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## The use of ZnO as optical spacer in polymer solar cells: Theoretical and experimental study

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For organic solar cells, insertion of an optical spacer between the active layer and the reflective electrode results in a redistribution of the optical electric field. In this paper, theoretical calculations using optical modeling are compared with experimental results for devices with ZnO as optical spacer. An excellent agreement was found for blends composed of poly(3-hexylthiophene) and a fullerene derivative [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester. © 2007 American Institute of Physics. [DOI: 10.1063/1.2784961]

Due to the depletion of fossil fuels, renewable energy sources such as solar and wind energies are of wide interest. Nowadays, much attention has been drawn to polymer solar cells for their advantages in low cost and light weight compared to traditional solar cells.<sup>1-3</sup> Most efficient polymer solar cells are based on a mixture of an electron rich conjugated polymer and a fullerene derivative [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) as electron acceptor, and recently, efficiencies up to 5.5% were published.<sup>4</sup>

One limiting parameter compared to more efficient, traditional silicon based devices is the low short circuit current ( $I_{sc}$ ). This is partially due to relatively narrow absorption bands and unfavorable overlap of these bands with the solar spectrum. Moreover, for many material combinations, the optimal layer thickness is too small to absorb all photons within the absorption bands. Thicker layers do absorb more light, but due to limited and/or unbalanced charge transport, this does not afford larger currents in general. However, it has been proposed that light absorption within these thin layers can be increased by changing the spatial distribution of the optical electric field inside the device.<sup>5,6</sup> Inserting an extra transparent electron transporting layer between the active layer and the metal top electrode can place the active layer in a more favorable region of the internal electrical field.

The use of TiO<sub>x</sub> as such an optical spacer has been reported before.<sup>5</sup> Previously, we demonstrated that incorporation of a ZnO layer between a poly(3-hexylthiophene) (P3HT):PCBM photoactive blend and aluminum metal electrode also affords higher photocurrents.<sup>7</sup> It has been suggested that, besides the optical incoupling effects, the addition of a metal oxide layer could also enhance the performance by creating an extra donor-acceptor interface<sup>5,8</sup> or by acting as an exciton blocking layer.<sup>9</sup> Here, we present theoretical and experimental results, assessing the origin of the increased current in P3HT:PCBM solar cells with a ZnO spacer layer.

Devices made and modeled in this study (Fig. 1) used indium tin oxide (ITO) patterned glass substrates (Philips Research) covered by 50 nm of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron® P VP AI 4083; HC Starck). For the active layer, a blend of

P3HT (Rieke Metals) and PCBM (Solenne BV) was used in a 1:1 weight ratio. The thin films up to 100 nm were spin coated from a 10 mg/ml chlorobenzene solution and thicker films from a 15 mg/ml solution at different spin speeds. ZnO layers were deposited by spin casting ZnO nanoparticles dissolved in acetone.<sup>7</sup> With 10 mg/ml, a 39 nm ZnO layer was obtained. After completion of the solution processing, the samples were moved into a glove box with a nitrogen atmosphere to evaporate 1 nm of LiF and 100 nm of Al as top electrode at 10<sup>-5</sup> mbar. After completion, the devices were annealed for 5 min at 140 °C in the glove box. Experimental currents were obtained from spectral response measurements convoluted with the AM1.5 spectrum. Layer thicknesses were determined with a Tencor® P-10 surface profiler.

Calculations of the optical electrical field were performed with the ESSENTIAL MACLEOD software package (Thin Film Center, Inc., Tucson, USA). The optical constants of PEDOT:PSS, P3HT:PCBM, and Al were obtained from literature.<sup>10-12</sup> The optical constants of glass and ITO were provided by Thin Film Center and those of ZnO were obtained with ellipsometry measurements.

Theoretical analysis by optical modeling is a powerful mean, increasingly often used to understand and predict optical effects in organic solar cells.<sup>13-18</sup> It is based on the transfer matrix formalism.<sup>13</sup> Absorption, transmission, reflection, and phase shift can all be described by the real and imaginary parts of the complex refractive index ( $\tilde{n}=n+ik$ , with  $n$  the refractive index and  $k$  the extinction coefficient) of each layer. The optical electric field at each position can be calculated with the resulting system transfer matrix.

Figure 2 shows calculated optical electric fields for a 40 nm thick P3HT:PCBM layer. Without optical spacer, the thin photoactive layer is situated well outside the maximum optical electrical fields of the relevant wavelengths of light,

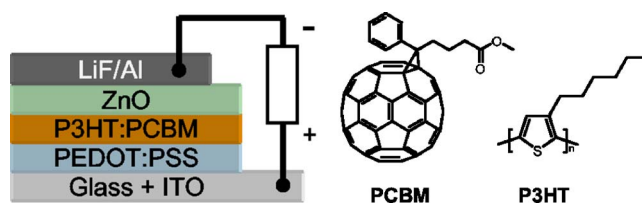


FIG. 1. (Color online) Device layout with a ZnO optical spacer and the molecular structure of the photoactive components.

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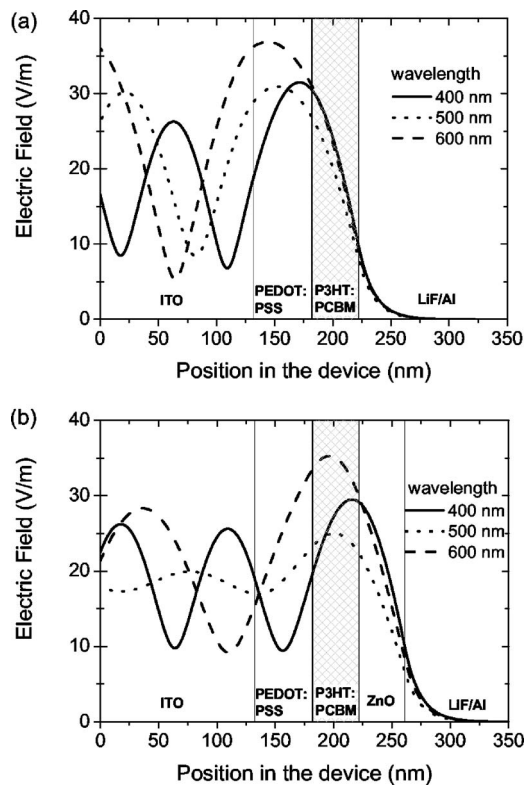


FIG. 2. Calculated optical electric field for light of different wavelengths in devices with a 40 nm thick active layer, (a) without and (b) with 39 nm ZnO.

and insertion of a 39 nm layer of ZnO shifts the position of the maximum into the absorbing layer. From these calculations, one would predict a significantly higher photocurrent for such a thin photoactive layer as a result of improved incoupling.

To quantify this effect, the maximum generated  $I_{sc}$  in active layer was calculated, assuming an internal quantum efficiency (conversion efficiency of absorbed photons to collected charges) of unity and illumination with AM1.5 at  $100 \text{ mW/cm}^2$ . For heterojunction solar cells based on P3HT:PCBM, the calculated  $I_{sc}$  oscillates with active layer thickness due to interference effects (Fig. 3, solid line). Maxima are observed at 80 and 210 nm. By inserting a ZnO layer, these maxima are shifted toward lower thicknesses. The extent of this shift corresponds to the thickness of the ZnO layer. Because  $I_{sc,max}$  is necessarily zero at zero thick-

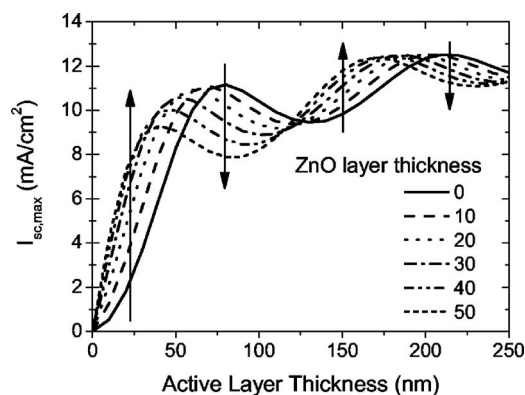


FIG. 3. Calculated active layer thickness dependent short circuit current, assuming a 100% IQE and illumination with AM1.5 ( $100 \text{ mW/cm}^2$ ) for different thicknesses of the ZnO layer.

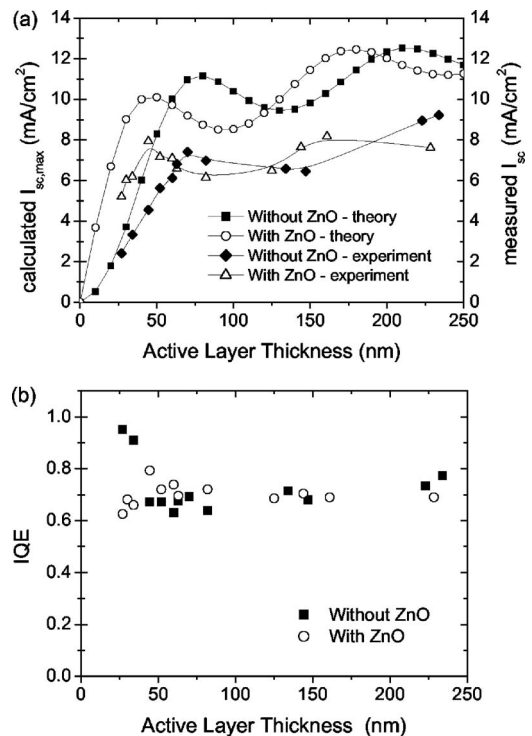


FIG. 4. (a) Theoretical vs experimental active layer dependence of short circuit current without and with a 39 nm ZnO optical spacer. (b) Internal quantum efficiency vs active layer thickness for solar cells with and without a ZnO spacer layer.

ness, the initial increase of the current with layer thickness becomes much steeper upon insertion of a ZnO layer, resulting in a large increase of the maximum obtainable  $I_{sc}$  for thin active layers. For a 40 nm thick active layer, there is an almost twofold increase by adding a 40 nm ZnO layer (Fig. 3). However, for thicker films, ranging from 70 to 130 nm, insertion of an extra layer is expected to be detrimental for the device performance. In this case, the active layer already is in the most effective position without ZnO, and adding the spacer layer shifts it away from the maximum of the optical electric field. Clearly, one would expect the magnitude of the perturbation caused by the ZnO to decrease for thicker layers.

To verify the calculations, devices with photoactive layer thicknesses ranging from 27 to 220 nm, without and with a 39 nm thick ZnO spacer layer, were made. Due to the out-of-phase progression of the predicted currents for cells with and without the ZnO layer, a number of crossover points are expected (Fig. 4). With active layers less than 60 nm cells with ZnO should give higher  $I_{sc}$ 's; between 60 and 130 nm, the devices without spacer are expected to generate higher currents. Figure 4 shows the excellent agreement between the theory and experiments. The difference in magnitude of the photocurrents between the model and the experiments is due to the fact that the actual internal quantum efficiency is less than unity, but the periodicity of both the experimental curves accurately corresponds to the calculated data. This demonstrates that optical modeling is an accurate tool to predict light absorption in these multilayer devices. Moreover, the good correlation between predicted and measured currents indicates that the observed effects of the extra ZnO layer can, at least in a qualitative way, be attributed to an optical effect. To further corroborate this, the internal quantum efficiency (IQE) was calculated, by dividing the mea-

sured currents by the calculated number of absorbed photons [Fig. 4(b)].<sup>16</sup> If the ZnO layer affects more than just the absorption profiles, for example by providing an additional donor-acceptor interface<sup>5,8</sup> or by acting as a exciton blocking layer,<sup>6</sup> this would afford higher IQE values for cells with ZnO, especially for thin photoactive layers, where the relative contribution of an interface effect should be the largest. However, with invariant values of  $0.7 \pm 0.1$ , the IQE of ZnO containing cells is at best equal to the IQE obtained for cells without ZnO. This observation indicates that a ZnO layer in P3HT:PCBM cells only significantly affects the incoupling of light and no additional electronic effects need to be considered to explain the moderation of the currents.

In conclusion, the increased photocurrent of P3HT:PCBM solar cells with an additional ZnO layer is caused by enhanced light absorption as a result of redistribution of the optical electrical field inside the device. The absorption is significantly enhanced for thin ( $<60$  nm) films. For thicker absorbing layers, the effect of the optical spacer is less pronounced, and may either enhance or decrease light absorption, depending on the thickness of the relevant layers. Especially organic solar cells where the film thickness is limited by a low charge carrier mobility can benefit from an optical spacer layer.

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