Relation between active-layer thickness and power conversion efficiency in P3HT:PCBM inverted organic photovoltaics

S. Nakami¹, T. Narioka¹, T. Kobayashi¹,², T. Nagase¹,², H. Naito¹,²

¹ Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuuencho, Naka, Sakai, 599-8531 Japan.
² Research Institute of Molecular Electronic Devices (RIMED), Osaka Prefecture University, 1-1 Gakuuencho, Naka, Sakai, 599-8531 Japan.

E-mail: tkobaya@pe.osakafu-u.ac.jp (TK); naito@pe.osakafu-u.ac.jp (HN)

Abstract. The dependence of active-layer thickness on the power conversion efficiency (PCE) of inverted organic photovoltaics (OPVs) based on poly(3-hexylthiophene) and [6,6]-phenyl-C₆₁-butyric acid methyl ester was investigated. When PCEs were measured immediately after device fabrication, the optimum thickness was ~100 nm. It was, however, found that thick OPVs exhibit higher PCEs a few months later, whereas thin OPVs simply degraded with time. Consequently, the optimum thickness changed with time. Considering this fact, we discuss the relationship between the active-layer thickness and PCE.

1. Introduction

Organic photovoltaics (OPVs) based on conjugated polymers and fullerene derivatives have been extensively studied. As the active-layer thickness increases, the number of absorbed photons increases but the charge collection efficiency is expected to reduce. These two opposite changes determine the relation between active-layer thickness and power conversion efficiency (PCE). This relationship has been experimentally and theoretically investigated by many researchers [1–14]. However, the reported experimental results are highly variable. For example, the optimum thickness for achieving the best PCE has been reported to be in the range of 85–830 nm even when the same materials were used, e.g., poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) [1, 2, 7–11]. The reason for this large variation in the optimum thickness may be the high sensitivity of PCE to processing conditions; however, this has not yet been fully clarified so that the true thickness dependence of PCE still remains unclear.

Recently, we found that thick inverted OPVs aged in the dark for a few months exhibit a higher PCE than OPVs that are measured immediately after device fabrication. As opposed to the PCE of thick inverted OPVs, that of thin inverted OPVs simply degrades with time. Consequently, the optimum thickness increases with time. As mentioned below, this change in PCE with time suggests that a processing condition leading to the best PCE for a particular thickness is not necessarily suitable for a different thickness. In short, a processing condition has to be optimized for each thickness. However, in many previous reports, OPVs with various thicknesses were fabricated with identical processing conditions. We thus conjecture that the large variation of the optimum thickness in literature is related to the use of an identical processing condition. In this report, we first present the change in PCE with time in inverted OPVs with various thicknesses and discuss the mechanism of the...
change. Then, by considering the observed change in PCE, we also discuss the true thickness dependence of PCE.

2. Materials and Methods
P3HT and PCBM were blended in a weight ratio of 1:0.8 and dissolved in chlorobenzene. The concentrations of the solutions were varied in the range of 1.8–5.6 wt% to change the resultant active-layer thickness. The solutions were stirred overnight to promote complete dissolution. ZnO nanoparticle ink was spin-coated onto cleaned ITO-coated substrates, and the substrates were then annealed at 200 °C for 10 min in an ambient atmosphere. Following the annealing process, the substrates were transferred into a glove box filled with dry nitrogen gas, and the active layer was spin-coated from the chlorobenzene solutions onto the ZnO surface at 800 rpm. The films were dried in vacuum for 1 h and subsequently annealed at 150 °C for 10 min unless otherwise noted. As the anode, MoO$_3$ and Al, instead of Au, was deposited in vacuum at $2 \times 10^{-3}$ torr. Compared with Au, Al has a higher reflectivity in the visible light region. Finally, the device was sealed by covering with a piece of glass and fixing it with epoxy. The current–voltage characteristics and PCE were measured under a simulated irradiation of 100 mW/cm$^2$ (AM 1.5 G) from a solar simulator. The samples were stored in the dark in an ambient atmosphere. Most of the aged samples were prepared by storing for 2 months, but some were prepared by storing for 3 months. The difference in the storing time was due to the uncontrollable, uneven degradation time.

3. Results and Discussion
Figure 1 shows the thickness dependence of PCE for inverted OPVs. In the case of fresh inverted OPVs, the optimum thickness is around 100 nm, above which PCE gradually decreases with increasing active-layer thickness. This result is consistent with one report on inverted OPVs [9] and some on conventional OPVs [1, 7]. When measured 2–3 months after device fabrication, PCEs of the inverted OPVs change depending on the thickness. As shown in Fig. 1, PCEs simply degrade at 110 and 160 nm, whereas PCEs improve in the thicker region above 430 nm. In Fig. 2, we show the current–voltage characteristics of some of the inverted OPVs. At 160 nm, the reduction in PCE is mainly due to the decrease in short-circuit current ($J_{sc}$); open-circuit voltage ($V_{oc}$) and fill factor (FF) are nearly unchanged. At 210 nm, $J_{sc}$ is similarly decreased but FF is improved enough that the decrease in $J_{sc}$ is compensated. As a result, PCE increases only slightly. At 430 nm, a decrease in $J_{sc}$ is no longer observed, and the increases in $J_{sc}$ and FF contribute to the improvement in PCE.

![Figure 1](image_url)

**Figure 1.** PCEs of inverted OPVs with various active-layer thicknesses. Open (black and white) and filled (red) circles represent PCEs measured immediately after device fabrication and after aging for 2–3 months, respectively.
Degradation mechanisms of OPVs have been intensively investigated [15–20]. The decrease in $J_{sc}$ is caused by chemical degradation of the semiconducting materials or a decrease in the P3HT/PCBM interface area (i.e., an increase in the size of the P3HT or PCBM domains). It has been confirmed that diffusion of fullerenes takes place, even below the glass transition temperature, which leads to acceleration of the phase segregation and to the formation of large domains [15–20]. If the domains become larger than the exciton diffusion length, $J_{sc}$ is expected to be lowered. In our fresh OPVs, the domain size is considered to be smaller than the optimum value. Thus, the increase in domain size with time would result in the development of carrier transport networks from the interface to the electrodes and in the enhancement of carrier drift mobility within the domains; both of these changes would contribute to the enhancement of $J_{sc}$ and FF. On the other hand, chemical degradation of the semiconducting materials may be a reason for the decrease in PCE observed in thin OPVs.

Figure 2. Current–voltage characteristics of inverted OPVs with active-layer thicknesses of (a) 160 nm, (b) 210 nm, and (c) 430 nm. In the insets, we show the typical photovoltaic properties.
In addition to the diffusion of fullerene and the chemical degradation, evaporation of residual solvent should be related to the observed change in PCE with time. Although our drying conditions are typical for P3HT:PCBM-based OPVs, there is a possibility that residual solvent reduces PCE, particularly in thicker OPVs, but gradually evaporates with time leading to an increase in PCE. In fact, when thick active layers were dried in a vacuum chamber for longer periods of time (e.g. 2 h), $J_{sc}$ was improved. As an example, we show the current–voltage characteristics of inverted OPVs with an active-layer thickness of 530 nm in Fig. 3. Their photovoltaic properties are summarized in Table 1. In the case of 530 nm-thick inverted OPVs, as a result of the improvement of $J_{sc}$, PCE is increased from 2.0% to 2.6%. If a longer drying time was used for thin OPVs (e.g. 100 nm-thick OPVs), their photovoltaic properties were not changed at all. This means that the drying time influences only the amount of residual solvent. It should be noted that no further increase in $J_{sc}$, FF, or PCE is obtained if thick active layers are dried for longer times. Thus, 2 h seems to be long enough to remove the residual solvent in the 530 nm-thick active layer. The point that we would like to stress here is that unlike $J_{sc}$, FF is not improved by removing the residual solvent (see Table 1). Compared with the aged OPVs with PCE of 3.6%, the fresh OPV that was dried for 2 h exhibited similar $V_{oc}$ and $J_{sc}$ but lower FF. This result suggests that the improved PCEs of aged, thick OPVs are realized by two factors: the increase in the domain size and the evaporation of the residual solvent.

![Figure 3](image-url)

**Figure 3.** Current-voltage characteristics of inverted OPVs with an active layer thickness of 530 nm. Fresh 1 (black) and 2 (blue) represent OPVs dried in a vacuum for 1 and 2 h, respectively. PCEs of those OPVs are 2.0 (Fresh 1), 2.6 (Fresh 2), and 3.6% (Aged). For other photovoltaic properties such as $V_{oc}$ and FF, see Table 1.

| Drying Time (h) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) |
|----------------|-------------|--------------------|-----|--------|
| 1              | 0.56        | 7.4                | 0.48| 2.0    |
| 2              | 0.56        | 9.4                | 0.49| 2.6    |
| 1$^{a}$        | 0.58        | 9.4                | 0.67| 3.6    |

$^{a}$ Measured 2 months after the device fabrication

As mentioned in the introduction, there is a large variation in the reported optimum thickness for the active layer in OPVs. Inadequate drying in thicker active layers may be one possible reason for the variation. The residual solvent can also be removed during thermal annealing and deposition of metal electrodes. Thus, in some reports, an additional drying process was not carried out. If drying of the active layer is not adequate, FF would decrease with increasing active-layer thickness. In other words,
such a tendency might indicate that the drying conditions are not adequate. As shown in Fig. 1, our fresh and aged OPVs exhibit the best PCEs of 3.2% at 110 nm and 3.6% at 530 nm, respectively. These values are close to the reported maximum PCE of P3HT:PCBM-based OPVs (around 4% under simulated 100 mW/cm² irradiation) [1, 5, 22, 23]. Therefore, further improvement of the PCE of our inverted OPVs may be limited. Considering this fact, it is expected that the true thickness dependence of the PCE of fully optimized OPVs is much weaker than those shown in Fig. 1 and in some previous reports. On the other hand, Moulé et al. reported that the PCEs of their OPVs employing a conventional architecture are almost constant in the thickness range 100–400 nm [5]. Based on our examination, among the various reports on the optimum thickness of P3HT:PCBM-based OPVs, the results of Moulé et al. seem to be the most reasonable.

4. Conclusions
In this work, P3HT:PCBM based inverted OPVs with various active layer thickness were fabricated. Fresh OPVs exhibit the best PCE around 110 nm, whereas the optimum thickness becomes more than 530 nm a few months after the device fabrication. We discussed three possible causes of the change in PCE, i.e. the residual solvent in particular in thick OPVs, the increase in the domain size of P3HT or PCBM, and the chemical degradation. It is found that the residual solvent mainly reduces $J_{sc}$. Considering the change in PCE with time, the active layer thickness dependence of PCE of fully optimized OPVs is expected to be much weaker than those observed in this work.

Acknowledgements
This work is supported in part by JSPS KAKENHI Grant Number 15H03883, and by a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks (No. 2401)” (No. JP24102011).

References
[1] Li G, Shrotriya V, Yao Y, Yang Y 2005 J. Appl. Phys. 98 043704
[2] Reyes-Reyes M, Kim K, Dewald J, López-Sandoval R, Avadhanula A, Curran S, Carroll D L 2005 Org. Lett. 7 5749
[3] Sievers D W, Shrotriya V, Yang Y 2006 J. Appl. Phys. 100 114509
[4] Moulé A J, Bonekamp J B, Meerholz K 2006 J. Appl. Phys. 100 094503
[5] Moulé A J, Meerholz K 2008 Appl. Phys. B 92 209
[6] Boland P, Namkoong G 2010 Jpn. J. Appl. Phys. 49 030205
[7] Nam Y M, Huh J, Jo W H 2010 Sol. Energ. Mat. Sol. Cells. 94 1118
[8] Zeng L, Tang C W, Chen S H 2010 Jpn. J. Appl. Phys. 49 053305
[9] Zhao D W, Tan S T, Kec L, Liu P, Kyaw A K K, Sun X W, Lo G Q, Kwong D L 2010 Sol. Energ. Mat. Sol. Cells. 94 985
[10] Jin H, Olkkonen J, Tuomikoski M, Kopola P, Maaninen A, Hast J 2010 Sol. Energ. Mat. Sol. Cells. 94 465
[11] Morvillo P, Bobeico E, Esposito S, Diana R 2012 Energy Procedia 31 69
[12] Kirchartz T, Agostinelli T, Campoy-Quiles M, Gong W, Nelson J 2012 J. Phys. Chem. Lett. 3 3470
[13] Apaydin D H, Yildiz D E, Cirpan A, Toppare L 2013 Sol. Energ. Mat. Sol. Cells. 113 100
[14] Rahman R, Karimi H, Ranjarbi L, Emadi M, Seyedmahmoudian M, Shafiabady A, Ismail R 2015 Plasmonics 10 495
[15] Yang X, van Duren J K J, Janssen R A J, Michels M A J, Loos J 2004 Macromolecules 37
[16] Hoppe H, Niggemann M, Winder C, Kraut J, Hiesgen R, Hinsch A, Meissner D, Sariciftci N S 2004 Adv. Funct. Mater. 14 1005
[17] Jo J, Kim S S, Na S I, Yu B K, and Kim D Y 2009 Adv. Funct. Mater. 19 866
[18] Watts B, Belcher W J, Thomsen L, Ade H, Dastoor P C 2009 Macromolecules 42 8392
[19] Conings B, Bertho S, Vandewal K, Senes A, D’Haen J, Manca J, Janssen R A J 2010 Appl.
Phys. Lett. 96 163301

[20] Grossiord N, Kroon, J M, Andriessen R, Blom P W M 2012 Org. Electron. 13 432
[21] Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K, Yang Y 2005 Nat. Mater. 4 864
[22] Huang W Y, Lee C C, Hsieh T L 2009 Sol. Energ. Mat. Sol. Cells. 93 382