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Fotovoltaik hücrelerin yüzey morfolojisi ve verimliliği üzerinde termal tavlama etkisi

Thermal annealing effect on the surface morphology and efficiency of photovoltaic cells

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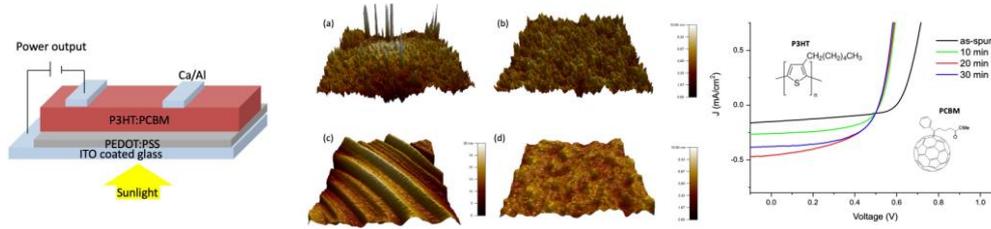
Thermal Annealing Effect on the Surface Morphology and Efficiency of Photovoltaic Cells

Highlights

- ❖ Importance of the thermal annealing in solar cell fabrication.
- ❖ Evaluation of the surface morphology with AFM.
- ❖ Measuring the device efficiency and its relation with the surface roughness.

Graphical Abstract

Solar cells were made with the blend of P3HT:PCBM. AFM images of the films were annealed at different annealing times. Current density and voltage measurements of the solar cells were performed.



Şekil. Güneş pili yapısı, filmlerin AFM görüntüleri, ve pillerin J-V karakteristikleri. / **Figure.** Device structure, AFM images of the films, J-V characteristics of the cells.

Aim

To observe if thermal annealing affects the device performance and the surface morphology.

Design & Methodology

Keithley 2400 Source Meter was used to measure voltage (V) and current (I). Solar cells were tested with xenon-lamp-based solar simulator (Solar Light 16S-150W) with AM1.5G irradiation (80 mW/cm²). Molecular force probe (MFP-3D) atomic force microscope was used to collect topographic images of the films.

Originality

The surface morphology of the produced films and the efficiency of the solar cells are affected by varying the thermal annealing time during the production phase.

Findings

It was found that the device, which was thermally annealed for 20 minutes, had the roughest surface. It was also the most efficient cell.

Conclusion

Thermal annealing time affects solar cell efficiency.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Fotovoltaik Hücrelerin Yüzey Morfolojisi ve Verimliliği Üzerinde Termal Tavlama Etkisi

Araştırma Makalesi / Research Article

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ÖZET

Fotovoltaikler, güneş ışığını elektrik akımına dönüştürür. Bu çalışmada silikon ile yapılan malzemeler yerine elektron verici ve alıcı içeren karışımlar kullanılmıştır. Karbon bazlı organik yarı iletkenlerin işlenmesi kolaydır ve üretim maliyetleri düşüktür. Fotovoltaik cihaz performansında, substrat hazırlama, karışımdaki polimer-alıcı oranları, aktif katmanın termal tavlama ve üst elektrot biriktirme gibi önemli rol oynayan birkaç üretim adımı vardır. Karışımın nano ölçekli morfolojisinin termal tavlama işlemi ile değiştirilebileceği gösterilmiştir. Sonuç olarak, verim yüzey pürüzlülüğünden etkilenir. İnce filmler ve fotovoltaik hücreler üretmek için donör: alıcı olarak P3HT: PCBM karışımı kullanıldı. Çeşitli zamanlarda tavlama cihazların güç dönüşüm verimleri ve yüzey morfolojileri ölçülmüştür. Atomik kuvvet mikroskobu (AFM) görüntüleri, aktif tabakanın yüzey pürüzlülüğünün esas olarak tavlama süresinden etkilendiğini ve en pürüzlü yüzeye sahip filmin en verimli güneş pili ile sonuçlandığını ortaya çıkardı.

Anahtar Kelimeler: AFM, polimerler, fotovoltaikler, termal tavlama.

Thermal Annealing Effect on the Surface Morphology and Efficiency of Photovoltaic Cells

ABSTRACT

Photovoltaics convert solar radiation into electrical current. For the present study, blends containing electron donor and acceptor are used instead of materials made with silicon. Carbon-based organic semiconductors are easy to process and have low fabrication costs. There are several fabrication steps playing important role in the photovoltaic device performance such as, substrate preparation, polymer-acceptor ratios in the blend, thermal annealing of the active layer and top electrode deposition. It has been shown that nanoscale morphology of the blend can be altered via thermal annealing treatment. As a result, efficiency is affected by surface roughness. The blend of P3HT: PCBM as donor: acceptor was used to fabricate thin films and photovoltaic cells. The power conversion efficiencies and surface morphologies of the devices annealed at various times were measured. Atomic force microscopy (AFM) images revealed that the surface roughness of the active layer is mainly affected by the annealing time, and the film with the roughest surface results in the most efficient solar cell.

Keywords: Atomic force microscopy, polymers, photovoltaics, thermal annealing.

1. INTRODUCTION

The unprecedented interest in developing low-cost renewable energy sources motivates scientific research for efficient photovoltaics (PVs). Organic e.g., polymer-based photovoltaic elements promise low cost of fabrication, material diversity, and mechanical flexibility [1–4]. Although organic PVs are more beneficial to work with, there are a few issues to be solved in order to make them commercially available, such as low operating lifetime and low power conversion efficiency (PCE). The bulk heterojunction (BHJ) made with the blend of poly (3-hexylthiophene) (P3HT): [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) has been the most studied and successful system so far [5, 6]. Both P3HT and PCBM are ideal photoactive materials individually to fabricate

BHJ photovoltaic cells. P3HT shows high carrier mobility, chemical stability, and 2.0 eV optical band gap [7]. P3HT has high hole mobility ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and it offers the potential of fabricating high-efficient photovoltaics [8, 9]. PCBM is the most used electron acceptor in polymer based solar cells because of its high affinity and high mobility [10, 11]

Although P3HT: PCBM solar cells are outstanding candidates among other polymer/fullerene blend devices, research is still going on to obtain higher efficiencies. Some of the parameters that affect the performance of the cells can be listed as film thickness, donor: acceptor ratio, processing conditions, dissolving solvent, and thermal annealing [9, 12–14]. In particular, thermal annealing changes the blend morphology, and is an essential step to increase the efficiency of polymer-based photovoltaics [15–20].

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Singh et al. has reported that P3HT polymer chain structure is reordered by thermal annealing which enhances the charge transfer efficiency and improves hole mobility among the polymer network [19]. Kim et al. has shown that annealing improves the light harvest and the interfacial contact between the active and cathode layer [16]. These two studies kept the annealing time same while varying the temperature. However, Li et al. showed that the device performance and the surface morphology can be enhanced via the annealing time, and the films with smoother surface had the largest power conversion efficiency [18].

were placed in a nitrogen-filled glovebox (< 0.1 p.p.m. H_2O and O_2).

For the active layer, we prepared a blend of 18 mg of P3HT (Rieke Metals) and PCBM (Nano-C) with 1:1 weight ratio in chlorobenzene. The device structure is shown in Figure 1. They were used without any purification. The blend was stirred around 14 hours at $40^\circ C$, and it was spin coated on PEDOT: PSS at 600 r.p.m. for 60 s (~ 220 - 250 nm) to prepare the active layer. The films were either annealed at $120^\circ C$ for various times, or they were placed in a petri dish at room

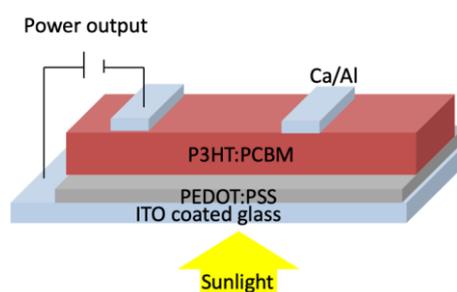


Figure 1. The device structure.

Herein, photovoltaic cells madewith P3HT : PCBM blend were fabricated and studied. The device structure was ITO / PEDOT : PSS / P3HT : PCBM / Ca-Al. PEDOT:PSS is a suitable electrode for hole injection, and we used it because of its high transmittance in the visible range and excellent thermal stability. Also, its work function is well matched with the highest occupied molecular orbital (HOMO) level of many of the polymer donors. Ca-Al is a commonly used top electrode since the work function of Ca matches with the lowest unoccupied molecular orbital (LUMO) level of the fullerene acceptor PCBM. Al layer is deposited on top of Ca layer to protect it from oxidation. The power conversion efficiency and the surface morphology were studied by varying the annealing time. Our current study shows that there is a strong relationship between thermal annealing time and the power conversion efficiency. To evaluate how the surface morphology changes by thermal annealing, atomic force microscopy (AFM) was used.

2. EXPERIMENTAL DETAILS

As the anode or hole-injecting contact, 40 nm thick indium tin oxide (ITO) on glass substrates (Delta Technologies) was used. The substrates were sequentially sonicated with detergent, acetone, deionized water, and isopropanol (10 min for each step). After removing the excess solvent with nitrogen gun, oxygen plasma cleaning was used to prepare the surface for the next step. A transparent conducting polymer poly(3,4-ethylenedioxythiophene)-poly (styrene- sulfonate) (PEDOT: PSS AI 4083) (Ossila Ltd.) was spin coated on the substrates at 8000 r.p.m. for 60 s (~ 30 nm), and they were annealed at $120^\circ C$ for 50 min. After annealing, they

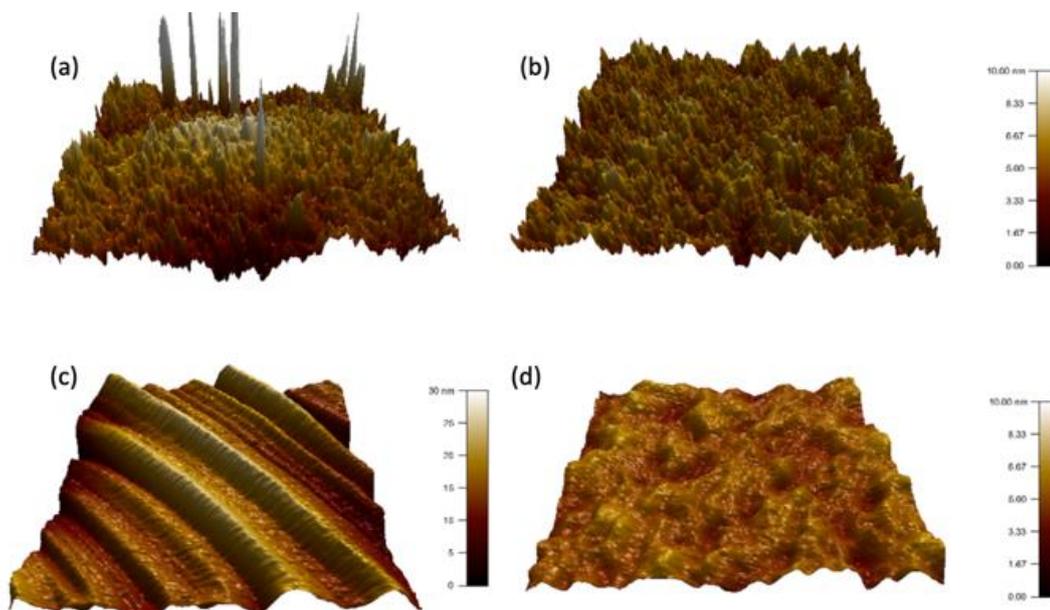
temperature. Ca (~ 30 nm) and Al (~ 100 nm) as the top electrode or the cathode were thermally evaporated. The device active area was roughly 1×1 mm². Solar cells were mounted in a closed cycle He cryostat, and measurements were completed at room temperature. Keithley 2400 Source Meter was used to measure voltage (V) and current (I). Solar cells were tested with xenon-lamp-based solar simulator (Solar Light 16S-150W) with AM1.5G irradiation (80 mW/cm²). Molecular force probe (MFP- 3D) atomic force microscope (Asylum Research, 36 Santa Barbara, CA) was used to collect topographic images of the films.

3. RESULTS AND DISCUSSION

The parameters of open circuit voltage (V_{OC}), short circuit current (I_{SC}), fill factor ($FF = P_{MAX}/V_{OC} I_{SC}$), and surface roughness are shown in Table 1. Power conversion efficiency ($PCE = P_{MAX}/P_{IN}$) is also calculated using these parameters. FF decreased for the device annealed for 20 min, then it increased for the 30 min annealed device. Figure 3 gives the current density-voltage (J-V) characteristics under solar light illumination. In J-V graph, short-circuit current density increases with increasing annealing time up to 20 minutes, resulting at smaller fill factor. AFM images of the films, before and after thermal annealing at various times are shown in Figure 2. From the surface images, it is clearly seen that the surface morphology changes with the annealing time. Annealing temperature was kept same at $120^\circ C$. For the unannealed film, the surface becomes smoother with r.m.s. roughness, σ , of ~ 0.7 nm (Figure 2a).

Table 1. The results for different annealing times.

Parameters	As spun	10 min	20 min	30 min
I_{sc} (μA)	1.8	3.1	5.5	4.5
V_{oc} (V)	0.6	0.52	0.52	0.51
Fill factor (%)	0.39	0.53	0.46	0.54
Efficiency (%)	0.018	0.035	0.053	0.051
Roughness (nm)	0.7	1.1	1.5	1.4

**Figure 2.** AFM images of the film morphology at different annealing times. (a) Left in a petri dish after spin coating. Annealed for 10 (b), 20 (c), 30 (d) minutes at 120°C.

The film after 10 min of annealing shows $\sigma \sim 1.1$ nm (Figure 2b), and the texture is rougher than that of unannealed film. Roughness becomes ~ 1.5 nm for the film after annealing for 20 min (Figure 2c). After annealing for 30 min, the roughness is very similar to that of 20 min annealed film, $\sigma \sim 1.4$ nm (Figure 2d). It is good to point out that the scale bar in Figure 2c is different than the other three images. Although 20 min annealed film shows very smooth texture, it has the roughest surface.

We note that AFM images of the devices look different from each other in terms of surface morphology. There are four samples fabricated under the same conditions except the annealing times. Indeed, the purpose of this study is to show that if there is any relationship between the surface roughness and the power conversion efficiency. The film with the roughest surface shows the largest efficiency. It was presented that the thermal annealing improves device rectification by forming better

vertical p-n junction morphology in the blend [17]. A similar study on thermal annealing effect on P3HT:PCBM blend devices was reported that the films become smoother after annealing, and this results in a better contact between organic and cathode layers. Another explanation for the improvement of power conversion efficiency is due to the decreased number of traps that is a result of reducing surface roughness [18]. In the same study, it was assumed that rough surface would increase the short-circuit current density and reduce the charge-transport distance. Thus, the internal light scattering, and light absorption are improved by nano scaled structures. However, we assume that this thermal annealing treatment to optimize the surface roughness may not have a positive effect on solar cell structures with well-ordered thick films.

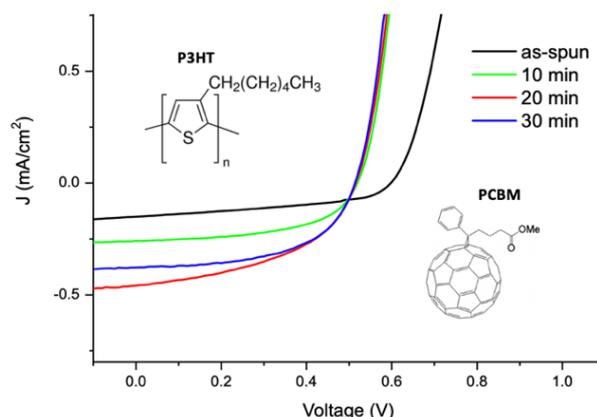


Figure 3. Thermal annealing effect on the J–V. The films before (black) and after thermal annealing at 120 °C for 10 (green), 20 (red) and 30 (blue) minutes.

4. CONCLUSION

In this study, devices were fabricated, and thermal annealing effect on current density and conversion efficiency was studied. According to results, different thermal annealing time of the active layer resulted in different surface morphology, surface roughness and device performance. AFM images revealed that the surface roughness increased with annealing time (up to 20mins) and the film with the roughest surface showed the highest power conversion efficiency amongst other films indicating a direct positive correlation between the surface roughness and the power conversion efficiency. As surface roughness increased from 0.7 nm to 1.5 nm, the efficiency of the device increased from 0.018% to 0.053 %, respectively, indicating a 195% increase in the efficiency. Thus, it can be concluded that there is a strong relationship between the efficiency of polymer solar cell and the surface morphology of the film. It is understood that the thermal annealing contributes to the device performance and improves the interfacial contact between the film and the top electrode.

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DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods they use in their studies do not require ethical committee approval and/or legal-specific permission.

AUTHORS' CONTRIBUTIONS

Keşer SAHİN TIRAS: Fabricated the films and solar cells and measured their performance. Writing the manuscript.

Thilini P. RUPASINGHE: Performed the AFM imaging and reviewing.

Markus WOHLGENANTT: Methodology and review & editing.

Alexei V. TIVANSKI: Advising and Methodology.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

REFERENCES

- [1] Brabec CJ, Sariciftci NS, Hummelen JC. "Plastic solar cells", *Advanced Functional Materials*, 11(1):15-26, (2001).
- [2] Hur SW, Kim TW, Chung DH, Oh HS, Kim CH, Lee JU, Park JW. "Organic photovoltaic effects depending on CuPc layer thickness", *Journal of the Korean Physical Society*, 45(3):627-9, (2004).
- [3] Kang H, Lee W, Oh J, Kim T, Lee C, Kim BJ. "From fullerene-polymer to all-polymer solar cells: The importance of molecular packing, orientation, and morphology control", *Accounts of Chemical Research*, 49(11):2424-34, (2016).
- [4] Kim FS, Ren G, Jenekhe SA. "One-dimensional nanostructures of π -conjugated molecular systems: assembly, properties, and applications from photovoltaics, sensors, and nanophotonics to nanoelectronics", *Chemistry of Materials*, 23(3):682-732, (2011).
- [5] Troshin PA, Hoppe H, Renz J, Egginger M, Mayorova JY, Goryachev AE, Peregudov AS, Lyubovskaya RN, Gobsch G, Sariciftci NS, Razumov VF. "Material solubility-photovoltaic performance relationship in the design of novel fullerene derivatives for bulk heterojunction solar cells", *Advanced Functional Materials*, 19(5):779-88, (2009).
- [6] Hoppe H, Sariciftci NS. "Morphology of polymer/fullerene bulk heterojunction solar cells", *Journal of Materials Chemistry*, 16(1):45-61, (2006).
- [7] Zhao Y, Yuan G, Roche P, Leclerc M. "A calorimetric study of the phase transitions in poly (3-hexylthiophene)", *Polymer*, 36(11):2211-4, (1995).
- [8] Brown PJ, Sirringhaus H, Harrison M, Shkunov M, Friend RH. "Optical spectroscopy of field-induced charge in self-organized high mobility poly (3-hexylthiophene)", *Physical Review B*, 63(12):125204, (2001).
- [9] Yang X, Loos J, Veenstra SC, Verhees WJ, Wienk MM, Kroon JM, Michels MA, Janssen RA. "Nanoscale morphology of high-performance polymer solar cells", *Nano Letters*, 5(4):579-83, (2005).
- [10] Anthopoulos TD, Tanase C, Setayesh S, Meijer EJ, Hummelen JC, Blom PW, De Leeuw DM. "Ambipolar organic field-effect transistors based on a solution-processed methanofullerene" *Advanced Materials*, 16(23-24):2174-9, (2004).

- [11] Wöbkenberg PH, Bradley DD, Kronholm D, Hummelen JC, de Leeuw DM, Cölle M, Anthopoulos TD. "High mobility n-channel organic field-effect transistors based on soluble C60 and C70 fullerene derivatives", *Synthetic Metals*, 158(11):468-72, (2008).
- [12] Rait S, Kashyap S, Bhatnagar PK, Mathur PC, Sengupta SK, Kumar J. "Improving power conversion efficiency in polythiophene/fullerene-based bulk heterojunction solar cells", *Solar Energy Materials and Solar Cells*, 91(9):757-63, (2007).
- [13] Zen A, Pflaum J, Hirschmann S, Zhuang W, Jaiser F, Asawapirom U, Rabe JP, Scherf U, Neher D. "Effect of molecular weight and annealing of poly (3-hexylthiophene)s on the performance of organic field-effect transistors", *Advanced Functional Materials*, 14(8):757-64, (2004).
- [14] Kim Y, Choulis SA, Nelson J, Bradley DD, Cook S, Durrant JR. "Device annealing effect in organic solar cells with blends of regioregular poly (3-hexylthiophene) and soluble fullerene", *Applied Physics Letters*, 86(6):063502, (2005).
- [15] Reyes-Reyes M, Kim K, Carroll DL. "High-efficiency photovoltaic devices based on annealed poly (3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6, 6) C 61 blends", *Applied Physics Letters*, 87(8):083506, (2005).
- [16] Kim H, So W, Moon S. "Effect of thermal annealing on the performance of P3HT/PCBM polymer photovoltaic cells", *Journal of the Korean Physical Society*, 48(3):441-5, (2006).
- [17] Kim H, Shin M, Kim Y. "Long time thermal annealing effects on the film morphology and performance of polymer solar cells with calcium electrode", *Macromolecular Research*, 17(6):445-7, (2009).
- [18] Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K, Yang Y. "High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends", *In Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*, 80-84, (2011).
- [19] Singh I, Madhwal D, Kumar J, Bhatia CS, Bhatnagar PK, Mathur PC. "Effect of thermal annealing on the efficiency of poly (3-hexylthiophene):[6, 6]-phenyl-C 61-butyric acid methyl ester bulk heterojunction solar cells", *Journal of Nanophotonics*, 5(1):053504, (2011).
- [20] Karagiannidis PG, Kassavetis S, Pitsalidis C, Logothetidis S. "Thermal annealing effect on the nanomechanical properties and structure of P3HT:PCBM thin films", *Thin Solid Films*, 519(12):4105-9, (2011).