Variation of the metal top electrode in bulk heterojunction solar cells*

Abstract

The performance of bulk heterojunction solar cells based on blends of conjugated polymers and fullerenes is known to be critically dependent on the nature of the metal top electrode. In contrast to the present understanding, it is demonstrated that the open-circuit voltage ($V_{OC}$) of the solar cells with non-Ohmic contacts is determined by the work function difference of the electrodes. For Ohmic contacts the $V_{OC}$ is governed by the LUMO and HOMO levels of the acceptor and donor, respectively, which pin the Fermi levels of the cathode and anode. The band bending created by accumulated charges at both interfaces due to Ohmic contacts produce a considerable loss in $V_{OC}$ of $\approx 0.38$ V at room temperature. Furthermore, the photocurrent obtained from the active layer of a solar cell, with a different metal work function, such as lithium fluoride topped with aluminum, silver, gold, or palladium, shows a universal behavior when scaled against the effective voltage across the device. Consequently, for any given metal, only the device’s $V_{OC}$ is required in order to be able to predict the remaining solar cell parameters.

4.1 Electrode dependence of the open-circuit voltage

4.1.1 Introduction

The essential parameters which determine the power conversion efficiency of thin film photovoltaic devices are the short-circuit current ($J_{SC}$), the open-circuit voltage ($V_{OC}$), and the fill factor (FF). It has been shown that the $J_{SC}$ is sensitive to the film morphology, solvent type, or deposition method [1, 2]. Formation of a bulk heterojunction by mixing the polymer (donor) and the fullerene (acceptor) lead to an enhancement of $J_{SC}$ due to an increased interface area for charge separation. However, the $J_{SC}$ is still much lower than the typical values reported for inorganic photovoltaic devices. This lower photocurrent is mainly due to the spectral mismatch between the sunlight and the absorption spectrum of the polymers (and fullerenes) used, as well as the limited transport of the separated charge carriers to the electrodes due to the low charge carrier mobility in organic materials.

On the other hand, organic solar cells produce quite respectable open-circuit voltages. It has been demonstrated that for a photodiode, based on a single layer of a conjugated polymer, the $V_{OC}$ scales with the work function difference between electrodes, and thus follows the metal-insulator-metal (MIM) model [1]. In bilayer devices made by electron- and hole-accepting polymers, the $V_{OC}$ also scales linearly with the work function difference, however, with an additional contribution depending on the light intensity [3]. This contribution is due to the accumulation of charge carriers at the organic/organic interface, giving rise to a diffusion current which must be compensated by a drift current at open-circuit. In bulk heterojunction (BHJ) solar cells, a linear correlation of the $V_{OC}$ with the variation of the oxidation potential of the donor conjugated polymers [4] and reduction potential of the acceptor [5, 6], has been reported. The fact that a slope

![Figure 4.1: Schematic variation of $V_{OC}$ with acceptor strength (solid double headed arrow, $V_{OC1}$) or/and electrode work function (dotted arrow, $V_{OC2}$), in a donor/acceptor bulk heterojunction solar cell. The electron transfer, occurring at the donor/acceptor interface after light excitation, is indicated by the bent arrow.](image-url)
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unity was obtained indicates a strong coupling of $V_{OC}$ to the reduction strength of the acceptors or oxidation potential of the donors. In case of Ohmic contacts, meaning that the negative and positive electrodes match the LUMO level of the acceptor and the HOMO level of the donor, respectively, such a correlation is expected. The maximum $V_{OC}$ for this case is schematically indicated by $V_{OC1}$ in Figure 4.1 and is thus governed by the bulk material properties. In case of non-Ohmic contacts, as is depicted in Figure 4.1, a reduced $V_{OC}$ with magnitude $V_{OC2}$ is expected, according to the MIM model. However, a very weak variation of the $V_{OC}$ of only 160 meV has been observed when varying the work function of the negative electrode from 5.1 eV (Au) to 2.9 eV (Ca) [5, 6]. This deviation from the MIM model has been explained by pinning of the electrode Fermi level to the reduction potential of the fullerene. For the design of future solar cells it is important to understand whether the $V_{OC}$ of BHJ devices can be adapted by the choice of the electrodes and whether the $V_{OC}$ is a bulk property (as shown by solid arrow in Figure 4.1) or an electrode property (shown by dotted line in Figure 4.1), or a combination of both. In this study we first investigated the electronic properties of various negative top electrodes on PCBM-only devices. The information regarding the alignment of the Fermi level of the various electrodes on PCBM is then applied to the experimental data on MDMO-PPV:PCBM based solar cells. We demonstrate that the $V_{OC}$ of the cells can be varied over more than 0.5 V by changing the work function of the top electrode.

4.1.2 Open-circuit voltage of pristine fullerene devices

In order to study a possible pinning of the Fermi level of the negative top electrode on PCBM, devices consisting of a single layer of PCBM were investigated as a reference. The devices were produced on top of a glass substrate, covered by indium-tin-oxide (ITO). As a bottom electrode, a hole transport layer of PEDOT:PSS was spin-coated under ambient condition, then the layer was dried in the oven. Subsequently, PCBM was spin cast from a chlorobenzene solution. Finally, gold (Au, 50 nm), silver (Ag, 80 nm), or lithium fluoride (LiF, 1 nm)/aluminum (Al, 100 nm) were thermally evaporated (pressure $< 10^{-6}$ mbar) as the top electrode.

When a metal is making intimate contact with a semiconductor or insulator, at equilibrium, the Fermi levels in the two materials will coincide. If the work function of the metal is higher then the LUMO level of the semiconductor, an interface barrier $\varphi_b$ for electrons will be formed [Figure 4.2(a)]. As indicated in Figure 4.2(a) for two of these blocking contacts, the $V_{OC}$ of the device is given by difference between the metals work functions. For the PCBM devices a schematic diagram is shown in Figure 4.2(a), where $M_2$ is the bottom electrode (PEDOT:PSS, $\varphi_{M2}=5.2$ eV) and $M_1$ is the evaporated top electrode (Ag, Au, LiF/Al). From Figure 4.2(a) it appears that

$$\varphi_b + qV_{OC} = \varphi_{M2} - LUMO,$$

where $q$ is the electric charge and LUMO is the position of the PCBM LUMO level with respect to vacuum (3.7 eV), respectively. Equation 4.1 indicates that for a given bottom electrode work function (in this case PEDOT:PSS), the sum
Figure 4.2: Schematic band diagram of a metal-insulator-metal (MIM) device with non-Ohmic contact for electrons and holes (a), and electron Ohmic contact (b). Before metal contact (upper image) and after contact and under short-circuit condition (lower image). The $\varphi_b$ and $\Delta V_b$ are injection barrier height for electrons at a non-Ohmic contact and the voltage loss at an Ohmic contact, respectively. $\varphi_{M1}$ and $\varphi_{M2}$ are the metal work functions.

of electron barrier height and $V_{OC}$ is constant for different top electrodes. It is important to note that in our PCBM devices both $\varphi_b$ and $V_{OC}$ can be independently determined from $J$-$V$ measurements. The barrier heights for electrons going from Ag and Au into the LUMO level of PCBM have been determined by investigation of the injection limited electron current (ILC). It was recently demonstrated that the injection limited current is well described by hopping of charge carriers from the Fermi level of the metal into energetically disordered localized states of the organic semiconductor [7, 8]. According to this hopping-based model, the ILC is determined by four parameters [7, 8]; the energy width of the density of localized states $\sigma$, the nearest hopping distance $a$, the dielectric constant $\epsilon_r$, and finally the energy distance from the Fermi level of the electrode to the center of the Gaussian DOS of the PCBM transport states (i.e., the barrier height $\varphi_b$). From the field- and temperature dependence of the electron mobility of PCBM $\sigma=0.073$ eV and $a=3.4\pm0.1$ nm have been extracted. Also, the dielectric constant of $\epsilon_r=3.9$ has been found from impedance measurement.

In Figure 4.3, the calculated ILC of PCBM, according to the hopping based model, is plotted, together with experimental data, obtained at different temperatures. Using a barrier heights $\varphi_b$ of 0.65 and 0.76 eV for Ag and Au, respectively, without any other free parameter, the calculated ILC is in a good agreement with the experimental results. Apparently, the injection barrier of the Au/PCBM contact is strongly reduced as compared to the band offset, from which a barrier of about 1.4 eV was expected. It has been demonstrated by ultraviolet photoemission spectroscopy (UPS) that at the Au/C$_{60}$ interface a strong
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Figure 4.3: Injection limited electron current (ILC) in the dark $J_D$ versus $V$ as a function of temperature (symbols) for an ITO/PEDOT:PSS/PCBM/top electrode device with thickness $L=110$ nm. The top electrode is Ag (a) or Au (b). The $J_D$-$V$ characteristics, calculated according to the hopping model, are plotted as solid lines. The estimated built-in voltage $V_{BI}$ has been subtracted from the applied bias.

interface dipole exists, which lowers the Au/C$_{60}$ interface barrier by 0.64 eV [9]. With the band offset of 1.4 eV this would give rise to an injection barrier of 0.76 eV, which exactly equals the barrier as extracted from the $J_D$-$V$ measurements. This interface dipole is then responsible for the relatively large injection-limited electron current of the Au/PCBM contact, indicating that the Au work function is pinned at about 4.46 eV, in contact with PCBM. The Ag electrode is in the position (4.35 eV) where is expected from its work function, as was also demonstrated by UPS measurements [9].

As a further control experiment, the $J_L$-$V$ characteristics under illumination for ITO/PEDOT:PSS/PCBM/cathode devices with Ag and Au cathodes were determined. These data are shown in Figure 4.4(a). The relatively low photocurrent exhibited by the pure PCBM device is due to the poor light absorption in visible range. The obtained $V_{OC}$ for Ag (0.84 V) and Au (0.74 V) were measured in the saturation regime (by checking at different light intensities). For both electrodes the sum of the barrier height (ILC measurements) and $V_{OC}$ (photocurrent) equals 1.5 V, which is equals to the energy distance between the Fermi level of the PEDOT:PSS (5.2 eV) and the LUMO of PCBM (3.7 eV), as predicted by Equation 4.1. Thus the position of the metal Fermi level with respect to the LUMO level of PCBM is confirmed by two independent measurements.

The next issue to address is the situation in which the metal work function $\varphi_{M1}$ is reduced to such an extent that it is even below the LUMO level of the semiconductor [as shown in Figure 4.2(b)]. In this case, alignment of the Fermi level is achieved by charge transfer of electrons from the metal into the semiconductor, and an Ohmic contact is formed. As a result, the electrode work function becomes pinned close to the LUMO level of the semiconductor, as shown in Figure 4.2(b) [10]. Furthermore, the accumulated charges at the interface will create a band bending, which leads to a reduction of the electric field in the bulk of the device [11]. The resulting voltage loss, indicated by $\Delta V_b$ in Figure 4.2(b), can be numerically calculated as a function of the barrier height $\varphi_b$, using a model by
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Figure 4.4: (a) $J_L$-$V$ of ITO/PEDOT:PSS/PCBM/cathode devices, illuminated with a white light halogen lamp (800 W/m$^2$). The cathodes are silver (dashed line) and gold (dotted line). The device was illuminated through the glass/ITO substrate. (b) Calculated voltage loss ($\Delta V_b$) due to the band bending, as a function of the barrier height ($\varphi_b$), for an Ohmic contact. The parameters used in calculation are thickness $L=95$ nm, temperature $T=295 \text{ K}$, effective density of states in the conduction band $N_c=3 \times 10^{26} \text{ m}^{-3}$ and the dielectric constant $\epsilon_r=3.9$.

Simmons [12]. In Figure 4.4(b) the result is shown for a device with thickness $L=95 \text{ nm}$, at room temperature. It appears that for a barrier height $\varphi_b>0.25 \text{ eV}$ the voltage loss is negligible, since the barrier prevents the flow of electrons from the metal into the semiconductor. However, for $\varphi_b<0.25 \text{ eV}$ the contact becomes Ohmic and for zero barrier, as shown in Figure 4.2(b), a voltage loss of typically 0.2 V has to be taken into account. Thus, for an Ohmic contact Equation 4.1 is modified to:

$$\varphi_b + qV_{OC} + q\Delta V_b = \varphi_{M2} - LUMO,$$

(4.2)

where $\Delta V_b$ is the voltage loss due to the band bending at the Ohmic contact.

The electron current injected from LiF/Al contacts was shown to be space-charge limited (SCL) (see Section 2.2), indicating that LiF/Al forms an ohmic contact for electron injection into the LUMO level of PCBM [13]. As a result, the current is limited by the bulk properties of the PCBM layer and no information about the contact, like a barrier height, can be obtained from the $J_D$-$V$ measurements. Furthermore, direct measurement of the $V_{OC}$ by using the photocurrent of an ITO/PEDOT:PSS/PCBM/ LiF/Al device was not possible due to the poor light absorption of the PCBM, leading to an unsaturated $V_{OC}$ for this device. Thus the experimental methods used on the Ag and Au devices do not apply to the PCBM devices with LiF/Al contacts. However, it is possible to determine the built-in potential in the device directly from the $J_D$-$V$ measurements. It should be noted that $V_{OC}$ is an accurate estimate for the built-in potential at low temperatures, but at room temperature it might underestimate the built-in potential [5]. In Figure 4.5 the dark $J_D$-$V$ characteristics of an ITO/PEDOT:PSS/PCBM/LiF/Al device is shown. It can be observed from Figure 4.5 that the dark $J_D$-$V$ characteristic of a PCBM device has three distinct regimes: At low voltage (0-0.8 V), the measured current is dominated by local leakage currents due to weak spots in the film, giving rise to ohmic behavior,
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which is symmetric for reverse bias. In the range 0.8-1.3 V, the current increases exponentially with voltage. In this regime the current is diffusion dominated, since the built-in electric field opposes the direction of the current. When the flat band condition is reached, the current becomes space-charge limited (drift dominated). Consequently, the built-in voltage can be read at the cross point between the exponential and SCLC regime, which amounts to $V_{BI} = 1.28 \pm 0.02$ V. This value can be taken as an upper limit for $V_{OC}$ in this device, but does not provide accurate information about the band bending at the LiF/Al-PCBM contact.

The results of the PCBM-only devices are summarized in Table 4.1. For non-Ohmic contacts (Ag, Au) the sum of barrier height and the $V_{OC}$ of the device is constant, being the difference between work function of the bottom electrode and the LUMO level of PCBM. In the case of an Ohmic contact the $V_{OC}$ is reduced due to band bending as a result of accumulated charges. These results are relevant for the understanding of the open-circuit voltage of the polymer/fullerene BHJ solar cells, which will be addressed in the next section.

**Table 4.1:** PCBM characteristics for $\phi_b$, $\Delta V_b$, and $V_{OC}$ for different cathodes together with calculation values according to Equation 4.2.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$\phi_b$ (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$\Delta V_b$ (V)</th>
<th>$\phi_b + V_{OC} + \Delta V_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF/Al</td>
<td>0</td>
<td>1.28$^a$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.65</td>
<td>0.84</td>
<td>0</td>
<td>1.49</td>
</tr>
<tr>
<td>Au</td>
<td>0.76</td>
<td>0.74</td>
<td>0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$Value estimated from the built-in field (Figure 4.5).
4.1.3 Open-circuit voltage of polymer:fullerene devices

With the position of the Fermi level of the Ag, Au, and LiF contact known, with regard to the LUMO of PCBM, the influence of the metal work function on the $V_{OC}$ of conjugated polymer:fullerene BHJ solar cells is investigated. The active layer consists of a blend of MDMO-PPV:PCBM. The PPV and PCBM was used in a ratio of 1:4 by weight and it was spin coated from a chlorobenzene solution on glass/ITO/PEDOT:PSS substrates. For the solar cells Au, Ag, Pd, or LiF (1 nm)/Al (100 nm) were thermally evaporated as a top electrode. The work function of PEDOT:PSS ($\varphi_{M2}=5.2$ eV) matches the HOMO level of MDMO-PPV (5.3 ± 0.1 eV), resulting in an Ohmic contact for holes in the BHJ solar cell, under forward bias condition. On the other side, LiF/Al makes an Ohmic contact for electron injection into the LUMO level of PCBM (3.7 eV). It should be noted that for PCBM-only devices with Au and Ag contacts, there is no band bending at either electrode, whereas for the solar cells with the same contacts there is an additional band bending at the PEDOT/MDMO-PPV interface. Furthermore, in the BHJ solar cell with a LiF/Al contact band bending occurs at both interfaces.

For this particular device Equation 4.2 modifies to:

$$q(V_{OC} + \Delta V_b) = \text{HOMO}_{\text{donor}} - \text{LUMO}_{\text{acceptor}},$$

(4.3)

where $\Delta V_b$ is the sum of the voltage losses due to the band bending at each contact. Equation 4.3 shows that for two Ohmic contacts the $V_{OC}$ is given by the difference between the HOMO level of the donor (MDMO-PPV) and the LUMO level of the acceptor (PCBM), minus the voltage losses at these contacts due to the band bending. Following the same approach as in PCBM only devices, we started with the investigation of the $V_{OC}$ dependence on the metal work function with non-Ohmic contacts.

Figure 4.6 shows the $J_L$-$V$ characteristics under illumination, of four typical devices. The $V_{OC}$ was found to be in saturation regime in all cases.
Table 4.2: MDMO-PPV:PCBM BHJ solar cells characteristics [$V_{OC}$; total voltage loss due to Ohmic contact ($\Delta V_b$) as a function of different top electrodes; electron barrier heights ($\varphi_b$) are taken from PCBM-only characteristics from Table 4.1; $\varphi_{M1}=\text{LUMO}_{PCBM}+\varphi_b$ is the estimated effective metal work function, taking the barrier height into account].

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$\varphi_b$ (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$\Delta V_b$ (V)</th>
<th>$\varphi_{M1}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF/Al</td>
<td>0</td>
<td>0.902</td>
<td></td>
<td>3.7</td>
</tr>
<tr>
<td>Ag</td>
<td>0.65</td>
<td>0.674</td>
<td>0.158</td>
<td>4.35</td>
</tr>
<tr>
<td>Au</td>
<td>0.76</td>
<td>0.59</td>
<td>0.158</td>
<td>4.46</td>
</tr>
<tr>
<td>Pd</td>
<td>0.944$^a$</td>
<td>0.398</td>
<td>0.158</td>
<td>4.644</td>
</tr>
</tbody>
</table>

$^a$Value calculated from Equation 4.2: the measured $V_{OC}$ from Figure 4.6, taking into account the average voltage losses at the Ag and Au interfaces.

ITO/ PEDOT:PSS/MDMO-PPV:PCBM/top electrode BHJ devices using either LiF/Al, Ag, Au, and Pd as the negative top electrode. The measured $V_{OC}$ values are summarized in Table 4.2, together with values for the respective electron barrier heights ($\varphi_b$). As stated above, in the BHJ solar cells with Au and Ag contacts, there is additional band bending at the anode as compared to the PCBM-only devices. As a result, the difference in $V_{OC}$ between the PCBM-only devices and the BHJ solar cells equals the voltage loss $\Delta V_b$ due to band bending at the Ohmic hole contact. For both Au and Ag this difference amounts to $0.16\pm0.02$ V, which is the voltage loss due to band bending at the anode. This demonstrates that the solar cells with Ag and Au electrodes, when corrected for the band bending at the anode, behave as expected from the results of the PCBM only devices. Furthermore, the position of the Ag and Au electrode with respect to the LUMO of the PCBM is not modified by the presence of the polymer in the blend.

![Figure 4.7: $V_{OC}$ as a function of temperature (open circles) for a device with active layer of MDMO-PPV:PCBM (1:4 w/w). The solid line represents the linear extrapolation to $T=0$ K.](image)
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For the LiF/Al contact the situation is more complicated: the upper limit for the $V_{OC}$ in a solar cell can be determined from the temperature dependence of $V_{OC}$ [14]. At $T=0$ K the diffusion of charges into the semiconductor and resulting band bending are suppressed, and $V_{OC}$ approaches its maximum value. In Figure 4.7 the temperature dependence of $V_{OC}$ is shown, and extrapolation to $T=0$ K gives a $V_{OC}$ of $\approx 1.3$ V, in agreement with an earlier reported result [14]. However, from the HOMO-LUMO difference between MDMO-PPV (5.3 eV) and PCBM (3.7 eV) an upper limit of 1.6 V for $V_{OC}$ would be expected. The question is why this maximum $V_{OC}$ amounts to only 1.3 V. It should be noted that the band diagrams as drawn in Figure 4.2 assume a well-defined band edge. However, both MDMO-PPV and PCBM are disordered semiconductors, in which the charge transport is characterized by hopping in an energetically broadened Gaussian density of states (DOS). The widths of the Gaussian DOS $\sigma$ for MDMO-PPV and PCBM amount to 0.11 and 0.072 eV, respectively. The transport levels in the Gaussian DOS are located at $-5/9 \times \sigma^2/k_B T$ from the center [15], implying that for MDMO-PPV and PCBM the transport levels are located 0.25 and 0.1 eV from the center of the DOS, respectively. Consequently, the HOMO(MDMO-PPV)-LUMO(PCBM) distance of 1.6 eV, deduced from the maxim of the Gaussian DOS, is effectively reduced to about 1.25 eV, which corresponds closely to the maximum obtainable $V_{OC}$ in the solar cells. Correcting the upper-limit of $V_{OC}=1.3$ V for the band bending at ambient temperature for two Ohmic contacts reduces the $V_{OC}$ further to 0.9 V, which is in close agreement with the experimentally observed value.

In an earlier study [5, 6] using Ca, Ag, Al, and Au as cathodes, it has been demonstrated that the obtained variation in $V_{OC}$ was less than 200 mV. Pinning of the Fermi level at PCBM surface states was suggested as a possible explanation. Also in our study the variation between LiF/Al, Ag, and Au is rather small. However, it is important to realize that the $V_{OC}$ of cells with Al and Ag cathodes behave in correspondence with the MIM model, without an additional contribution by pinning. As we have shown, Ag is exactly at the position where it is expected from its work function. Furthermore, the Fermi level of LiF is pinned close to that of the LUMO of PCBM [shown in Figure 4.2(b)] due to the accumulated charge carriers. Because of this pinning, the $V_{OC}$ will be independent of the work function of the cathode whenever its work function is lower than the LUMO of PCBM. Therefore, cells with such electrodes, like Ca and LiF/Al, should not be included in the analysis of a work function dependence of $V_{OC}$. The only cell of which the measured $V_{OC}$ strongly deviates from the MIM model is the one with the Au cathode. There are two possible explanations for its specific behavior: First, the energy level of Au at the PCBM interface is close to those of Ag and Al because all metals are pinned at that position due to the presence of a large number of interface states. The alternative is that Al and Ag are not pinned by surface states and that the energy level of Au by coincidence is at the same position because of a strong interface dipole [9]. In order to discriminate between these options we also investigated a Pd electrode, which has a work function comparable to Au. As can be seen in Figure 4.6, the $V_{OC}$ of cells with a Pd electrode is strongly reduced to 0.39 V. Although Pd is apparently shifted by 0.3 V with regard to its work function, a total variation of more than
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Figure 4.8: $V_{OC}$ as a function of effective position of the Fermi level of the negative electrode (symbols) for devices with MDMO-PPV:PCBM active layer, at room temperature. The solid line represents the calculated value according to the MIM model. The dotted line indicates the linear dependence of $V_{OC}$ with the acceptor strength of the fullerene.

0.5 V of the $V_{OC}$ was observed by varying the negative electrodes. These results indicate that pinning of the metal Fermi level at a specific surface state of the methanofullerene is unlikely, but that Au is a special case because of its large interface dipole.

In Figure 4.8 the results obtained in this study are summarized: the measured $V_{OC}$ is plotted versus the position of the Fermi level of the negative electrode, given by LUMO$_{PCBM} + \varphi_b$ as obtained from our measurements. The dotted line shows the behavior as expected from the MIM model [12]. According to this model, $V_{OC}$ increases linearly with the energy level of the cathode and then pins when the PCBM LUMO level at 3.7 V is reached. The solid line represents the calculated $V_{OC}$ when the voltage loss due to band bending at the anode interface ($\approx 0.2$ V) is taken into account. For metals approaching the LUMO of PCBM, band bending at both interfaces ($\approx 0.4$ V) is taken into account. For cells with non-Ohmic contacts, the observed $V_{OC}$ is in agreement with the expected values. In this case, $V_{OC}$ is determined by the work function differences of the electrodes. However, for the Ohmic contact the measured value of 0.9 V is lower than the predicted value of around 1.1 V, possibly due to the energetic disorder of the charge transport levels.

4.1.4 Conclusion

In this section it is shown that by variation of the negative electrode the open-circuit voltage of the polymer/fullerene BHJ solar cell varies by more than 0.5 V, which excludes the presence of a large number of PCBM surface states. A clear distinction between Ohmic and non-Ohmic contacts was elucidated: for non-Ohmic contacts the experimental $V_{OC}$ is in agreement with the work function difference of the electrodes as expected from the MIM model. In case of Ohmic contacts, the negative and positive electrodes match the LUMO of the acceptor...
and the HOMO of the donor, respectively, which govern the $V_{OC}$. Furthermore, the band bending at the Ohmic contacts reduces the $V_{OC}$ by typically 0.2 V for each contact. These voltage losses strongly reduce the maximum attainable $V_{OC}$ in an MDMO-PPV:PCBM BHJ solar cell at room temperature.

### 4.2 Effect of metal electrodes on solar cell performance

#### 4.2.1 Introduction

In addition to attempt to optimize the components and composition of the MDMO-PPV:PCBM-based solar cells, modification of the electrodes has led to an improvement of the device performance [5, 6, 16]. In the previous section, the attention has mainly been focused on the effect of the metal electrodes on the open-circuit voltage $V_{OC}$ of the solar cells. As such, it has been demonstrated that the $V_{OC}$ of a cell is governed by the work function of the negatively charged electrode, although interface dipoles might complicate this behavior. The role of the metal electrodes on other important parameters as the short-circuit current ($J_{SC}$), fill factor (FF), and maximum output power ($P_{max}$) has not been addressed. However, it has been observed that when employing Al as the top electrode, the insertion of LiF between organic layers and the metal not only enhances the $V_{OC}$, as expected from its work function, but also increases both the $J_{SC}$ and FF [13, 17]. The origin of this increase, and the resulting 20% enhancement in the efficiency, is less clear. One explanation which has been proposed is that the insertion of a subnanometer LiF layer lowers the series resistance of the device by a factor of 3 or 4, which thereby increases the observed FF [13]. However, it must be stressed that in solar cells the top electrode extracts electrons from the device, in contrast to light-emitting diodes (LEDs) in which charge injection is important [18]. In the previous section, the injection of electrons from various metal electrodes into the LUMO level of the acceptor PCBM has been investigated. For electron injection the energy barrier $\varphi_b$ between the metal electrode and the LUMO level of PCBM is relevant, and has been determined to be 0 eV for LiF/Al (Ohmic contact), 0.65 eV for Ag, 0.76 eV for Au, and 0.94 eV for Pd. The respective processes for the transfer of electrons (injection in LEDs; extraction in solar cells) between PCBM and each metal are schematically represented in Figure 4.9. The main distinctions between the two processes are that in the case of extraction, the electrons are not inhibited from leaving the active layer by an energy barrier, and are therefore collected with equal efficiency whatever the electrode. Additionally, since the charge carrier generation process in the PPV:PCBM blend is not affected by the electrodes it is also not obvious why a change in the metal electrode would dramatically affect the series resistance.

In this section, we have investigated the role of various metal electrodes on the performance of polymer/fullerene bulk heterojunction solar cells. We demonstrate that when scaled with the internal electric field, the photocurrent ($J_{ph}$) of the cell shows a universal behavior, which proves to be independent
4.2. Effect of metal electrodes on solar cell performance

Figure 4.9: Schematic energy diagram of an interface between an organic semiconductor and different top electrodes. The extraction current is independent of the work function of the top electrode.

of the metal electrode used. The differences in device performance between the various metals therefore originates from the change in the electric field in each device, since for each metal a different part of the universal photocurrent-voltage curve is probed. Consequently, once the $V_{OC}$ has been established for a given metal, the $P_{max}$, FF, and $J_{SC}$ can be directly predicted from our device model.

4.2.2 Results and discussion

The experimental photocurrent-voltage characteristics of the ITO/PEDOT:PSS/MDMO-PPV:PCBM/cathode (cathode=LiF/Al, Ag, Au, Pd) devices are illustrated in Figure 4.6. The $V_{OC}$ of these devices after correction for the dark current are: LiF/Al=0.90 V; Ag=0.70 V; Au=0.59 V; Pd=0.40 V, respectively. The $J_{SC}$ decreases from 28 A/m$^2$ for LiF/Al to only 17 A/m$^2$ for Pd. Although the experimental data in Figure 4.6 are measured at the same light intensity, a difference in the reflectivity and/or interface roughness of the top electrode materials means that the quantity of photons absorbed by the active layer is almost certainly not equal [19], thus resulting in a slight variation in the $J_{ph}$. In the case of Au and Pd, the lower surface reflectivity means that the $J_{ph}$ is typically 11% less than that of Ag and LiF/Al.

In Section 3.1 of this thesis, it is shown that when subjected to a large reverse bias ($\geq -10$ V) the $J_{ph}$ saturates and becomes voltage and temperature independent. This implies that all photogenerated charge carriers are extracted from the active layer before recombining, and that their rate of generation approaches the maximum possible. The existence of such a saturated $J_{ph}$ allows us to correct the experimental data for the maximum generation rate, which subsequently more correctly reflects the number of photons absorbed by the active layer for the data presented. The corrected $J_{ph}$-$V$ characteristics are plotted against $V_{OC}$-$V$ in Figure 4.10, which reflects the internal electric field in the device, together with the model calculations. In all cases, the individual curves coincide with one universal curve, demonstrating that, as expected, the photogeneration processes in the photoactive layer are not dependent on the nature of the top electrode. Moreover, it shows that no additional contact resistance is induced when the top
contact is changed from Ohmic (LiF/Al) to non-Ohmic (Ag, Au, Pd) as depicted by Figure 4.9. With a change in the top electrode the $V_{OC}$ is affected due to modification of the metal work function. The reason for the observed changes in $J_{SC}$, $FF$, and $P_{max}$ is now clear from Figure 4.10: the voltage area between the origin ($V=V_{OC}$) and the arrow ($V=0$ V) reflects the active (fourth-quadrant) part of the device for each top electrode. Consequently, a different region of the $J_{ph}$-$V_{OC}$ curve shown in Figure 4.10 is probed when $V_{OC}$ is modified. The fact that a universal photocurrent-voltage dependence is observed when varying the work function of the metal top electrode (see Figure 4.10) proof that the MIM model is applied to organic bulk heterojunction solar cells.

In Section 3.1 we have addressed the relationship, and ultimate dependence, of the photocurrent of devices with LiF/Al top electrodes on temperature-and the applied voltage. Recently, Koster et al. developed a device model which solves numerically the Poisson equation, continuity equations, and current equations including both drift and diffusion [20]. A similar model has been presented by Barker et al. [21] for bilayer devices. As shown in Figure 4.10 these model calculations describing the $J_{ph}$ of PPV:PCBM BHJ solar cells are in excellent agreement with the experimental photocurrents. For electrodes in which the Fermi level aligns as expected according to their work function, such as silver, the $V_{OC}$ of the solar cell can be directly calculated (as shown in the previous section). Consequently, for these electrodes only knowledge about their work function is required to predict the $J_{SC}$, $FF$, and $P_{max}$. However, this is not the case when considering gold electrodes, in which interface dipoles are known to play a role. Accordingly, there is not a direct linear correlation between the $V_{OC}$ and the metal’s work function, and therefore $V_{OC}$ has to be measured. The
4.3. Experimental section

Figure 4.11: Experimental short-circuit current $J_{SC}$ and the maximum output power $P_{max}$ as a function of $V_{OC}$ (symbols) for four different electrodes at 295 K. The solid and dotted lines represent the numerical calculation for $J_{SC}$ and $P_{max}$, respectively.

experimentally determined $J_{SC}$ and maximum output power $P_{max}$ values as a function of $V_{OC}$ (symbols; calculated values, lines), at 295 K, for four different electrodes are shown in Figure 4.11. In each instance, the device thickness totaled 95 nm. The increase in $P_{max}$ with increasing $V_{OC}$ reflects the movement of the maximum power point along the $J_{ph}$-($V_{OC}$-$V$) curve of Figure 4.10. Furthermore, from considering Figure 4.11 it is also possible to determine exactly how much the power conversion efficiency will rise when the $V_{OC}$ itself is increased, as would occur with a shift in the PCBM LUMO level.

4.2.3 Conclusion

We have been able to demonstrate that the photocurrent in BHJ solar cells is not affected by varying the negatively charged metallic top electrode when scaled against the effective voltage over the device. In addition, the dependence of the photocurrent on the effective voltage is responsible for the difference in performance of the various top electrodes. Moreover, model calculations demonstrate that all of the applicable device parameters can readily be elucidated once the open-circuit voltage is known.

4.3 Experimental section

Device Preparation: All devices used during the course of this study were prepared using indium-tin-oxide (ITO) coated glass substrates. To supplement this bottom electrode, a hole transport layer was prepared by first spin coating an aqueous suspension of PEDOT:PSS (Baytron P VP Al 4083) on top of the ITO surface, under ambient conditions, before drying the substrates at 140 °C in an oven. In addition, the active layer was fabricated by spin coating a solution of MDMO-PPV and PCBM (1:4 ratio, by weight) in chlorobenzene on top of the
PEDOT:PSS coated substrate. To complete the devices, the metal and LiF/metal top electrodes were deposited by thermal evaporation (pressure $< 10^{-6}$ mbar). The respective electrodes and their thicknesses were: gold (Au), 50 nm; palladium (Pd), 50 nm; silver (Ag), 80 nm; lithium fluoride (LiF), 1 nm/aluminum (Al), 100 nm. In order to have a better comparison, all MDMO-PPV:PCBM devices were prepared from the same solution, evaporated and characterized in the same day. The stability of the devices was found to be more than sufficient to perform all the necessary measurements.

**Device Characterization:** In order to measure a reliable photocurrent ($J_L$), the devices were illuminated by a white light halogen lamp with an intensity of 800 W/m$^2$, under a dry nitrogen atmosphere. $J$-$V$ measurements were performed with a Keithley 2400 Sourcemeter. In forward bias ITO electrode was positively biased. A determination of the net photocurrent ($J_{ph}$) was made by also recording the current density in the dark ($J_D$) and subtracting it from the $J_L$, and the $V_{OC}$ was determine from the resulting $J_{ph}$-$V$ curve.
References


Chapter 4: Variation of the metal top electrode in bulk heterojunction solar cells


