Morphological Analysis of Co-evaporated Blend Films Based on Initial Growth for Organic Photovoltaics

Yosei Shibata^{a*}, Tetsuya Taima^{a, b}, Ying Zhou^a, Noboru Ohashi^a,

Takahiro Kono^a, and Yuji Yoshida^{a*}

^a Research Center for Photovoltaic Technologies, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan

^b Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

Journal: *Applied Surface Science*

KEYWORDS: co-evaporation, initial growth, bulk heterojunction, blend morphology, organic photovoltaics

*Corresponding Authors

Research Center for Photovoltaic Technologies, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
Zip-code: 305-8565

- 1) Dr. Yosei Shibata E-mail: yosei.shibata@aist.go.jp
Phone: +81-29-861-8780 Fax: +81-29-861-6232
- 2) Dr. Yuji Yoshida E-mail: yuji.yoshida@aist.go.jp
Phone: +81-29-861-9423 Fax: +81-29-861-6232

ABSTRACT

Bulk heterojunction structures composed of electron donor and acceptor molecules for application in high-performance organic photovoltaics studied. To fabricate these structures, the co-evaporation method in vacuum is commonly applied; however, the details of the crystal growth process during co-evaporation have not yet been established.

Here, we focused on structural analysis of blend films composed of phthalocyanine and fullerene based on initial growth stage. Similar crystal growth behavior to that typically observed in single-component molecules is obtained for the films. These results suggest that the competitive crystal growth between donors and acceptors occurs during co-evaporation process. The balance of thin film growth among donor and acceptor molecules can be related to improved photovoltaic performance. The homogeneous blend structure leads to improvement of the power conversion efficiency from 1.2 % to 3.0 %.

Graphical Abstract

1. Introduction

Vacuum-processed organic photovoltaics (OPVs) based on small molecules have been studied as a means of realizing tandem-structured OPVs to stack certain single cells [1, 2]. The application of the bulk heterojunction (BHJ) structure, which is a mixture of electron donor and acceptor molecules, in high-performance single OPV has been investigated since the 1990s [3]. The exciton (photoexcited electron-hole binding pair) diffusion length in organic thin films is extremely short (limited to within several nanometers), and the presence of an interface area between the donor and acceptor contributes to exciton dissociation. The concept of BHJ structure is widely-distributed interface area in thin films. Therefore, the BHJ structure has the potential to yield enhanced photocurrent density. Co-evaporation method has been commonly used in order to fabricate OPV cells incorporating the BHJ structure. In this method, donor and acceptor molecules are sublimed by separate sources in vacuum [3]. The BHJ structures composed of metal-phthalocyanines and fullerene (C_{60}) have been reported, with materials being chosen on account of their high absorption coefficients and chemical stability, respectively. The metal phthalocyanines having high molecular planarity such as zinc-phthalocyanine (ZnPc) establish high mobility and light absorption at the Q-band, because of the strong π - π overlap [4]. Hence, OPV devices incorporated BHJ

structure composed of ZnPc and C₆₀ exhibit a photocurrent density (J_{sc}) exceeding 10 mA/cm² [5-8].

Recently, it was reported that structural control of co-evaporated films leads to improved photovoltaic performance [9], for example, in case of phase-separated structures [10] and nano-sized crystal grains [11]. However, the growth process during the co-evaporation of film used in high-performance BHJ structures has not been explored; this is because of the difficulty in analyzing these structures. To date, the film morphology and crystallinity of BHJ films has been controlled by tuning the substrate temperature (T_{sub}) only [8, 11, 12]. The quality of vacuum-evaporated films including the morphology and the crystal size depends on the rate of crystal nucleation, and T_{sub} and deposition rate (V_{depo}) during deposition are well-recognized as factors affecting the crystal size control [13]. Therefore, we may reasonably suppose that the crystallinity of the co-evaporation films can be controlled by varying T_{sub} and V_{depo} during co-evaporation in vacuum.

Here, we report on the relationship between OPV device performance and growth control of the ZnPc:C₆₀ blend films used in these devices. We also report on a structural analysis of the co-evaporated films, based on the initial donor and acceptor growth

modes. We discuss the optimal growth process for the production of co-evaporated films suitable for high-performance OPVs.

2. Experimental Details

2.1. Device fabrication

The OPV devices were fabricated in a vacuum evaporation system at a pressure of 10^{-5} Pa. ZnPc (purity 97 %) and C₆₀ (purity 99.9 %) were purchased from Sigma-Aldrich and Materials Technologies Research, Ltd., respectively. The organic materials were purified by repeated sublimation prior to evaporation. The OPV devices were fabricated as follows: (1) Indium-tin-oxide (ITO) -coated glass substrates (purchased from Sanyo Vacuum Industry Co., Ltd) were cleaned in oxygen plasma for 30 min. The thickness and sheet resistance of the ITO films were 150 nm and less than $15 \Omega/\square$, respectively. (2) A BHJ layer composed of ZnPc and C₆₀ was simultaneously evaporated onto the ITO. The growth conditions of the ZnPc:C₆₀ BHJ layer were controlled by tuning T_{sub} and V_{depo} during the evaporation process, within ranges of 30—150 °C and 0.02—0.08 nm/s, respectively. Here, V_{depo} was defined as $V_{\text{depo}} \equiv V_{\text{ZnPc}} = V_{\text{C60}}$, where V_{ZnPc} and V_{C60} are ZnPc and C₆₀ deposition rate, respectively. Therefore, the volume ratio of the ZnPc:C₆₀ BHJ films was fixed at ZnPc:C₆₀ = 1:1 (v/v %). V_{depo} was monitored by two separate quartz crystal oscillators. (3) The substrate was cooled to room temperature. (4)

Finally, C₆₀ films (60-nm thickness), bathocuproine (BCP: 6-nm thickness), and aluminum (Al: 100 nm), as an electron transport layer, exciton blocking layer [14], and an electrode, respectively, were evaporated sequentially. The OPV device configuration was ITO/ZnPc:C₆₀=1:1/C₆₀ (60 nm)/BCP (6 nm)/Al (80 nm). To prevent morphological change of the electron blocking layer during substrate heating, we excluded typical poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and molybdenum oxide [15] from the device design. The device area was 0.04 cm².

2.2. Measurements

The current-voltage (*J-V*) characteristics were measured using a source meter (KEITHLEY 2400 series, Keithley Instruments Inc.), and the light source (air mass: 1.5G, light intensity: 100 mW/cm²) used for the light irradiation test of the OPVs was calibrated with a silicon-photodiode (Bunko Keiki Co., Ltd). *J-V* curves of the OPV devices were measured in an N₂ atmosphere without exposure to ambient air. Here, we calculated the series resistance (*R_s*) and parallel resistance (*R_p*) from curve fitting of the dark current with the Shockley diode model, in accordance with references [16-18] and using.

$$V = n \frac{k_B T}{q} \ln \left(\frac{J}{J_0} \right), \quad (1)$$

where V is the applied voltage, k_B is the Boltzmann constant, T is the temperature, q is the electronic charge, n is the ideal factor, J_0 the is reverse saturation current density, and J is the current density.

The light absorption spectra of the ZnPc:C₆₀ films were measured using a SM-25K xenon lamp (Bunko Keiki Co.,Ltd) equipped with a monochrometer. The film morphology was observed using atomic force microscope (AFM; Nanonavi E-sweep: Seiko Instruments Inc.) with dynamic force mode and a scanning electron microscopy (SEM, JSM-6340F: JEOL Co., Ltd) with accelerate voltage of 10 kV. To observe the initial growth mode, molecules were deposited onto a cleaned silicon oxide (SiO₂) substrate. In initial growth stage, the monitored thickness by crystal quartz oscillators was 5–10 nm. The grazing incidence wide-angle X-ray scattering (GIWAXS) utilizing synchrotron irradiation was measured at beam line BL46XU (at the SPring-8 synchrotron radiation which was equipped with a two-dimensional counter, PILATUS 300K (DECTRIS Ltd.)). The X-ray wavelength and camera length were 1.2 Å and 148.8 mm, respectively.

3. Results and Discussion

3.1. Optical properties of growth-controlled ZnPc:C₆₀ co-evaporated films

Fig. 1 shows the ultraviolet(UV)/visible-light absorption spectra of the co-evaporated ZnPc:C₆₀ films. The 300—500- and 550—800-nm absorbance corresponds to C₆₀ and ZnPc, respectively. ZnPc also has absorption peak around 350-nm wavelength. Further, the absorption peaks at 550—800-nm wavelength are strongly dependent on the crystal phase of the ZnPc molecules, because of the polymorphic phase [19, 20]. The α -phase ZnPc crystalline films have two absorption peaks at 620- and 696-nm wavelength [21]. It is apparent that co-evaporated ZnPc:C₆₀ films having α -phase ZnPc crystals were obtained regardless of the growth condition, as shown in Fig. 1 (a-b). In contrast, it was reported that the crystal structures of the single-component ZnPc films are strongly dependent on T_{sub} and V_{depo} [13]. Therefore, these results indicate that the crystal growth of co-evaporated films is limited, owing to the competitive growth between the donors and acceptors during the co-evaporation process.

Fig.1. Ultraviolet(UV)/visible light absorption spectra of co-evaporated ZnPc:C₆₀ films (20-nm thickness) on glass/ITO substrate. (a) **Deposition rate** (V_{depo}): 0.02 nm/s (b) V_{depo} : 0.08 nm/s.

3.2. Surface morphology of ZnPc:C₆₀ co-evaporated films

Fig. 2 shows AFM images of the co-evaporated ZnPc:C₆₀ film surfaces and their root-mean-square (RMS) roughness values. The surface morphologies of these ZnPc:C₆₀ films were dependent on both T_{sub} and V_{depo} , under different condition. When T_{sub} was increased from 30 °C to 90 °C, a relatively smooth surface and nano-sized grains were obtained, regardless of V_{depo} , as shown in Fig.2 (a, b, d, e). The ZnPc:C₆₀ film surfaces became extremely rough at a T_{sub} of 150 °C, as shown in Fig. 2 (c, f). The corresponding increase in the RMS values can be attributed to molecular-aggregation structures, such as islands, protruding in the out-of-plane direction from the ITO substrate. Compared with slow V_{depo} (0.02 nm/s), fast V_{depo} (0.08 nm/s) condition led to the formation of numerous island structures. The calculated number densities of the island-like structures shown in Fig. 2 (c) and (f) were 14.5 and 61.5 μm^{-2} , respectively. The heights of these structures, which were evaluated from the contrast bars in AFM images, were ca. 30-45 nm. Thus, the surface roughness of the ZnPc:C₆₀ BHJ films was dramatically increased by increases in T_{sub} rather than by adjustment of V_{depo} . In order to investigate the surface morphologies of ZnPc:C₆₀ BHJ films in more detail, we examined the large-scale AFM topography images, such as those shown in Fig. 2 (e, f). It was confirmed that the grain size at a T_{sub} of 150 °C was larger than that at 90°C.

With a view to analyzing the ZnPc and C₆₀ distributions in the aggregation structures protruding perpendicular to the ITO substrate, we examined the phase images of the large-scale AFM images, as shown in Fig. 2 (i, j). In principle, a phase indicates the presence of distinct materials. However, in this case, it is difficult to distinguish the ZnPc from C₆₀ because there is no obvious difference in contrast. Then, we focused on the individual growth modes of the ZnPc and C₆₀ molecules, because organic molecules have specific crystal habits.

Fig.2. Atomic force microscopy images of co-evaporated ZnPc:C₆₀=1:1 v/v% (20-nm thickness) film surface onto ITO substrate and root-mean-square (RMS) roughness values. (a–f) Topography images. (g, h) Large-scale topography images. (i, j) Phase images of large-scaled images. T_{sub} : substrate temperature, V_{depo} : deposition rate.

3.3. Effects of substrate temperature on initial growth mode

Fig. 3 (a–d) shows AFM images of the initial growth stages of single-component ZnPc and C₆₀ molecules. In the single-component C₆₀ growth shown in Fig. 3 (a) and (b), a large number of grains can be observed. It can also be seen that the sizes of the grains composed of C₆₀ molecules increase with increasing T_{sub} , while the crystal nucleation rate decreases. A ca. 1.8-fold height increase, which evaluated from the contrast bar, was obtained from these figures. Note that the C₆₀ molecules tended strongly towards three-dimensional aggregation with increasing T_{sub} , whereas the evaporated C₆₀ molecules exhibited the Volmer-Weber growth mode. On the other hand, a ca.8-fold height increase (as evaluated from the contrast bar) obtained for T_{sub} values 90 °C–150 °C for the single-component ZnPc molecules, as shown in Fig. 3 (c, d). A relatively smooth surface was obtained at a T_{sub} of 90 °C for this substance. This indicates that ZnPc has strong molecular interaction in the π - π stacking direction, similar to the Stranski-Krastanov growth mode. When T_{sub} was increased to 150 °C, the ZnPc molecules preferentially protruded outward from the ITO substrate. Senthilarasu et.al has reported that needle-like or one-dimensional crystal growth of ZnPc occurred at 150 °C [21, 22]. This difference in growth mode can be attributed to the the ZnPc molecules crystal phase.

From the above results, we found that the crystal growth modes of the C₆₀ and ZnPc molecules differed. Considering these results, we also observed the initial growth modes of the co-evaporated ZnPc:C₆₀, as shown in Fig. 3 (e, f). At a T_{sub} of 90 °C, a blend morphology composed of plate-like and island-like crystallites was observed. The maximum bar height increased with T_{sub} . Interestingly, the maximum height in the contrast bar of single-component ZnPc at a T_{sub} of 150 °C was consistent with that of the co-evaporated ZnPc:C₆₀ blend at the same T_{sub} 150 °C. Therefore, there is a possibility that the enhancement of the surface roughness observed in the co-evaporated ZnPc:C₆₀ films at a T_{sub} of 150 °C (Fig. 2 (f)) can be attributed to the one-dimensional growth trend of the ZnPc crystals on the substrates.

We also show SEM images of the initial growth stages of the ZnPc:C₆₀ blend at T_{sub} values of 90 and 150 °C in Fig. 3 (g, h). Here, monitored thickness was increased up to 10 nm in order to track the crystal growth in co-evaporated films. In the case of a T_{sub} of 90 °C, homogeneous growth and a smooth surface were obtained. This indicates that balanced film growth occurred between the C₆₀ and ZnPc. In contrast, at a T_{sub} = 150 °C, the surface morphology exhibited not only three-dimensional grains near the substrate surface, but also a needle-like structure elsewhere in the sample. The C₆₀ molecules cannot show the one-dimensional or needle-like growth mode in thin films because

fullerene molecules have three-dimensional molecular interaction due to spherical molecule [23]. From the cross-sectional SEM image in Fig. 3 (i), it is clear that the needle-like structure particularly contributes to the enhanced surface roughness. Therefore, these SEM images also support the crystal growth mechanism suggested above.

Compared with the initial growth stage of the co-evaporated films at a T_{sub} of 150 °C, we found that balanced film growth between the C_{60} and ZnPc occurred during the co-evaporation process conducted at a T_{sub} of 90 °C.

Fig. 3. Atomic force microscopy (AFM) images of initial growth stages (5-nm thickness, $V_{\text{depo}}=0.02$ nm/s) and molecular structures of: (a, b) Single-component C_{60} , (c, d) single-component ZnPc, and (e, f) co-evaporated ZnPc: $C_{60}=1:1$. (g, h) In-plane scanning electron microscopy (SEM) images of co-evaporated ZnPc: C_{60} at 10-nm thickness, $V_{\text{depo}}=0.02$ nm/s. (i) Cross-sectional SEM images of (h).

3.4. Photovoltaic device

In order to understand the suitable BHJ structure for high-performance, the relationship between the growth-controlled BHJ structures and the photovoltaic performance of devices incorporating these films which was incorporated these films is of importance. Fig.4 (a) and Table 1 show the J - V characteristics of devices produced at T_{sub} values of 90 and 150 °C under light irradiation and extracted photovoltaic parameters, respectively. The power conversion efficiency (PCE) of the co-evaporated ZnPc:C₆₀ films at a T_{sub} of 90 °C is higher than that at a T_{sub} of 150 °C. In particular, the open-circuit voltage (V_{oc}) and fill factor decreased at a T_{sub} of 150 °C. In addition, we calculated the series resistance (R_s) and parallel resistance (R_p) of devices produced at T_{sub} values of 90 °C and 150 °C; these results are shown in Fig. 4 (b) and Table. 2. The calculated R_s values are approximately identical regardless of growth condition. This indicates that carrier transport network is fully established in BHJ films. On the other hand, a difference was observed in the R_p values, which indicate current leakage in the devices. It is well known that the optimal V_{oc} is determined by difference between the lowest unoccupied molecular orbital (LUMO) level of acceptor and the highest occupied molecular orbital (HOMO) level of donor [24, 25]. For the ZnPc and C₆₀ combination, the optimal V_{oc} was calculated ca. 0.6 V [26]. V_{oc} loss in OPV devices is

conventionally explained by the Langevin recombination model [27, 28], where reductions of the optimal V_{oc} are determined by the exciton generation rate and the dissociation probability of the electron-hole pairs into free carriers. To obtain efficient exciton dissociation, a broad donor-acceptor interface area and large exciton diffusion length are required. Thus, it is that the unbalanced film growth shown in Fig. 3 (f, h) leads to a morphologically narrow donor-acceptor interface area because of the low J_{sc} .

For further improvement of device performance, we optimized the co-evaporated film thickness. The maximum PCE of ca. 3.0 % was obtained at 50-nm thickness without electron blocking layer, as can be seen in Table 1. As the thickness increased slightly, J_{sc} increased dramatically, up to 11 mA/cm². This is attributed to the greater light absorption capacity of BHJ devices.

Fig. 4 (c) shows a GIWAXS image of a co-evaporated ZnPc:C₆₀ film (50-nm thickness, $T_{sub} = 90$ °C and $V_{depo} = 0.02$ nm/s) on ITO/glass substrate. In the GIWAXS image, a diffraction ring pattern appears at approximately scattering vector $q_z = 0.49$ Å⁻¹, and the calculated d -spacing value was ca. 13 Å. This is attributed to randomly-oriented α -phase ZnPc crystals, as evidenced by Fig. 1. The C₆₀ molecules exhibit amorphous configuration, as indicated by the non-diffraction pattern. In the co-evaporation process, the C₆₀ crystal growth was limited despite the growth control, and the co-evaporated

ZnPc:C₆₀ films with PCE ca. 3% were constructed using with ZnPc nano-sized crystal and amorphous C₆₀, shown in illustrated Fig. 4 (d). Balanced crystal growth between the donors and acceptors is one of important factors in the fabrication of a BHJ structure using a vacuum process.

Fig. 4. (a) Current-voltage (J - V) characteristics under light irradiation with air mass 1.5G, intensity of 100 mW/cm². (b) Semilogarithmic J - V plots in dark. (c) Grazing incidence wide-angle X-ray scattering image of glass/ITO/ZnPc:C₆₀ (50-nm thickness), substrate temperature (T_{sub}): 90 °C, deposition rate (V_{depo}): 0.02 nm/s). (d) Illustration of high-performance ZnPc:C₆₀ co-evaporated film structure.

Table 1. Photovoltaic parameters extracted from light J - V curves.

Device	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill Factor	PCE (%)
T_{sub} 90 °C (20-nm thickness)	8.93 ± 0.14	0.51 ± 0.01	0.54 ± 0.01	2.46 ± 0.14
T_{sub} 150 °C (20-nm thickness)	8.31 ± 0.23	0.30 ± 0.03	0.48 ± 0.01	1.20 ± 0.19
T_{sub} 90 °C (50-nm thickness)	11.69 ± 0.24	0.53 ± 0.01	0.47 ± 0.01	2.91 ± 0.11

Table 2. Diode parameters extracted from dark J - V curves.

Device	J_o (μ A/cm ²)	n	R_s (Ω cm ²)	R_p (k Ω cm ²)
T_{sub} 90 °C (20-nm thickness)	5.1	1.1	0.2	3.28
T_{sub} 150 °C (20-nm thickness)	2.9	1.7	0.1	1.56

4. Conclusion

In summary, we investigated the relationship between the surface morphologies of growth-controlled ZnPc:C₆₀=1:1 bulk heterojunction films and the performance of organic photovoltaic devices incorporating these films. It was found that the surface morphology of the co-evaporated ZnPc:C₆₀ samples was affected both the substrate temperature and the deposition rate. Further, the crystal growth of co-evaporated ZnPc:C₆₀ films was limited during the evaporation process. We also conducted morphological analysis of the co-evaporated thin films, focusing initial growth modes. We suggest that balanced film growth between donor and acceptor molecules during the evaporation process results in high-performance BHJ structures suitable for use in organic photovoltaics.

Acknowledgements

This work was supported by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency (JST). The synchrotron GIWAXS measurements were conducted at SPring-8 (BL46XU beam line, Japan) with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Nos. 2013A1629 and 2013A1781). We thank Dr. Tomoyuki Koganezawa (JASRI) for advice on the GIWAXS measurement. The SEM measurements were supported by Ms. Yuka Yoshinuma and Dr. Masashi Kuwahara (National Institute of Advanced Industrial Science and Technology (AIST)).

References

- [1] X. Che, X. Xiao, J.D. Zimmerman, D. Fan, S.R. Forrest, High-efficiency, vacuum-deposited, small-molecule organic tandem and triple-junction photovoltaic cells, *Adv. Energy Mater.* 4 (2014) 1400568.
- [2] J.D. Zimmerman, B.E. Lassiter, X. Xiao, K. Sun, A. Dolocan, R. Gearba, D.A. Vandembout, K.J. Stevenson, P. Wickramasinghe, M.E. Thompson, S.R. Forrest, Control of interface order by inverse quasi-epitaxial growth of squaraine/fullerene thin film photovoltaics, *ACS Nano.* 7 (2013) 9268–9275.
- [3] M. Hiramoto, H. Fujiwara, M. Yokoyama, Three-layered organic solar cell with a photoactive interlayer of codeposited pigments, *Appl. Phys. Lett.* 58 (1991) 1062–1064.
- [4] S. Senthilarasu, R. Sathyamoorthy, S. Lalitha, A. Sabbarayan, K. Natarajan, Thermally evaporated ZnPc thin films—Band gap dependence on thickness, *Sol. Energy Mater. Sol. Cells* 82 (2004) 179–186.
- [5] W. Zheng, K.S. Yong, Z.M. Kam, F. Zhu, Y. Li, Effect of blend layer morphology on performance of ZnPc:C₆₀-based photovoltaic cells, *Appl. Phys. Lett.* 97 (2010) 133304.
- [6] B. Yu, L. Huang, H. Wang, D. Yan, Efficient organic solar cells using a high-quality crystalline thin film as a donor layer, *Adv. Mater.* 22 (2010) 1017–1020.
- [7] K. Iketaki, T. Kaji, S. Nakao, M. Hiramoto, Structural studies of the codeposited i-layer of ZnPc:C₆₀ p-i-n solar cells *Phys. Status. Solidi C*, 8 (2011) 637–639.
- [8] S. Pfuetzner, J. Meiss, A. Petrich, M. Riede, K. Reo, Thick C₆₀:ZnPc bulk heterojunction solar cells with improved performance by film deposition on heated substrates, *Appl. Phys. Lett.* 94 (2012) 253303.

- [9] Y. Shibata, T. Kono, N. Komura, Y. Yoshida, Structural control of bulk heterojunction films based on oligothiophene with sterically-bulky groups, *Org. Electron.* 14 (2013) 1073–1080.
- [10] Z. Wang, T. Miyadera, T. Yamanari, Y. Yoshida, Templating effects in molecular growth of blended films for efficient small-molecule photovoltaics, *ACS Appl. Mater. Interfaces.* 6 (2014) 6369–6377.
- [11] S. Pfuetzner, J. Meiss, A. Petrich, M. Riede, K. Reo, The influence of substrate heating on morphology and layer growth in C₆₀:ZnPc bulk heterojunction solar cells, *Org. Electron.* 12 (2011) 435–441.
- [12] K.-C. Chiu, L.-T. Juey, C.-F. Su, S.-J. Tang, M.-N. Jong, S.-S. Wang, J.-S. Wang, C.-S. Yang, W.-C. Chou, Effects of source and substrate temperatures on the properties of ITO/CuPc/C₆₀ heterostructure prepared by physical vapor deposition, *J. Cryst. Growth.* 310 (2008) 1734–1738.
- [13] F. Yang, M. Shtein, S.R. Forrest, Morphology control and material mixing by high-temperature organic vapor-phase deposition and its application to thin-film solar cells *J. Appl. Phys.* 98 (2005) 014906.
- [14] H. Gommans, B. Verreert, B.P. Rand, R. Muller, J. Poortmans, P. Heremans, J. Genoe, On the role of bathocuproine in organic photovoltaic cells, *Adv. Funct. Mater.* 18 (2008) 3686.
- [15] J. Jung, D. Kim, W.S. Shin, S.-J. Moon, C. Lee, S.C. Yoon, Highly efficient organic photovoltaic cells with molybdenum oxide buffer layer, *Jpn. J. Appl. Phys.* 49 (2010) 05EB05.

- [16] S. Yoo, B. Domercq, B. Kippelen, Intensity-dependent equivalent circuit parameters of organic solar cells based on pentacene and C₆₀, J. Appl. Phys. 97 (2005) 103706.
- [17] W. J. Potscavage Jr., A. Sharma, B. Kippelen, Critical interfaces in organic solar cells and their influence on the open-circuit voltage, ACS. Chem. Res. 42 (2009) 1758–1767.
- [18] T. Kim, H. Shim, M. Choi, H. Kim, J. Kim, Multilayer epitaxial growth of lead phthalocyanine and C₇₀ using CuBr as a templating layer for enhancing the efficiency of organic photovoltaic cells, ACS Appl. Mater. Interfaces, 6 (2014) 4286–4291.
- [19] M. Szybowicz, W. Bała, K. Fabisiak, K. Paprocki, M. Drozdowski, The molecular structure ordering and orientation of the metallophthalocyanine CoPc, ZnPc, CuPc, and MgPc thin layers deposited on silicon substrate, as studied by micro-Raman spectroscopy, J. Mater. Sci. 46 (2011) 6589–6595.
- [20] M. Hiramoto, K. Kitada, K. Iketaki, T. Kaji, Near infrared light driven organic p-i-n solar cells incorporating phthalocyanine J-aggregate, Appl. Phys. Lett. 98 (2011) 023302.
- [21] S. Senthilarasu, R. Sathyamoorthy, S.K. Kulkarni, Substrate temperature effects on structural orientations and optical properties of zincphthalocyanine (ZnPc) thin films, Mater. Sci. Eng. B. 122 (2005) 100–105.
- [22] S. Senthilarasu, Y.B. Hahn, S.-H. Lee, Structural analysis of zinc phthalocyanine (ZnPc) thin films: X-ray diffraction study, J. Appl. Phys. 102 (2007) 043512.
- [23] Thomas D. Anthopoulos, B. Singh, N. Marjanovic, N. S. Sariciftci, Alberto M. Ramil, H. Sitter, M. Cölle, Dago M. de Leeuw, High performance *n*-channel

- organic field-effect transistors and ring oscillators based on C₆₀ fullerene films, Appl. Phys. Lett. 89 (2006) 213504.
- [24] T. Yamanari, T. Taima, J. Sakai, K. Saito, Origin of the open-circuit voltage of organic thin-film solar cells based on conjugated polymers, Sol. Energy Mater. Sol. Cells 93 (2009) 759–761.
- [25] M.C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells—Towards 10 % energy-conversion efficiency, Adv. Mater. 18 (2006) 789–794.
- [26] R. Pode, On the problem of open circuit voltage in metal phthalocyanine/C₆₀ organic solar cells Adv. Mat. Lett. 2 (2011) 3–11.
- [27] F. Zhang, F. Sun, Y. Shi, Z. Zhuo, L. Lu, D. Zhao, Z. Xu, Y. Wang, Effect of an ultra-thin molybdenum trioxide layer and illumination intensity on the performance of organic photovoltaic devices, Energy Fuels 24 (2010) 3739–3742.
- [28] L.J.A. Koster, V.D. Mihailetschi, R. Ramaker, P.W.M. Blom, Light intensity dependence of open-circuit voltage of polymer:fullerene solar cells, Appl. Phys. Lett. 86 (2005) 123509.