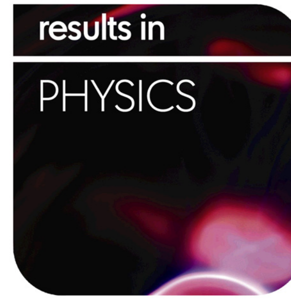
Accepted Manuscript



The influence of annealing temperature and time on the efficiency of pentacene:ptcdi organic solar cells

Mehmet Biber, Şakir Aydoğan, Zakir Çaldıran, Bülent Çakmak, Tevhit Karacalı, Abdulmecit Türüt

PII: S2211-3797(17)30570-3
DOI: http://dx.doi.org/10.1016/j.rinp.2017.09.014
Reference: RINP 930

To appear in: *Results in Physics*

Received Date: 4 April 2017
Revised Date: 23 August 2017
Accepted Date: 5 September 2017

Please cite this article as: Biber, M., Aydoğan, S., Çaldıran, Z., Çakmak, B., Karacalı, T., Türüt, A., The influence of annealing temperature and time on the efficiency of pentacene:ptcdi organic solar cells, *Results in Physics* (2017), doi: http://dx.doi.org/10.1016/j.rinp.2017.09.014

THE INFLUENCE OF ANNEALING TEMPERATURE AND TIME ON THE EFFICIENCY OF PENTACENE:PTCDI ORGANIC SOLAR CELLS

Mehmet Biber[1], Şakir Aydoğan[2a*], Zakir Çaldıran[2], Bülent Çakmak[3], Tevhit Karacalı[3], Abdulmecit Türüt[4]

[1]Department of Biotechnology, Necmettin Erbakan University, Science Faculty, Konya, Turkey

[2]Department of Physics, Science Faculty, Atatürk University, Erzurum, Turkey

[a]Department of Environmental Engineering, Faculty of Engineering, Ardahan University, Ardahan, Turkey

[3]Department of Electrical and Electronics Engineering, Erzurum Technical University, Erzurum, Turkey

[4]Department of Physics Engineering, Faculty of Science, Istanbul Medeniyet University, Turkey

Keywords: Organic solar cells; PTCDI; pentacene; annealing.

Abstract

In this study, fabrication of a polycyclic aromatic hydrocarbon/Perylene Tetracarboxylic Di-Imide (PTCDI), donor/acceptor solar cells are presented using physical vapour deposition technique in a 1000 class glove box. An ITO/PEDOT:PSS/Pentacene/PTCDI/Al (ITO=Indium Tin Oxide and PEDOT:PSS= poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) solar cell has been obtained and the power conversion efficiency, PCE (η) of about **0.33**% has been obtained under simulated solar illumination of 300 W/m^2. Furthermore, the effects of annealing temperatures (at 100 and 150 ^{0}C) and of annealing (at 100 ^{0}C) times for 5 and 10 min. on the power conversion efficiency, η of the solar cells have also been

*Corresponding author: email: **saydogan@atauni.edu.tr**

investigated. In general, it has been seen that the thermal annealing deteriorated the characteristics parameters of Pentacene/PTCDI solar cell such that both fill factor, *FF* and η decreased after annealing and with increase of annealing time. Atomic force microscopy (AFM) images showed that the phase segregation and grain size increased and the surface roughness of Pentacene film decreased and these effects reduced the η value. The η values of the solar cell have been determined as 0.33%, 0.12% and 0.06% for pre-annealing, annealing at 100 and 150 ^{0}C, respectively.

1 Introduction

Developing countries produce electricity mostly from nuclear and limited oil resources. However, these resources pollute our atmosphere and environment. Therefore, researchers search for renewable and inexpensive energy resources around the world. Renewable energy resources exist over wide geographical areas, in contrast to other energy sources which are concentrated in a limited number of countries. Among renewable energy resources, solar cells are the most powerful candidates for the generation of low-cost electricity, by directly converting sun light into electricity. In recent years, photovoltaic devices have gained an important role among the alternative renewable energy sources and researches on these devices are increasingly ongoing today. Solar cell devices made up of organic semiconductors have attracted because of their light weight, mechanical flexibility, clean conversion of solar energy and low cost of fabrication [1–3], light weightlessness, and the potential for large scale production [4,5]. Researches on the power conversion efficiency of organic photovoltaic (OPV) cells have been extended and significantly improved due to the use of new materials and device architectures. Among few organic materials, pentacene has strong absorption property in the visible solar spectrum, large exciton diffusion length and high field effect hole mobility (1 cm^2 V^{-1} s^{-1}) [6]. Furthermore, PTCDI has been used as an

*Corresponding author: email: saydogan@atauni.edu.tr

electron acceptor (electron mobility is 0.6 $cm^2V^{-1}s^{-1}$), which ensures balanced field-effect motilities for n- and p-channels within the device. The chemical structures of pentacene and PTCDI are shown in Fig.1.

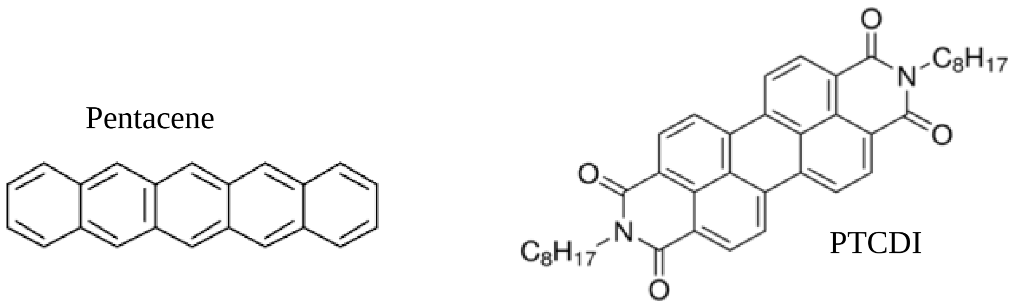


Fig.1 The chemical structures of pentacene and PTCDI

Performance of the organic solar cells depends on the preparation conditions or annealing conditions such as annealing temperature and annealing time. After annealing, morphology of the active layer may be altered and this modification may affect the performance of a solar cell. The morphology of an organic material may change under different annealing time or temperatures because different recombination mechanisms may present in different structures. In this study, we have studied the effect of annealing temperatures and annealing times on the performance (the power conversion efficiency) of heterojunction based on Pentacene/PTCDI, donor/acceptor solar cells.

2 Experimental Procedures

Fabrication steps of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells have been given here. ITO has been cleaned by chemically (ultrasonic washing in acetone, drying in N_2 atmosphere, dipping in deionised (DI) water, ultrasonic washing in isopropyl alcohol (IPA), drying in N_2 atmosphere, dipping in DI water and then drying in N_2). PEDOT:PSS layer has been formed on ITO (having 8-12 Ω resistance) by spin coating (15 s ramp up, 35 s 1500 rpm, 10 s 2000 rpm, 2 min. annealing at 180°C, 40 nm thickness). Later, a 50 nm pentacene

*Corresponding author: email: saydogan@atauni.edu.tr

layer has been evaporated on PEDOT:PSS layer, at a pressure of $3x10^{-7}$ Torr and an evaporation rate of 1 Å/sec. Then, PTCDI layer, with 50 nm thickness has been evaporated on pentacene, at a pressure of $3x10^{-7}$ Torr and an evaporation rate of 1 Å/sec. Finally, Al metallic contacts with 100 nm thickness have been evaporated on PTCDI layer at a pressure of $3x10^{-7}$ Torr and an evaporation rate of 1 Å/sec. The device configuration of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell is given in Fig. 2.

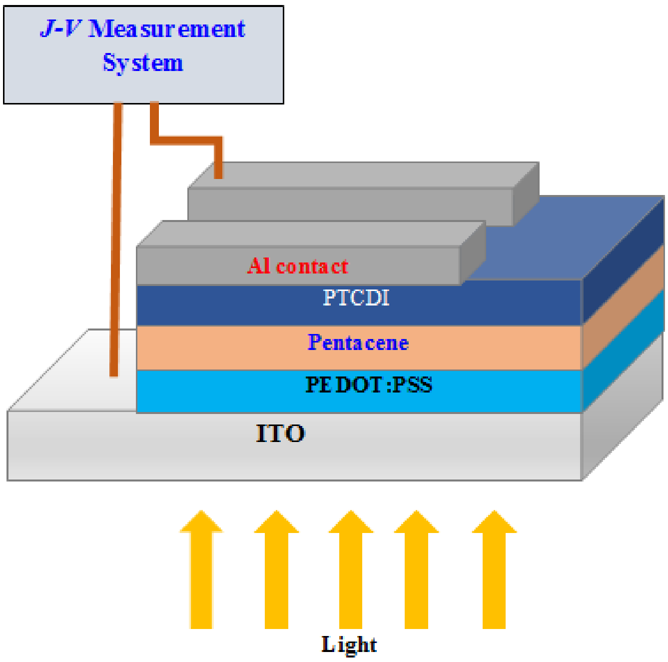


Figure 2. The device configuration of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell fabricated in this study.

3 Results and Discussion

We have fabricated two different group samples to determine the effect of the annealing temperatures (annealing process was performed in inert (argon) environment, in a glove box) and annealing time on the power conversion efficiency of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells. These samples are:

*Corresponding author: email: **saydogan@atauni.edu.tr**

- Group I: pre-annealing at different temperatures (room temperature RT (ref.), 100°C, and 150°C) for 5 minutes.
- Group II: pre-annealing, at constant annealing temperature of 100°C for different times (5 min. and 10 min.)

Absorption spectra of the pentacene, PTCDI and Pentacene:PTCDI blend have been obtained for visible range and given in Fig.3. As seen, all the films have good spectrum characteristics in this range.

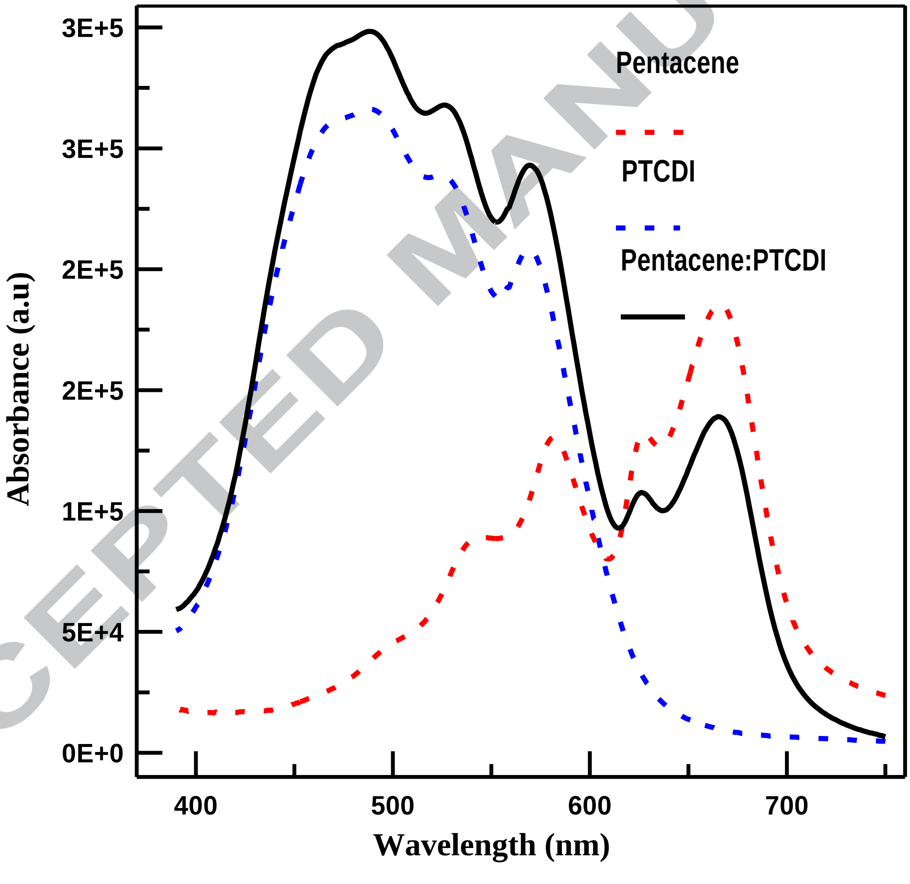


Fig.3 Absorption spectra of the pentacene, PTCDI and Pentacene:PTCDI blend

*Corresponding author: email: **saydogan@atauni.edu.tr**

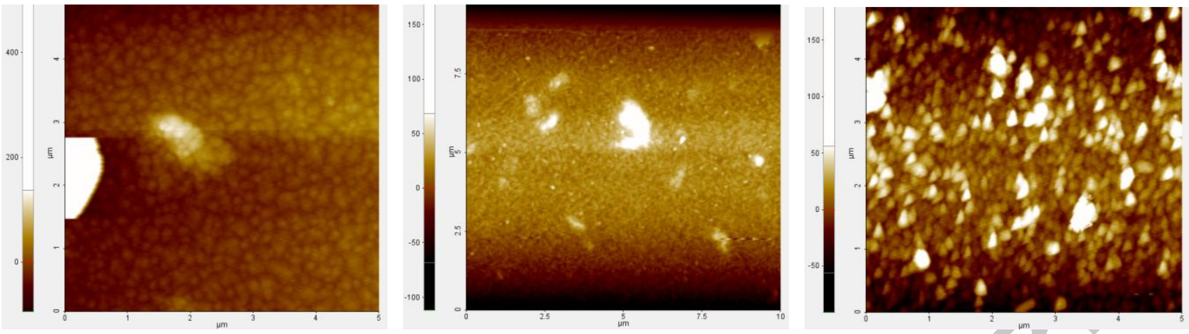
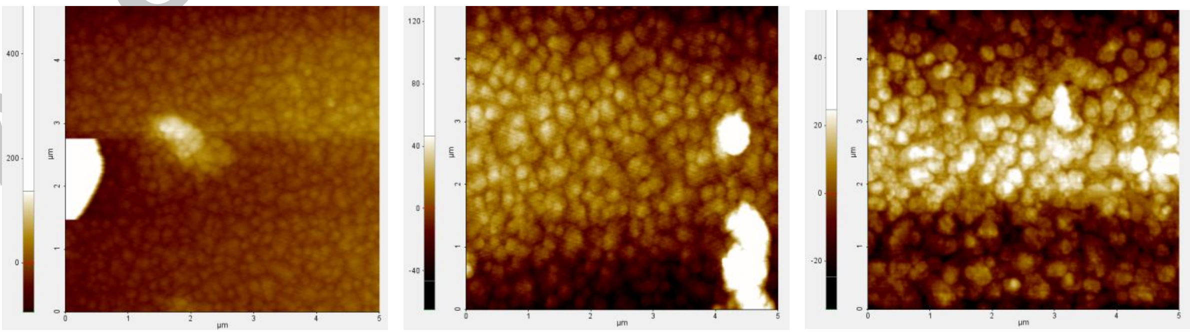


Fig.4: AFM images of the Pentacene, PTCDI and PTCDI/Pentacene films on PEDOT:PSS at pre-annealing.

The morphology of the organic blend layer plays an important role in determining the performance of the solar cell. In order to clarify the morphological changes, AFM images of the Pentacene, PTCDI and PTCDI/Pentacene films on PEDOT:PSS at pre-annealing are given in Fig. 4. AFM images of the Pentacene films on PEDOT:PSS at pre-annealing (**a**) and after annealing of at 100°C (**b**) and at150°C (**c**) are illustrated in Fig. 5. Furthermore, AFM images of the PTCDI films on Pentacene at pre-annealing (**a**) and after annealing of at 100°C (**b**) and at 150°C (**c**) are given in Fig. 6. In addition, AFM images of the PTCDI/Pentacene films on PEDOT:PSS at pre-annealing (**a**) and after annealing at 100°C (**b**) and at 150°C (**c**) are shown in Fig.7. AFM images denoted that thin films annealed at high temperatures yielded more homogeneous structure as rougher surface roughness with respect to non-annealed ones, at low temperature. After annealing, the enhance of roughness might produce extra locations for crystallization of PTCDI, and the increase in the roughness may be due to an increase in phase separation of the coated PTCDI/Pentacene films. Namely, annealed films lead to varying degrees of phase separation and a result of annealing effects might be attributed to improved microscopic phase separation between PTCDI and Pentacene [7]. It is known that surface roughness in blended films significantly affects some processes such as the charge carrier collection, the efficiency of charge carrier transfer or transport [8-

*Corresponding author: email: **saydogan@atauni.edu.tr**

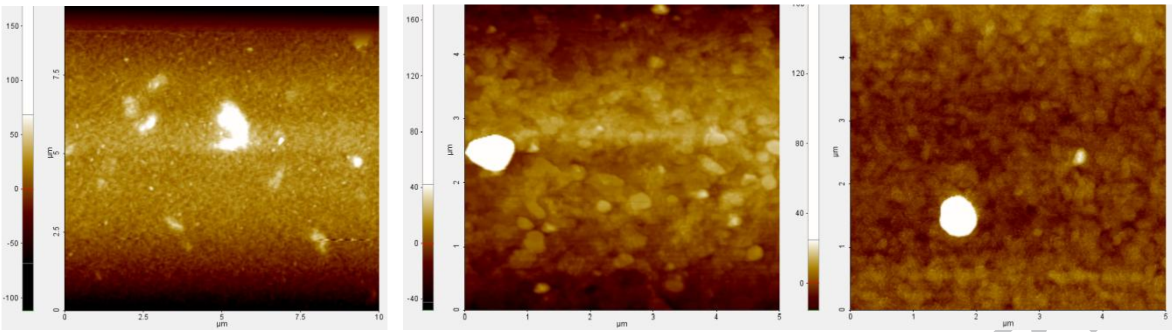
11]. Furthermore, an enhancement in higher roughness of the thin film layers (PEDOT:PSS and PTCDI/PENTACENE) yields a larger contact surface in the interface of the device materials' layers and this boosts charge collection efficiency at electrodes giving a higher power conversion efficiency [12]. In summary, high annealing temperature provides more activation energy to material atoms which leades to larger grain size. In conclusion, the images indicate that as annealing temperatures are increased, the surface roughness of the Pentacene film decreased and, grain sizes and phase separation became larger. It should be noted that the higher roughness of the film is, the higher efficiency we get [13]. When the surface roughness increased, internal reflection will increase which leads to improve light collection. This results in an increase in the efficiency of the solar cell. [14]. These results in the literature indicate that determination of the diffusion length of excitons is difficult after annealing. In other words, the contact area may increase for the higher surface roughness and then, more charges may be collected in the interface of organic film and Al. However, our results showed exactly opposite results after heat treatment. Therefore, it should be expected lower power conversion efficiency for ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells after annealing.



(a) (b) (c)

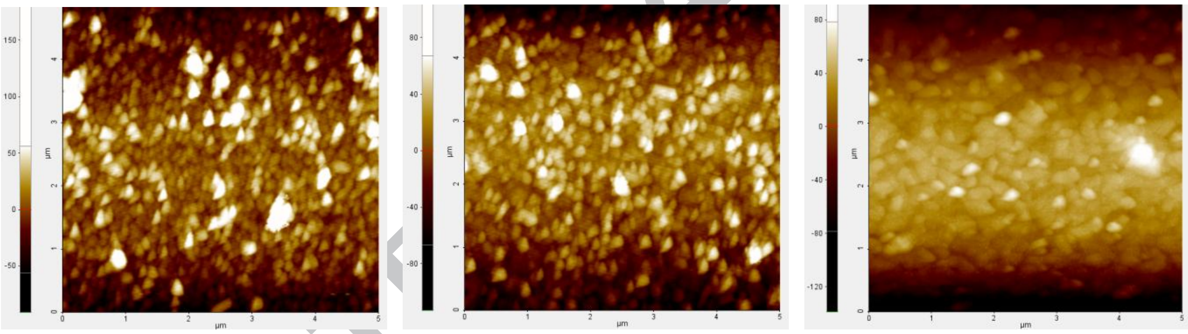
Fig.5: AFM images of the Pentacene films on PEDOT:PSS at pre-annealing (**a**) and after annealing of at 100°C (**b**) and at 150°C (**c**).

*Corresponding author: email: **saydogan@atauni.edu.tr**



(a) (b) (c)

Fig.6: AFM images of the PTCDI films on Pentacene at pre-annealing (**a**) and after annealing of at 100°C (**b**) and at 150°C (**c**).



(a) (b) (c)

Fig.7: AFM images of the PTCDI/Pentacene films on PEDOT:PSS at pre-annealing (**a**) and after annealing at 100°C (**b**) and at 150°C (**c**).

J-V characteristics of the reference ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell have been measured in dark and under illumination with a power density of 300 W/m^2. The *J*-V characteristics of ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell is seen in Fig.8. *J-V* characteristics of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells for different annealing temperatures is given in Fig. 9 under illumination Characteristic parameters such as short circuit current density Jsc, open circuit voltage Voc, current density Jmp and voltage

*Corresponding author: email: **saydogan@atauni.edu.tr**

Vmp corresponding to maximum power of the solar cell are given in Table 1. Experimental results showed that the power conversion efficiency η of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell decreased with increasing of annealing temperature. As a result, the solar cell without heat treatment resulted in a better PCE of 0.33%.

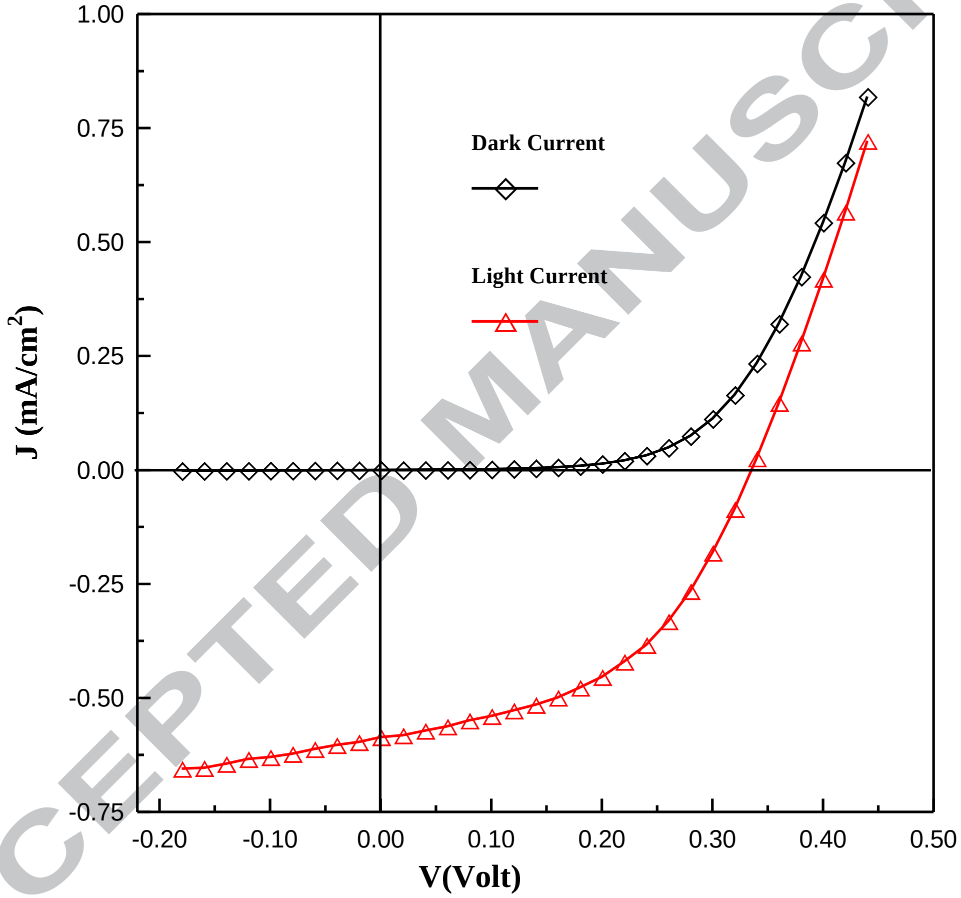


Fig. 8: *J-V* characteristics of the reference ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell in dark and under illumination of 300 W/m^2

*Corresponding author: email: **saydogan@atauni.edu.tr**

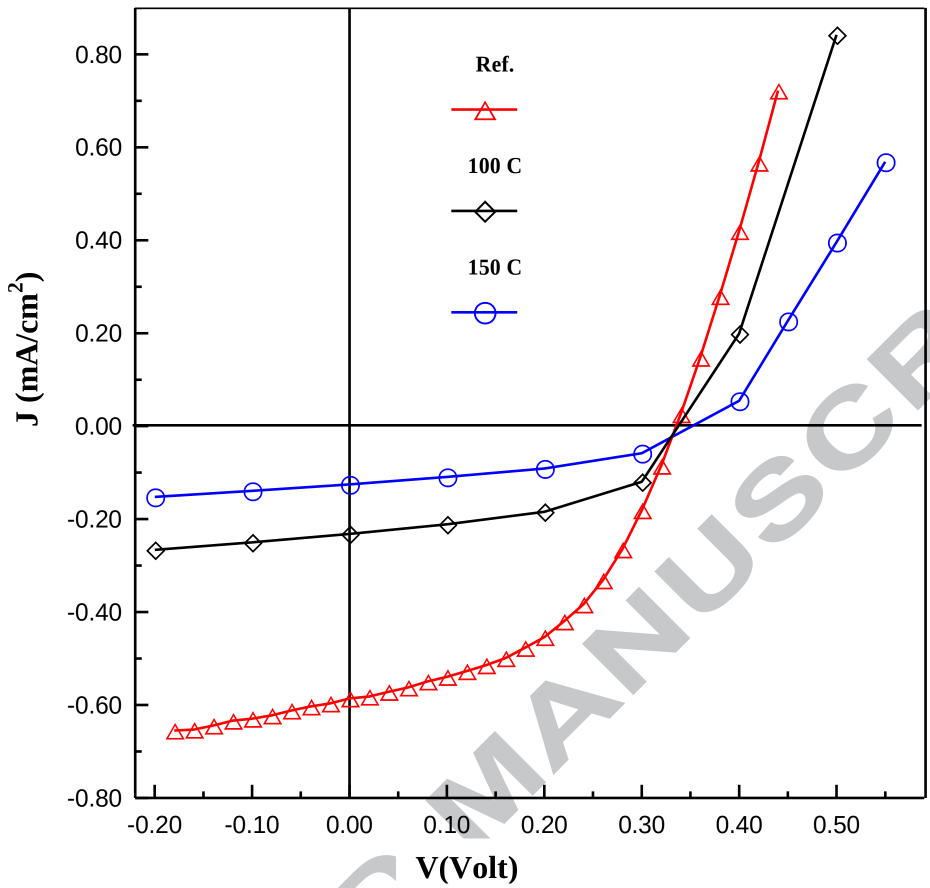


Fig. 9: The *J-V* characteristics of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells before and after annealing at 100 and 150 ^{0}C temperatures, under illumination of 300 W/m^2.

Figure 10 depicts *J-V* characteristics of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells which are annealed at 100 ^{0}C for annealing time of 5 and 10 minutes under illumination of 300 W/cm^2. Experimental characteristic parameters such as J_{sc}, V_{oc} and J_{mp} and V_{mp} are also given in Table 1. As seen in the table efficiency η of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell decreased after increasing annealing time such that its values are determined as 0.12 and 0.08 for 5 and 10 min. annealing times, respectively. In addition, these values are also lower than that of the reference sample.

*Corresponding author: email: **saydogan@atauni.edu.tr**

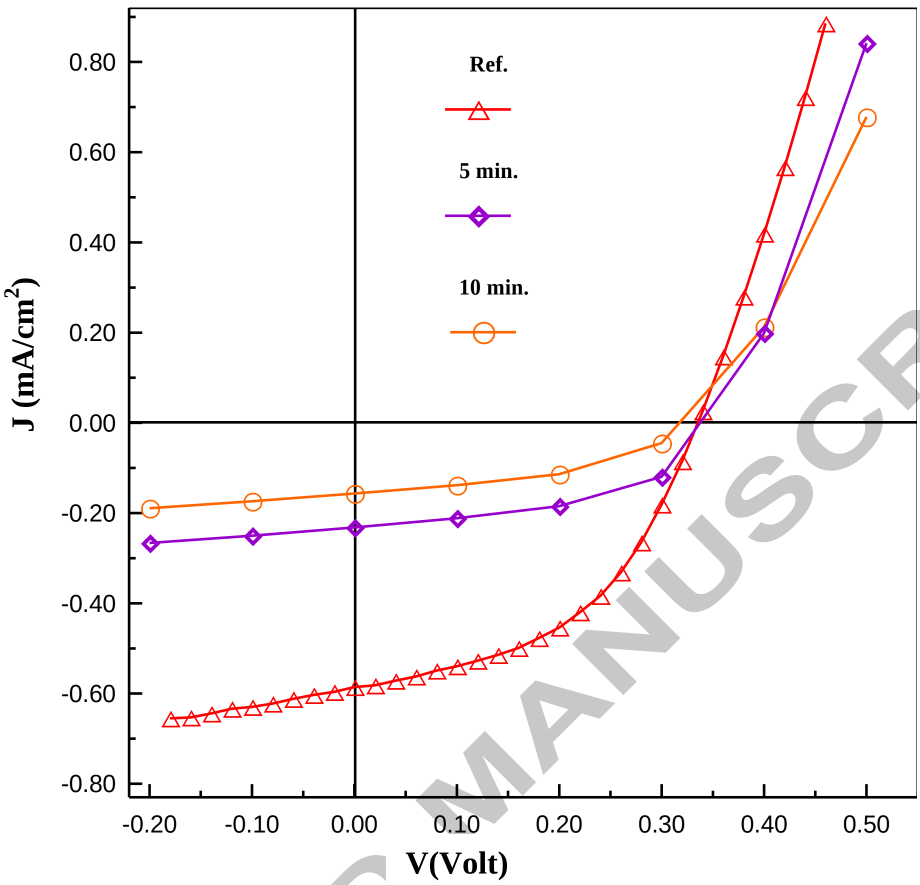


Fig.10: Under illumination of 300 W/m^2 *J-V* characteristics of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells at 5 and 10 minutes annealing time at an annealing temperature of 100 ^{0}C ones.

Table 1: The characteristics parameters of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells for different annealing temperatures and annealing times..

Sample	**J_{SC} (mA/cm^2)**	**V_{OC} (V)**	**J_{MP} (mA/cm^2)**	**V_{MP} (V)**	**FF (%)**	**PCE (%)**
Ref.	0.60	0.34	0.45	0.22	49	0.33
100 °C 5 min.	0.23	0.34	0.18	0.20	47	0.12

*Corresponding author: email: **saydogan@atauni.edu.tr**

150 °C 5 min.	0.12	0.40	0.09	0.20	37	0.06
100 °C 10 min.	0.16	0.32	0.11	0.20	44	0.08

According to the as-cast device, annealing of the organic solar cells fabricated caused a deterioration of ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell performance, characterized by an increase in V_{oc} and a reduction in J_{sc}. This can be explained by an increased mixing of the components causing a degradation of the transport properties in the Pentacene/PTCDI blend [13,15]. The surface roughness is determined to be 18 nm and 13 nm, for annealing temperatures of 100, 150 ^{0}C, respectively. Our results indicate that the diffusion length of excitons in organic material might be increased after annealing which results in a decrease in photocurrent. The decreased surface roughness after annealing might also decrease internal reflection and reduce light collection. As a conclusion the PCE of ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell would also decrease.

3 Conclusions

We have fabricated ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells and have investigated the influence of thermal annealing on power conversion efficiency, PCE. We demonstrate that the device combination exhibits light harvesting throughout the visible region of the solar spectrum. It is seen that open circuit voltage increased and efficiency of the solar cells decreased with increasing annealing temperature and both decreased with increasing annealing time. Surface roughness of pentacene film decreased and grain sizes increased with increasing annealing temperatures. These results could be explained by a reduction in charge

*Corresponding author: email: saydogan@atauni.edu.tr

collection which causes a decrease in photocurrent due to an increase in the diffusion length of excitons in organic material.

Acknowledgement

This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) with research project number of 212T012.

*Corresponding author: email: **saydogan@atauni.edu.tr**

4 REFERENCES

[1] S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, “2.5% efficient organic plastic solar cells”, Appl. Phys. Lett. 78 pp. 841–843 (2001)

[2] S.Yoo, B.Domercq, B.Kippelen, “Efficient thin-film organic solar cells based on pentacene/C60 heterojunctions, Appl. Phys. Lett. 85 (2004) pp. 5427–5429

[3] A. K. Pandey, J. M. Nunzi, “Efficient flexible and thermally stable pentacene/C60 small molecule based organic solar cells”, Appl. Phys. Lett. 89 (2006) pp. 213506- 213509

[4] Y. Su, S. Lan, K. Wei, K. Organic Photovoltaics. Mater. Today 2012, 15, pp. 554−562

[5] S. Lizin, S. Van Passel, E. De Schepper, W. Maes, L. Lutsen, J. Manca, D. Vanderzande, D. Life Cycle Analyses of Organic Photovoltaic: A Review. Energy Environ. Sci. 2013, 6, pp. 3136−3149.

[6] S. Karak, V.S. Reddy, S.K. Ray, A. Dhar, Organic photovoltaic devices based on pentacene/N,N0-dioctyl-3,4,9,10-perylenedicarboximide heterojunctions, Organic Electronics 10 (2009) pp. 1006–1010.

[7] A. P. Wanninayake, Li Shengyi, C. Benjamin Church, N. Abu-Zahra, Thermal Annealing on P3HT/PC_{70}BM Solar Cells Incorporated with Au and CuO Nanoparticales, Int. J. Renew. En Res. (2015), pp. 1080-1091.

[8]T. M. Lloyd, J. E. Anthony and G. G. Malliaras, Photovoltaics from soluble small molecules, Mater. Today (Oxford, U. K.), (2007), 10, pp. 34–41

[9]X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, Nanoscale morphology of high-performance polymer solar cells, Nano Lett., (2005), 5, pp. 579–583.

*Corresponding author: email: **saydogan@atauni.edu.tr**

[10]A. Tamayo, T. Kent, M. Tantitiwat, Mark A. Dante, J. Rogers and Thuc-Quyen Nguyen, Influence of alkyl substituents and thermal annealing on the film morphology and performance of solution processed, diketopyrrolopyrrole-based bulk heterojunction solar cells, Energy Environ. Sci., (2009), 2, pp. 1180-1186.

[11]H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner and N. S. Sariciftci, Nanoscale morphology of conjugated polymer/fullerene- based bulk- heterojunction solar cells, Adv. Funct. Mater., (2004), 14, pp. 1005–1011.

[12] F. A. George, A. Dibb, M. A. Muth, T. Kirchartz, S. Engmann, H. Hoppe, G. Gobsch, M. Thelakkat, N. Blouin, S. Tierney, M. Carrasco Orozco, J. R. Durrant, and J. Nelson, Influence of doping on charge carrier collection in normal and inverted geometry polymer:fullerene solar cells", Scientific Reports, 3, (2013), pp. 3335.

[13] T-L. Wang, C-H. Yang, Y-T. Shieh, A-C. Yeh, C-H. Chen, T-H. Ho, Effects of annealing on the polymer solar cells based on CdSe–PVK electron acceptor, Materials Chemistry and Physics, 132 (2012) pp.131–137.

[14] G. Li, V. Shrotriya, Y. Yao, and Y. Yang, Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly(3-hexylthiophene), J. Appl. Phys. 98, (2005), 043704.

[15] Y. Kim, S. A. Choulis, J. Nelson, D. D. C. Bradley, S. Cook, and J. R. Durrant, Device annealing effect in organic solar cells with blends of regioregular poly(3-hexylthiophene) and soluble fullerene, Appl. Phys. Lett. 86, (2005), 063502 .

*Corresponding author: email: **saydogan@atauni.edu.tr**

FIGURE CAPTIONS

Fig.1 The chemical structures of pentacene and PTCDI

Fig 2. The device configuration of ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell fabricated in this study

Fig.3 Absorption spectrums of the pentacene, PTCDI and Pentacene:PTCDI blend

Fig.4: AFM images of the Pentacene, PTCDI and PTCDI/Pentacene films on PEDOT:PSS at pre-annealing.

Fig.5: AFM images of the Pentacene films on PEDOT:PSS at pre-annealing (**a**) and after annealing of 100°C (**b**) and 150°C (**c**).

Fig.6: AFM images of the PTCDI films on Pentacene, at pre-annealing (**a**) and after annealing of 100°C (**b**) and 150°C (**c**).

Fig.7: AFM images of the PTCDI/Pentacene films on PEDOT:PSS at pre-annealing (**a**) and after annealing at 100°C (**b**) and at 150°C (**c**).

Fig. 8: *J-V* characteristics of the reference ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cell for in dark and under illumination of 300 W/m^2

Fig. 9: The *J-V* characteristics of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells before and after annealing at 100 and at 150 ^{0}C temperatures, under illumination, 300 W/m^2.

Fig.10: Under illumination of 300 W/m^2, the *J-V* characteristics of the ITO/PEDOT:PSS/Pentacene/PTCDI/Al solar cells at 5 and 10 minutes annealing time for annealed at 100 ^{0}C ones.

*Corresponding author: email: **saydogan@atauni.edu.tr**