Role of Poly(Ethylenedioxythiophene)/Poly(Styrene Sulphonate) on the Performance of Nanocrystalline Titanium Dioxide/Poly(3-Hexylthiophene) Polymer Solar Cells

S. Sarathchandran, K. Prashanthan, and P. Ravirajan*

Department of Physics, University of Jaffna, Jaffna, JA 40 000, Sri Lanka

Hybrid nanocrystalline titanium dioxide (TiO_2)/polymer solar cells draw intense interest due to the potential advantages of nanocrystalline TiO_2. The poly(styrenesulfonate)-doped poly(ethylenedioxy thiophene) (PEDOT:PSS) layer spin-coated below the top electrode in these solar cells had shown enhanced performance in previous studies, which motivated to explore the dependence of the thickness of the PEDOT:PSS layer on its performance. This study focused on the characterization of solar cells fabricated with poly(3-hexylthiophene) (P3HT) polymer with a silver electrode and different PEDOT:PSS layer thicknesses, in the dark and under AM 1.5 stimulated illumination with the intensity varying from 10 to 100 mW/cm². The variations in the photovoltaic parameters, particularly the open-circuit voltage, proved that the PEDOT:PSS layer significantly affects the photovoltaic parameters through the characteristic changes in the morphology as well as the electrical properties. Discussed herein is the possible influence wielded by the thickness of the PEDOT:PSS layer on different factors, such as the series and shunt resistances, the mode of recombination, the reduction of the energy barrier, and the diffusion of silver. The optimum power conversion efficiency was observed for the as-prepared devices with 50-nm-thick PEDOT layers. The optimum power conversion efficiency, however, shifted to that corresponding to the 80 nm thick PEDOT:PSS layer about 30 weeks after the fabrication. A sublinear variation of the short-circuit current density with the intensity was found in the aged cells with relatively lower PEDOT:PSS layer thicknesses, supporting the view of dominant recombination contributed from bimolecular recombination in the cells with lower PEDOT:PSS thicknesses. The significantly increased open-circuit voltage and the more stable current density in the aged devices are the main causes of the improved performance of the cells generally with above 60 nm thick PEDOT:PSS layers. These, along with the long-term stability found in the cells with reasonably thick PEDOT:PSS layers, may be a figure of merit, most probably attributable to the comparatively minimized diffusion of silver nanoparticles.

Keywords: Solar Cells, PEDOT:PSS, Polymer, TiO_2, Thickness, Photovoltaic Device.

RESEARCH ARTICLE

1. INTRODUCTION

Solar cells utilizing molecular materials are currently under intensive research as potential replacements for the traditional microcrystalline solar cells, because of their relative ease of fabrication with cost-efficient methods. A class of solar cells fabricated with blends of polymers and fullerene derivatives at nanoscale has yielded the highest efficiency among the organic solar cells. The use of fullerenes as electron acceptors has some disadvantages, however, such as the phase segregation of the components during aging, and the relatively poor photostability. Stable metal oxides such as TiO_2, ZnO, and SnO_2 are promising as alternative electron acceptors that could offer good electron transport properties, fabrication via facile techniques, nontoxicity, and heterojunction morphology control.[1–8] These hybrid solar cells fabricated with metal oxide and polymer can further assume the advantages of both types of materials.[8, 9] The hybrid TiO_2/polymer solar-cell system is more attractive as the titania templates can be made with continuous pores with the size matching the exciton diffusion length, which improves exciton harvesting. The performance of these hybrid TiO_2/polymer solar

---

*Author to whom correspondence should be addressed.
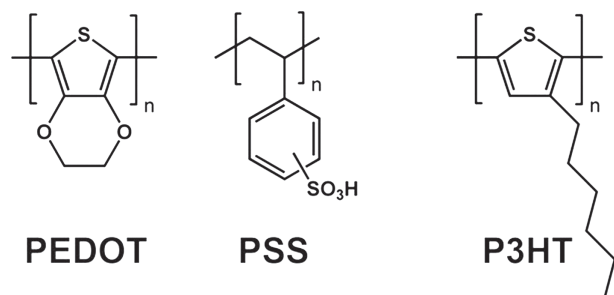
Fig. 1. Chemical structure of poly(ethylenedioxy thiophene: poly(styrenesulfonate)-(PEDOT:PSS) and poly(3-hexylthiophene) (P3HT).

cells, however, are still lower than that of the reported best polymer:fullerene solar cells mainly due to the limited photogeneration rate and the quality of the interfaces.[3] Several attempts to modify the TiO$_2$/polymer interface have been made and reported.[10] The polymer/top-electrode interface modified with poly(styrenesulfanate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) has also been determined to improve the performance of the TiO$_2$/polymer solar cells.[3, 4, 10, 11] The PEDOT:PSS underlayer has been found to enhance the hole collection by establishing ohmic contact with the polymer layer[12] while serving as an electron-blocking layer. Furthermore, the degraded current density–voltage (J–V) characteristics owing to the energy barrier at the polymer/top hole-collecting metal electrode were reported to have been reduced by the introduction of the PEDOT:PSS underlayer.[3–5] The PEDOT:PSS underlayer can also serve as a protective layer from the damages that can be caused by metal penetration during thermal evaporation, which may enhance the exciton quenching near the interface. With this background, a study related to the quality of the PEDOT:PSS layer in the hybrid TiO$_2$/polymer solar cells is important for optimizing the performance of the layer.

The present study focused on the effect of the thickness of the PEDOT:PSS layer on the performance of the hybrid TiO$_2$/P3HT multilayer solar cell fabricated with a silver top electrode. The possible influence of the PEDOT:PSS layer thickness on several factors, including the reduction of the interfacial energy barrier, recombination, compatibility between the interface layers, and the diffusion of the silver nanoparticles, are discussed in this paper.

2. EXPERIMENTAL DETAILS

Indium-tin-oxide-(ITO)-coated glass substrates (25 Ω/cm^2) were cleaned using acetone and isopropyl alcohol, and were then annealed to remove any organic residue. The precursor solution that was used to deposit the dense TiO$_2$ nanolayer, prepared as described in Ref. [13], was sprayed onto the cleaned ITO-coated glass substrates and were subsequently sintered at 450 °C for 30 min. This dense TiO$_2$ layer prevents direct contact between

poly(3-hexylthiophene) (P3HT) and the ITO-coated glass substrate, which would short-circuit the device. The porous nanocrystalline TiO$_2$ film was deposited on the dense TiO$_2$ layer by spin-coating the diluted TiO$_2$ paste purchased from Dysol (Australia), and was then sintered at 450 °C for 30 min. After allowing sufficient time for the substrates to cool down, they were dipped in the P3HT (purchased from Merck Chemicals Ltd.) solution in 1,2 dichlorobenzne for 24 h. After being blown with nitrogen gas, they were soft-baked at 50 °C for 5 min, and the P3HT layer (∼50 nm thick) was spun on this substrate.

To fabricate the PEDOT:PSS underlayer, the aqueous solution of PEDOT:PSS (BAYTRON) after filtering with a 0.45-μm filter was heated at 90 °C for 5 min. It was then spin-coated at different spin rates, ranging from 1050 to 10100 rpm, onto the P3HT layer. The samples were again baked at 100 °C for 5 min in a nitrogen-filled, home-built annealing box. Solar cells were fabricated through the deposition of a silver film on the PEDOT:PSS layer under vacuum, below 10^{-5} Torr, in the chamber of the thermal evaporator. A dot of silver paint was applied on top of this silver film and on the ITO bottom electrode for better contact, and was subsequently annealed at 120 °C in a nitrogen environment.

The J–V characteristics were obtained with a Keithley 2400 Source Measure unit. The cells were characterized in the dark and under illumination with a solar simulator (SCIENCETECH) at varying intensities.

3. RESULTS AND DISCUSSION

The J–V characteristics of the hybrid TiO$_2$/P3HT multilayer devices with different PEDOT:PSS thicknesses characterized in the dark and under AM 1.5 simulated illumination with a typical intensity of 70 mW/cm^2 are shown in Figures 2(a and b), respectively.

The forward-biased dark current of the nanostructured TiO$_2$/polymer solar cells with varying PEDOT:PSS underlayer thicknesses showed a significant increase compared to those without such layer, in accord with the previous studies.[3–5, 10] The dark-current rectification ratio, however, was observed to decrease when the thickness of the PEDOT:PSS layer was continuously increased up to about 80 nm, but was observed to increase when the thickness exceeded 90 nm. The PEDOT:PSS layer whose thickness exceeded 100 nm, however, was peeled off from the substrate. For this reason, the analysis was restricted to the moderately thick PEDOT:PSS layers, although techniques like encapsulation may remedy the aforementioned problem identified with thick PEDOT:PSS layers.

The previous reports attribute the drop in serial resistance, the subsequent increase in the dark current and current under illumination, the absence of a distorted feature near the open-circuit voltage, and the minimal reduction in the open-circuit voltage to the reduction of the
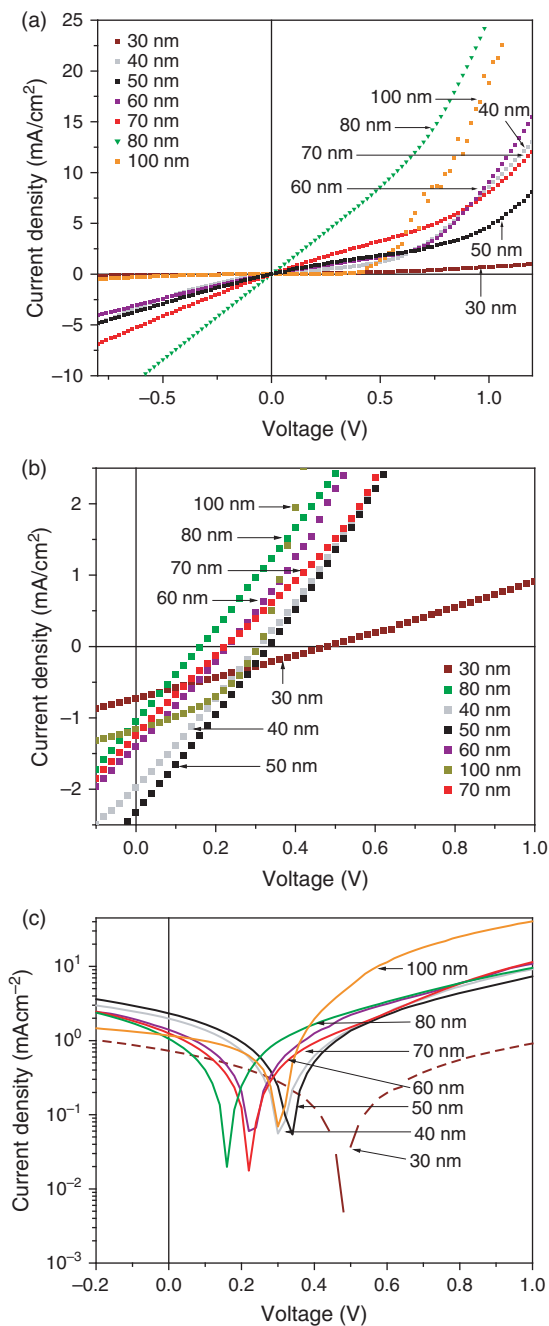
Fig. 2. *J–V* characteristics of the hybrid TiO$_2$/P3HT multilayer solar cells with different PEDOT thicknesses (a) in the dark and (b) under AM 1.5 illumination with a solar simulator with an intensity of 70 mW/cm^2. (c) Replotted in semilogarithmic scale for better observation of the change in the open-circuit voltage.

polymer/metal electrode energy barrier resulting from the inclusion of a PEDOT:PSS layer.[4–7] In the present study, the open-circuit voltage (V$_{OC}$) started to fall continuously, reaching the minimum level, and seemed to increase again for the cells with reasonably thick PEDOT:PSS layers (~100 nm), as can be seen in Figure 2. The short-circuit current density (J$_{SC}$) was maximized with the around 50 m PEDOT:PSS layer thickness. The optimum power

conversion efficiency was observed with the about-50-nm-thick PEDOT:PSS layer, as shown in Figure 3. The comparatively inferior power conversion efficiencies shown by the 70- and 80-nm-thick PEDOT:PSS layers of the solar cells mainly resulted from the poor V$_{OC}$.

It should be noted that the power conversion efficiency was not absolutely optimized but only entailed relative variation with the PEDOT:PSS thickness in this work because some of the steps, such as dye dipping prior to dipping in the polymer solution, were skipped in this study, for simplicity. Similarly, the identical steps followed in the preparation of the dense TiO$_2$ hole-blocking layer, which is known as vital for the optimization of the performance of the nanocrystalline TiO$_2$/P3HT polymer solar cells, removed the influence of the quality of the dense TiO$_2$ hole-blocking layer on the results of this comparative study.

A number of factors associated with the PEDOT:PSS layer will be identified to explain the PEDOT:PSS-controlled photovoltaic parameters. The morphology-related factors, such as surface roughness, compactness, distribution of voids, uniformity, and quality of adherence to the surface of P3HT, possibly influence the polymer/metal electrode energy barrier, series and shunt resistance, and recombination mode, and may thereby control the photovoltaic parameters. Better compatibility, which leads to a reduced energy barrier, as has already been confirmed in the previous studies,[5,6] cannot be expected to be attained with very thin PEDOT:PSS layers. The reduction of the surface roughness and the filling of voids may contribute positively to the reduction of the series resistance with increasing thickness. It is reasonable to expect a saturated reduced-barrier level, and its consequence of enhancing the charge collection, due to the aforementioned morphology-related factors, up to a certain thickness. When the thickness increased to a certain extent,
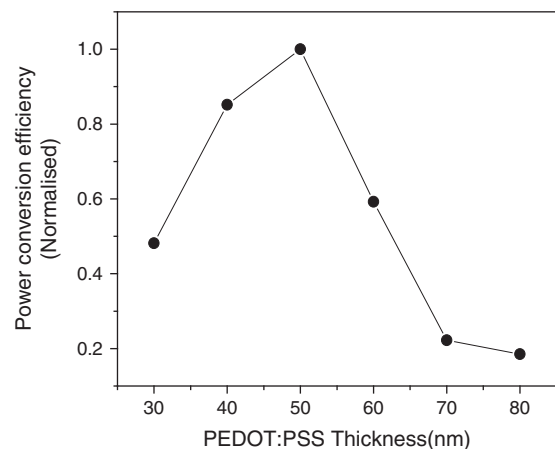
Fig. 3. Normalized power conversion efficiency of the hybrid TiO$_2$/P3HT multilayer solar cells with different PEDOT:PSS thicknesses (30, 40, 50, 60, 70, and 80 nm) under stimulated illumination with 70 mW/cm^2 light intensity.

the series resistance tended to increase, mainly receiving contributions from the layer resistance itself. Furthermore, the layer resistance obtains importance due to the hygroscopic nature of the PEDOT:PSS layer, which decreases the conductivity.

The shunt resistance, on the other hand, is a measure of the inverse of the slope of the J–V curve near J_{SC}. The shunt resistance in this analysis showed an initial steep fall followed by a gentle decrease and another steep increase with increased PEDOT:PSS thickness, reflecting the trend shown by V_{OC}. Noncompact and nonuniform films probably lead to pinholes acting as shunt pathways that degrade the performance. The effect of the diffusion of silver nanoparticles towards P3HT through the PEDOT:PSS layer is not well understood, but if the diffusion reaches a critical stage, the increased shunt pathways will definitely decrease the shunt resistance.

The PEDOT:PSS layer may also influence the charge carrier recombination, which generally depends on the macroscopic film properties, such as the sizes and shapes of the cells and the nanoscale phase-separated regions, percolation paths,[14] molecular arrangement, and traps. In the cells with too thin or too thick PEDOT:PSS layers, a slower rate of hole collection can be expected compared to the rate of generation, which in turn makes the recombination and/or space-charge-limited current dominant. The effect of the recombination and/or space-charge-limited current will become even more dominant in the thin PEDOT:PSS layer cells due to the inefficient electron-blocking function carried out by the thin PEDOT:PSS layer.

Another important observation is the aging effect, which affects the performance of the solar cells in a somewhat unexpected manner. The optimum power conversion efficiency shifted to that corresponding to the 80-nm-thick PEDOT:PSS layer about 30 weeks after the fabrication. The significantly increased V_{OC} and the more stable J_{SC} in the aged devices were the main causes of the improved performance of the cells with generally more-than-60-nm-thick PEDOT:PSS layers. These, along with the long-term stability found in the cells with reasonably thick PEDOT:PSS layers, may be merits most probably attributable to the comparatively minimized diffusion of silver nanoparticles.

Both the aged and the as-prepared cells depicted the same trend of variation in J_{SC} and V_{OC} when exposed to varying light intensity. The degree of variation, however, was lower in the as-prepared cells. Figure 4 shows the variation of the J_{SC} and V_{OC} of the aged cells with varying light intensity.

Figure 4(a) shows the significant increase in the V_{OC} at a particular intensity compared to the as-prepared cells. The sublinear variation of J_{SC} with the intensity could be seen in the aged cells with relatively lower PEDOT:PSS layer thicknesses, supporting the view of the dominant recombination contributed from the bimolecular recombination in
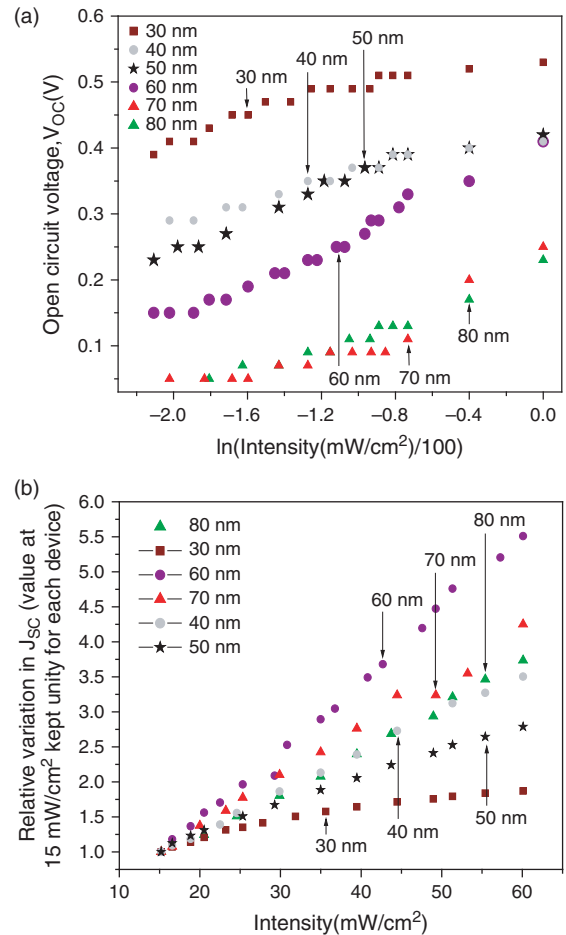
Fig. 4. Variation in the (a) open-circuit voltage with ln (intensity) and (b) short-circuit current density with the intensity relative to a very low intensity of 15 mW/cm² of the ITO/dense TiO₂ layer/porous TiO₂ layer/P3HT/PEDOT:PSS/Ag cells with varying PEDOT:PSS thicknesses (x nm) after 30 weeks elapsed time (kept under vacuum).

these cells with lower PEDOT:PSS layer thicknesses. The possibility, however, that the space-charge-limited current resulted in this sublinear variation cannot be ruled out.

4. CONCLUSION

It was found that the photovoltaic parameters controlled by the thickness of the PEDOT:PSS layer in a multi-layer hybrid TiO₂/polymer cell can be attributed to the characteristic changes in the morphology and electrical properties, including the series and shunt resistances, the reduction of the energy barrier, the diffusion of the silver top metal contact, and the recombination mode. The optimum power conversion efficiency was observed with the 50-nm-thick PEDOT:PSS layers. Improved performance with aging was observed, however, in the cells with much thicker PEDOT:PSS layers, which is attributed to the more stable current density in these cells and the significant increase in the open-circuit voltage, which had been found to be very low in the as-fabricated cells.

References and Notes

1. T. Ishwara, D. D. C. Bradley, J. Nelson, P. Ravirajan, I. Vanseveren, T. Cleij, D. Vanderzande, L. Lutsen, S. Tierney, M. Heeney, and I. McCulloch, *Appl. Phys. Lett.* 92, 053308 (**2008**).
2. P. Ravirajan, S. A. Haque, J. R. Durant, D. Poplavaskyy, D. D. C. Bradley, and J. Nelson, *J. Appl. Phys.* 95, 1473 (**2004**).
3. P. Ravirajan, S. A. Haque, J. R. Durant, D. D. C. Bradley, and J. Nelson, *Adv. Funct. Mater.* 15, 609 (**2005**).
4. P. Ravirajan, D. D. C. Bradley, J. Nelson, S. A. Haque, J. R. Durrant, H. J. P. Smit, and J. M. Kroon, *Appl. Phys. Lett.* 86, 143101 (**2005**).
5. P. Ravirajan, A. Green, S. A. Haquec, J. R. Durrant, D. D. C. Bradley, and J. Nelson, *Proc. of SPIE.* 5520, 232 (**2004**).
6. P. Atienzar, T. Ishwara, B. N. Illy, M. P. Ryan, B. C. O'Regan, J. R. Durrant, and J. Nelson, *J. Phys. Chem. Lett.* 1, 708 (**2010**).
7. J. Bouclé, H. J. Snaith, and N. C. Greenham, *J. Phys. Chem.* 114, 3664 (**2010**).
8. S. Sarathchandran, K. Haridas, Y. Kim, and P. Ravirajan, *J. Nanoelect. Optoelectron.* 5, 243 (**2010**).
9. W. J. E. Beek, M. W. Wienk, and R. A. J. Janssen, *Adv. Funct. Mater.* 16, 1112 (**2006**).
10. B. Johaan, P. Ravirajan, and J. Nelson, *J. Mater. Chem.* 17, 3141 (**2007**).
11. M. Y. Song, K. J. Kim, and D. Y. Kim, *Sol. Energy Mater. Sol. Cells* 85, 31 (**2005**).
12. G. Khrypunov et al., *Physics and Chemistry of Solid State* T. 11, 249 (**2010**).
13. L. Kavan and M. Gratzel, *Electrochim. Acta* 40, 643 (**1995**).
14. J. G. Müller, J. M. Lupton, J. Feldmann, U. Lemmer, M. C. Scharber, N. S. Sariciftci, C. J. Brabec, and U. Scherf, *Physical Review B* 72, 195208 (**2005**).

RESEARCH ARTICLE