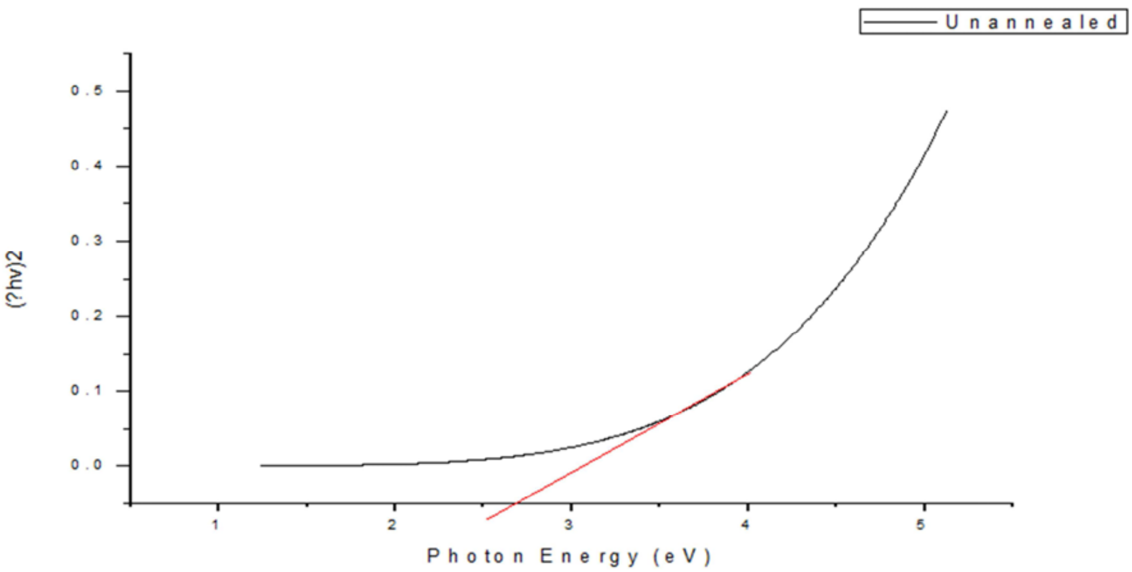

Figure 11. *Band gap of unannealed sample.*

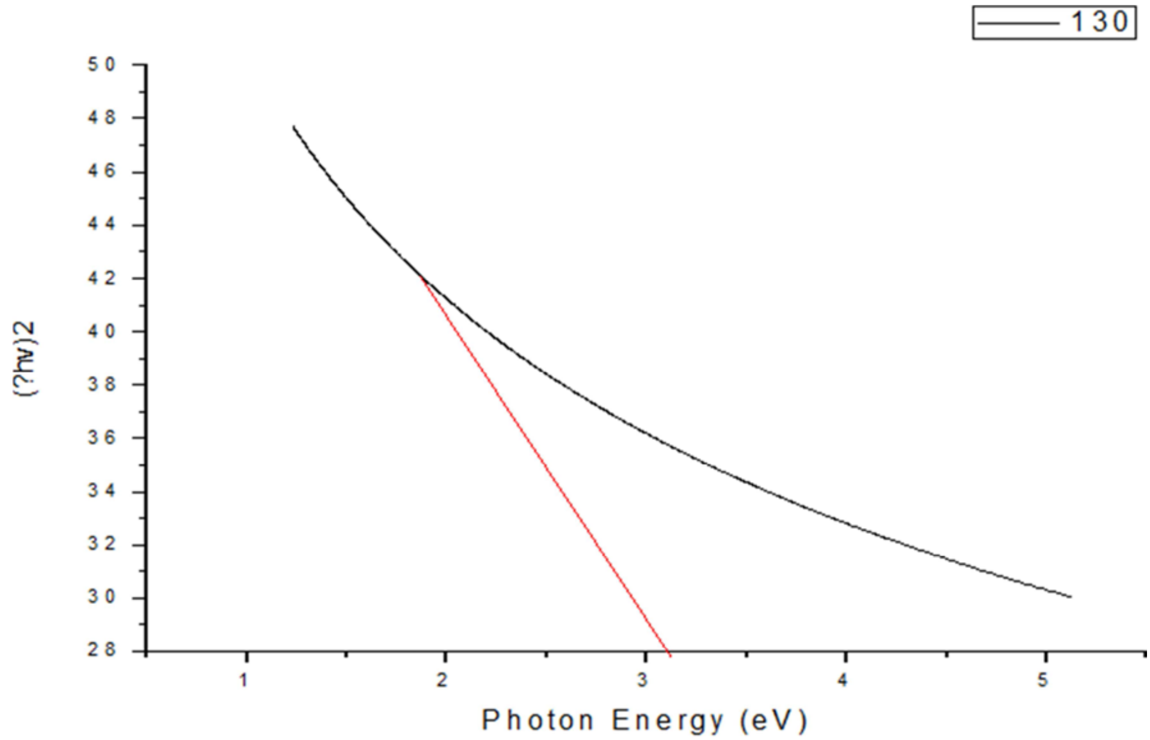

Figure 12. *Band gap at 130 degree annealing.*

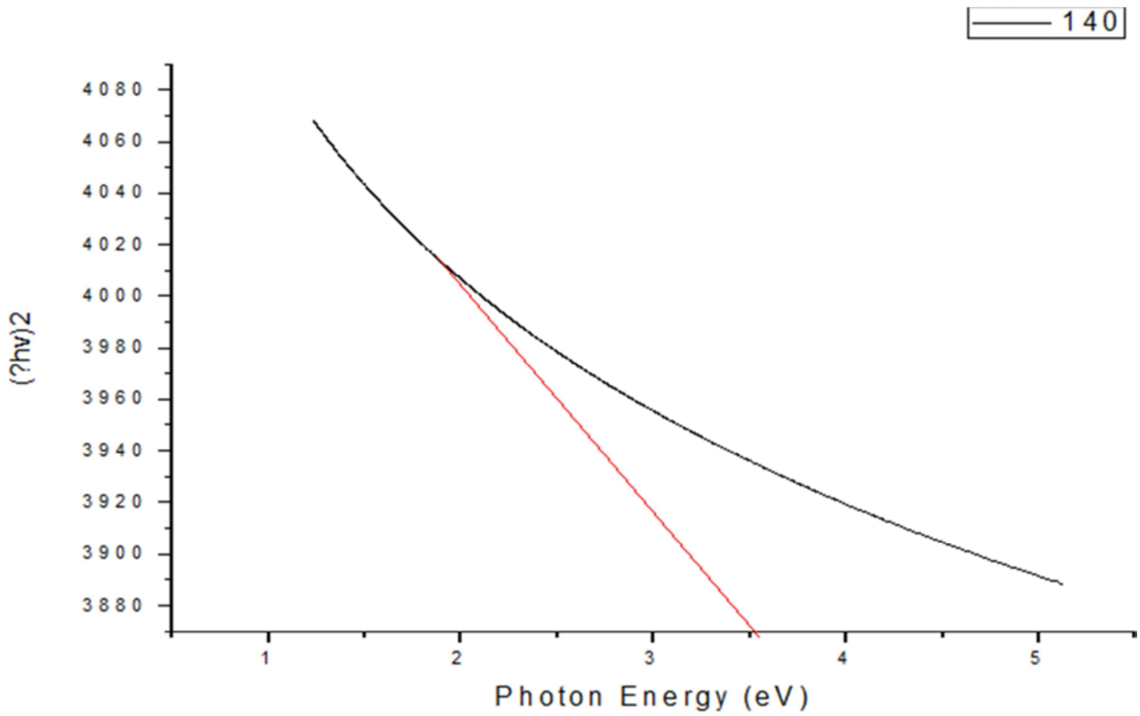

Figure 13. *Band gap at 140 degree annealing.*

The photon energy (hν) and absorption coefficient (α) for direct optical transition are related by the following equation [18, 19].

$$\alpha = A\ h\nu\ (h\nu - E g)^{/2}$$

where hυ is the photon energy, α is the absorption coefficient, E_g is the optical band gap, A is a constant and n = 1 or 4. The energy band gap could obtain from straight line plot of $(\alpha h\upsilon)^{2/}$ vs. hυ by extrapolating of the line to base line. If a straight-line graph is obtained for n=1, it is attributed to direct electron transition from valence band to conduction band whereas n=4, there is indirect transition of electrons from valence band to conduction band [13]. For calculation of the optical band gap of films, the curve of $(\alpha h\upsilon)^2$ vs. hυ was plotted. The E_g value of the films was determined from

Figure 11-13 and was found that the energy band gap increases from 2.7 eV to 3.5 eV as annealing temperature increases.

4. Conclusion

The thin film based on P3HT: $PC_{60}BM$ blend film was deposited and annealed at 120°C, 130°C, and 140°C temperature, respectively. The result shows that the film annealed at 140°C has the highest absorption peak at 520nm wavelength in the visible region followed by annealing done at 130°C. The treatment at 140°C has the highest band gap energy 4.7ev. Heat treatment improves the stability or efficiency of thin film. Also, the band gap energy of the films increases as the annealing temperatures increase.

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