

Photovoltaics of interconnected networks

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Abstract

All three types of organic solar cells *i.e.* sensitised photoelectrochemical cells, molecular organic and polymeric “plastic” cells, work best when utilising interpenetrating networks. Although the basic construction is equal, the current understanding and the modelling of devices by different groups are contradictory. Whereas photoelectrochemists use classical models based on the solid/electrolyte junctions, the polymeric, organic device community seems to prefer to treat the network system as an intrinsic material sandwiched between metals of different work function (metal-insulator-metal MIM devices). Both approaches will be discussed with recent experiments performed with molecular organic solar cells.

Keywords: Solar Cells, Bi-continous polymer network interfaces, Fullerenes and derivatives, Organic semiconductors based on conjugated molecules, Semiconductor/semiconductor interfaces, Evaporation and Sublimation

1. Introduction

Organic photovoltaics, started in 1986 by Tang [1], only recently became of broader interest. Starting with relatively small molecules [2] the efficiency remained for a long time at the record set in the first papers. In our own investigations we could show that the main problem is the width of the charge generation layer which for organic solar cell is much smaller than in an inorganic cell [3,4]. Another new approach, the sensitisation solar cell, which is on the verge of industrial utilisation, uses only one monolayer of an organic dye to absorb the light [5]. Here, a new concept was developed in 1985 when for the first time extremely rough electrode surfaces developed by J. Augustynski [6] were used by J. Desilvestro [7]. Thereby the first interpenetrating networks of materials, an electron conductor (TiO₂) with a monolayer of dye at the interface on the one hand, and an ion conductive electrolyte used for charge transport from the counter electrode to the oxidised dye on the other hand. This in photoelectrochemistry is discussed as a nanoporous or even fractal junction.

A similar concept was developed independently, when about 10 years later the first polymer/C₆₀ based solar cell was demonstrated [8]. Here a discussion started between the concept of a “bicontinuous network of internal donor-acceptor heterojunctions” [8] and a MIM-device controlled by the “work function difference of the metal electrodes” [9].

Later it was shown that C₆₀ networks could also be used to extend the flat interface of the Tang-type organic heterojunction [10]. Thereby the first organic solar cell with a solar AM1.5 efficiency higher than 1 % was demonstrated.

In the following we mainly report on further investigations of this type of organic solar cells based on zinc phthalocyanine (ZnPc) and the methyl substituted perylene pigment (MPP) N,N-bismethyl-perylen-3,4,9,10 -tetracarboxylic acid diimide.

2. Experiment

The p/n-junction solar cells were produced by successive evaporation of the organic dyes on ITO coated substrates in a high vacuum evaporation system ($p < 3 \cdot 10^{-6}$ mbar). As a back electrode gold was evaporated onto the

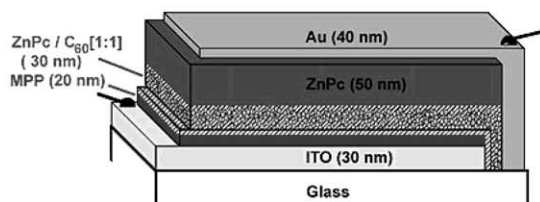


Fig. 1: Structure of a sandwich organic solar cell consisting of substrate / ITO / MPP / ZnPc / Au containing an ZnPc/C₆₀-composite interlayer

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top organic dye layer. Figure 1 shows a typical structure of our sandwich solar cells. Interconnected network solar cells were prepared by coevaporating a ZnPc/ C₆₀-composite layer between the MPP and ZnPc.

The short circuit photocurrent spectra were measured using a xenon arc lamp and a monochromator. For the I/V-characteristics under illumination an AM 1.5 solar simulator (K. H. Steuernagel Lichttechnik GmbH) was used. The photocurrent spectra as well as the I/V-characteristics were monitored using a Keithley SMU 236 [10]. Luminescence and luminescence quenching experiments were performed illuminating the solar cells with an Ar laser (488 nm) in a Zeiss MCS 400 spectrometer protected by a Notch-filter.

For electroabsorption measurements, light from a Xenon lamp was dispersed through a monochromator and focused onto the organic semiconductor device through the transparent ITO contact. The light reflected at the back metal electrode was then focused onto a silicon photodiode. A combined DC and AC electric field was applied to the device. The AC test field modulated at 3.3 kHz was taken from the reference output of the lock-in amplifier and a programmable voltage source provided the DC bias [11]. All measurements were performed in ambient air.

3. Results and discussion

All results obtained with flat interfaces are in perfect accordance with those expected for a voltage dependent space charge region as known from inorganic semiconductor junctions. These results were:

- the photo current increases for voltages in reverse direction with the square root of applied voltage,
- the luminescence of solar cells is quenched with the square root of voltage applied in reverse direction for low voltages (the voltage dependence following a kind of "diode behaviour")
- the electroreflectance signal [11] consisting of two components of which one (the one we therefore attribute to the space charge region) showing again a square root increase with voltage.

This square root dependence reflects the voltage dependence of the thickness of the space charge region as given by the well know dependence

$$d = (\epsilon\epsilon_0 V_b / 2 \pi e N_A)^{1/2}$$

Here V_b is the barrier height which is proportional to the applied voltage, ϵ the dielectric constants and N_A the doping concentration.

Since in our case the absorption within the extremely thin space charge region is negligible, the light intensity does not decrease much throughout the film and the amount of light absorbed within the film is about constant. Therefore the number of electron hole pairs (or excitons) created within the films is about constant. But the charge separation (and thereby the photocurrent generation and luminescence quenching) occurs only within the electric field of the space charge region, thereby reflecting the voltage dependence of its thickness. As the electric field leading to a reflectivity change also the photocurrent and the luminescence quenching therefore reflect the voltage dependence of the space charge layer thickness.

4. Conclusions

Also molecular organic photovoltaic solar cells are determined by charge separation within the electric field at the interface with a contact material, just the same way as classical solid state PV or photoelectrochemical solar cells work. This interface can be made extremely rough (e.g. even by etching, in most cases though by preparing the electrodes from nanoparticles), thereby creating a nanoporous structure also called interpenetrating network. But as in photoelectrochemical solar cells the junction still remains that between the two contact materials.

The two contact materials forming the interpenetrating network will therefore determine the behaviour of the solar cell, especially their maximum photovoltage or built in potential. The contact metals used need to form ohmic low resistance contacts to only one of the two materials. They can diminish the maximum photovoltage, but do not determine it (as was assumed in the MIM description of polymer/ C₆₀ cells).

5. Acknowledgements

We gratefully acknowledge financial support by the European Commission under contract number JOR3-CT96-0106, and by the Bundesministerin für Bildung und Forschung under contract number 13N6906/1.

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