Conducting and transparent single-wall carbon nanotube electrodes for polymer-fullerene solar cells

Aurelien Du Pasquier, Husnu Emrah Unalan, Alokik Kanwal, Steve Miller, and Manish Chhowalla

Rutgers University, Materials Science and Engineering Department, 607 Taylor Road, Piscataway, New Jersey 08854

We describe the use of single-wall carbon nanotube (SWNT) thin films as transparent and conducting electrodes for hole collection in poly(hexyl)thiophene-[6-6]phenyl-C_{61}-butyric acid methyl ester (P3HT-PCBM) organic photovoltaics. We report a power conversion efficiency of 1%, with a fill factor of 0.3 and a short-circuit current of 6.5 mA/cm^2 under 100 mW/cm^2 polychromatic white light illumination measured in air. These values are comparatively higher than reference cells of similar thickness made on indium tin oxide (ITO) glass substrates. This is attributed to the three-dimensional nature of the interface between the SWNTs and the P3HT-PCBM nanocomposite. Our results indicate that solution processed SWNT thin films are a viable alternative to ITO for photovoltaic devices, eliminating an expensive vacuum deposition step in the fabrication of organic solar cells. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2132065]

Organic solar cells are a promising low-cost alternative to silicon solar cells and thus a great deal of effort is being devoted, in both academic and industrial laboratories, to increase the power conversion efficiency and scale-up production processes. One of the most studied systems is based on mixtures of conjugated polymers and fullerenes.[1–5] To date, phenyl-C_{61}-butyric acid methyl ester (PCBM) with conjugated polymers has become the standard for fabrication of plastic solar cells with the highest efficiency.[6–8] In addition to efficient exciton dissociation from PCBM, maximum charge collection also requires efficient hole transport through the polymer. P3HT appears to be the best candidate as the hole transport medium owing to its relatively high mobility of around 10^{-3} cm^2 V^{-1} s^{-1} (Ref. 9) and higher field effect mobility which can be as high as 0.1–0.2 cm^2 V^{-1} s^{-1} in high quality samples.[10,11] P3HT has a band gap ranging from 1.8 to 2.1 eV and is relatively stable. Indeed, solar to electrical power conversion efficiency of the P3HT-PCBM system has steadily improved during the past few years. In 2004, efficiency of 3.8% and short-circuit current up to 15 mA/cm^2 measured under air mass (AM) 1.5 simulated solar light and in a controlled atmosphere were reported.[12] However, it should be noted that such high efficiencies ($>2\%$) are only achieved if the devices are fabricated and measured in a controlled atmosphere such as a glovebox.

In most photovoltaic devices, the transparent conducting electrode is indium tin oxide (ITO) coated. Recent studies[13] have pointed out that the conductivity of ITO is a source of series resistance which decreases the fill factor and hence decreasing power conversion efficiency, especially in large area devices. It is also desirable to increase the work function of the transparent electrode in order to increase the built in potential of the photovoltaic devices.

Recently, Wu *et al.*[14] reported that a continuous film of high purity single-wall carbon nanotubes (SWNTs) could be a new class of transparent conducting material with transparency and sheet resistance comparable to ITO. Here we report on the use of transparent and conducting SWNT thin films as the hole collection electrode in organic photovoltaics.

Kymakis and Amaratunga[15] used SWNTs as electron acceptors via creation of nano heterojunctions with poly(3-octyl)thiophene (P3OT) for exciton dissociation. In their work,[15] subsequent to exciton dissociation, the electrons are injected into the SWNTs which act as the electron transport medium (similar to PCBM in our devices). In contrast, the exciton dissociation in our devices occurs at the P3HT/PCBM interface and holes are transported through the polymer to the transparent and conducting SWNT electrode. Thus, SWNT thin films are simply a replacement of ITO for hole collection. Our results indicate that photovoltaic devices with the SWNTs are superior to comparable devices fabricated using ITO when tested under the same conditions.

A range of six different film thicknesses (30–200 nm) was deposited by varying the volume of SWNT suspension filtered by 10 ml increments, from 10 to 60 SWNTs used in this work were purchased from Carbon Nanotechnologies, Inc. (batch R0496). The scanning electron microscopy images of a continuous SWNT thin film deposited using a 50 ml suspension and one discontinuous film deposited using 10 ml solution are shown in Fig. 1. The image in Fig. 1(a) shows that the SWNTs are distributed uniformly on the surface of the glass substrate while uncovered regions on the substrate can be clearly seen in Fig. 1(b).

The transmission spectra of the six thin films prepared from the suspensions are shown in Fig. 2(a). The data in the figure show a relatively homogeneous transmission from 250
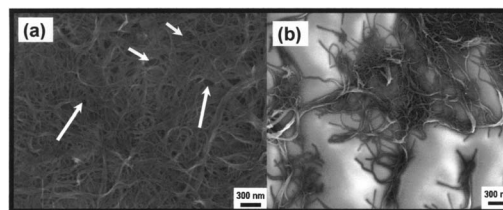

FIG. 1. SEM images of SWNT films deposited on glass, from 50 ml SWNT solution (a) and 10 ml SWNT solution (b). The arrows on image (a) indicate the presence of voids that illustrate the three-dimensional nature of the coating.
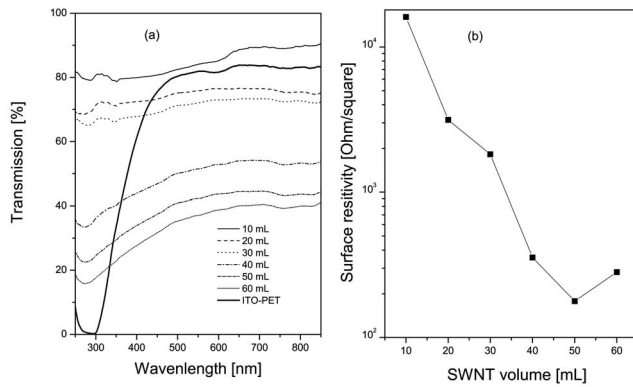
FIG. 2. Transmission spectra of the SWNT-glass samples and an ITO-PET substrate. (a) The panel (b) shows surface resistivity vs SWNT volume used for filtration coating of all the SWNT-glass samples.

to 850 nm and illustrate the influence of film thickness on transparency. Thin films ($<$100 nm, suspension volume less than 30 ml), exhibit higher transparency than ITO-PET (up to 80% transmission). It is also worth noting that the films are transparent in the UV, which is not the case for ITO-PET.

The surface resistivity measurements were obtained by performing a $+/-1$ V I-V scan at a sweep rate of 100 mV/s between two gallium contacts of diameter $D=1.5$ mm and separated by a distance $L=3$ mm. The formula used to calculate surface resistivity was $\rho=(V/L)/(I_s/D)$, where V is the voltage and I_s is the current across the measured area. The V/I_s ratio was obtained from the slope of the I-V scans, which were perfectly linear over the voltage range tested. The lowest resistivity measured was 282 Ω/square for 50 ml SWNT. This compares to 25 Ω/square for the ITO-glass substrates. The variation of the surface resistivity with the SWNT volume of the suspension used to prepare the samples is shown in Fig. 2(b).

Bulk-heterojunction solar cells [see schematics in Fig. 3(a) and 3(b)] were prepared from a 2.5 g/l solution of P3HT:PCBM 1:1.1 in chlorobenzene. A layer of poly(eth-ylenedioxy) thiophene:poly(styrene) sulfonate (PEDOT:PSS) (Baytron P: MeOH 1:2) was spin coated on the SWNT-quartz substrates and on the ITO-glass reference substrates. Gallium–indium eutectic was used for the contacts to the SWNT and the P3HT: PCBM layer. The photoactive area tested was 0.07 cm^2. An o ring of 3 mm diameter was used to contain the gallium–indium droplet and control the back contact area. Gallium–indium which melts at 15.7 °C is convenient for making contacts without an evaporator and has a work function of 4.2 eV, slightly lower than the 4.3 eV of aluminum. The higher sensitivity of Ga to oxygen in comparison to Al is a concern because it may limit device performance and lifetime. Therefore, the actual device characteristics with Al may be better than those reported here.

The photovoltaic characteristics were evaluated using glass-SWNT/PEDOT: PSS/P3HT: PCBM 1:1/Ga devices fabricated using the 6 SWNT films as well as a reference ITO-glass substrate. PEDOT: PSS was used in the SWNT thin film devices because we also used it in the reference cells. The devices were optimized by annealing up to 100 °C in air by illumination while monitoring the evolution of photovoltaic device characteristics. When a maximum conversion efficiency was achieved, the devices were allowed to cool to room temperature and I-V measurements at various light intensities were taken. The current density versus volt-
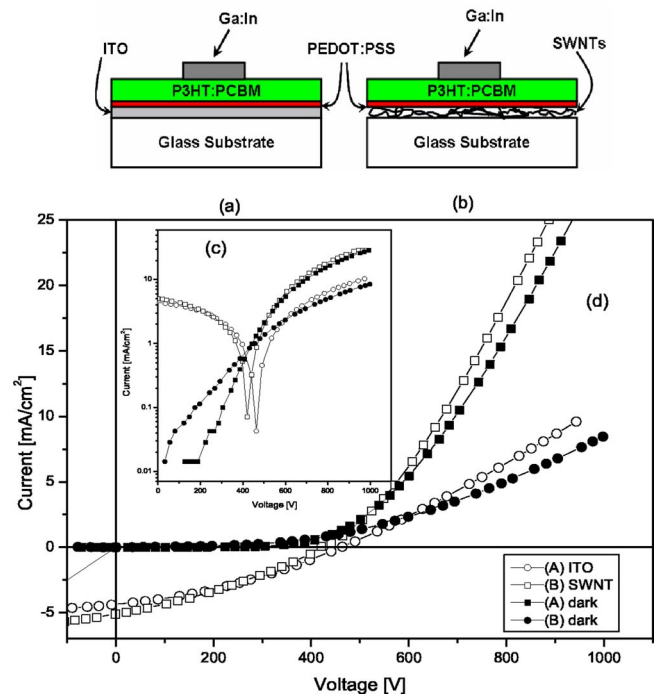

FIG. 3. Schematic of the devices with ITO (a) and SWNT thin film (b) as the anodes are shown in the upper panel. The corresponding I-V curves at 100 mW/cm^2 halogen white light and in the dark of reference solar cell on ITO-glass substrate and best solar cell using a SWNT-glass current collector are shown. (c) The log I-V characteristics of the ITO and SWNT thin film devices under illumination are shown in the inset.

age in dark and under illumination (100 mW/cm^2) with ITO and SWNT hole collector electrodes, respectively, are plotted in Fig. 3(c). The significantly higher dark current under forward bias (positive voltage on transparent and conducting electrode) indicates distinct diode behavior. The log I-V characteristics of our devices are shown in the inset of Fig. 3(c). Fill factor and open-circuit voltage for our devices are lower than best published results, which we attribute to the fact that we fabricated and measured our devices in air and used Ga–In as the electrode material. In addition, these devices have yet to be optimized. Thicker than optimum (800 vs 100 nm) polymer thin films by drop casting were used in the experiment reported here. Nevertheless, the drop-cast reference cells of same thickness on glass-ITO/PEDOT:PSS from the same solution yielded a similar fill factor of 0.3 but lower photocurrents of 5 mA/cm^2 compared to 6.65 mA/cm^2 at 100 mW/cm^2 of white light [see Figure 3(c)]. Hence, the cells using SWNT anode had a higher conversion efficiency of 0.99%, vs 0.69% for the reference cells.

In order to confirm that the improved efficiency in our devices is attributed to the incorporation of SWNT thin film electrode and not PEDOT:PSS, we fabricated additional cells without the PEDOT:PSS layer on SWNT electrodes. Our experiments revealed that for thin P3HT-PCBM films (2.5 g/l), the devices shorted in the absence of PEDOT:PSS. However, working cells with efficiency values lower than our best devices were obtained for thicker P3HT-PCBM films (10 g/l). On the other hand, devices fabricated using only PEDOT: PSS coated on glass as the anode layer without SWNT thin films yielded extremely low currents. Therefore we argue that SWNT thin film electrodes play an essential role in hole collection and in-plane conductivity of our photovoltaic devices. Our interpretation is that since SWNTs are a mixture
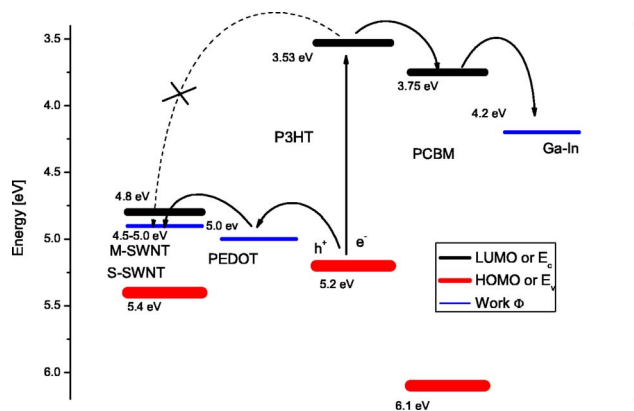
FIG. 4. Energy level diagram adjusted in relation to the vacuum level for the SWNT/ PEDOT/ P3HT: PCBM/Ga–In device. The arrows indicate hole and electron flows. The references used to build this energy diagram are the following: Ref. 16, Ref. 17, Ref. 18. M-SWNTs and s-SWNTs refer to metallic and semiconducting SWNTs, respectively.

of metallic and *p*-doped nanotubes, PEDOT:PSS is necessary to adjust the SWNT work function for hole collection and avoid device shorting by having the metallic nanotubes transport electrons from the PCBM network to the transparent electrode. The charge transfer and transport in the SWNT/P3HT+PCBM/Ga system can be understood from the energy diagram shown in Fig. 4. Excitons are generated in the P3HT, and hole transfer is possible through the PEDOT and the conduction band of the semiconducting SWNTs (s-SWNTs). Electrons are injected in the lowest unoccupied molecular orbital of PCBM, then collected by the Ga–In contact. In theory, electron transfer is also possible in the metallic SWNTs (*m*-SWNTs), which could account for some exciton dissociation. However, in our device configuration, the SWNT network is not in direct contact with the top Ga–In electrode, making electron collection unlikely. Thus, in our case, the SWNTs only serve as hole conducting network.

Although we found the maximum transmission in the 10 ml sample, we obtained the best photovoltaic characteristics with the 50 ml sample ($t=300$ nm), the one having the lowest surface resistivity. We also observed a general trend of an increase in performance with the increase in SWNT thickness. A comparison of the photovoltaic characteristics of devices fabricated on ITO and transparent and conducting SWNTs is given in Table I. It can be seen that the photovoltaic performance of the SWNT devices is significantly improved relative to those with ITO. A similar improvement in hole collection by multiwall carbon nanotubes (MWNTs) over a planar ITO contact has been demonstrated by Ago *et al.* with MWNT/PPV/Al devices.[19] Here, we combined this effect with the efficient exciton dissociation provided by in-

corporating a fullerene derivative in the conjugated polymer.

A closer observation of the scanning electron microscope (SEM) image in Fig. 1(a) reveals the presence of voids in the SWNT thin film 3D network. The substrate is clearly visible at the bottom of these voids as indicated by the arrows in Fig. 1(a). The presence of the voids is an important factor in understanding our results. We argue that the PEDOT:PSS and P3HT+PCBM mixture infiltrate the voids when deposited on top of the SWNT thin films. Thus some of the PEDOT:PSS and P3HT+PCBM is essentially deposited on the surface of the glass substrate while being in intimate electrical contact with the SWNTs. That is, although the overall transparency of the 50 ml film is lower in comparison to ITO, the presence of the voids in the 3D SWNT network provides sufficient exposure of the nanocomposite to the illumination to efficiently create excitons at the P3HT/PCBM interface and collect holes at the SWNT electrode. Thus, in contrast to planar configuration of ITO, beneficial effects of bulk heterojunction are also likely to play a role in enhancing the performance of SWNT electrode devices. We attribute the main limitation in efficiency to the excessive thickness of the devices (800 nm).

In conclusion, our promising result suggests that SWNT thin films can be used as transparent conducting current collectors in organic solar cells and could even be a source of performance improvement due to the 3D connection with the photoactive composite. The work function of the SWNTs has been reported to be between 4.5 and 5 eV, which is in the same range as ITO and thus it is very well suited for hole collection.

TABLE I. Solar cell parameters at 100 mW/cm^{2} illumination for the reference cell on ITO-PET substrate and the best solar cell on SWNT-glass substrate.

Values@100 mW/cm^2	ITO-glass drop cast reference	Best SWNT-glass drop cast
% efficiency	0.69	0.99
FF	0.32	0.3
I_{sc}(mA/cm^2)	5	6.65
V_{oc}(mV)	426	500

[1]N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).

[2]G. Zerza, C. J. Brabec, G. Cerullo, S. De Silvestri, and N. S. Sariciftci, Synth. Met. **119**, 637 (2001).

[3]N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Synth. Met. **59**, 333 (1993).

[4]C. J. Brabec, G. Zerza, G. Cerullo, S. De Silvestri, S. Luzzati, J. C. Hummelen, and S. Sariciftci, Chem. Phys. Lett. **340**, 232 (2001).

[5]K. Yoshino, X. H. Yin, S. Morita, T. Kawai, and A. A. Zakhidov, Solid State Commun. **85**, 85 (1993).

[6]G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).

[7]C. J. Brabec, F. Padinger, J. C. Hummelen, R. A. J. Janssen, and N. S. Sariciftci, Synth. Met. **102**, 861 (1999).

[8]D. Chirvasse, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, and J. C. Hummelen, Synth. Met. **138**, 299 (2003).

[9]S. S. Pandey, W. Takashima, S. Nagamatsu, T. Endo, M. Rikukawa, and K. Kaneto, Jpn. J. Appl. Phys., Part 1 **39**, 94 (2000).

[10]Z. Bao, A. Dodabalapur, and A. J. Lovinger, Appl. Phys. Lett. **69**, 4108 (1996).

[11]H. Sirringhaus, N. Tessler, and R. H. Friend, Science **280**, 1741 (1998).

[12]C. Waldauf, P. Schilinsky, J. Hauch, C. J. Brabec, Thin Solid Films **451–452**, 503 (2004).

[13]J. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, Appl. Phys. Lett. **84**, 3013 (2004).

[14]Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler, Science **305**, 1273 (2004).

[15]E. Kymakis, I. Alexandrou, and G. A. J. Amaratunga, J. Appl. Phys. **93**, 1764 (2003).

[16]B. J. Landi, S. L. Castro, H. J. Ruf, C. M. Evans, S. G. Bailey, and R. P. Raffaelle, Sol. Energy Mater. Sol. Cells **87**, 733 (2005).

[17]D. Chirvase, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, and J. C. Hummelen, Synth. Met. **138**, 299 (2003).

[18]Maher Al-Ibrahim, Steffi Sensfuss, Jutta Uziel, Gernot Ecke, Oliver Ambacher, Sol. Energy Mater. Sol. Cells **85**, 277 (2005).

[19]H. Ago, K. Petritsch, M. S. P. Shaffer, A. H. Windle, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **11**, 1281 (1999).