

Flexible polymer solar cells prepared using hard stamps for the direct transfer printing of polymer blends with self-organized interfaces†

Fang-Chung Chen,^{*a} Ming-Kai Chuang,^b Shang-Chieh Chien,^b Jheng-Hao Fang^c and Chih-Wei Chu^c

Received 30th March 2011, Accepted 18th May 2011

DOI: 10.1039/c1jm11336d

A transfer printing technique allows the development of flexible photovoltaic devices. Blending poly(ethylene glycol) (PEG) in the photoactive layer causes the PEG molecules to migrate spontaneously to and weaken the bonding at the interface between the polymer film and the Si wafer, thereby facilitating the transfer process from a hard stamp to the receiving flexible substrate. The device fabricated using this transfer printing process had characteristics similar to those of the corresponding device prepared using a spin-coating process. Using hard stamps should help to realize the low-cost, high-throughput roll-to-roll fabrication of flexible solar cells.

Introduction

Electronically functional polymers are being investigated extensively for their applications in such electronic devices as light emitting diodes, field effect transistors, and solar cells.^{1–4} The advantageous features of these organic devices include their low cost, light weight, and fabrication at low temperature.^{1–4} In addition, their mechanical properties allow the fabrication of devices using roll-to-roll and/or large-area processing on flexible substrates.^{5–9} Nevertheless, complicated multilayer structures or thin films exhibiting complex patterning^{10–12} are usually required to enhance device performance. The realization of multilayer structures is constrained, however, by dissolution of the initial layer in subsequent wet fabrication processes.^{13–15} Consequently, the mass-fabrication of devices incorporating electronically functional polymers requires the development of methods that contrast and complement those (*e.g.*, photolithography) used for the processing of conventional semiconductors in inorganic devices.

Many lamination and transfer printing processes have been proposed for the fabrication of organic devices. These approaches have been applied to construct metal–organic,^{16,17} organic–metal,^{16,18–21} and organic–organic^{22–25} interfaces in organic electronic devices to overcome the problem of solvent compatibility. Among these transfer printing or lamination processes, polydimethylsiloxane (PDMS) stamps have been used most widely for the fabrication of various structures in organic

functional electronic devices. Nevertheless, the fabrication of PDMS stamps can be complicated and modification of their surfaces is usually required to obtain the specific properties required for the transfer process.^{26,27} Herein, we report a simple transfer printing methodology—using hard stamps—for the fabrication of flexible organic photovoltaic devices. We have found that blending an inert polymer into the photoactive layer benefits the transfer printing of polymer films. The blended organic layer was readily transferred from a rigid substrate, such as a Si wafer, to a flexible polyethylene terephthalate (PET) substrate pre-coated with indium tin oxide (ITO). After deposition of metal cathodes on the thin films, the devices exhibited performance comparable with that of corresponding solar cells prepared using conventional spin-coating processing. We suspect that the inert polymer migrated to the interface between the polymer film and the Si wafer, weakening the bonding between the polymer films and the substrate; subsequently, the polymer thin film could be transferred from the wafer to the receiving flexible substrate.

Experimental section

The photoactive layer in this study consisted of P3HT and PCBM; the P3HT:PCBM weight ratio in the blend was maintained at 1 : 1. The molecular weight of PEG was 600 g mol⁻¹. The J–V characteristics of the solar cells were measured using a computer-controlled Keithley 2400 apparatus. The device photoresponse was measured under the illumination (100 mW cm⁻², AM 1.5G) provided by an Oriel 150 W solar simulator. The intensity of the light source was corrected using a standard Si photodiode.²⁸ The surface morphology of the thin films was visualized using a Digital Instruments Dimension 3100 atomic force microscope. XPS spectra were recorded using a PHI 5000 VersaProbe system.

^aDepartment of Photonics and Display Institute, National Chiao Tung University, Hsinchu, 30010, Taiwan. E-mail: fcchen@mail.nctu.edu.tw

^bDepartment of Photonics and Institute of Electro-optical Engineering, National Chiao Tung University, Hsinchu, 30010, Taiwan

^cResearch Center for Applied Sciences, Academia Sinica, Nankang, Taipei, 11529, Taiwan

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1jm11336d

Results and discussion

To facilitate the transfer of the thin film, we doped poly(ethylene glycol) (PEG) into a photoactive layer comprising poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Fig. 1 outlines the fabrication of the flexible organic solar cells. The donor substrate for the transfer process was a clean Si wafer presenting a layer of thermally grown SiO₂ (200 nm) on its surface [Fig. 1(a)]. After UV-O₃ treatment on the SiO₂ surface, the polymer blend was spin-coated from a solution in 1,2-dichlorobenzene. The thin film was then subjected to solvent annealing for at least 20 min.^{29,30} The sample was thermally annealed at 110 °C for 15 min prior to performing the transfer process. Herein, we denote the Si wafers presenting deposited polymer blends as “donor” samples. Patterned ITO-coated PET films were used as the “target” substrates. A layer of poly(ethylene dioxythiophene):polystyrenesulfonate (PEDOT:PSS) was spin-coated on the PET substrate and then the sample was annealed at 120 °C for 60 min. Prior to performing the transfer process, we further annealed the target PET substrates at 110 °C for 5 min [Fig. 1(b)]. Note that the transfer procedure was conducted at 110 °C. Subsequently, we attached the flexible target substrates onto the donor wafer [Fig. 1(c)]. After applying pressure (~18 psi), the photoactive layer was readily transferred to the PEDOT:PSS surface upon delamination of the flexible target substrate [Fig. 1(d)]. Finally, the device was completed through thermal evaporation of 80 nm Al as the cathode [Fig. 1(e)]. Fig. 1(e) also displays a standard device having the same structure, except that its photoactive layer was spin-coated directly on top of the PEDOT:PSS layer; all of the materials and manufacturing conditions were the same as those used to prepare devices through transfer printing.

Using the transfer printing procedure (Fig. 1), the unmodified P3HT:PCBM blend thin film could not be transferred successfully. After doping PEG into the polymer blend, however, the photoactive layer was readily lifted-off and transferred from the Si wafer to the plastic substrate. To understand the mechanism of the transfer printing process, we investigated the morphologies of the thin films deposited on the SiO₂ surfaces [Fig. 2(a), (b), (d) and (e)]; these surfaces directly contacted the PEDOT:PSS layer

on the flexible target substrate. The height- [Fig. 2(a) and (b)] and surface-mode [Fig. 2(d) and (e)] images reveal that the surface morphologies of the P3HT:PCBM films remained almost unchanged after the addition of PEG. Fig. 2(c) and (f) present AFM images (height and phase modes, respectively) of the transfer-printed thin film containing PEG on the flexible target substrate; this surface was originally in contact with the SiO₂ surface on the rigid Si wafer. The morphology of this surface [Fig. 2(f)] was significantly different from that of the other side [Fig. 2(e)]. We suspected that this surface featured a large number of PEG molecules, whereas the other interface was covered almost entirely by P3HT and PCBM molecules, resulting in entirely different surface textures in the AFM images. In addition, when we increased the weight ratio of PEG to 15%, we observed an even more obvious change in morphology (see Figure S1, ESI†), further supporting the notion that the compositions of the two surfaces were different. In other words, the distribution of PEG in the thin films was uneven; therefore, we infer that vertical phase separation occurred between PEG and the P3HT:PCBM blends in the thin film.³¹

Vertical phase separation in polymer blends has been reported widely.^{31–36} For example, Arias *et al.* demonstrated that the substrate surface can initiate phase separation of the lower-energy phase in polymer mixtures, leading to spontaneous formation of an encapsulation layer [poly(methyl methacrylate)] on top of a semiconducting film (P3HT) in thin-film transistors.³⁴ Recently, we also observed that PEG molecules tended to undergo vertical phase separation to the top surfaces of P3HT/PCBM blends.³¹ In this present study, the PEG molecules preferred to reside at the interface between the top of the Si wafer and the bottom of the thin film, presumably because of the hydrophilicity of the SiO₂ surface after UV-O₃ treatment.

To validate our assumptions, we immersed the thin film samples—prepared with and without PEG on the Si wafers—into a water bath (see Fig. 3). The polymer film containing PEG was readily lifted-off from the substrate [Fig. 3(a)]. We suspect that the water-soluble PEG molecules located at the polymer–SiO₂ interface were readily dissolved. As a result, the polymer film detached from the Si wafer after the PEG molecules were removed by water. On the other hand, the thin film lacking PEG molecules remained strongly bonded to the Si wafer after treatment in the water bath [Fig. 3(b)]. Because the hydrophobic P3HT and PCBM species repelled water molecules, the polymer–SiO₂ interface was barely affected after treatment in the water bath.

We used X-ray photoelectron spectroscopy (XPS) to further study the surfaces of the transferred thin films. Fig. 4 presents the O 1s core level spectra of the polymer blends containing PEG spin-coated on the Si wafers. The spectrum of the surface of the thin film on the Si wafers after UV-O₃ treatment exhibited a peak at 532.5 eV, which we assign to the C–O bonds of the PCBM and/or PEG molecules. In contrast, the O 1s core level spectrum of the thin film on the PET substrate, which had been transferred from the Si wafer, featured an intense peak at a binding energy of 531.5 eV, which we assign to the O–H bonds of the PEG molecules. The high intensity of this peak suggests that this surface contained a high concentration of PEG. The dramatic difference between the two spectra indicates that the concentration of PEG on the top surface of the thin film on the Si wafer was much lower

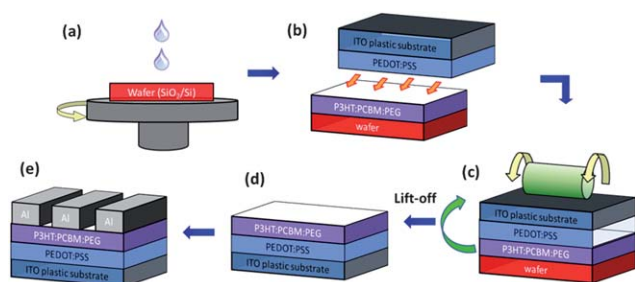


Fig. 1 Schematic representation of the transfer printing process for the preparation of flexible solar cells. (a) A photoactive layer is spin-coated on a Si wafer. (b) A PEDOT:PSS layer is spin-coated on a flexible PET substrate; the sample is then annealed at 110 °C for 15 min. (c) The two parts of the device are laminated together under moderate pressure. (d) The flexible substrate is lifted-off from the wafer; the photoactive layer is then transferred from the donor substrate to the plastic substrate. (e) The cathode is thermally deposited.

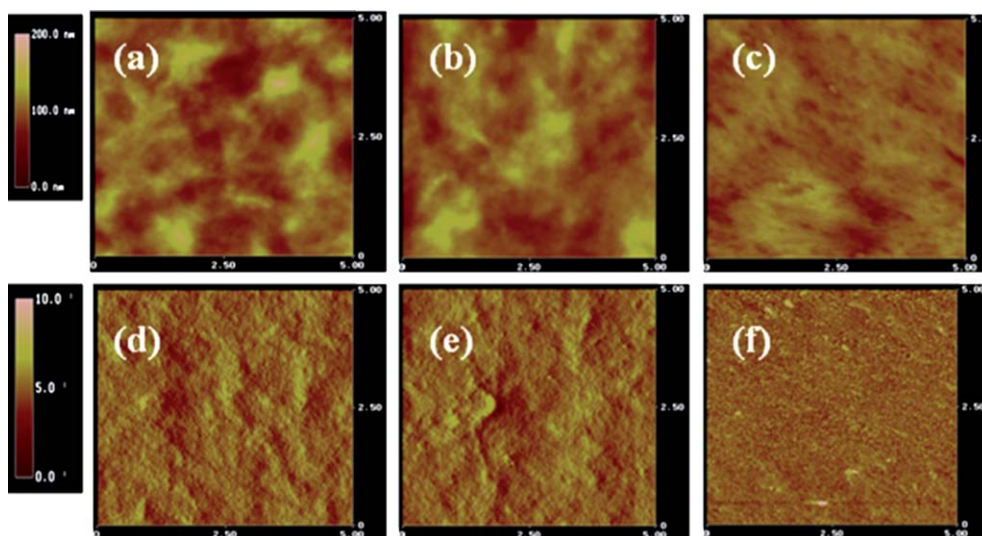


Fig. 2 (a, b) AFM height-mode images of the P3HT:PCBM films deposited on a SiO₂ surface (a) before and (b) after the addition of 5 wt% PEG. (d, e) AFM phase-mode images of the P3HT:PCBM films deposited on a SiO₂ surface (d) before and (e) after the addition of 5 wt% PEG. (c) Height-mode and (f) phase-mode AFM images of P3HT:PCBM:PEG blend films, incorporating weight ratios of PEG of 5 wt%, transferred from SiO₂ surfaces to PET substrates. All the image sizes are 5 μm × 5 μm.

than that on the bottom surface. Thus, the XPS data support the formation of a PEG “layer” at the polymer–SiO₂ interface.

To further investigate the origin of the self-organized interfaces, we treated the SiO₂ surface with hexamethyldisilazane (HMDS) vapors and then used XPS to study the interfaces of the polymer films deposited on the treated wafers. Fig. 4 reveals that the spectrum of the surface of the thin film transferred from the HMDS-treated wafer exhibited a peak near to 532.5 eV, suggesting a composition similar to that of the film deposited on the SiO₂ surface after UV-O₃ treatment. We could not, however, find any signals representing the presence of the O–H bonds of PEG molecules. Thus, the distribution of PEG molecules was different after the transfer printing of the two different polymer films. Because the HMDS-modified surface was relatively hydrophobic, its surface properties might not have been favorable for the vertical phase segregation of PEG to the SiO₂ substrate surface. Notably, the spectrum of the surface of the film on the HMDS-treated Si wafer (prior to transfer printing) exhibited a peak at 533.0 eV, which we attribute to the C–O–C bonds of PCBM. Although PEG also contains C–O–C bonds, the absence of O–H bonds (531.5 eV) excludes the possibility that it was responsible for this signal. Because the SiO₂ surface became

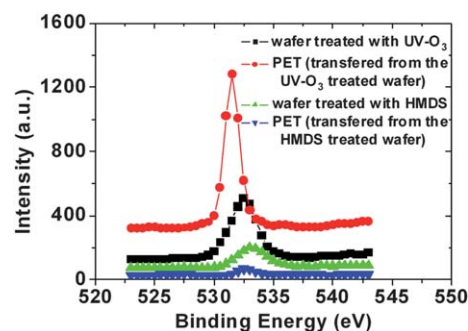


Fig. 4 Normalized O 1s core level spectra recorded from the surfaces of thin films (i) deposited on a wafer treated with UV-O₃; (ii) transferred from the treated wafer to a PET substrate; (iii) deposited on a wafer treated with HMDS vapor; and (iv) transferred from the HMDS-treated wafer to a PET substrate. The PEG concentration in each thin film was 5 wt%.

hydrophobic after treatment with HMDS, the PCBM molecules tended to appear at the top surface of the polymer blend. More interestingly, after we dipped the HMDS-treated sample into a water bath, the polymer film was shed and turned into many small pieces [Fig. 3(c)]. We infer that water molecules readily

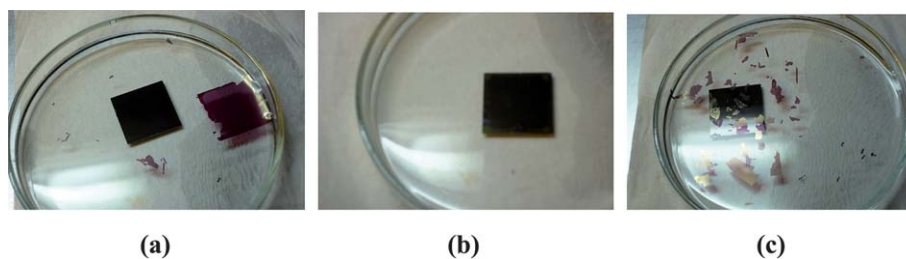


Fig. 3 Photographs of samples prepared under various conditions after treatment in a water bath. (a) Sample prepared with PEG; the substrate had been treated with UV-O₃. (b) Sample prepared without PEG; the substrate had been treated with UV-O₃. (c) Sample prepared with PEG; the substrate had been treated with HMDS.

passed through the polymer film after dissolution of the PEG units, due to the rather uniform distribution of PEG. Thus, the water bath experiments (Fig. 3) revealed that the surface properties of the substrate had a pronounced effect on the distribution of the PEG molecules.

Our results suggest that the self-organized PEG molecules functioned to weaken the chemical bonds between the polymer blends and the SiO₂ surface. In the transfer printing process, after we had applied appropriate pressure and moderate thermal treatment to the substrates, the adhesion strength between the molecules at the top of the polymer thin film and the PEDOT:PSS molecules became stronger than the bonding between the polymer blend and the SiO₂ surface. Hence, the photoactive layer could be delaminated and transferred onto the flexible target substrate.

Fig. 5 presents the photocurrent–voltage (J – V) curves of the devices prepared on ITO-coated PET substrates under AM 1.5 illumination (100 mW cm⁻²). The standard device, in which the P3HT:PCBM thin film was prepared through spin-coating, exhibited a short-circuit current density (J_{sc}) of 8.21 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.47 V, and a fill factor (FF) of 0.52, yielding a power conversion efficiency (PCE) of 2.02%. This slightly lower efficiency, relative to that of the device prepared on a glass substrate, was probably due to the higher resistance of the ITO films on the PET substrates; the sheet resistance of an ITO film on a typical glass substrates is 6 Ω sq⁻¹, increasing to 30 Ω sq⁻¹ on PET substrates. After the addition of 5 wt% of PEG in the photoactive layer, the values of J_{sc} and V_{oc} were both improved (to 0.51 V and 9.47 mA cm⁻², respectively); although the FF decreased to 0.47, the PCE underwent a slight increase (to 2.25%). The improved device performance of the PEG-containing device is consistent with previous reports.^{31,37} We suspect that the addition of PEG improved the device performance as a result of better contact at the cathode. The device fabricated using the transfer printing process exhibited a value of J_{sc} of 7.86 mA cm⁻², a value of V_{oc} of 0.53 V, and a FF of 0.52; its calculated PCE of 2.16% is comparable with the value of the standard device prepared using spin-coating. Notably, the value of V_{oc} (0.53 V) was larger than those of the other devices, presumably because the residual PEG molecules on the thin film surface after transfer printing reacted with the Al atoms and decreased the energy

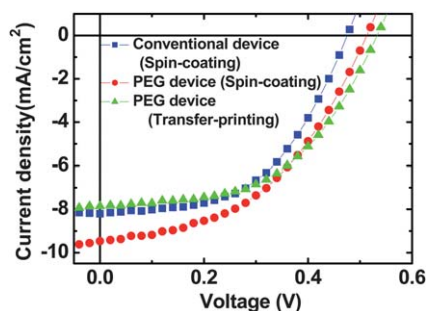


Fig. 5 J – V characteristics (measured under AM 1.5 G illumination at 100 mW cm⁻²) of a conventional P3HT:PCBM-containing device prepared through spin-coating (■), a device featuring an active layer containing PEG fabricated through spin-coating (●), and a device featuring an active layer containing PEG fabricated through transfer-printing (▲).

barrier at the cathode.^{31,38} The other possibility of the improvement is the increase of the build-in potential across the device, thereby improving the charge transportation.³⁷ In other words, residual PEG on the surface might also have a beneficial effect on device performance.

Conclusions

We have fabricated flexible polymer photovoltaic devices using a transfer printing process without the need for elastic stamps (e.g., PMDS). Doping PEG molecules into the P3HT/PCBM blend allowed the photoactive layer to be readily lifted-off and transferred from a rigid stamp (e.g., Si wafer) to a flexible substrate. A device fabricated using this transfer printing process had characteristics similar to those of the corresponding device prepared using a spin-coating process. Using hard stamps should help to realize the low-cost, high-throughput roll-to-roll fabrication of flexible solar cells; in addition, it should improve the reliability of the process and eliminate the complicated fabrication of elastic stamps.

Acknowledgements

This study was supported by the National Science Council (grant Nos. NSC 99-2221-E-009-181 and NSC 98-ET-E-009-005-ET) and the Ministry of Education through the ATU Program.

References

- 1 S. Reineke, F. Lindner, G. Schwartz, N. Sidler, K. Walzer, B. Lüssem and K. Leo, *Nature*, 2009, **459**, 234.
- 2 S. R. Forrest, *Nature*, 2004, **428**, 911.
- 3 L. M. Chen, Z. Hong, G. Li and Y. Yang, *Adv. Mater.*, 2009, **21**, 1434.
- 4 G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323.
- 5 T. Someya, Y. Kato, S. Iba, Y. Noguchi, T. Sekitani, H. Kawaguchi and T. Sakurai, *IEEE Trans. Electron Devices*, 2005, **52**, 2502.
- 6 X. Xu, M. Davanco, X. F. Qi and S. R. Forrest, *Org. Electron.*, 2008, **9**, 1122.
- 7 S. H. Ahn and L. J. Guo, *ACS Nano*, 2009, **3**, 2304.
- 8 H. J. Park, M. G. Kang, S. H. Ahn and L. J. Guo, *Adv. Mater.*, 2010, **22**, E247.
- 9 F. C. Chen, J. L. Wu, C. L. Lee, W. C. Huang, H. M. P. Chen and W. C. Chen, *IEEE Electron Device Lett.*, 2009, **30**, 727.
- 10 D. H. Wang, D. G. Choi, K. J. Lee, S. H. Im, O. O. Park and J. H. Park, *Org. Electron.*, 2010, **11**, 1376.
- 11 J. B. Emah, R. J. Curry and S. R. P. Silva, *Appl. Phys. Lett.*, 2008, **93**, 103301.
- 12 J. F. Chang and H. Sirringhaus, *Adv. Mater.*, 2009, **21**, 2535.
- 13 K. H. Yim, Z. J. Zheng, Z. Liang, R. H. Friend, W. T. S. Huck and J. S. Kim, *Adv. Funct. Mater.*, 2008, **18**, 1012.
- 14 Y.-H. Niu, M. S. Liu, J.-W. Ka, J. Bardeker, M. T. Zin, R. Schofield, Y. Chi and A. K.-Y. Jen, *Adv. Mater.*, 2007, **19**, 300.
- 15 W. Ma, P. K. Iyer, V. Gong, B. Liu, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2005, **17**, 274.
- 16 Y.-L. Loo, R. L. Willett, K. W. Baldwin and J. A. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 7654.
- 17 Y. L. Loo, R. L. Willett, K. W. Baldwin and J. A. Rogers, *Appl. Phys. Lett.*, 2002, **81**, 562.
- 18 M. L. Chabiny, A. Salleo, Y. Wu, P. Liu, B. S. Ong, M. Heaney and I. McCulloch, *J. Am. Chem. Soc.*, 2004, **126**, 13928.
- 19 T. W. Lee, J. Zaumseil, Z. Bao, J. W. P. Hsu and J. A. Rogers, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 429.
- 20 T. W. Lee, J. Zaumseil, S. H. Kim and J. W. P. Hsu, *Adv. Mater.*, 2004, **16**, 2040.
- 21 T. W. Lee, *Adv. Funct. Mater.*, 2007, **17**, 3128.
- 22 M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson and R. H. Friend, *Nature*, 1998, **395**, 257.

- 23 T. F. Guo, S. Pyo, S. C. Chang and Y. Yang, *Adv. Funct. Mater.*, 2001, **11**, 339.
- 24 J. Huang, G. Li and Y. Yang, *Adv. Mater.*, 2008, **20**, 415.
- 25 H. Kim, B. Yoon, J. Sung, D. G. Choi and C. Park, *J. Mater. Chem.*, 2008, **18**, 3489.
- 26 L. C. Chen, P. Degenaar and D. D. C. Bradley, *Adv. Mater.*, 2008, **20**, 1679.
- 27 J. H. Huang, Z. Y. Ho, T. H. Kuo, D. Kekuda, C. W. Chu and K. C. Ho, *J. Mater. Chem.*, 2009, **19**, 4077.
- 28 V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Adv. Funct. Mater.*, 2006, **16**, 2016.
- 29 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 4864.
- 30 G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang and Y. Yang, *Adv. Funct. Mater.*, 2007, **17**, 1636.
- 31 F. C. Chen and S. C. Chien, *J. Mater. Chem.*, 2009, **19**, 6865.
- 32 X. Zheng, L. M. Chen, G. Yang, C. H. Huang, J. Hou, Y. Wu, L. Gang, C. S. Hsu and Y. Yang, *Adv. Funct. Mater.*, 2009, **19**, 1227.
- 33 S. Goffri, C. Muller, N. Stingelin-Stutzmann, D. W. Breiby, C. P. Radano, J. W. Andreasen, R. Thompson, R. A. J. Janssen, M. M. Nielsen, P. Smith and H. Sirringhaus, *Nat. Mater.*, 2006, **5**, 950.
- 34 A. C. Arias, F. Endicott and R. A. Street, *Adv. Mater.*, 2006, **18**, 2900.
- 35 L. Qiu, J. A. Lim, X. Wang, W. H. Lee, M. Hwang and K. Cho, *Adv. Mater.*, 2008, **20**, 1141.
- 36 Q. Wei, T. Nishizawa, K. Tajima and K. Hashimoto, *Adv. Mater.*, 2008, **20**, 2250.
- 37 T. Zhang, M. Ceder and O. Inganas, *Adv. Mater.*, 2007, **19**, 1835.
- 38 T. H. Lee, J. C. A. Huang, G. L. Pakhomov, T. G. Guo, T. C. Wen, Y. S. Huang, C. C. Tsou, C. T. Chung, Y. C. Lin and Y. J. Hsu, *Adv. Funct. Mater.*, 2008, **18**, 3036.