

## Fabrication of bulk heterojunction plastic solar cells by screen printing

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We demonstrate the use of screen printing in the fabrication of ultrasmooth organic-based solar cells. Organic films on the order of several tens of nanometers in thickness and 2.6 nm surface roughness were made. The first-generation screen-printed plastic solar cells demonstrated 4.3% in power conversion efficiency when using an aluminum electrode and 488 nm illumination. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413501]

Recent improvements in the power conversion efficiencies of organic solar cells have brought renewed attention to the possibility of practical, large scale use of these devices.<sup>1–3</sup> Efficiencies of 2.5% and 4.5% have been demonstrated for conjugated polymer/fullerene bulk heterojunction solar cells and halogen doped single crystal pentacene solar cells, respectively, under AM1.5 solar illumination. Although these values fall below those of inorganic technologies, organic devices have the advantage of simple processing at relatively low temperature, and therefore low fabrication cost. Polymer based devices, in which a thin film is deposited by a solution casting technique such as spin casting, are particularly easy and cost effective to fabricate. In addition, polymer based devices can be scaled up for production of large areas without significant loss of device efficiency by using dye printing techniques such as doctor blading,<sup>4</sup> or ink jet printing.<sup>5</sup>

In the present work, we demonstrate the implementation of screen printing technology in the fabrication of an organic-based bulk heterojunction solar cell. Screen printing is a commonly used industrial technique for fast, inexpensive deposition of dye films over large areas. From this standpoint, it is an ideal technology for large scale fabrication of polymer based solar cells. In addition, screen printing allows patterning to easily define which areas of the substrate receive deposition. This is important, for instance, for fabricating a photovoltaic device that is integrated onto a substrate containing other electronic devices. Also, in the production of a large area energy collection system, it is necessary to fabricate many individual solar cells that are wired together. Using screen printing, individuals devices can easily be defined on the same substrate in order to optimize the power generation of the entire system. In industrial processes, films fabricated with screen printing usually have a thickness greater than 0.5  $\mu\text{m}$ . The use of screen printing to fabricate a polymer layer with a thickness less than 100 nm, serving as the hole transport layer in an organic light-emitting diode, has been recently demonstrated.<sup>6</sup> However, in this case, the printed films were not smooth and the screen footprint was visible to the naked eye. Here, we use screen printing to deposit an ultrathin and smooth active layer in a bulk heterojunction photovoltaic device, consisting of a con-

jugated polymer/fullerene blend, with a thickness of 40 nm and root-mean-square (rms) surface roughness of 2.6 nm. This device yields a power conversion efficiency of 4.3% when illuminated by monochromatic light with a wavelength of 488 nm.

The structure of the bulk-heterojunction solar cell is shown in Fig. 1(a). The principles of operation of this device are described elsewhere.<sup>1,7–9</sup> A 150 nm thick film of poly(ethylene dioxythiophene) doped with polystyrene sulphonic acid [(PEDOT:PSS), Bayer AG] was first spin cast from a water solution onto an indium tin oxide (ITO)/glass substrate, where the ITO has a thickness of 120 nm (about 40  $\Omega/\text{square}$ ) and 85%–90% transmission in the visible range. The PEDOT:PSS layer was then dried in vacuum for 3 h at 140 °C. The active layer, consisting of a blend of the conjugated polymer [poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene)] (MDMO-PPV) and the methanofullerene ([6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester) (1:4 by weight) (PCBM) was then deposited onto the PEDOT:PSS layer from a chlorobenzene solution using the screen printing technique. The average thickness of the active layer was 40 nm. A description of the screen printing process, depicted in Fig. 1(b) follows. During deposition, the screen is placed a few millimeters above the surface of the substrate. Upon loading the polymer solution onto the screen, a rubber

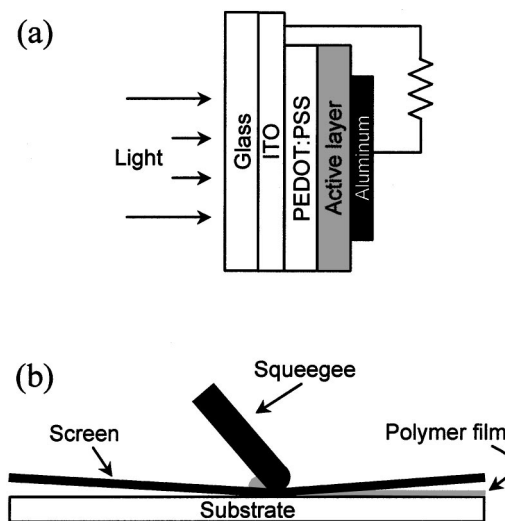


FIG. 1. Schematic diagrams of (a) the device structure of the bulk heterojunction solar cell connected to an external resistive load and (b) the screen printing technique.

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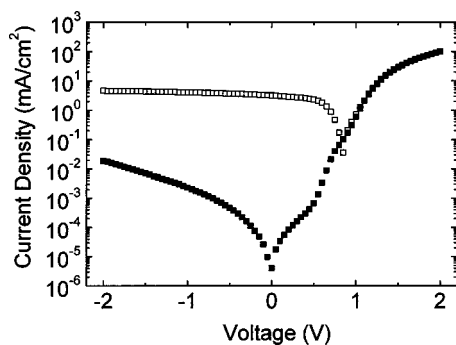


FIG. 2. Plot of the current density (absolute value) versus voltage for the solar cell operated in the dark (filled squares) and under illumination (hollow squares) by monochromatic light with a wavelength of 488 nm and an intensity of 27 mW/cm<sup>2</sup>. The short-circuit current, open-circuit voltage, fill factor, and power conversion efficiency are 3.16 mA/cm<sup>2</sup>, 841 mV, 0.44, and 4.3%, respectively. The temperature of the device during measurement was approximately 25 °C.

“squeegee” is then swept with a velocity of several centimeters per second across the surface of the screen, momentarily contacting it to the substrate. At this point, solution flows from the screen to the surface of the substrate. As the squeegee then passes over a region, the screen separates from the substrate, leaving behind solution that dries to yield a continuous film. For this study, a screen with a thread diameter of 30  $\mu\text{m}$  and a mesh count of 181/cm was used. For the cathode, a 130 nm thick film of aluminum was thermally deposited onto the active layer through a shadow mask to define an active device area of 0.12 cm<sup>2</sup>. The aluminum was deposited in a high vacuum at 0.2–0.7 nm/s from a thermal source under an operating pressure of  $10^{-6}$  Torr. For characterization, the device was illuminated with the 488 nm line of an argon laser with an intensity of 27 mW/cm<sup>2</sup>. The temperature of the device during characterization, performed in an inert environment, was approximately 25 °C.

The current density–voltage characteristics of the device under illumination and in the dark are shown in Fig. 2. The rectification of the device in the dark is approximately 5000 at  $\pm 2$  V. This indicates a good diode behavior and a high shunt (parallel) resistance as a result of conformal coverage of the PEDOT:PSS layer by the screen printed MDMO-PPV:PCBM active layer. Under illumination, the short-circuit current density is 3.16 mA/cm<sup>2</sup>, which corresponds to an external quantum efficiency (incident photons to converted electrons) of 30%. The open-circuit voltage and fill factor are 841 mV and 0.44, respectively, and the resulting power conversion efficiency is 4.3%. The external quantum efficiency of the device is limited by the optical absorption of the 40 nm thick active layer. By comparing the amount of light reflected from the device compared to the amount of light reflected from a glass/ITO/PEDOT:PSS/aluminum reference sample, the optical absorption of the active layer was measured to be approximately 33%. Thus, the internal quantum efficiency (absorbed photons to converted electrons) of the device under short-circuit conditions is approximately 90% at an incident wavelength of 488 nm. For a plot of the shape of the spectral response of the device, the reader is referred to previous work.<sup>1</sup>

An atomic force microscopy (AFM) image of the surface of the active layer is shown in Fig. 3(a). As indicated in Fig. 3(a), the surface is quite smooth, with a rms roughness of 2.6

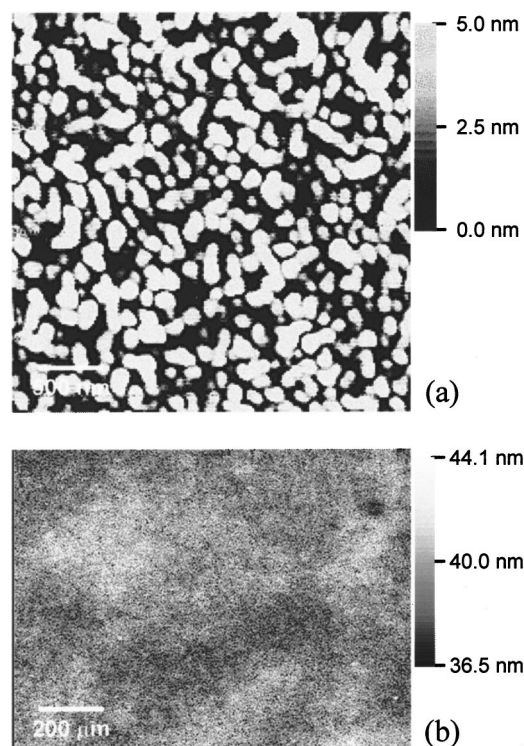


FIG. 3. (a) AFM (Digital Instruments Nanoscope) image of the surface of a 3  $\mu\text{m} \times 3 \mu\text{m}$  region of the active layer. The rms roughness is 2.6 nm. (b) Optical interferogram (Wyko) of a 1.2 mm  $\times$  0.9 mm region of the screen-printed active layer.

nm. Structural features seen in the image have not been studied, but we suspect them to be phase segregated regions that contain higher concentrations of PCBM. Phase segregation to this degree was not seen in previous work using spin casting (also from a chlorobenzene solution) to deposit the active layer.<sup>1</sup> This may be a result of the different dynamics and slower timescale for solvent evaporation in the case of the screen print technique. An interferometric image of the thickness of the active layer is shown in Fig 3. The thickness is seen to deviate by not more than 4 nm from average across the image area of approximately 1 mm<sup>2</sup>. No micron-scale structuring of the film surface resulting from the mesh pattern of the printing screen is evident in these experiments. However, such structuring of the active layer would potentially increase the efficiency of the solar cell, since thermal deposition of aluminum onto a structured surface would result in a nonplanar geometry of the reflecting back electrode. This is expected to increase the light absorbed within the active layer, since the optical path length is increased for light reflected at angles other than normal to incident. Efforts are underway to achieve such structuring to increase the power conversion efficiency of the cell.

In summary, the screen printing technique has been used to deposit the active layer in a bulk heterojunction “plastic” solar cell. The power conversion efficiency of the device was 4.3% under monochromatic illumination. We expect that the power conversion efficiency will be improved as the film thickness is increased and interfaces are modified. These results illustrate that screen printing can be a powerful technique for the fast, inexpensive fabrication of roll-to-roll polymer optoelectronic devices while retaining nanometer-scale control of the film thickness. The application of this tech-

nique to the fabrication of an organic solar cell further increases the strong potential that these devices have for practical use.

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