Metal grid/conducting polymer hybrid transparent electrode for inverted polymer solar cells

Jingyu Zou, Hin-Lap Yip, Steven K. Hau, and Alex K.-Y. Jen

View Online

Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Metal grid/conducting polymer hybrid transparent electrode for inverted polymer solar cells

Jingyu Zou,[1] Hin-Lap Yip,[1,2] Steven K. Hau,[1] and Alex K.-Y. Jen[1,2,a]

[1]*Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195, USA*
[2]*Institute of Advanced Materials and Technology, University of Washington, Seattle, Washington 98195, USA*

A simple method was developed using metal grid/conducting polymer hybrid transparent electrode to replace indium tin oxide (ITO) for the fabrication of inverted structure polymer solar cells. The performance of the devices could be tuned easily by varying the width and separation of the metal grids. By combining the appropriate metal grid geometry with a thin conductive polymer layer, substrates with comparable transparency and sheet resistance to those of ITO could be achieved. Polymer solar cells fabricated using this hybrid electrode show efficiencies as high as ~3.2%. This method provides a feasible way for fabricating low-cost, large-area organic solar cells. © *2010 American Institute of Physics*. [doi:10.1063/1.3394679]

Polymer solar cells (PSCs) are becoming as a viable technology for low-cost power production.[1] Indium tin oxide (ITO) is the most commonly used transparent electrode for PSCs because it offers good transparency in the visible range of the solar spectrum as well as good electrical conductivity. However, there are several deficiencies that exist for using ITO such as poor mechanical properties of ITO-coated plastic substrates,[2] limited conductivity for fabricating large-area solar cells, limited availability of indium, and complicated vacuum sputtering process tend to increase the cost for ITO. These limitations set a potential barrier for the commercialization of low-cost PSCs. To alleviate this problem, alternative materials for transparent conducting electrodes are needed to replace ITO. There has been some research on exploring conductive polymers,[2] carbon nanotubes,[3] graphenes,[4] and silver nanowires[5] as potential candidates to replace ITO. However, lower transparency and higher sheet resistance compared to ITO strongly hinder their use for transparent electrode. Metal grids have also been investigated as a promising alternative for transparent electrode.[6,7] Utilizing microfluidic deposition and nanoimprinting methods, metal grids coated substrates have been used for fabricating conventional PSCs with PCE as high as 2%.

Previously, inverted architecture PSC using ITO as cathode and evaporated silver (Ag) as anode has been proved to be more stable in ambient than the conventional devices using sensitive metal as cathode.[8] Moreover, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) has also been demonstrated by Hau *et al.*[9] as a potential replacement of ITO for fabricating inverted PSCs. However, the relatively high sheet resistance of PEDOT:PSS compared to ITO may limit the performance of PSCs The combination of conductive metal grids with PEDOT:PSS provides a good solution to solve this problem and obtain ITO-free and ambient stable PSCs.

Here, we report a simple method to fabricate high-efficiency ITO-free inverted structure PSCs using a metal grid/conducting polymer hybrid transparent electrode. By us-ing soft lithography and chemical etching, the metal grids can be easily fabricated on substrates. The inverted device architecture is used to fabricate PSCs with Ag as anode to collect holes and zinc oxide (ZnO) as an electron selective layer at the metal grid/conducting polymer interface to help collect electrons. To prepare the metal grids, a 1 nm aluminum (Al) film was deposited first followed by evaporating a 30 nm thick silver film onto the glass substrates. It was found that the very thin Al layer improves adhesion between the substrate and the Ag film.

A micropatterned photoresist (SU-8, MicroChem) film, fabricated by standard photolithography, was used as a master to replicate stamps for microcontact printing (μCP). A typical stamp was made by casting a 10:1 (v/v) mixture of polydimethyl siloxane (PDMS) and curing agent against a silanized master. The PDMS stamp was first soaked with an "ink" containing 1 mM of mecaptoundecanoic acid (MUA) in ethanol, then brought into contact with the surface of silver for 60 s. After the removal of the stamp, the patterned Ag film was developed by wet etching with aqueous Fe^{3+}/thiourea using the patterned SAM as resist.[10] MUA was chosen for both generating better wettability for the processing of upper layer film. and facilitating better charge collection.[11]

Three types of designed grids patterns were utilized as width and separation with (1) 5 μm and 50 μm (5 μm/50 μm), (2) 10 μm and 100 μm (10 μm/100 μm), (3) 20 μm and 200 μm (20 μm/200 μm), respectively. The optical transmittance of as-fabricated Ag grids was measured by UV-Vis spectroscopy (Fig. 1). The sheet resistance for metal grids with different geometries was also measured.

The transmittance of ITO at 550 nm is 85.7%. When the transmittance of glass (~93%) is taken into account, the maximum expected transmittance of the metal grids coated glass substrate is calculated to be ~83–84%. It was found that the average transmittance of metal grid coated glass substrates in the range of 250–1200 nm is 78%, 80%, and 82%, respectively, for grids of 5 μm/50 μm, 10 μm/100 μm, and 20 μm/200 μm. The lower transmission may be due to

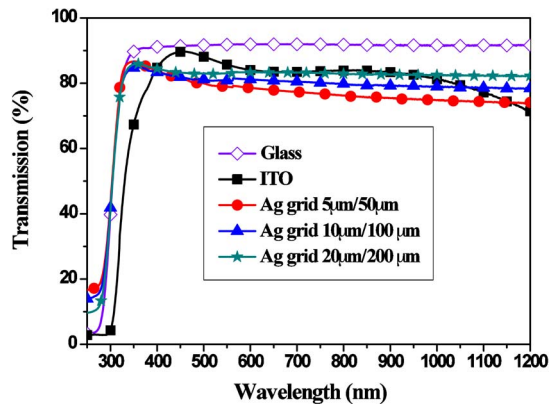[a]Electronic mail: ajen@u.washington.edu.

FIG. 1. (Color online) Transparency vs wavelength of different geometry Ag grids on glass as compared to transparency of ITO and glass, as referenced against air.

some diffusion of MUA during contact printing on the metal surface. As the result, the actual Ag grid patterns expand $1-2$ μm in width. Figure 2(a) shows the optical microscope images of an as-fabricated metal grid electrode on a glass substrate.

Another important parameter for transparent conducting electrodes is the sheet resistance. The sheet resistance of commercial available ITO substrates is 15 $\Omega\square^{-1}$, $\Omega\square$ while the Ag grid electrodes exhibited sheet resistances of 9.1 $\Omega\square^{-1}$,   146.3 $\Omega\square^{-1}$,   and   254.1 $\Omega\square^{-1}$,   for 5 μm/50 μm, 10 μm/100 μm, and 20 μm/200 μm, respectively. Lower sheet resistances will minimize the loss of photocurrent during charge transport due to the lowered lateral resistance of the electrode. In general, the transmittance and sheet resistance for thin conductive films are related by the equation of

$$T(\lambda) = \left[1 + \frac{188.5}{R_s} \frac{\sigma_{Op}(\lambda)}{\sigma_{DC}} \right]^{-2},$$

where $\sigma_{Op}(\lambda)$ is the optical conductivity (here we quoted at $\lambda = 550$ nm) and σ_{DC} is the conductivity of the film. σ_{DC}/σ_{Op} is a commonly used term to describe transparent conductors.[12] For ITO with R_s of $15\Omega\square^{-1}$ and T(550 nm) of 85.7%, the σ_{DC}/σ_{Op} is 156.7. The best results that have been achieved for the graphene-based films[13] and carbon nanotubes[14] are 0.5 and 25, respectively. Based on the best metal grid geometry used in this work (5 μm/50 μm), R_s =9.1 $\Omega/\square$, and T(550 nm)=79.0%, a σ_{DC}/σ_{Op} ratio as high as 165.6 could be achieved.

To fabricate solar cells, the ITO substrate and the metal grids coated substrate were cleaned using standard cleaning procedures. A thin layer of ZnO nanoparticles (ZnO NPs)
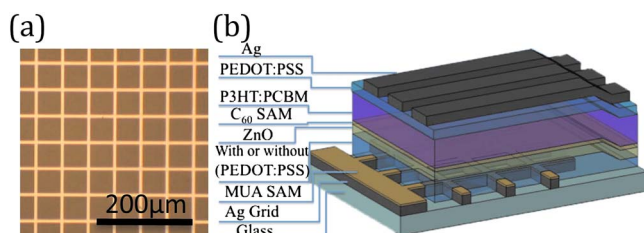

FIG. 2. (Color online) (a) Optical microscope image of silver grid with 5 μm width separated by a distance of 50 μm. (b) Device configuration of the polymer solar cell using Ag grid as the transparent electrode with or without conductive PEDOT:PSS layer.
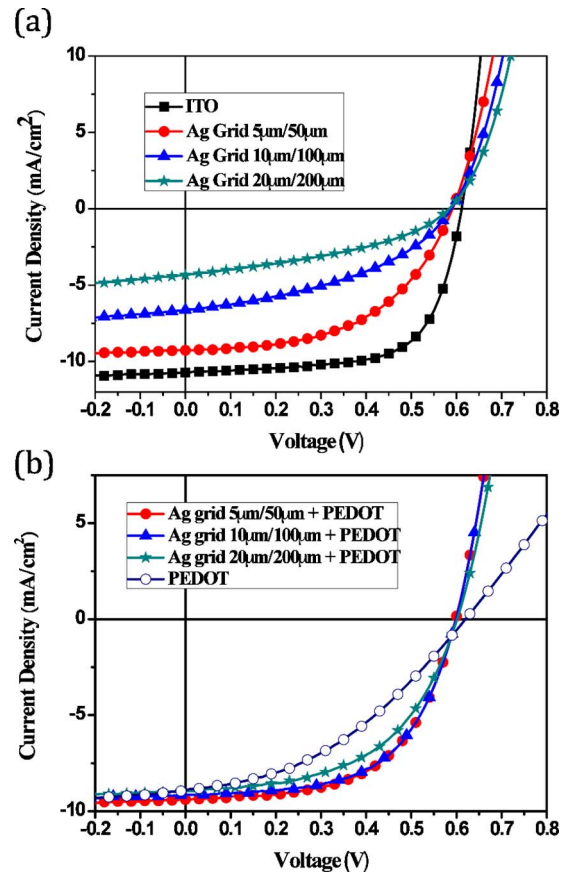

FIG. 3. (Color online) The current density-voltage ($J-V$) characteristics of polymer solar cells with (a) different Ag grid geometries (b) different Ag grid geometries combining 40nm PEDOT:PSS PH500 film measures under AM1.5 illumination from a calibrated solar simulator with a light intensity of 100 mW cm^{-2}.

was spin-coated onto these substrates. A C_{60}-based SAM (C_{60}-SAM) was deposited onto the ZnO surface using a spin-coating process as reported previously.[15] A 200nm bulk-heterojunction film comprising of poly (3-hexylthiophene) (P3HT) (Rieke Metals) and [6,6] phenyl C_{61} butyric acid methyl ester (PCBM) (American Dye Source) was then spin-coated in an argon-filled glove box.

After depositing a 50 nm of PEDOT:PSS film (H. C. Starck, CLEVIOS™ P VP 4083).[8] A layer of Ag was vacuum deposited on top of PEDOT:PSS as anode. The solar cells were tested under ambient using a Keithley 2400 SMU and an Oriel Xenon lamp (450 W) with an AM 1.5 filter. The light intensity was calibrated to 100 mW/cm^2.

The device architectures are shown in Fig. 2(b). The J-V characteristics under illumination and the solar cells performance are summarized in Fig. 3(a) and Table I, respectively. The device with the 5 μm/50 μm Ag grid has the best performance with PCE of 2.97%. The lower efficiency of the metal grid substrate derived device is mainly due to lower J_{sc} and fill factor.

An important parameter that needs to be considered for the design of metal grids is that the charges generated from the voids between the grid lines need to be efficiently collected. The inverted device structure utilizes a ZnO NP layer as an electron selective layer between the active layer and the metal grids to collect electrons. The inhomogeneous and poor charge collection in the voids due to high sheet resistance of ZnO decrease both J_{sc} and fill factor. In addition,

TABLE I. Summary of PSCs performance with different Ag grids width and separation.

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	R_s (Ω cm^2)	R_p (Ω cm^2)
ITO	0.61	10.72	0.66	4.35	0.9	780.2
Ag Grid 5 μm/50 μm	0.60	9.57	0.52	2.97	2.8	1341.6
Ag Grid 10 μm/100 μm	0.59	6.62	0.42	1.65	3.0	327.4
Ag Grid 20 μm/200 μm	0.58	4.33	0.49	1.00	3.1	322.1
Ag Grid 5 μm/50 μm-PEDOT	0.60	9.39	0.57	3.21	2.8	1118.0
Ag Grid 10 μm/100 μm-PEDOT	0.60	9.14	0.58	2.93	2.9	1213.2
Ag Grid 20 μm/200 μm-PEDOT	0.60	8.95	0.53	2.85	3.0	956.3
PEDOT	0.62	8.91	0.40	2.20	30.7	365.1

the lower transmittance of the 5 μm/50 μm Ag grids ($\sim$78%) compared to ITO ($\sim$85%) also contributes to the decrease in J_{sc}.

Increasing the width and separation while maintaining the same aspect ratio dramatically reduces the J_{sc} and fill-factor. To alleviate the problem for poor charge collection, a PEDOT:PSS (H. C. Starck, CLEVIOS™ PH 500) conducting polymer was inserted between the silver grids and the ZnO layer to form the hybrid electrode.

To demonstrate the function of the hybrid electrode, an inverted photovoltaic device with 220 nm thick PEDOT:PSS PH500 film without metal grids as the bottom electrode was fabricated. The *J-V* characteristics under illumination and the solar cells performance are summarized in Fig. 3 and Table I, respectively. For the smaller separation Ag grids (5 μm/50 μm), the addition of the conducting PEDOT:PSS polymer layer improved the device performance to 3.21% due to the reduced lateral resistance. For devices using larger separation grid lines (10 μm/100 μm and 20 μm/200 μm), the addition of the PEDOT:PSS layer significantly improved the performance of the devices. For grids with separation distance of over 10 μm, additional layer of PEDOT:PSS is necessary to reduce the lateral resistance. All three silver grids electrodes can achieve near 3% PCE using the additional PEDOT:PSS layer. The potential benefit of using larger size grid patterns is the ease for device fabrication especially for cost efficient industrial roll-to-roll processing. Without Ag grids, PEDOT:PSS PH 500 bottom electrode devices can only have efficiency of $\sim$2.2% which is due to the high sheet resistance.

In conclusion, we have demonstrated that silver metal grid electrodes fabricated by microcontact printing and wet chemical etching can replace conventional ITO electrodes for fabricating organic solar cells. The patterned metal electrodes on glass show high optical transmittance as well as good electrical conductivity. Organic solar cells with optimized grid geometry show encouraging device performance. It was also found that silver grid electrodes with smaller width and separation with the same aspect ratio facilitated better charge collection from the ZnO NP layers leading to increased FF, J_{sc}, and PCE. By adding a PEDOT:PSS PH500 conducting polymer between Ag grid and ZnO, even devices with larger Ag grid spacing can achieve good performance. The use of inexpensive Ag grids compared to ITO allows the possibility of employing roll-to-roll process to realize low-cost, large-area organic solar cells.

[1]G. Dennler, M. C. Scharber, and C. J. Brabec, Adv. Mater. (Weinheim, Ger.) **21**, 1323 (2009).
[2]S. I. Na, S. S. Kim, J. Jo, and D. Y. Kim, Adv. Mater. (Weinheim, Ger.) **20**, 4061 (2008).
[3]M. W. Rowell, M. A. Topinka, M. D. McGehee, H. J. Prall, G. Dennler, N. S. Sariciftci, L. Hu, and G. Gruner, Appl. Phys. Lett. **88**, 233506 (2006).
[4]G. Eda, Y. Y. Lin, S. Miller, C. W. Chen, W. F. Su, and M. Chhowalla, Appl. Phys. Lett. **92**, 233305 (2008).
[5]J. Y. Lee, S. T. Connor, Y. Cui, and P. Peumans, Nano Lett. **8**, 689 (2008).
[6]K. Tvingstedt and O. Inganas, Adv. Mater. (Weinheim, Ger.) **19**, 2893 (2007).
[7]M. Kang, M. Kim, J. Kim, and L. J. Guo, Adv. Mater. (Weinheim, Ger.) **20**, 4408 (2008).
[8]S. K. Hau, H. L. Yip, N. S. Baek, J. Zou, K. O'Malley, and A. K.-Y. Jen, Appl. Phys. Lett. **92**, 253301 (2008).
[9]S. K. Hau, H. L. Yip, J. Zou, and A. K.-Y. Jen, Org. Electron. **10**, 1401 (2009).
[10]J. M. McLellan, M. Geissler, and Y. Xia, J. Am. Chem. Soc. **126**, 10830 (2004).
[11]H. L. Yip, S. K. Hau, N. S. Baek, and A. K.-Y. Jen, Appl. Phys. Lett. **92**, 193313 (2008).
[12]S. De, T. M. Higgins, P. E. Lyons, E. M. Doherty, P. N. Nirmalraj, W. J. Blau, J. J. Boland, and J. N. Coleman, ACS Nano **3**, 1767 (2009).
[13]X. Wang, L. Zhi, and K. Mullen, Nano Lett. **8**, 323 (2008).
[14]H. Z. Geng, D. S. Lee, K. K. Kim, G. H. Han, H. K. Park, and Y. H. Lee, Chem. Phys. Lett. **455**, 275 (2008).
[15]S. K. Hau, H. L. Yip, H. Ma, and A. K.-Y. Jen, Appl. Phys. Lett. **93**, 233304 (2008).