Open circuit voltage enhancement due to reduced dark current in small molecule photovoltaic cells

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We demonstrate high open circuit voltage photovoltaic cells achieved by reducing the electron leakage current through the introduction of both organic and inorganic electron blocking layers between the donor layer and the anode contact. As an example, the blocking layers reduce the dark current in tin (II) phthalocyanine (SnPc)/C60 solar cells with response across the visible and near infrared spectral region up to a wavelength of 1000 nm, is decreased by two orders of magnitude compared to cells lacking the layers, resulting in a doubling of the open circuit voltage. The structure: indium tin oxide/electron blocker/SnPc (100 Å)/C60 (400 Å)/bathocuproine (100 Å)/Al, has a power conversion efficiency of (2.1 ± 0.1)% at 1 sun, standard AM1.5G solar illumination. This work demonstrates the importance of reducing dark current to achieve high organic thin film photovoltaic cell efficiencies. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072807]

Photovoltaic (PV) cells based on small molecular weight organic thin films have the potential advantages of being low-cost, lightweight, and flexible.1 The power conversion efficiency ($\eta_p$) of molecular organic PV cells has steadily improved due to the use of new materials and device architectures, although it is still too low to make such cells commercially viable.2 One means to achieve further increases in $\eta_p$ is to increase the open circuit voltage ($V_{oc}$), which is a three to four times less than the photon energy in most organic PV cells. For example, the high dark current in such cells results in a significant reduction in $V_{oc}$. Previously, current blocking layers were used in polymer bulk heterojunction PV cells to eliminate shorts from anode to cathode characteristics of these structures.3 In this way we show that inserting electron blocking layers between the anode contact and donor layer in a bilayer cell can result in a significant decrease in thermally generated dark current, and hence a doubling of $V_{oc}$, leading to a proportionate increase in $\eta_p$.

Among small molecule organic materials, tin (II) phthalocyanine (SnPc) has demonstrated significant absorption at wavelengths from $\lambda=600$–$900$ nm, with a cutoff $\lambda$ =1000 nm. Indeed, approximately 50% of the total solar photon flux is in the red and near-infrared (NIR) spectrum at wavelengths from $\lambda=600$ to 1000 nm. However, long wavelength absorbing materials such as SnPc generally result in cells with low open circuit voltages due to their small energy gap and high dark currents. Previously, a $50$ Å thick SnPc layer was included at a copper phthalocyanine (CuPc)/C60 heterojunction to expand the absorption spectral range of this otherwise short wavelength ($\lambda<700$ nm) sensitive PV cell.4 Alternatively,5 SnPc has been grown into discontinuous islands between CuPc and C60 to achieve long wavelength sensitivity. A SnPc tandem cell6 using C70 as the acceptor material has also been reported. Here, we demonstrate a SnPc cell structure with low dark current and high $V_{oc}$. This is achieved by inserting an electron blocking layer between SnPc and the indium tin oxide (ITO) anode, leading to a doubling of $V_{oc}$. The power conversion efficiency measured under 1 sun AM1.5G (air mass 1.5 global) of the cell is improved from (0.45 ± 0.1)% without the blocking layer, to (2.1 ± 0.1)% when the electron blocker is included.

Devices were fabricated on 1500 Å thick layers of ITO (sheet resistance of 15 Ω/sq) precoated onto glass substrates. The solvent-cleaned ITO surface was treated in ultraviolet/O3 for 5 min immediately before loading into a high vacuum chamber (base pressure $<4 \times 10^{-7}$ Torr), where the organic layers and a 1000 Å thick Al cathode were sequentially deposited via thermal evaporation. The deposition rate of the purified7 organic layers was $\sim 1$ Å/s. The Al cathode was evaporated through a shadow mask with 1 mm diameter openings to define the device active area. The current density versus voltage ($J$–$V$) characteristics were measured in the dark and under simulated AM1.5G solar illumination. Illumination intensity and quantum efficiency measurements were conducted using standard methods employing a NREL calibrated Si detector.8

Figure 1 shows the current density–voltage ($J$–$V$) characteristics of an ITO/SnPc (100 Å)/C60 (400 Å)/bathocuproine (BCP) (100 Å)/Al PV cell, and an ITO/CuPc (200 Å)/C60 (400 Å)/BCP (100 Å)/Al PV cell. Compared to the CuPc cell, the SnPc-based device has a higher dark current, which can be understood in terms of differences in energy levels between the two structures. The highest occupied molecular orbital (HOMO) energies of both SnPc and CuPc are at 5.2 eV below the vacuum level.4,9 The lowest unoccupied molecular orbital (LUMO) energy for CuPc is 3.2 eV, as measured by inverse photoemission spectroscopy.9 For SnPc, the LUMO energy is estimated from the optical band gap to be 3.8 eV. Since the LUMO energy of C60 is 4.0 eV,10 this results in a 0.8 eV barrier to electron transport from the C60 acceptor to the anode for a CuPc/C60 cell, but only 0.2 eV for the SnPc/C60 device. As a result, the dark current in the CuPc/C60 cell arises mainly from generation and recombination at the CuPc/C60 hetero-

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FIG. 1. Current density vs voltage characteristics of an ITO/SnPc (100 Å)/C60 (400 Å)/BCP (100 Å)/Al PV cell (open squares) and an ITO/CuPc (200 Å)/C60 (400 Å)/BCP (100 Å)/Al PV cell (open triangles) in the dark and under 0.2 and 1 sun, AM1.5 illumination. The dark current fitting results are also shown (solid lines).

 Junction, whereas in the SnPc/C60 cell, the electron leakage current from cathode to anode dominates.

The relationship between dark current and $V_{oc}$ is inferred from

$$J = \frac{R_p}{R_s + R_p} \left[ J_s \exp \left( \frac{q(V - J R_p)}{n k T} \right) - 1 \right] + \frac{V}{R_p} - J_{ph}(V),$$

where $J$ is the total current, $J_s$ is the reverse dark saturation current, $n$ is the ideality factor, $R_s$ is the series resistance, $R_p$ is the parallel resistance, $V$ is the bias voltage, and $J_{ph}$ is the photocurrent. Setting $J = 0$,

$$V_{oc} = \frac{n k T}{q} \ln \left[ \frac{J_{ph}(V_{oc})}{J_s} + 1 - \frac{V_{oc}}{R_p J_s} \right].$$

When $J_{ph}/J_s \gg 1$, $V_{oc}$ is proportional to $\ln(J_{ph}/J_s)$, suggesting that a large $J_s$ results in a reduction in $V_{oc}$. From Eq. (1), fits to the dark $J$-$V$ characteristics in Fig. 1 yield $n = 1.5$ and $J_s = 5.1 \times 10^{-2}$ mA/cm² for the SnPc-based cell, and $n = 2.0$ and $J_s = 6.3 \times 10^{-4}$ mA/cm² for the cell employing CuPc as the donor. We then can calculate $V_{oc}$ using Eq. (2) assuming a constant $J_{ph}(V) = J_{oc}$ (short circuit current). At one sun illumination, we obtain $V_{oc} = 0.19$ V for SnPc, and 0.46 V for CuPc cell by ignoring the small parallel resistance term. These calculated values of $V_{oc}$ obtained from dark current fitting parameters are consistent with the measured values of 0.16 ± 0.01 and 0.46 ± 0.01 V, respectively.

To decrease $J_s$ and hence increase $V_{oc}$ in a SnPc/C60 cell, we insert an electron blocking layer between the anode and the SnPc donor layer. According to the energy level diagram in the inset of Fig. 2, the electron blocking layer must (i) have a higher LUMO energy than that of the donor, (ii) have a relatively high hole mobility, and (iii) not introduce significant dark current due to generation and recombination at the interface with the donor resulting from a small blocking layer HOMO to donor LUMO “interfacial gap” energy. Following these considerations, we employed the inorganic material MoO3, boron subphthalocyanine chloride (SubPc), and CuPc as electron blocking layers. According to their energy levels (see Fig. 2), they all effectively impede the electron current from the donor to the anode contact. Among these materials, MoO3 has previously been used in polymer PV cells to prevent reactions between ITO and the polymer PV active layers.

The $J$-$V$ characteristics of three devices: one with a 100 Å thick MoO3 blocker, one with a 40 Å thick SubPc blocker, and one with a 40 Å CuPc blocker, are shown in Fig. 2. For comparison, the characteristics of the SnPc cell without a blocker are also shown. The dark currents of devices with blocking layers are significantly suppressed, and as a result, $V_{oc}$ measured under 1 sun illumination increased to >0.40 V in all cases.

The performances of all devices are summarized in Table I. The values for $V_{oc}$, $J_{sc}$ fill factor (FF), and power conversion efficiency ($\eta_{PV}$) were measured at 1 sun standard AM1.5G solar illumination. The high $V_{oc}$ leads to a concomitant increase in power conversion efficiency from (0.45 ± 0.1)% for a SnPc device without the blocking layer to a maximum of (2.1 ± 0.1)% Note that the SubPc blocking layer introduces an energy barrier to holes in addition to electrons. Increasing its thickness from 20 to 40 Å leads to a decrease in FF possibly due to the small barrier to hole conduction (0.4 eV, see inset, Fig. 2), and hence a slight decrease in power conversion efficiency.

Equation (1) is used to fit the dark current of all devices, with the resulting fitting parameters listed in Table I. When the MoO3 layer thickness exceeds 100 Å, or the SubPc layer thickness is >20 Å, $J_s$ is only 1% of devices lacking the blocking layers. If the electron blocking layer thickness is further increased, the additional decrease in $J_s$ is marginal, indicating that these thin layers effectively eliminate electron leakage. As indicated in the table, the calculated $V_{oc}$ is consistent with the measured values for all devices.

Figure 3 shows the external quantum efficiency (EQE) spectra of PV cells with the different structures studied. The EQE of the CuPc cell decreases to <10% at $\lambda > 730$ nm, whereas the EQE of all SnPc cells are >10% at $\lambda$
TABLE I. Performance of SnPc solar cells at 1 sun, AM1.5 illumination.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$\eta_e$ (%)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$n$</th>
<th>$R_s$ ($\Omega$ cm$^2$)</th>
<th>$R_p$ ($\Omega$ cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No blocker</td>
<td>0.16</td>
<td>0.44</td>
<td>6.4</td>
<td>0.45</td>
<td>5.1 x 10^{-2}</td>
<td>1.5</td>
<td>0.19</td>
<td>2.9 x 10^{3}</td>
<td>0.19</td>
</tr>
<tr>
<td>30 Å MoO$_3$</td>
<td>0.37</td>
<td>0.62</td>
<td>7.4</td>
<td>1.7</td>
<td>1.2 x 10^{-3}</td>
<td>1.7</td>
<td>0.19</td>
<td>1.1 x 10^{5}</td>
<td>0.39</td>
</tr>
<tr>
<td>100 Å MoO$_3$</td>
<td>0.40</td>
<td>0.63</td>
<td>6.7</td>
<td>1.9</td>
<td>6.0 x 10^{-4}</td>
<td>1.7</td>
<td>0.19</td>
<td>1.6 x 10^{5}</td>
<td>0.22</td>
</tr>
<tr>
<td>300 Å MoO$_3$</td>
<td>0.42</td>
<td>0.61</td>
<td>7.4</td>
<td>1.9</td>
<td>5.5 x 10^{-4}</td>
<td>1.8</td>
<td>0.19</td>
<td>3.5 x 10^{5}</td>
<td>0.45</td>
</tr>
<tr>
<td>20 Å SubPc</td>
<td>0.40</td>
<td>0.62</td>
<td>8.4</td>
<td>2.1</td>
<td>5.9 x 10^{-4}</td>
<td>1.7</td>
<td>0.17</td>
<td>1.4 x 10^{5}</td>
<td>0.42</td>
</tr>
<tr>
<td>40 Å SubPc</td>
<td>0.41</td>
<td>0.55</td>
<td>8.8</td>
<td>2.0</td>
<td>5.9 x 10^{-4}</td>
<td>1.7</td>
<td>0.16</td>
<td>1.4 x 10^{5}</td>
<td>0.44</td>
</tr>
<tr>
<td>40 Å CuPc</td>
<td>0.41</td>
<td>0.59</td>
<td>7.9</td>
<td>1.9</td>
<td>9.5 x 10^{-4}</td>
<td>1.9</td>
<td>0.27</td>
<td>1.4 x 10^{5}</td>
<td>0.44</td>
</tr>
</tbody>
</table>

<900 nm. The efficiencies of devices employing MoO$_3$ are the same as those without blocking layers, suggesting that the increased power conversion efficiency is due entirely to the reduced leakage current. In addition, devices with a SubPc blocking layer have a higher efficiency than those with MoO$_3$ due to the increased absorption in the green spectral region and subsequent exciton generation from SnPc.

In summary, we have shown the effects that dark current have on the open circuit voltage of small molecular weight organic PV cells. Specifically, we have employed several different organic and inorganic electron blocking layers in SnPc/C$_60$ heterojunction solar cells as a means to significantly reduce the electron leakage current resulting in a two-fold increase in $V_{oc}$ compared to cells lacking the blocking layers. As a result, a power conversion efficiency of (2.1 ± 0.1)% is achieved. Our findings lead to a deeper understanding of the origins of the open circuit voltage while also opening up possibilities for achieving very high efficiency in thin film organic solar cells with sensitivity into the NIR.

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