



Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Study of the open circuit voltage dependence on incident light intensity of planar heterojunction organic solar cell

Anukul Prasad Parhi^a, Durgesh C. Tripathi^b, Devika Kataria^{c,*}^a Department of Physics, Indira Gandhi Institute of Technology, Sarang 759146, Odisha, India^b Department of Electrical Engineering, Israel Institute of Technology, Haifa 32000, Israel^c Institute of Engineering & Technology, J K Lakshmi Pat University, Jaipur 302026, India

ARTICLE INFO

Article history:

Received 23 May 2020

Received in revised form 21 August 2020

Accepted 27 August 2020

Available online xxxx

Keywords:

Organic photovoltaic

Open circuit voltage

Heterojunction

Defect states

Intensity dependent characteristics

CuPc:C60 bilayer solar cell

ABSTRACT

Organic photovoltaic is an emerging technology employing organic molecules as absorbers has gained tremendous attention in the past two decades due to its potential utilization as a renewable energy source. Contrary to conventional solar cells, excitons are formed under illumination which diffuse towards the heterojunction interface for dissociation into the photo charge-carriers. Heterojunction in the organic photovoltaic devices are formed either by stacking the layers of donor and acceptor molecules or by blending the both. Due to weak van-der Waals interaction between the molecules, intermixed states, in addition to the pure states of donor and acceptor molecules, are formed at the heterojunction interface which affects the electronic process and the power conversion efficiency. Significant efforts have been made to understand the photovoltaic process particularly in the bulk heterojunction solar cells however, least efforts have been devoted to investigate the governing mechanisms in the planar heterojunction solar cells. The motive of this study is to characterize the planar heterojunction solar cells based on the Copper Phthalocyanine (CuPc) and Fullerene (C₆₀) molecules under light illumination. The devices were fabricated under controlled condition in the normal device configuration, ITO (150 nm) | PEDOT:PSS (50 nm) | CuPc(20 nm) | C₆₀(40 nm) | BCP(10 nm) | Ag(80 nm), and characterized performing the light intensity dependent measurement in the wide illumination range. The solar cell parameters such as open circuit voltage, short circuit current and the power conversion efficiency have been discussed as a function of illumination intensity in the wider illumination range.

© 2020 Elsevier Ltd. All rights reserved.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Innovation in Technology & Management for Achieving Sustainable Development Goals (SDGs): Materials Science.

1. Introduction

Organic photovoltaics (OPVs) devices have received great attention in the past three decades due to its potential as attractive, low cost and sustainable energy source [1–6]. Both academic and industry researchers have put immense efforts to optimize the processing conditions and to characterize the physical process for improving the OPVs performance [7–14]. It is well established that the charge carrier processes in such class of materials are very different than the conventional semiconductors due to the weak intermolecular interaction [15,16]. For instance, the excitons are formed under the illumination, diffuse to the heterojunction

interface where they get dissociated resulting the charge carrier's generation [17,18]. It is well known that the defect states in the organic semiconductors, originated due to impurities, structural disorder, or processing, are commonly distributed within the energy gap. Such defect states are responsible for deteriorating the charge carrier mobility in the bulk, exciton quenching, and carrier recombination at heterojunction interface [19–22]. Therefore, a detailed understanding of physical processes at the heterojunction interface is extremely important for further improving the solar cells performance.

The current–density voltage (J–V) characteristics of an OPV under the dark and illumination conditions are usually found to be similar as reported for conventional p–n junction diodes [23–25]. Having this in mind, the generalized Shockley diode equation, originally developed for the inorganic devices, are often utilized to

* Corresponding author.

E-mail address: devikakataria@jkl.u.edu.in (D. Kataria).<https://doi.org/10.1016/j.matpr.2020.08.682>

2214-7853/© 2020 Elsevier Ltd. All rights reserved.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Innovation in Technology & Management for Achieving Sustainable Development Goals (SDGs): Materials Science.

model the J-V characteristics of OPVs for extraction of the relevant parameters. This approach provides reasonable descriptions up to some extent however, it is usually failed and lacked the physical meaning of extracted parameters since the charge transport mechanisms are very different. In view of this, Forrest and co-workers [26] developed a Shockley type of diode equation for organic heterojunction diodes by taking into account the polaron pair generation and recombination at the heterojunction interfaces. The model not only propose the occurrence of two different ideality factors due to trap assisted recombination at the heterojunction interface but also predicts the intensity and temperature dependence of the dark current, the open-circuit voltage (V_{oc}) and the short-circuit current (J_{sc}) and also provides their interpretations.

In this study, we will characterize the Copper Phthalocyanine (CuPc) and Fullerene (C_{60}) based planer heterojunction organic solar cells performing the illumination intensity dependent J-V measurement in the wider illumination range. The relevant solar cell parameters, such as V_{oc} and J_{sc} are derived from the illumination intensity dependent J-V characteristics and their dependency on the illumination intensity are discussed using the diode equation developed for the bi-carrier organic devices.

2. Experimental methods

The devices were fabricated on commercially available ITO coated glass substrates from SANYO HVAC with ITO thickness of 150 nm and sheet resistance 10 to 15 Ω/m . These substrates were cleaned in soap solution followed by sonication in de-ionised (DI) water at room temperature and then rinsed in boiling DI water. Subsequently, the substrates were dried with a nitrogen gun and kept inside an oven at 120 $^{\circ}C$ in air for half an hour. The cleaned ITO coated glass substrates were patterned into rectangular strips and pixelated to define the device area using the photolithography. The pixelated substrates were kept inside an oven at 140 $^{\circ}C$ in air for half an hour for photoresist hardening. The pixelated substrates were then treated in ozone for 10 min before coating the PEDOT: PSS solution. Thereafter, the substrates were dried at 130 $^{\circ}C$ in air for half an hour and loaded into the deposition chamber. Double sublimed pure organic materials as obtained from Sigma Aldrich were deposited through shadow mask. The silver cathode layer was deposited using a different shadow mask after BCP layer deposition. The contacts for electrical measurements were made using silver paste on the deposited metal layer. The J-V measurements were performed using Keithley 2400 SourceMeter[®]. The solar cell performance was recorded using Newport AM1.5 Solar Simulator

(Model 91191). Neutral density filters were used to vary the light intensity from 0.001 sun to 1 sun. The final device structure and the energy level diagram are shown in Fig. 1. The value of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the work functions have been taken from literatures [27,28].

3. Result and discussion

The J-V characteristic of the fabricated solar cells under the dark and illuminations are shown in Fig. 2(a) and (b), respectively. The devices were kept inside a closed black box to ensure no light illumination during the dark J-V measurements. The light intensities are varied in the wider range of 0.001, 0.01, 0.03, 0.1, 0.2, 0.3 0.5 and 1 Sun of AM 1.5 spectrum using the neutral density filters during the light J-V measurements. The J-V characteristics under the dark condition shows rectifying behavior with approximate two orders of current density difference between the forward and reverse bias. In the forward bias operation, two distinct exponential regimes can easily be identified in the semi-log plots before device enters into the space charge limited regime. To understand the observed behavior, Forrest and co-workers developed the diode equation considering the polaron pair generation and recombination at heterojunction interfaces of an organic diode. According to this model, the trap-limited recombination due to disorder at the donor-acceptor (D-A) heterojunction interface leads to introduction of two distinct ideality factors (n_D and n_A) in the dark current of organic diode as given in the following expression[26].

$$J = J_{SD}[\exp(qV_a/n_D k_B T) - 1] + J_{SA}[\exp(qV_a/n_A k_B T) - 1] - q\eta_{ppd}J_X \quad (1)$$

where J_{SD} and J_{SA} are the dark saturation current density, V_a is the applied voltage, η_{ppd} is the exciton (polaron) pair dissociation efficiency, n_D and n_A are the ideality factors, and J_X the exciton density under illumination.

The solar cell performance was measured under illumination at various intensities as shown in the Fig. 2(b). The values of J_{sc} and V_{oc} are observed to be 4.6 mA/cm² and 0.49 V at 1 Sun illumination intensity. Furthermore, these parameters increase monotonically with increase of illumination intensity. The relation governing the variation of V_{oc} with illumination intensity is given by the expression[26].

$$qV_{oc} = \Delta E_{HL} - k_B T \ln \left[\left(\frac{k_{ppr}}{k_{ppd}} \right) \frac{k_{rec} N_{HOMO} N_{LUMO}}{J_X/a_0} \right] \quad (2)$$

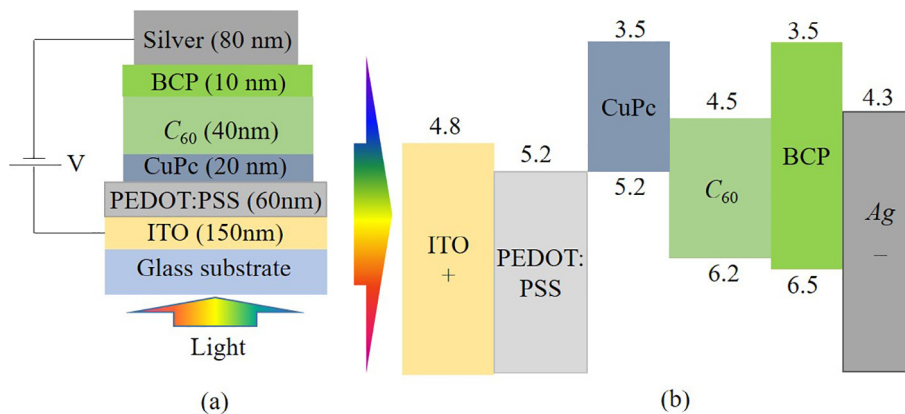


Fig. 1. Device structure with thickness of the constituting layers. (b) The energy level of constituting layers taken from literatures [27,28]

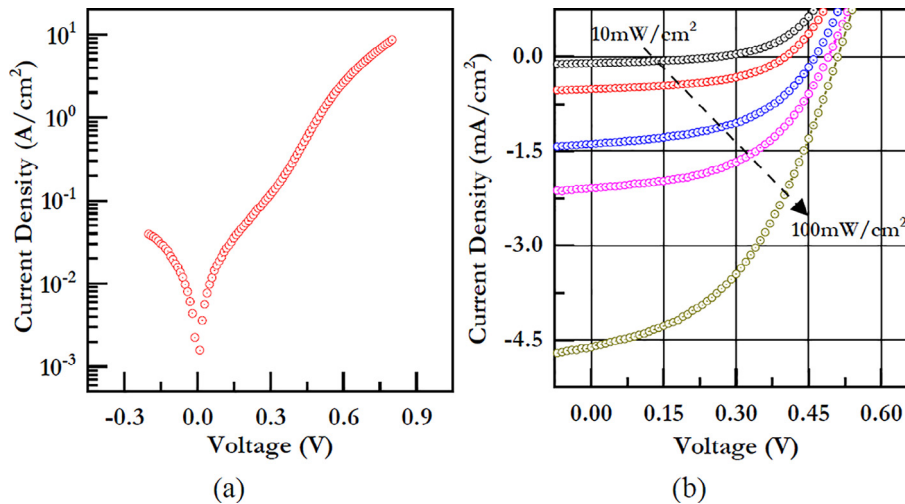


Fig. 2. J-V characteristics of CuPc:C₆₀ planar heterojunction solar cell (a) under dark and (b) varying illumination conditions such as 0.1, 0.2, 0.3 0.5 and 1 Sun.

ΔE_{HL} is the energy gap between the donor HOMO and acceptor LUMO, k_{ppr} is the polaron pair recombination rate, k_{ppd} is the polaron pair dissociation rate, k_{rec} is the bimolecular recombination rate, a_o is the polaron pair spatial extent or width of donor-acceptor heterojunction width, N_{HOMO} and N_{LUMO} is the densities of states in the donor HOMO and acceptor LUMO level respectively. The equation suggests that the V_{OC} is always less than the ΔE_{HL} and competition between the polaron pair recombination and dissociation determine the extent of loss. Furthermore, the V_{OC} should increase logarithmic with exciton density, J_X , which is directly proportional to the incident intensity.

In this study, the CuPc molecule is used as donor whose (HOMO) is located at 5.2 eV and C₆₀ as acceptor whose (LUMO) is located at 4.5 eV. Thus, the theoretical ΔE_{HL} at the heterojunction interface would be 0.7 eV which not only help in polaron dissociation but also determine the V_{OC} value as given in Eq. (2). The built-in field, V_{bi} , of the structure is difference of work function of electrodes which is equal to 0.5 eV. It facilitates polaron extraction after the dissociation at the heterojunction interface.

The J_{SC} and V_{OC} value obtained from the Fig. 2 (b) is plotted as a function of logarithm of illumination intensity as shown in Fig. 3 (a). Indeed, V_{OC} increases with higher slope at lower intensities (less than 20 mW/cm²) and lower slope at higher intensities from

20 mW/cm² to 100 mW/cm². These two slopes at low and high intensities respectively result in two different ideality factors for the diode equation in these two regions as given in Eq. (1). These two ideality factors, n_D and n_A , are occurred due to trap limited recombination in the donor and acceptor within the heterojunction region [26]. The ideality factors values are found to be 4.65 and 2.15 at lower and higher intensity regimes, respectively. Our results show strong consistency with theoretical prediction reported in the reference [26].

The width of the heterojunction region which is also the polaron pair spatial extent ' a_o ', formed due to intermixing of the donor and acceptor materials while deposition of acceptor layer over the donor layer to form the sandwiched structure. Such intermixing happens due to punching of the acceptor molecules into the donor layer because of their kinetic energy and facilitated by the uneven surface of the donor. The uneven morphology of the CuPc donor surface before acceptor layer deposition can be seen in the Field Emission Scanning Electron Microscope image as shown in the Fig. 3(b). The roughness in the morphology supports the observation that the current density is limited due to some irregularities in the photoactive layer of OSC. The island type of morphology of CuPc film surface is formed due to the Stransky-Krastanov or Layer plus Island growth mode in which a film grows initially forming

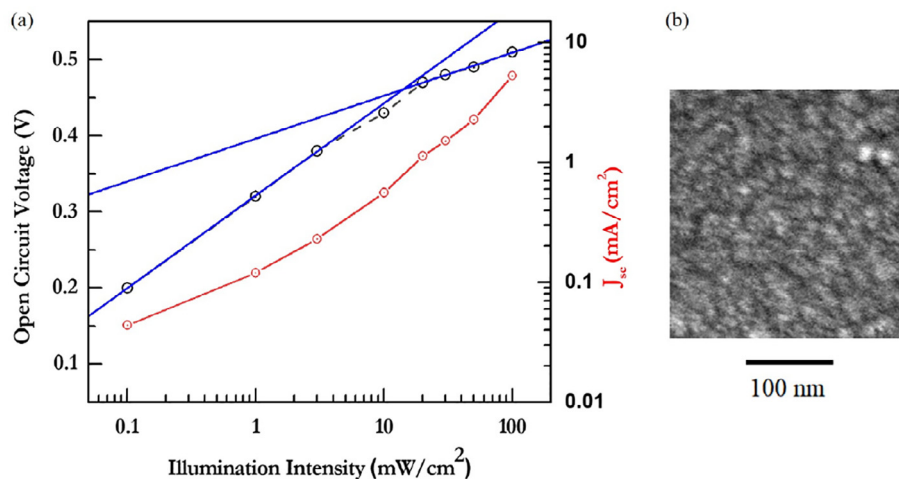


Fig. 3. (a) Open circuit voltage and short circuit current as a function of illumination intensity from 0.001 to 1 Sun. Note that two distinct slopes are identified for V_{OC} and fitted excellently with straight lines. (b) FESEM image shows unevenness on the CuPc film surface which helps intermixing of donor-acceptor forming the junction.

continuous layers and then deviates with the formation of island like structures. The stress imposed by the substrate on the CuPc layer gradually reduces with the film thickness allowing to form islands over continuous layer [29]. Possibly the stress in the film is responsible for the trap states in between the HOMO and LUMO. The short circuit current density, J_{sc} , should show linear dependence on the incident intensity [26], however Fig. 3(a) shows deviation, which also indicates the presence of trap states in thin film. A slight upward deviation of J_{sc} from linearity with intensity can be attributed to better charge collection due to trap filling at higher intensity.

The fill factor and power conversion efficiency are plotted as the function of logarithm of illumination intensity as shown in Fig. 4. It can be observed that the power conversion efficiency increases monotonically with illumination intensity while the fill factor (FF) shows non-monotonic dependence. The fill factor initially increases with illumination intensity up to 10 mW/cm² and then, decreases gradually. At higher intensities, above 50 mW/cm², the fall of fill factor can be attributed to recombination of mobile carriers or Langevin recombination. Photocarrier concentrations within the active materials increases significantly with illumination intensity. Since the transport properties of these materials are very poor, all the photogenerated charge carriers do not reach to the respective electrodes rather gets recombine within the bulk through the Langevin bimolecular recombination processes. Therefore, the competition between the recombination and extraction of photocarriers principally determine the FF at the voltage bias between the short circuit and open circuit conditions [30,31]. The reduction of fill factor at higher illumination intensity may possibly be happened because of poor extraction of photocarriers from the donor-acceptor heterojunction region.

4. Conclusion

The study of J - V characteristics under varying illumination intensities helps us to understand the effect of traps on V_{oc} and consequently, on the PCE of the organic bilayer heterojunction solar cells. At low illumination intensity the trap limited recombination is dominated by recombination between the free electrons with trapped holes in donor showing ideality factor n_D which is higher than the ideality factor at higher intensities for the test bilayer heterojunction solar cells. At higher intensities the recombination between free holes with trapped electrons in acceptor

shows n_A . The upper limit of V_{oc} is bound as interfacial gap between HOMO level of donor and LUMO level of acceptor and is observed to saturate at 0.5 V for CuPc:C₆₀ interface. Contrary to the theoretical predictions, a slight upward deviation of J_{sc} from linearity with intensity can be attributed to better charge collection due to trap filling at higher intensity.

CRediT authorship contribution statement

Anukul Prasad Parhi: Conceptualization, Investigation, Writing - original draft. **Durgesh C. Tripathi:** Formal analysis, Writing - review & editing. **Devika Kataria:** Validation, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We acknowledge funding support from The Ministry of New and Renewable Energy (MNRE), Government of India, through the R&D project 31/18/2009-10/PVSE titled 'Design and Development of Organic Solar Cell Sub-Modules' which helped in carrying out the experiments. We thank Prof. S. Sundar Kumar Iyer for availing his laboratory to carry out the experiments.

References

- [1] Y. Cui, Y. Wang, J. Bergqvist, H. Yao, Y.e. Xu, B. Gao, C. Yang, S. Zhang, O. Inganäs, F. Gao, J. Hou, Wide-gap non-fullerene acceptor enabling high-performance organic photovoltaic cells for indoor applications, *Nat Energy* 4 (9) (2019) 768–775.
- [2] R. Zhou, Z. Jiang, C. Yang, J. Yu, J. Feng, M.A. Adil, D. Deng, W. Zou, J. Zhang, K. Lu, W. Ma, F. Gao, Z. Wei, All-small-molecule organic solar cells with over 14% efficiency by optimizing hierarchical morphologies, *Nat Commun* 10 (1) (2019), <https://doi.org/10.1038/s41467-019-13292-1>.
- [3] O. Inganäs, Organic Photovoltaics over Three Decades, *Adv. Mater.* 30 (35) (2018) e1800388.
- [4] L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R.A. Street, Y. Yang, 25th Anniversary Article: A Decade of Organic/Polymeric Photovoltaic Research, *Adv. Mater.* 25 (46) (2013) 6642–6671.
- [5] L. Duan, A. Uddin, Progress in Stability of Organic Solar Cells, *Adv. Sci.* 7 (11) (2020) 1903259.
- [6] J. Liu, Y. Cui, Y. Zu, C. An, B. Xu, H. Yao, S. Zhang, J. Hou, Organic photovoltaic cells for low light applications offering new scope and orientation, *Organic Electronics* 85 (2020) 105798, <https://doi.org/10.1016/j.orgel.2020.105798>.
- [7] M.C. Scharber, D. Mühlbacher, 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 (6) (2006) 789–794.
- [8] S. Liu, J. Yuan, W. Deng, M. Luo, Y. Xie, Q. Liang, Y. Zou, Z. He, H. Wu, Y. Cao, High-efficiency organic solar cells with low non-radiative recombination loss and low energetic disorder, *Nat. Photonics* 14 (5) (2020) 300–305.
- [9] S.K. Gupta, A. Sharma, S. Banerjee, R. Gahlot, N. Aggarwal, Deepak, A. Garg, Understanding the role of thickness and morphology of the constituent layers on the performance of inverted organic solar cells, *Solar Energy Materials and Solar Cells* 116 (2013) 135–143.
- [10] A. Barito, M.E. Sykes, B. Huang, D. Bilby, B. Frieberg, J. Kim, P.F. Green, M. Shtein, Universal Design Principles for Cascade Heterojunction Solar Cells with High Fill Factors and Internal Quantum Efficiencies Approaching 100%, *Adv. Energy Mater.* 4 (13) (2014) 1400216, <https://doi.org/10.1002/aenm.201400216>.
- [11] R.A. Street, Localized state distribution and its effect on recombination in organic solar cells, *Phys. Rev. B* 84 (7) (2011), <https://doi.org/10.1103/PhysRevB.84.075208>.
- [12] R. Xue, J. Zhang, Y. Li, Y. Li, Organic Solar Cell Materials toward Commercialization, *Small* 14 (41) (2018) 1801793.
- [13] Y. Park, K. Vandewal, K. Leo, Optical In-Coupling in Organic Solar Cells, *Small Methods* 2 (10) (2018) 1800123.
- [14] Forrest, S.R., Q. Burlingame, and C. Coburn, Organic photovoltaic devices having a lateral charge transport channel. 2020: US Patent App. 16/722, p. 709.
- [15] A. Prasad Parhi, S.S. Kumar Iyer, Static electric field enhanced recrystallization of copper phthalocyanine thin film during annealing, *Journal of Crystal Growth* 380 (2013) 123–129.

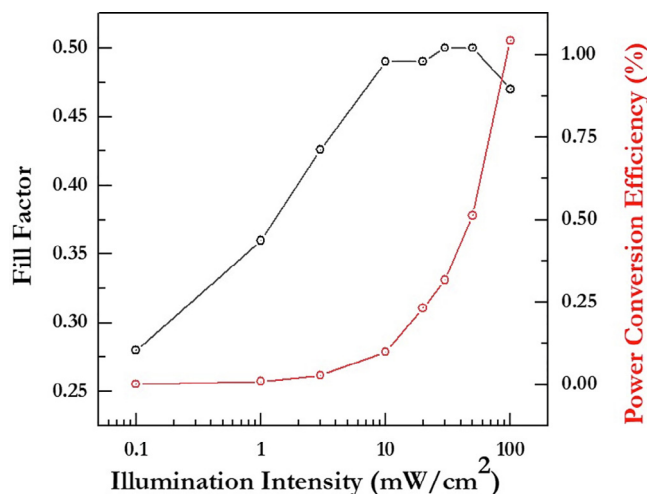


Fig. 4. Fill factor and power conversion efficiency of the solar cell is plotted as a function of illumination intensities.

- [16] A.P. Parhi, S.S.K. Iyer, Effect of external electric field on morphology of copper phthalocyanine-fullerene blended films during annealing, *Electron. Mater. Lett.* 12 (2) (2016) 260–269.
- [17] V.D. Mihailescu, L.J.A. Koster, J.C. Hummelen, P.W.M. Blom, Photocurrent Generation in Polymer-Fullerene Bulk Heterojunctions, *Phys. Rev. Lett.* 93 (21) (2004), <https://doi.org/10.1103/PhysRevLett.93.216601>.
- [18] A. Petersen, T. Kirchartz, T.A. Wagner, Charge extraction and photocurrent in organic bulk heterojunction solar cells, *Phys. Rev. B* 85 (4) (2012), <https://doi.org/10.1103/PhysRevB.85.045208>.
- [19] U.K. Verma, D.C. Tripathi, Y.N. Mohapatra, Direct determination of defect density of states in organic bulk heterojunction solar cells, *Appl. Phys. Lett.* 109 (11) (2016) 113301, <https://doi.org/10.1063/1.4962827>.
- [20] K. Sudheendra Rao, Y.N. Mohapatra, Open circuit voltage decay transients and recombination in bulk-heterojunction solar cells, *Appl. Phys. Lett.* 104 (20) (2014) 203303, <https://doi.org/10.1063/1.4879278>.
- [21] J. Wagner, M. Gruber, A. Wilke, Y. Tanaka, K. Topczak, A. Steindamm, U. Hörmann, A. Opitz, Y. Nakayama, H. Ishii, J. Pflaum, N. Koch, W. Brütting, Identification of different origins for s-shaped current voltage characteristics in planar heterojunction organic solar cells, *Journal of Applied Physics* 111 (5) (2012) 054509, <https://doi.org/10.1063/1.3692050>.
- [22] T. Kirchartz, B.E. Pieters, J. Kirkpatrick, U. Rau, J. Nelson, Recombination via tail states in polythiophene:fullerene solar cells, *Phys. Rev. B* 83 (11) (2011), <https://doi.org/10.1103/PhysRevB.83.115209>.
- [23] V. Dyakonov, Mechanisms controlling the efficiency of polymer solar cells, *Appl. Phys. A* 79 (1) (2004) 21–25.
- [24] B.P. Rand, D.P. Burk, S.R. Forrest, Offset energies at organic semiconductor heterojunctions and their influence on the open-circuit voltage of thin-film solar cells, *Phys. Rev. B* 75 (11) (2007), <https://doi.org/10.1103/PhysRevB.75.115327>.
- [25] W.J. Potscavage Jr., S. Yoo, B. Kippelen, Origin of the open-circuit voltage in multilayer heterojunction organic solar cells, *Appl. Phys. Lett.* 93 (19) (2008) 193308, <https://doi.org/10.1063/1.3027061>.
- [26] N.C. Giebink, G.P. Wiederrecht, M.R. Wasielewski, S.R. Forrest, Ideal diode equation for organic heterojunctions. I. Derivation and application, *Phys. Rev. B* 82 (15) (2010), <https://doi.org/10.1103/PhysRevB.82.15530>.
- [27] J. Xue, B.P. Rand, S. Uchida, S.R. Forrest, Mixed donor-acceptor molecular heterojunctions for photovoltaic applications. II. Device performance, *Journal of Applied Physics* 98 (12) (2005) 124903, <https://doi.org/10.1063/1.2142073>.
- [28] H. Park et al., Interface engineering of graphene for universal applications as both anode and cathode in organic photovoltaics, *Sci Rep* 3 (2013) 1581.
- [29] S.R. Forrest, Ultrathin Organic Films Grown by Organic Molecular Beam Deposition and Related Techniques, *Chem. Rev.* 97 (6) (1997) 1793–1896.
- [30] T.M. Burke, S. Sweetnam, K. Vandewal, M.D. McGehee, Beyond Langevin Recombination: How Equilibrium Between Free Carriers and Charge Transfer States Determines the Open-Circuit Voltage of Organic Solar Cells, *Adv. Energy Mater.* 5 (11) (2015) 1500123, <https://doi.org/10.1002/aenm.201500123>.
- [31] D. Bartsaghi et al., Competition between recombination and extraction of free charges determines the fill factor of organic solar cells, *Nat Commun* 6 (2015) 7083.