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Research Article

Investigation of Dependence of Optoelectronic Properties of P3HT: PCBM Based Organic Solar Cells on Active Layer Thickness

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ABSTRACT

This paper presents the production and results of optoelectronic characterization process for ITO/PEDOT:PSS/P3HT:PCBM/Al organic solar cells (OSC). OSCs were produced in open air environment with various P3HT:PCBM active layer thicknesses of 70, 110, 140, 175 and 190 nm. The diode properties of the solar cells in the dark have been investigated by using current-voltage (I-V) measurements. The absorption characteristics have been investigated by using transmission spectroscopy, and optical band gap energy (E_g) for each sample has been calculated. Solar cell parameters for each solar cell has been investigated by using current density-voltage (J-V) measurements under AM 1.5 solar raditation, and important solar cell parameters have been calculated. It was observed that fill factor (FF) value of the solar cells increase between 0.3239 and 0.3409 with decreasing diode ideality factor (n) value. The highest value of PCE was found to be 0.59, which belongs to the cell having 140 nm P3HT:PCBM thickness.

Keywords: *Solar Cell, P3HT, PCBM, Electrical Characterization, Optical Characterization*

P3HT:PCBM Tabanlı Organik Güneş Hücrelerinin Opteoelektronik Özelliklerinin Aktif Katman Kalınlığına Bağlı İncelenmesi

ÖZET

Bu çalışmada ITO/PEDOT:PSS/P3HT:PCBM/Al organik güneş hücrelerinin (OSC) üretimi ve optoelektronik karakterizasyon süreci üzerine yapılan araştırmanın sonuçlarını sunmaktadır. OSC'ler, 70, 110, 140, 175 ve 190 nm P3HT:PCBM aktif tabaka kalınlıklarına sahip olacak şekilde açık hava ortamında üretildi. Güneş hücrelerinin diyot özellikleri karanlıkta yapılan akım-gerilim (I-V) ölçümleri kullanılarak incelenmiştir. Soğurma karakteristikleri optik geçirgenlik spektroskopisi kullanılarak incelenmiş ve her numune için yasak enerji bant aralığı (E_g) hesaplanmıştır. Her bir güneş hücresi için hücre parametreleri, AM 1.5 güneş radyasyonu altında akım yoğunluğu-voltaj (J-V) ölçümleri kullanılarak incelenmiş ve önemli güneş hücresi parametreleri hesaplanmıştır. Güneş hücrelerinin FF değerinin 0,3239 ile 0,3409 arasında diyot idealite faktörü (n) düştükçe arttığı gözlendi. PCE'nin en yüksek değerinin 140 nm P3HT: PCBM kalınlığına sahip hücreye ait 0,59 olduğu bulunmuştur.

Anahtar Kelimeler: *Güneş Hücresi, P3HT, PCBM, Elektriksel Karakterizasyon, Optik Karakterizasyon*

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I. INTRODUCTION

Optoelectronic applications of solution processable organic semiconductors have attracted much attention in the past years mainly due to their low fabrication cost, flexibility and tuneable optoelectronic properties [1-5]. Amongst these applications, composite polymer and fullerene based organic solar cells (OSCs) have received a special attention by researchers [6,7]. Bulk heterojunction (BHJ) OSCs having an active layer blend of polymer, poly (3-hexylthiophene) (P3HT) and fullerene [6,6],-phenyl-C61-butyric acid methyl ester (PCBM) have been extensively studied by several researches in the last decade [8-14]. The power conversion efficiencies (PCE) of OSCs are mainly affected by the structure of BHJ active layers, which has a significant effect on charge generation and transport mechanisms [15,16]. Among various device arthitecture types, ITO/PEDOT:PSS/P3HT:PCBM/Al cells are known to have the simplest structure of P3HT:PCBM based OSCs, where PEDOT:PSS layer is used as a hole transport layer to enhance device characteristics. It has been reported that PCE of P3HT:PCBM based OSCs can be enhanced by changing thicknesses of different cell layers [17-19]. PCEs can further be enhanced by annealing of PEDOT:PSS layers at several temperatures with several durations [20]. The highest PCE of P3HT:PCBM OSCs at 150 °C annealing temperature with 10 minutes of annealing time was reported to be 3.84 % [13]. The characterization of produced OSCs were made by several techniques including absorption spectroscopy, optical microscopy, photoluminescence spectroscopy, Xray diffraction, DC masurements, and AC impedance spectroscopy [21-29]. When literature is taken into account, it is seen that most of the time P3HT:PCBM OSCs were produced in a closed system under vacuum or inert gas enviroment. It is also seen that, the diode characteristics and their effects measured under dark conditions have not been investigated in detail systematically, despite several methods have been used to characterize P3HT:PCBM based OSCs.

In the present study, we represent the results of the study on ITO/PEDOT:PSS/P3HT:PCBM/Al OSCs produced in open air environment with various P3HT:PCBM active layer thicknesses. The diode properties of the solar cells in the dark have been investigated by using Current-Voltage (I-V) measurements. By using the results of the measurements, the most important diode parameter, ideality factor (n), has been calculated. In addition, the absorption characteristics have been investigated by using transmission spectroscopy and forbidden band gap energy (E_g) for each sample has been calculated. Finally, solar cell parameters for each solar cell has been investigated by using I-V measurements under AM 1.5 solar raditation. Important solar cell parameters such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), maximum cell power (P_{max}), fill factor (FF), and PCE have been calculated. The dependence of the optoelectronic properties of the cells on the thickness of P3HT:PCBM active layer has been revealed by means of detailed analysis on measured data and result of calculations.

II. EXPERIMENTAL DETAILS

A. PRODUCTION OF SOLAR CELLS

PCBM and P3HT organic polymer materials used in this study are provided by Sigma Aldrich Ltd. Company. PEDOT:PSS, which is used as a hole carrier layer, was purchased from Heraeus Deutschland GmbH Company. ITO/PEDOT:PSS/P3HT:PCBM/Al organic solar cells were produced by preparing a mixture to form an organic interface layer. The hole carrier layer PEDOT:PSS was mixed with DMSO with the help of magnetic fishes to have a volumetric ratio of 3% for 24 hours at room temperature by stirring. In order to prepare the active layer, P3HT:PCBM mixture, the powdered P3HT and PCBM had first to be converted into liquid solutions by dichlorobenzene (DCB) solvent. Stirring was carried out by magnetic fishes in different tubes to form 25mg/mL solutions at 45° C for 6 hours. Separately prepared solutions were then transferred to the same vessel in a 1: 1 ratio through a 0.45 µm filter and stirred for 24 hours.

The first stage of the ITO/PEDOT:PSS/P3HT:PCBM/Al organic solar cell production process is the cleaning of ITO coated glass to be used as wafers for solar cells. These wafers are commercially available, cut to a size of 15x15mm and coated with ITO on one side, approximately 150 nm thick. Before starting the experimental procedures, the wafers were cleaned in an ultrasonic bath at room temperature for 10 min in purified water, 10 min in acetone and 10 min in isopropyl alcohol. After cleaning, drying with N_2 gas was carried out in order to prevent oxide layers on ITO coated surface.

After these preliminary steps, all wafers were spin coated with 50µL PEDOT:PSS solution at 1000 rpm with a Specialty Coating Systems G3 spin coater. The initial coating was followed by annealing at 150° C for 10 minutes and then allowing to cool. For the coating of the active layer, P3HT:PCBM, 50 µL of solution was used for each sample. The determining parameter of the coating thickness of the samples was the rpm value of the spin coater. These values were selected as 500rpm, 1000rpm, 2000rpm, 3000rpm, 4000rpm.

Al contacts required for the characterization of the device coated on the active layer by a Nanovak NVBJ-300TH thermal evaporator. The structures of the produced solar cells are shown schematically in Figure 1. The circular contacts with radius of 1mm were produced by help of a metal mask. By this method, several contacts were formed on each sample.

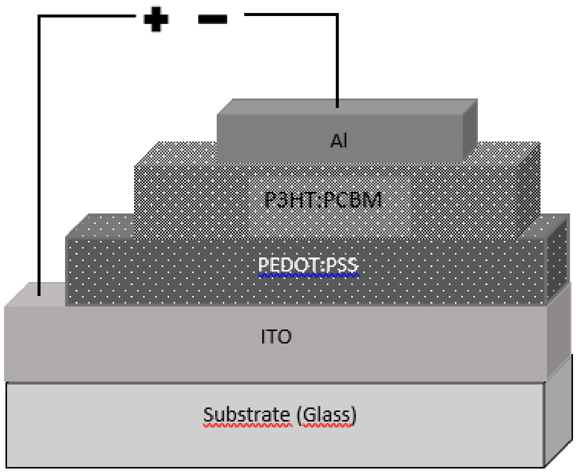


Figure 1. *Schematic representation showing the structure of ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells.*

B. CHARACTERIZATION OF SOLAR CELLS

The optoelectronic characterization of produced solar cells were done by several methods. The electrical characterization of the cells were done by means of Current(I)-Voltage(V) measurements with a Keithley 2400 measurement system which has a built-in power supply and an ampermeter. The optical characterization of the cells were done by using optical transmission spectroscopy. For this purpose, a PG Instruments T70+ model spectrophotometer with 0.5 nm spectral bandwith was used. The recorded spectra were corrected for both optical detector efficiency and effect of substrates. Final characterization of solar cells were done by using a FY 7000 solar simulator under AM 1.5 solar radiation. The thicknesses of PEDOT:PSS and P3HT:PCBM layers were measured by a FEI Quanta FEG 250 scanning electron microscope by taking the image of the cross section of the cells.

III. RESULTS AND DISCUSSION

As a first step in the characterization process of ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells, the thicknesses of the corresponding layers were measured by taking SEM images of the cross sections of the cells. As a result of measurements, the thicknesses of the PEDOT:PSS layers were found to be around 50 nm for all the cells. The thicknesses of the P3HT:PCBM active layers were found to be 190 nm, 175 nm, 140 nm, 110 nm and 70 nm for the layers produced at 500 rpm, 1000 rpm, 2000 rpm, 3000 rpm, and 4000 rpm, respectively.

To reveal electrical characteristics of the produced solar cells, I-V measurements were performed in the voltage range betweeen -3 V and 3 V. The results of the measurements were shown in Figure 2 in semi-logharitmic scale due to exponential behaviour of the I-V characteristics. From the figure, it is obviously seen that all cells show a rectifying behaviour as expected. This means that forward currents are exponentially increasing with the voltage, while the reverse currents show somehow weaker voltage dependencies. This shows that internal electric field was succesfully generated in the produced cells.

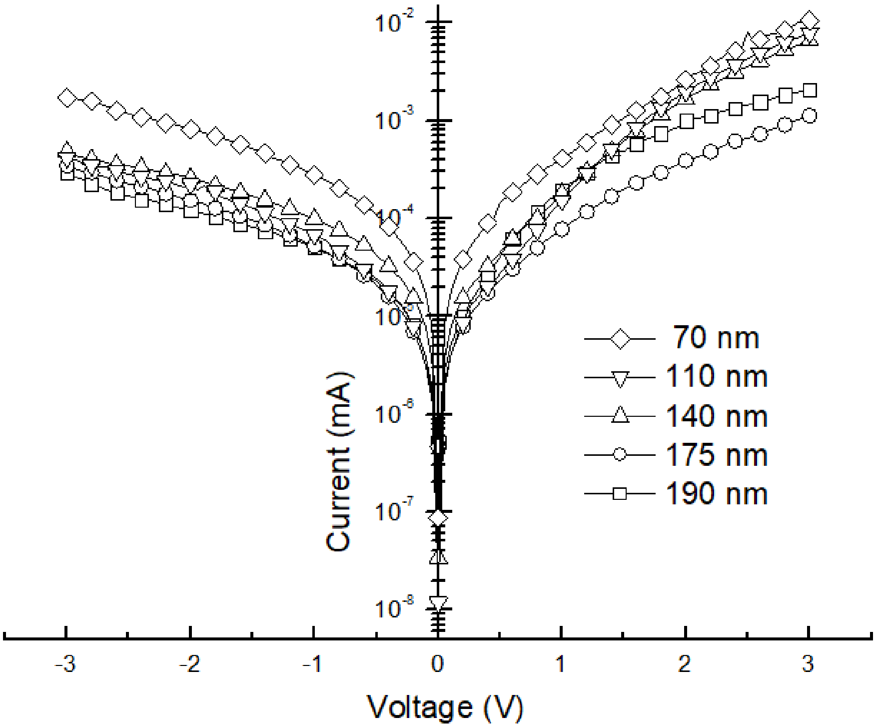


Figure 2. *I-V characteristics of ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells.*

For a more detailed analysis on the electrical properties of the cells, several diode parameters can be calculated. The I-V characteristic of a diode can be defined by [30],

$$I = I_0 exp\left(\frac{qV - IR}{nkT}\right)\left[1 - exp\left(\frac{q(V - IR)}{kT}\right)\right] \tag{1}$$

and

$$I_0 = AR^*T^2 exp\left(-\frac{q\Phi_0}{kT}\right) \tag{2}$$

Here I_0 denotes the saturation current, q denotes electronic charge, V denotes applied voltage, n denotes ideality factor of a diode, k denotes Boltzman constant, R denotes Richardson constant, T denotes absolute temperature in Kelvin, A denotes diode area, and ϕ_0 denotes zero potential barrier height. It is well known that n indicates the proximity of the diode characteristics to the ideal one. The area of the produced cells were measured to be $3{,}14\times10^{-6}$ m^2. The ideality factor n can be calculated by,

$$n = \frac{q}{kT}\frac{d(V)}{d(\ln(I))} \quad (3)$$

The values of *n* were calculated by using the slopes of the linear regions of the curves shown in figure2 in the forward bias region, and the results of the calculations were shown in figure 3. As seen from the figure, the value of the ideality factor changes between 3.29 and 3.96, and increases with active layer thickness. The ideality factor is a measure of how much a diode follows pure thermo-ionic emission behaviour, and its value is expected to be 1 in the ideal case, or closer to 1 in non ideal cases [31]. In general, it is thought that recombination of the charge carriers occur in the neutral areas of the device in the regions where the value of the ideality factor is around 1, whereas it occurs in the depletion area in the regions where the value of the ideality factor is 2 or higher [32]. The values of the ideality factor also affects fill factor (FF) of the solar cell. It is expected that the increase in the value of ideality factor of the produced cells will result in a decrease in the value of solar cell fill factor, and decrease its power conversion efficiency PCE.

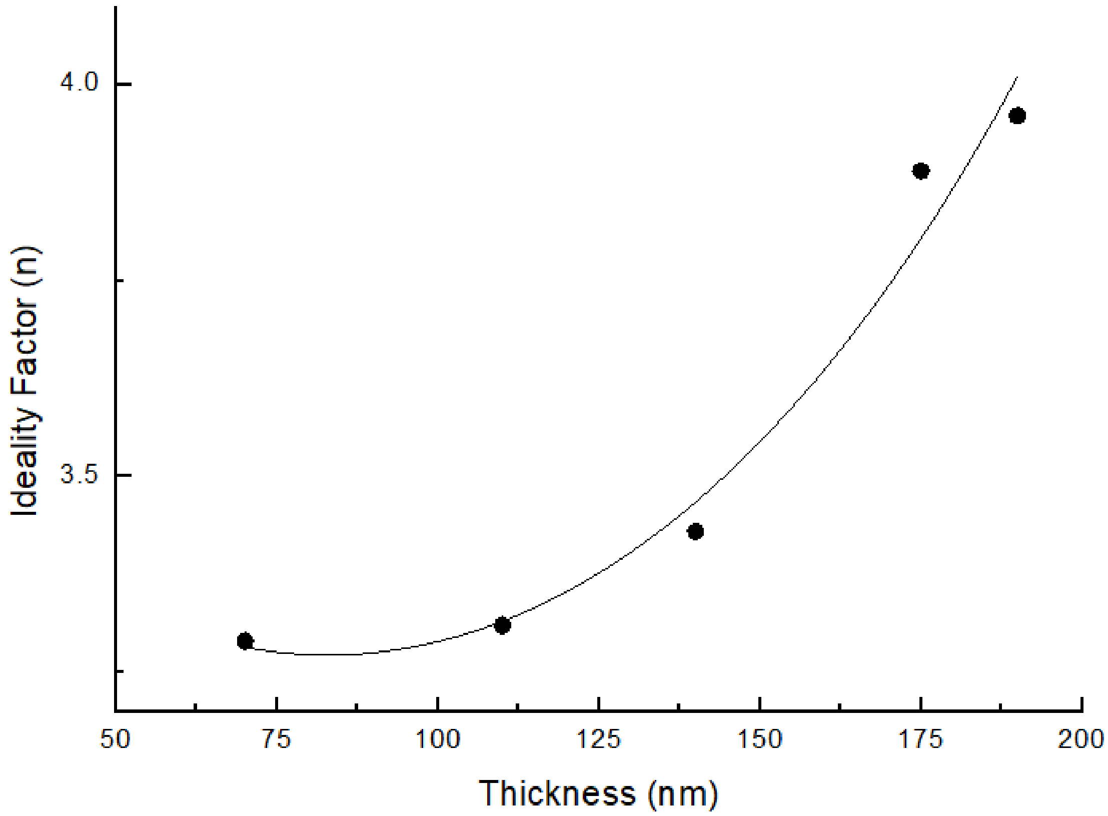


Figure 3. *Dependence of the values of n on P3HT:PCBM active layer thickness.*

To reveal optical properties ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells, optical transmission spectroscopy was employed. After transmission experiments, the experimental data were corrected both for detector efficiency and substrate effects. Figure 4 shows corrected transmission spectra for all cells recorded between 525 nm and 800 nm wavelength interval. It is obviously seen from the figure that absorption of incident light increases as the active layer thickness increases. It is an expected result, since as the active layer thickness increases, the length of the path light has to travel across this layer and possibility of photons being captured by charge carriers also increases. If all the other parameters are not taken into account, it is expected that cells having the highest absorption would have the highest value of PCE. It is also directly seen from the figure that all cells have a soft absorption edge, that is, high absorption region covers roughly 150 nm, which is relatively a wide interval. In general, cristallinity of the material increases as the absorption edge gets sharper.

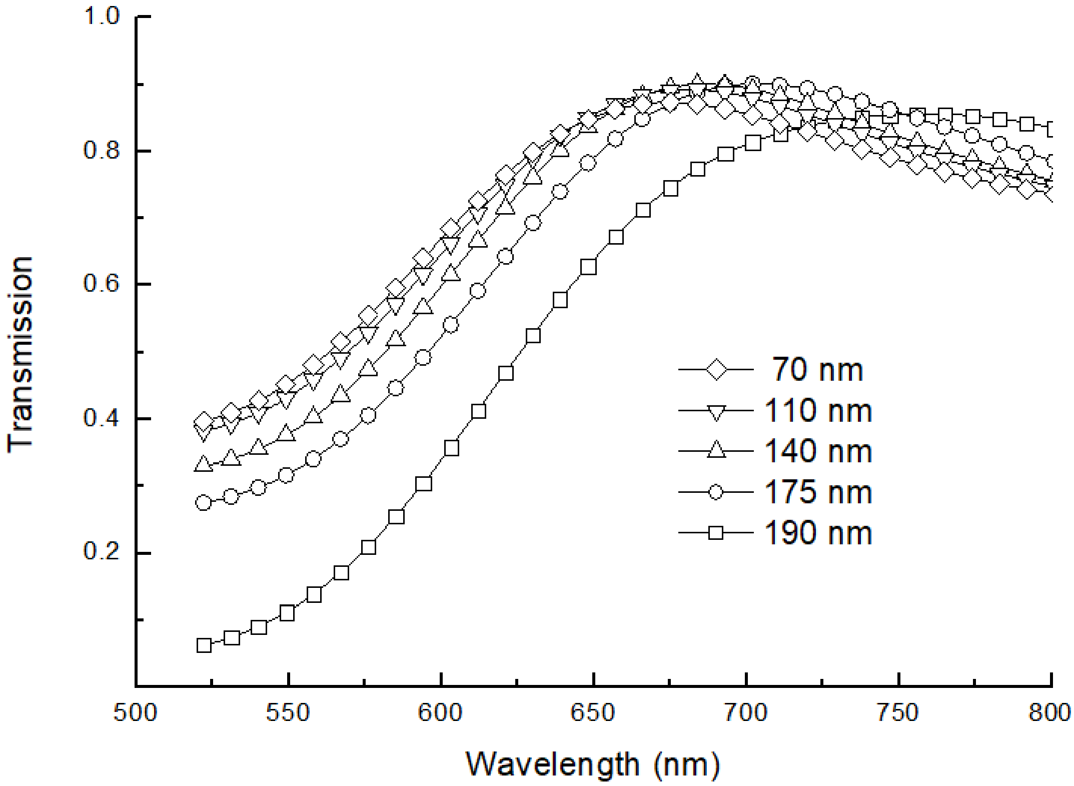


Figure 4. *Dependence of the transmission spectra of produced cells on active layer thickness.*

For a detailed analysis of the optical properties of the cells, Beer Lambert law of the form [33]

$$I = I_0 e^{-\alpha d} \tag{4}$$

can be used. Here, α denotes absorption coefficent, I_0 denotes incident light intensity, I denotes the light intensity passing through the active layer of the cell, and d denotes the distance light travels through active region, i.e., active region thickness. By using equation 4, α can be calculated by

$$\alpha = \frac{1}{d} ln\left(\frac{I_0}{I}\right) \tag{5}$$

Figure 5 shows the variation of calculated values of α with respect to incident light photon energy. Optical band gap of the material can also be calculated by using the values of α, and Tauc relation given by [33]

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^p \tag{6}$$

where $h\upsilon$ corresponds to photon energy, E_g corresponds to optical band gap, A corresponds to a constant depending on transition probability. In addition, p value characterizes the type of the optical absorption process. Its value is theoretically equal to 0.5 for allowed direct, and 2 for allowed indirect transitions. The values of p can easily be determined by analyzing figure 5, in which all the curves show a parabolic behaviour. This behaviour can simply be verified by drawing a line connecting first and last data points. The parabolic behaviour shows that the value of p is 2 for all of the active layers of the cells. By taking squareroot of the equation 6, we get

$$(\alpha h\nu)^{0.5} = B^{0.5}\left(h\nu - E_g\right) \tag{7}$$

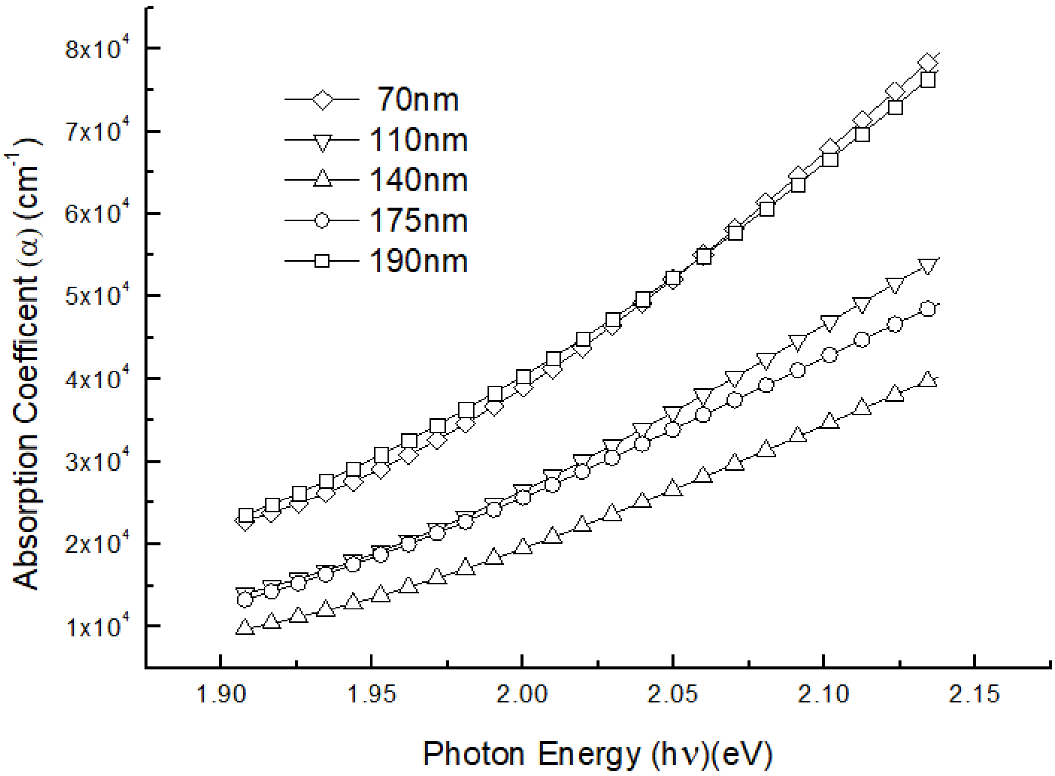


Figure 5. *Dependence of the absorption coefficent on photon energy for all produced solar cells.*

From equation 7, it is seen that the $h\nu$ intercept of $(\alpha h\nu)^{0,5}$ vs. $h\nu$ graph gives the value of E_g. To calculate E_g, figure 6 is drawn. The values of optical band gaps of active layers of the cells were found to be 1.67 eV, 1.69 eV, 1.70 eV, 1.71 eV, and 1.71 eV for 70 nm, 110 nm, 140 nm, 175 nm, and 190 nm, respectively.

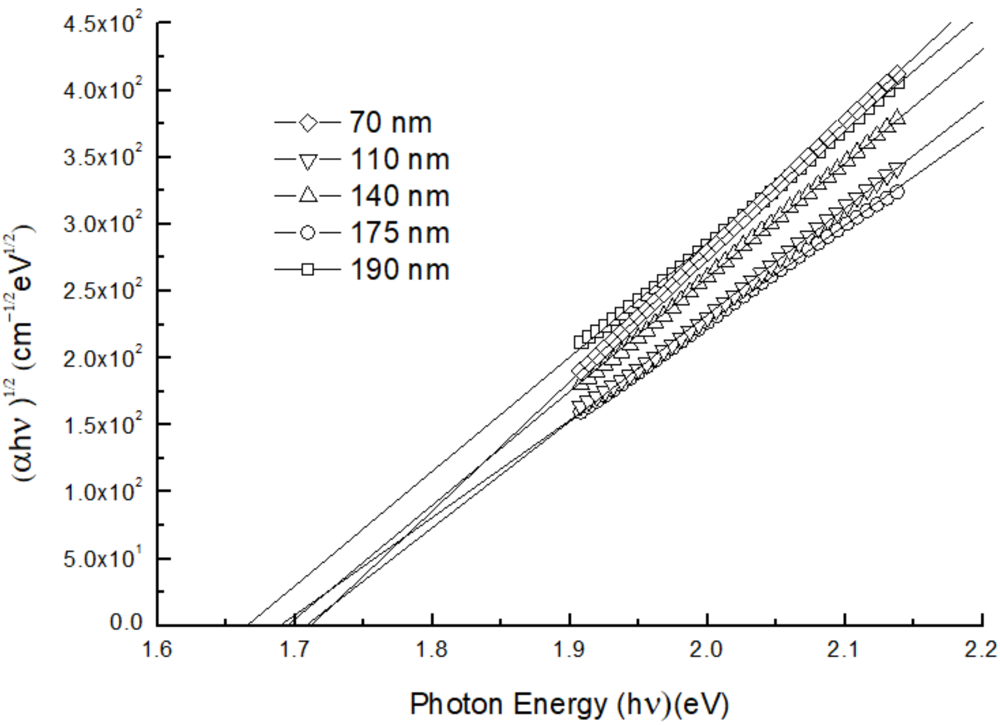


Figure 6. *The graph drawn to reveal optical band gap energy of active region of all produced solar cells.*

It is seen from the figure that the thickness of the active layer has no significant effect on value of E_g. This is an expected result, since the composition of the active layer does not change. In general, the size of band gap is very important for a solar cell, since it directly affects the energy that can be absorbed from light. If incoming photon energy is higher than E_g, the photon is absorbed by the electron and excess energy will be lost due to relaxation of the electron to band minimum, which causes loss of energy. However, if ncoming photon energy is lower than E_g, it will not be absorbed, which again causes loss of energy. For our produced cells, it is out of corcern, since E_g values do not differ from each other much.

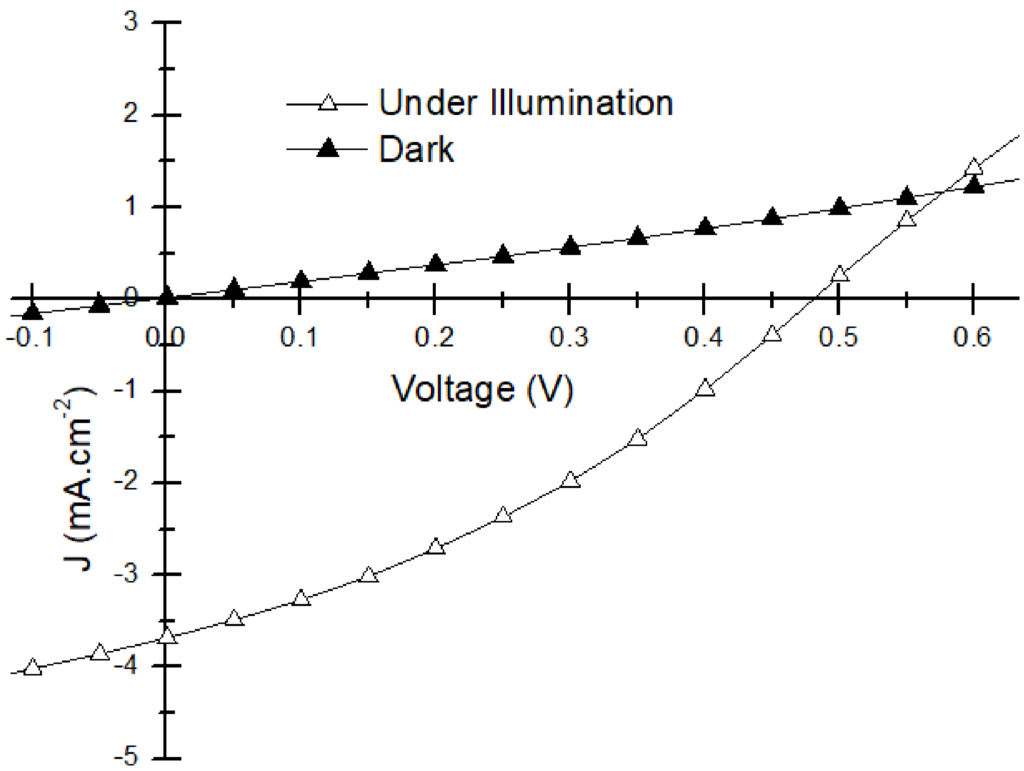
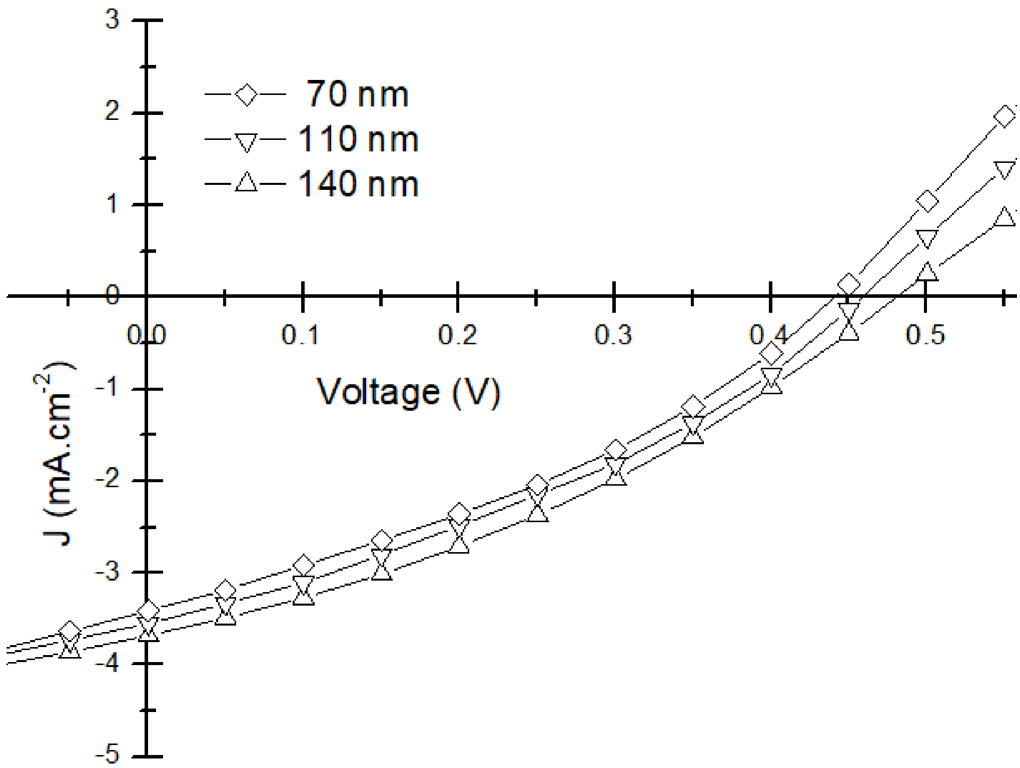


Figure 7. *J-V characteristic of the solar cell having 140 nm thick P3HT:PCBM layer*.

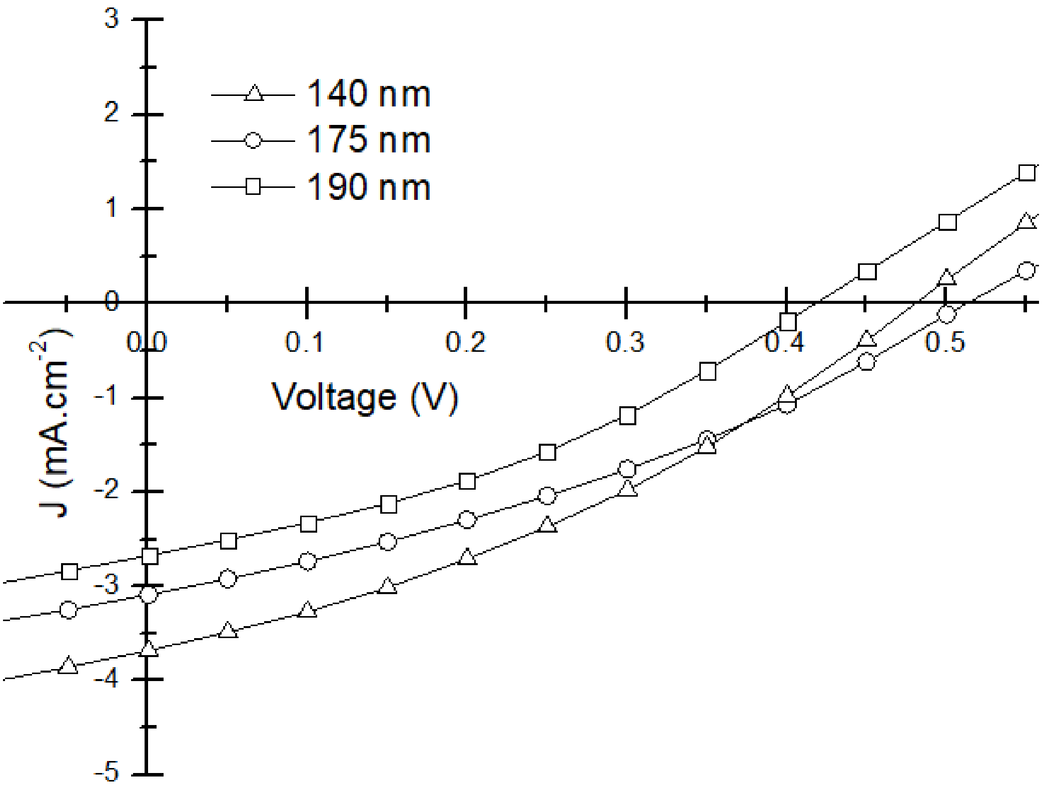
To reveal characteristic properties of produced solar cells, current density (J) – Voltage (V) experiments were employed. Figure 7 shows the results of J-V experiments under dark and AM 1.5 solar raditation conditions of the cell having 140 nm thick P3HT:PCBM layer, for comparison. The graph shows a shift in the curve when exposed to solar radiation, which proves photo response of the solar cell as expected. Figure 8 is drawn to analyse the characteristic parameters of all solar cells under illumination. By using the figure, important solar cell parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), maximum cell power density (P_{max}), fill factor (FF) and power conversion efficiency (PCE). While J_{sc} and V_{oc} can directly be determined from the figure by using J-axis and V-axis intercepts of the curves, the other parameters should be calculated. P_{max} can easily be calculated by calculating the power generated by the solar cell at each voltage value and taking the maximum. FF of a solar cell can be calculated by [34],

$$FF = \frac{P_{max}}{J_{SC} \times V_{OC}} = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} \tag{8}$$

where J_{max} is the value of current density, and V_{max} is the value of voltage at maximum cell power.



(a)



(b)

Figure 8. *J-V characteristic of the solar cells having **a)** 70, 110, and 140 nm, **b)** 140, 175, and 190 nm thick P3HT:PCBM layers.*

Furthermore, PCE, showing how much light energy can be converted to electrical energy of a solar cell, can be calculated by [34]

$$\text{PCE} = \frac{P_{max}}{P_{incident}} \tag{9}$$

where P_{incident} is the optical power density incident on the solar cell. All of the calculated solar cell parameters are given in Table 1. The most important parameter showing the cell performance is PCE. As seen from the table, the most effective solar cell with the highest PCE is the one having 140 nm thick P3HT:PCBM layer.

Table 1. *Characteristic parameters of ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells for different P3HT:PCBM layer thicknesses.*

Thickness *(nm)*	$\mathbf{J_{sc}}$ *(mA.cm^{-2})*	$\mathbf{V_{oc}}$ *(V)*	$\mathbf{P_{max}}$ *(mW.cm^{-2})*	**% FF**	**% PCE**
70	3.4	0.44	0.51	34.09	0.51
110	3.5	0.46	0.54	33.54	0.54
140	3.7	0.48	0.59	33.22	0.59
175	3.1	0.52	0.53	32.88	0.53
190	2.8	0.43	0.39	32.39	0.39

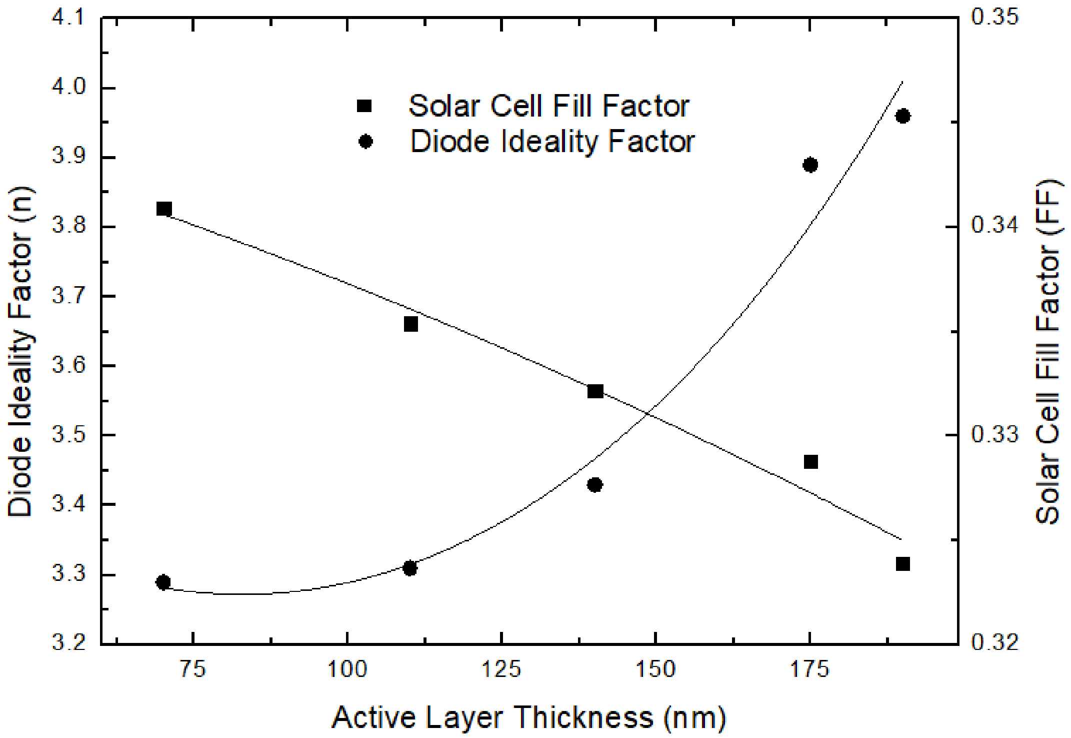


Figure 9. *The behaviors of the ideality factors and fill factors of the produced ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells for different P3HT:PCBM layer thicknesses.*

Solar cell efficiency may be affected by several factors. Firstly, light should be captured by the active layer of the cell, which could be affected by E_g, absorption coefficent and thickness of the material. For organic materials, E_g is generally thought to represent energy difference between the highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) energy level. As mentioned before, since E_g of the cells do not differ from each other significantly (figure 6), light is best absorbed by 190 nm thick cell, which has the thickest P3HT:PCBM layer (figure 4). Secondly, the absorbed light should be converted to electrical energy with minimum loss. As the electrical properties of the cells are investigated, it is seen from the figure 3 that the cells having 70 nm thick P3HT:PCBM layer is the one closest to an ideal diode. The ideality factor for a cell does not directly affect the PCE of a solar cell, however it is expected that an increase in the value of ideality factor will result in a decrease in the value of solar cell fill factor, and decrease its PCE. To see this behavior, figure 9 is drawn. As seen from the figure, n and FF values of the solar cells are inversely proportional to each other, as expected. It is understandable that a solar cell with a lower n and higher FF might have a higher PCE, although its absorption is lower when compared to others.

Figure 10 is drawn to see the dependence of the PCE on P3HT:PCBM layer thickness. It is seen from the figure that the solar cell with the highest PCE is the one having 140 nm thick P3HT:PCBM layer. It is seen that this cell has a % PCE of 0.59 %. By using the results of all available data, it can be concluded that this cell satisfies an optimum condition between optical and electrical properties of produced ITO/PEDOT:PSS/P3HT:PCBM/Al solar cell with an optimum P3HT:PCBM layer thickness.

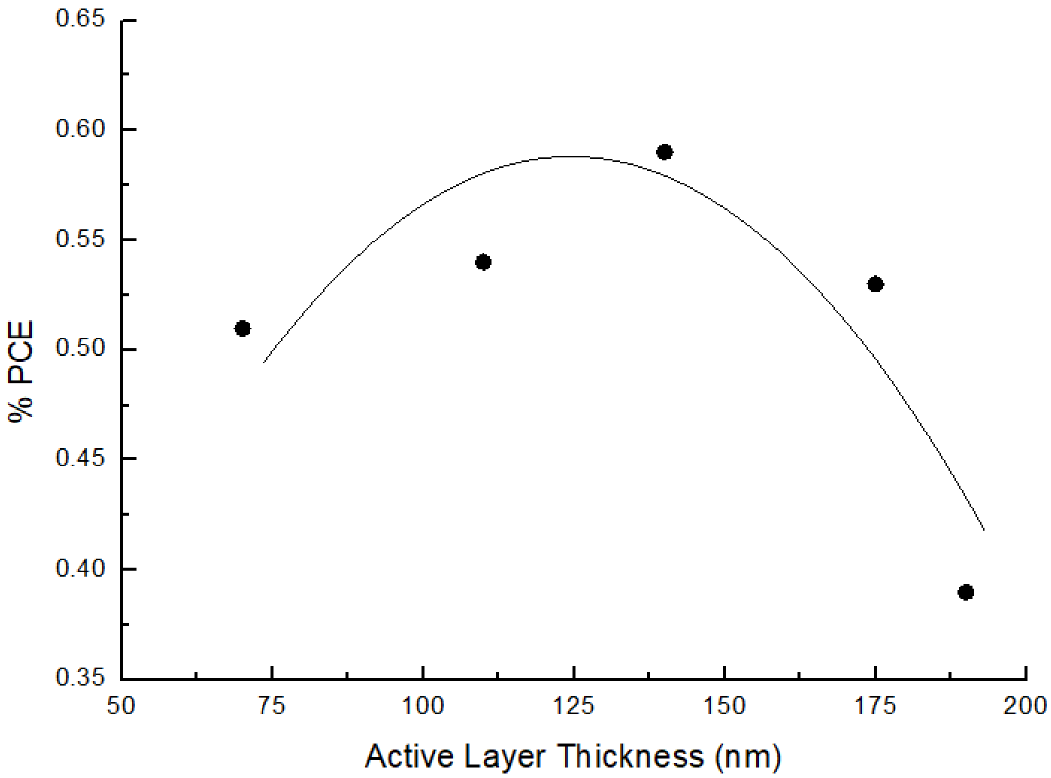


Figure 10. *Dependence of PCE % of ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells for different P3HT:PCBM layer thicknesses.*

Table 2 is drawn to compare the results of the present study to latest studies performed in the literature. It is seen from the table that the value of PCE for the produced solar cell is not higher than the most PCEs reported. From the table, it is also seen that the highest PCE values were obtained for the cells produced in vacuum environment. After a thorough analysis of the data, it is seen that V_{oc} value of the produced cell is somehow close to the ones in the literature, and the difference in PCE mainly comes from J_{sc} values. This leads to thinking about the metal contact quality of the cell. It is also seen from the data that increasing contact thickness also resulted in a higher PCE values. It was mentioned in the text that solar cells produced in this study were produced in open air conditions, and relatively thinner metal contact layers. Therefore, it seems reasonable to be able to achieve only a low PCE value. Producing solar cells with thicker metal contact layer was not performed, since it exceeds the scope of the present study. However, a future study with the subject of investigation of the dependence of PCE on metal contact thickness should be performed to achieve higher PCE values.

Table 2. *Characteristic parameters of recently produced ITO/PEDOT:PSS/P3HT:PCBM/Al solar cells in the literature. Thermal evaporation and magnetron sputtering methods were denoted by TE and MS abbreviations.*

Active Layer Thick. *(nm)*	**Al Contact Thick.** *(nm)*	J_{sc} *(mA.cm^{-2})*	V_{oc} *(V)*	**FF**	**% PCE**	**Annealing Env.**	**Ref. No**
140	50 (TE)	3.70	0.48	0.33	0.59	Air	This Study
150	100 (TE)	11.62	0.57	0.58	3.84	Vacuum	[35]
100-250	100 (TE)	4.61	0.60	0.21	0.57	Vacuum	[36]
100-250	50 (MS)	2.16	0.34	0.19	14×10^{-5}	Vacuum	[36]
160	-	8.74	0.62	0.51	2.77	Vacuum	[37]
160	-	8.51	0.63	0.52	2.76	N_2	[37]
160	-	7.86	0.62	0.54	2.64	Ar_2	[37]
160	-	7.45	0.63	0.48	2.29	Air	[37]

IV. CONCLUSION

In the present study, the results of the investigations on ITO/PEDOT:PSS/P3HT:PCBM/Al OSCs produced in open air environment with various P3HT:PCBM active layer thicknesses were reported. The active layer thicknesses of the produced cells were measured to be 190 nm, 175 nm, 140 nm, 110 nm and 70 nm, by SEM imaging. Several methods have been employed to reveal electrical and optical properties of the produced solar cells. The diode properties of the solar cells in the dark have been investigated by using I-V measurements. By using the results of the measurements, the most important diode parameter n has been calculated to be 3.96, 3.89, 3.43, 3.31, and 3.29, respectively. Besides, the absorption characteristics have been investigated by using transmission spectroscopy. By using the results of the transmission measurements, E_g for each sample has been calculated to be 1.71, 1.71, 1.70, 1.69, and 1.67 eV, respectively. It is thought that the values of E_g are not determining parameters, since they are very close to each other. Furthermore, solar cell parameters for each solar cell has been investigated by using J-V measurements under AM 1.5 solar raditation. Important solar cell parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), maximum cell power (P_{max}), fill factor (FF), and PCE have been calculated. The values of % PCE were found to be 0.39, 0.53, 0.59, 0.54, and 0.51, respectively. It was also observed that FF value of the solar cells increase between 0.3239 and 0.3409 with decreasing *n* value. It was revealed that the cell with highest PCE is the one having 140 nm P3HT:PCBM thickness. The reason for relatively low value of PCE was proposed to be the production of cells in open air environment, and with a thin layer of metal contact. Although the PCE value of the produced cells seems to be lower when compared to ones in the latest literature, a future study proposal was made to achieve cells having thicker metal contacts with higher expected PCE values.

V. REFERENCES

[1] P. Heremans, D. Cheyns, B.P. Rand, "Strategies for increasing the efficiency of heterojunction

organic solar cells: Material selection and device architecture," *Accounts of Chemical Research*, vol. 42, no. 11, pp. 1740-1742, 2009.

[2] J. Nelson, "Polymer: Fullerene bulk heterojunction solar cells," *Materials Today*, vol. 14, no. 10, pp. 462-470, 2011.

[3] F.C. Krebs, "Fabrication and processing of polymer solar cells: A review of printing and coating techniques," *Solar Energy Materials and Solar Cells*, vol. 93, no. 4, pp. 394-412, 2009.

[4] P. Vanlaeke, G. Vanhoyland, T. Aernouts, D. Cheyns, C. Deibel, J. Manca, P. Heremans, J. Poortmans, "Polythiophene based bulk heterojunction solar cells: Morphology and its implications," *Thin Solid Films*, vol. 511, pp. 358-361, 2006.

[5] L. Blankenburg, K. Schultheis, H. Schache, S. Sensfuss, M. Schrödner, "Reel-to-reel wet coating as an efficient up-scaling technique for the production of bulk heterojunction polymer solar cells," *Solar Energy Materials and Solar Cells*, vol. 93, no. 4, pp. 476, 2009.

[6] R. Hegde, N. Henry, B. Whittle, H. Zang, B. Hu, J. Chen, K. Xiao, M. Dadmun, "The impact of controlled solvent exposure on the morphology of structure and function of bulk heterojunction solar cells," *Solar Energy Materials and Solar Cells*, vol. 107, pp. 112–124, 2012.

[7] P.P. Khlyabich, B. Burkhart, A.E. Rudenko, B.C. Thompson, "Optimization and simplification of polymer-fullerene solar cells through polymer and active layer design," *Polymer*, vol. 54, pp. 5267–5298, 2013.

[8] G. Li, R. Zhu, Y. Yang, "Polymer solar cells," *Nature Photonics*, vol. 6, pp. 153–161, 2012.

[9] K. Kawano, J. Sakai, M. Yahiro, C. Adachi, "Effect of solvent on fabrication of active layers in organic solar cells based on poly(3-hexylthiophene)and fullerene derivatives," *Solar Energy Materials Solar Cells*, vol. 93, pp. 514–518, 2009.

[10] B.C. Thompson, J.M.J. Fréchet, "Polymer - fullerene composite solar cells," *Angewandte Chemie*, vol. 47, pp. 58–77, 2018.

[11] M.T. Dang, L. Hirsch, G. Wantz, "P3HT: PCBM, best seller in polymer photovoltaic research," *Advanced Materials*, vol. 23, pp. 3597–3602, 2011.

[12] A.M. Ballantyne, T.A.M. Ferenczi, M. Campoy – Quiles, T.M. Clarke, M. Maurano, K.H. Wong, W. Zhang, N. Stingelin-Stutzmann, J.-S. Kim, D.D.C. Bradley, J.R. Durrant, I. McCulloch, M. Heeney, J. Nelson, "Understanding the influence of morphology on poly(3-hexylselenothiophene): PCBM solar cells," *Macromolecules*, vol. 43, pp. 1169–1174, 2010.

[13] O. Oklobia, T. Sadat-Shafai, "A quantitative study of the formation of PCBM clusters upon thermal annealing of P3HT/PCBM bulk heterojunction solar cell," *Solar Energy Materials and Solar Cells*, vol. 117, pp. 1–8, 2013.

[14] M. Campoy – Quiles, T. Ferenczi, T. Agostenilli, P.G. Etchegoin, Y. Kim, T.D. Anthapoulos, P.N. Stavrinou, D.D.C. Bradley, J. Nelson, "Morphology evolution via self-organisation and lateral and vertical diffusion in polymer: Fullerene solar cell blends," *Nature Materials*, vol. 7, pp. 158–164. 2008

[15] V.D. Mihailetchi, H. Xie, B. de Boer, L.J.A. Koster, P.W.M. Blom, "Charge transport and photocurrent generation in poly(3-hexylthiophene): Methanofullerene bulkheterojunction solar cells," *Advanced Functional Materials*, vol. 16, pp. 699–708, 2006.

[16] T.M. Clarke, J.R. Durrant, “Charge photogeneration in organic solar cells,” *Chemical Reviews*, vol. 110, pp. 6736–6767, 2010.

[17] Z. Zhao, L. Rice1, H. Efstathiadis, P. Haldar, “Thickness dependent effects of thermal annealing and solvent vapor treatment of poly(3-hexylthiophene) and fullerene bulk heterojunction photovoltaics,” *Materials Research Society Symposium P – Photovoltaic Materials and Manufacturing Issues,* Boston, 2008.

[18] C.Y. Nam, D. Su, C.T. Black, “High-performance air-processed polymer–fullerene bulk heterojunction solar cells,” *Advanced Functional Materials,* vol. 19, pp. 3552–3559, 2009.

[19] J. Jo, S.S. Kim, S.I. Na, B.K. Yu, D.Y. Kim, “Time-dependent morphology evolution by annealing processes on polymer: Fullerene blend solar cells,” *Advanced Functional Materials*, vol. 19, pp. 866–874, 2009.

[20] O. Oklobia,T.S.Shafai, “A quantitative study of the formation of PCBM clusters upon thermal annealing of P3HT/PCBM bulk heterojunction solar cell,” *Solar Energy Materials and Solar Cells*, vol. 117, pp. 1–8, 2013.

[21] F.C. Jamieson, E.B. Domingo, T. McCarthy-Ward, M. Heeney, N. Stingelin, J.R. Durrant, “Fullerene crystallisation as a key driver of charge separation in polymer: Fullerene bulk heterojunction solar cells,” *Chemical Science*, vol. 3, pp. 485–492, 2012.

[22] P. M.Buschbaum, “The active layer morphology organic solar cells probed with grazing incidence scattering techniques,” *Advanced Materials,* vol. 26, pp. 7692–7709, 2014.

[23] T. Erb, U. Zhokhavets, H. Hoppe, G. Gobsch, M. Al-Ibrahim, O. Ambacher, “Fullerene crystallisation as a key driver of charge separation in polymer: Fullerene bulk heterojunction solar cells,” *Thin Solid Films*, vol. 511–512, pp. 483–485, 2006.

[24] G. Li, V. Shrotriya, Y. Yao, Y. Yang, “Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly(3-hexylthiophene),” *Journal of Applied Physics*, vol. 98, pp. 1-5, 2005.

[25] D. Chirvase, J. Parisi, J.C. Hummelen, V. Dyakonov, “Influence of nanomorphology on the photovoltaic action of polymer-fullerene composites,” *Nanotechnology*, vol. 15, pp. 1317–1323, 2004.

[26] T. Kuwabara, Y. Kawahara, T. Yamaguchi, K. Takahashi, “Characterization of inverted-type organic solar cells with a ZnO layer as the electron collection electrode by ac ımpedance spectroscopy,” *Applied Materials & Interfaces*, vol. 1, pp. 2107–2110, 2009.

[27] F. Fabregat-Santiago, J. Bisquert, E. Palomares, L. Otero, D. Kuang, S.M. Zakeeruddin, M. Grätzel, “Correlation between the photovoltaic performance and impedance spectroscopy of dye-sensitized solar cells based on ionic liquids,” *The Journal of Physical Chemistry* C, vol. 111, pp. 6550–6560, 2007.

[28] Q. Wang, J.-E. Moser, M. Grätzel, “Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells,” *The Journal of Physical Chemistry B,* vol. 109, pp. 14945–14953, 2005.

[29] L. Han, N. Koide, Y. Chiba, T. Mitate, “Modelling of an equivalent circuit for dyesensitized solar cells,” *Applied Physics Letters*, vol. 84, pp. 2433, 2004.

[30] E. H. Rhoderick, "Current-transport mechanisms," in *Metal–Semiconductor Contacts,* 1st ed., New York, USA: Oxford University Press, 1978, pp. 121–136.

[31] C. Temirci, B. Bati, M. Saglam, A. Türüt, “High-barrier height Sn/p-Si schottky diodes with interfacial layer by anodization process,” *Applied Surface Science*, vol. 172, pp. 1–7, 2001.

[32] M. Campos, L. O. C. Bulhoes, C. A. Lındıno, “Gas-Sensitive characteristics of metal/semiconductor polymer schottky device,” *Sensors and Actuators A: Physical*, vol. 87, pp. 67, 2000.

[33] J. Pankove, “Absorption,” in *Optical Processes in Semiconductors,* 1st ed., New Jersey, USA: Prentice-Hall Press, 1971, pp. 34-81.

[34] J. Nelson, “Introduction,” in *The Physics of Solar Cells*, 1st ed., UK: Imperial College Press, 2003, pp. 1–16.

[35] O. Oklobiaa, S. Komilianb, T. Sadat-Shafaib, “Impedance spectroscopy and capacitance–voltage measurements analysis: Impact of charge carrier lifetimes and mapping vertical segregation in bulk heterojunction P3HT: PCBM solar cells,” *Organic Electronics*, vol. 61, pp. 276–281, 2018.

[36] A. Iwan, M. Palewicz, M. Ozimek, A. Chuchmala, G. Pasciak, “Influence of aluminium electrode preparation on PCE values of polymeric solar cells based on P3HT and PCBM,” *Organic Electronics*, vol. 13, no. 11, pp. 2525–2531, 2012.

[37] J.W. Jeong, J. W. Huh, J.I. Lee, H.Y. Chu, I.K. Han, B.-K. Ju, “Effects of thermal annealing on the efficiency of bulk-heterojunction organic photovoltaic devices,” *Current Applied Physics*, vol. 10, no. 3, pp. S520–S524, 2010.