

TiO₂ as Electron-Extraction-Layer in Reverse Type P3HT/ICBA Organic Solar Cells

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INTRODUCTION

Amongst the different types of solar cells, organic solar cells consist of carbon-based materials and therefore are light-weight and have low production costs per unit. However, the exciton binding energy in organic semiconductors is very high compared to that in inorganic semiconductors. Low carrier mobilities also limit the thickness of the active layer and therefore the energy conversion efficiency (η). With a so called bulk-heterojunction (BHJ), i.e. a blend film of a conjugated polymer donor and a soluble fullerene derivative acceptor, the active layer thickness can be increased significantly. To facilitate charge extraction, a typical cell-configuration is support/ITO/hole-extraction-layer/BHJ/electron-extraction-layer/low work-function metal.

However, PEDOT:PSS, a common hole-extraction-layer, is known to react with ITO [1]. By inversion of the configuration, direct contact between ITO and PEDOT:PSS, as well as the use of low work-function metals can be avoided. Such reverse structures have been shown to be more stable [2]. Furthermore, reverse structures allow for a more controlled processing of metal oxides, i.e. TiO₂, as electron-extraction-layers. The crystallinity and microstructure of TiO₂ significantly influence the layer conductivity and recombination sites within. However, the influence of the TiO₂ morphologies on the functionality as electron-extraction-layers in organic solar cells is still unknown.

In this work, we fabricated reverse type organic cells of the structure glass/ITO/TiO₂/P3HT:ICBA/PEDOT:PSS/Ag. Indene-C60 bisadduct (ICBA) has a higher LUMO level (-3.67 eV) than the commonly used [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, -3.85 eV), which leads to a higher open circuit voltage (V_{OC}) [3]. With this type of cell, we investigated the influence of the crystallinity and microstructure of the TiO₂ layer on the photocurrent generation and quantum efficiency (QE).

EXPERIMENTAL

To fabricate the cells, a TiO₂ layer was deposited on an ITO coated glass slide. On top of this, first a mixture of P3HT and ICBA in *o*-xylene and then PEDOT:PSS in water were spin-coated. After annealing at 120°C, the Ag counter electrode was deposited in vacuum and the cell heated again to 120°C and sealed. The TiO₂ layers were deposited either by spray pyrolysis or by sputtering. For the former method, an ethanolic solution of TiC₁₆H₂₈O₆ was sprayed onto ITO coated glass heated to 250°C, 350°C or 420°C. For the latter method, ITO coated glass was heated to 100°C, 200°C, 300°C or 440°C in Ar with 5% O₂ and a total pressure of 0.3 Pa and a TiO₂ sputtering target and 70 W RF power were used. Haze rates were measured for TiO₂ layers fabricated under the same conditions on glass slides. The cells were characterized by UV-VIS spectra of the respective layers, external quantum efficiency (EQE) spectra, current density – voltage (J–V) curves and photocurrent generation profiles.

RESULTS AND DISCUSSION

Reverse-type organic solar cells with P3HT as donor and ICBA as acceptor were fabricated successfully. A short circuit current (J_{SC}) of 5.85 mA/cm², V_{OC} of 0.71 V, fill factor (FF) of 0.38, η of 1.6% and a peak EQE of 0.48 at 475 nm was achieved with a TiO₂ layer fabricated at 420°C by spray pyrolysis. The light absorption of the cell was dominated by the absorbance of the BHJ, with a peak at about 510 nm. The absorbance of the BHJ at wavelengths longer than 400 nm was dominated by the absorbance of P3HT, at shorter wavelengths by the absorbance of ICBA. Variation of the fabrication method or temperature did not seem to influence the light absorption of the cell.

The EQE, however, decreased significantly with decreasing

fabrication temperature with both methods (Fig. 1). At relatively high fabrication temperatures, the EQE spectra had two peaks each, one of which can be attributed to light absorption of ICBA, the other to absorption of P3HT. At the lowest fabrication temperatures, only the peak due to ICBA absorption was measured. Exciton formation on ICBA and subsequent hole transfer to P3HT has an energetic advantage over exciton formation on P3HT and electron transfer to ICBA. At low fabrication temperatures, this energetic advantage significantly influenced the shape of the EQE spectra. At higher fabrication temperatures, the energetic difference did not seem to have much influence.

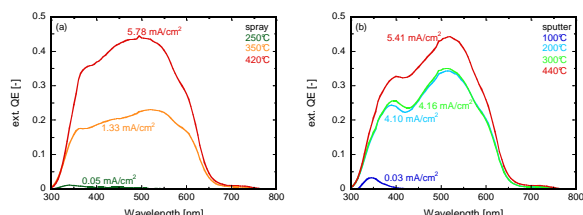


Fig. 1: EQE spectra of ITO/TiO₂/P3HT:ICBA/PEDOT:PSS/Ag cells with TiO₂ layers fabricated at different temperatures. (a) TiO₂ layers fabricated by spray pyrolysis, (b) sputtered TiO₂ layers.

J–V curves showed a similar trend as the EQE spectra (data not shown). Dark current measurements showed, that at low fabrication temperatures, the TiO₂ layers acted as insulators, which led to low photocurrent generation. In TiO₂ layers fabricated by spray pyrolysis, there was a risk of remaining organic impurities at low fabrication temperatures, which might have increased the insulator characteristics. Further analysis suggested that the series resistance of cells with sprayed TiO₂ layers decreased with increasing fabrication temperature. This decrease in series resistance is one probable reason for the increase in photocurrent generation. The resistance of cells with sputtered TiO₂ layers, however, did not change significantly, so that the difference in photocurrent generation cannot be explained by the resistance alone. At the highest fabrication temperatures (over 400°C), both sprayed and sputtered TiO₂ layers were anatase and therefore had a higher conductivity compared to amorphous TiO₂. At lower fabrication temperatures, part or all of the TiO₂ might be amorphous. Anatase TiO₂ therefore seems to facilitate electron extraction and thus measurable photocurrent.

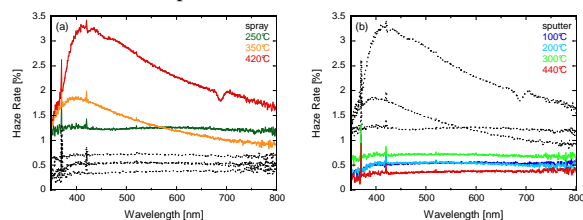


Fig. 2: Haze rate of TiO₂ layers on glass substrates fabricated at different temperatures. (a) TiO₂ layers fabricated by spray pyrolysis, (b) sputtered TiO₂ layers. (dotted lines: respective other method)

Furthermore, with sputtered TiO₂ layers, the P3HT peak and the ICBA peak in the EQE spectra could be distinguished easily, while with sprayed TiO₂ layers, the two peaks were broadened and thus difficult to distinguish (Fig. 1). Haze rate measurements showed an increased scattering effect of sprayed layers with increasing fabrication temperature with maximal scattering around 400 nm (Fig. 2a). This scattering effect can explain the peak broadening of the EQE, especially since the wavelength of the haze rate peak roughly corresponds to the wavelength of the valley between the two EQE peaks. In contrast to this, the haze rate of sputtered layers was very low for all fabrication temperatures (Fig. 2b). The EQE peaks of cells with sputtered layers therefore were relatively sharp.

In conclusion, the crystallinity and the haze rate of the TiO₂ layers significantly influence the height and shape of the EQE spectra of organic solar cells and might therefore be used to regulate the cell characteristics

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