

# Scientific Report

about an

## Short Visit Grant

within the

## ORGANISOLAR-Program

## of the European Science Foundation

Grantee: Harald Hoppe

Grantee Institution: Institute of Physics, Weimarer Str. 32, 98693 Ilmenau, Germany

Host: Professor Nyazi Serdar Sariciftci

Host Institution: Linz Institute for Organic Solar Cells, Altenberger Straße 69, 4040 Linz,  
Austria

Exchange Period: 7<sup>th</sup> December 2008 – 21<sup>st</sup> December 2008

Reference Number: 2683

# 1 Introduction

Within the last decade polymer solar cells – as part of organic electronics – have undergone a tremendous development in terms of understanding principal device function and power conversion efficiency. By surpassing certified efficiencies of 5% within the last three years, the polymer solar cell concept has reached application levels and is on the way to commercialization. However, today there is still a need for improved understanding of the fundamental physics behind and its influence on further improved device performance.

A powerful method to investigate internal electrical properties of organic semiconductor thin film devices is impedance spectroscopy. Among the main advantages of this technique is that it is non-invasive, non-destructive and that the frequency and hence the timescale on which the physical processes of charge transport and recombination is observed can be varied over several orders of magnitude. From impedance data various important device and material parameters such as its capacitance and conductance, the width of a space charge region, charge carrier density, charge carrier mobility and dielectric constants can be determined. It is well established that e.g. the charge carrier mobility [1,2] and trapping/detrapping processes [3] influence on impedance spectra. All of these parameters are usually obtained by fitting the experimental data to model equivalent circuits.

Another feature still under discussion is the phenomenon of a negative capacitance. This negative capacitance was found to dominate the low frequency regime under bipolar injection in organic semiconductor thin film devices. Eitan Ehrenfreund et al. have recently introduced an analytical model describing negative capacitance in organic semiconductor devices [4], by attributing this phenomenon to electron-hole recombination.

The main purpose of this scientific collaboration was to improve the understanding of negative capacitance in polymer-fullerene bulk heterojunction solar cells by analyzing the influence of different parameters, among which the film thickness, the work function of the electron extracting electrode, the operating temperature, and finally a replacement of the active layer by an insulator.

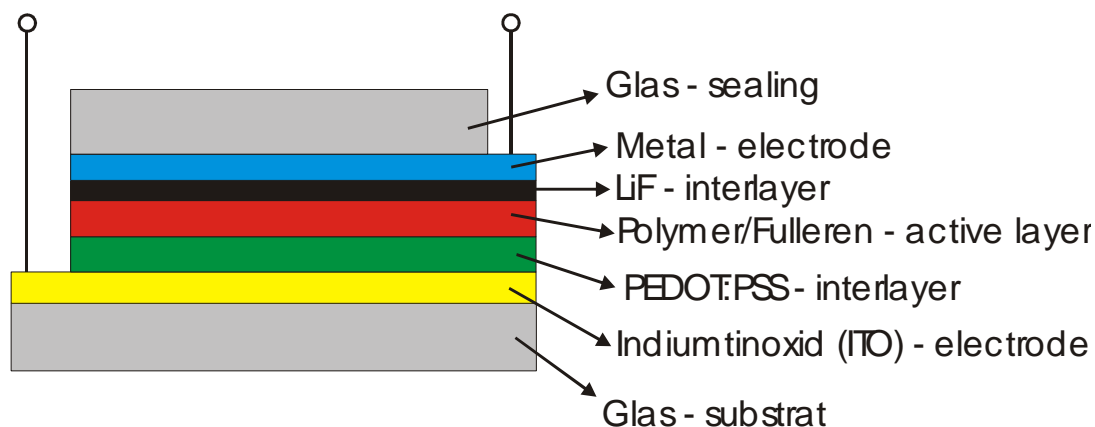
Especially the charge recombination process needed to be shed more light at: does the occurrence of negative capacitance requires the injection of charge carriers at specific energy

levels into HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)– controlled by the work function of the electrodes, or rather are the energetics and place of charge recombination of minor importance and only the presence of recombination inside the polymer thin film controls negative capacitance? In previous measurements we could identify that with increasing work function on the cathode side, the effect of negative capacitance was increased. However, this was accompanied by generally larger currents and a loss of diode behaviour. These data suggested either the negative capacitance to depend mainly on the overall current passed through the device or indeed the control of energy level dependent injection.

## 2 Experimental

### 2.1 Device Preparation

Organic semiconductor thin film devices studied herein were prepared in sandwich geometry (see Figure 1). Substrates for these devices are 1.5 x 1.5 cm large glass sheets covered with Indium-Tin-Oxide (ITO, purchased from Merck, KGa Darmstadt). To ensure secure connection of the metal top electrode without the risk of punching through the metal layer and shortcut to the ITO, part of the ITO was removed by chemical wet etching. This was done by exposing the surface to a strong acid (HCl conc : HNO<sub>3</sub> conc: H<sub>2</sub>O = 4.6 : 0.4 : 5) for 20 minutes. To protect the part of the substrate from acid where the ITO-layer should remain, it was coated with a sticky tape. For thorough cleaning substrates subsequently underwent 20 minutes in acetone and isopropanol supersonic bath. After drying, the substrates were either covered first with PEDOT:PSS and/or directly with the organic semiconductor layer by spin coating, depending on the desired device structure.



**Figure 1: Common design for an organic solar cell.**

Active layers were prepared from regio-regular poly(3-hexylthiophene-2,5-diyl) (P3HT, purchased from Rieke Metals, Inc.) and (1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C<sub>60</sub>) (PCBM, purchased from Solenne) in different mixing ratios either by spin coating from a solution in chlorobenzene (CB) or by doctor blading from a solution in chloroform (CF), in order to achieve different film thicknesses. For the extreme case of an insulating polymer layer, polystyrene (PS) was spin cast from toluene solution as replacement for P3HT:PCBM.

Top electrodes were deposited by thermal sublimation through a shadow mask in a vacuum better than  $5 \times 10^{-6}$  mbar. Tungsten boats were used as source. Last but not least, all samples

were heat treated at 120°C for 5 minutes in order to reach better diode and solar cell performance.

## 2.2 Experimental Methods

After device preparation the I-V-characteristics (or DC-behavior) of all organic solar cells were determined by a Keithley 2400 sourcemeter, in order to allow selection of the best cells for further investigation.

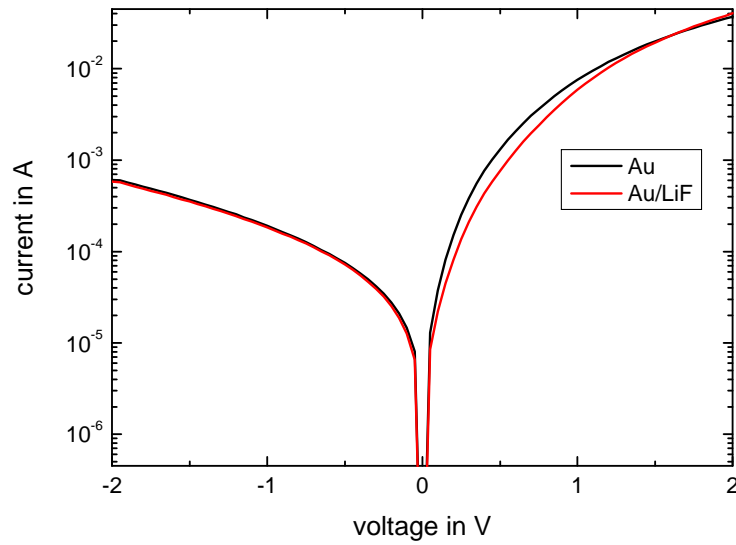
Impedance spectroscopy was carried out with a “Novocontrol Technologies Alpha-A High Performance Frequency Analyzer” (range: 3  $\mu$ Hz till 20 MHz) under dark conditions and different forward biases. In order to carry out temperature dependent impedance spectroscopy test devices were placed into an Oxford Instruments cryostat and cooled down with liquid nitrogen. An accessible temperature range from 77 K to 280 K was obtained for the capacitance measurements. Taking into account both, working as close to equilibrium as possible and reaching a good signal to noise ratio an AC signal amplitude of 20 mV was chosen.

## 3 Results

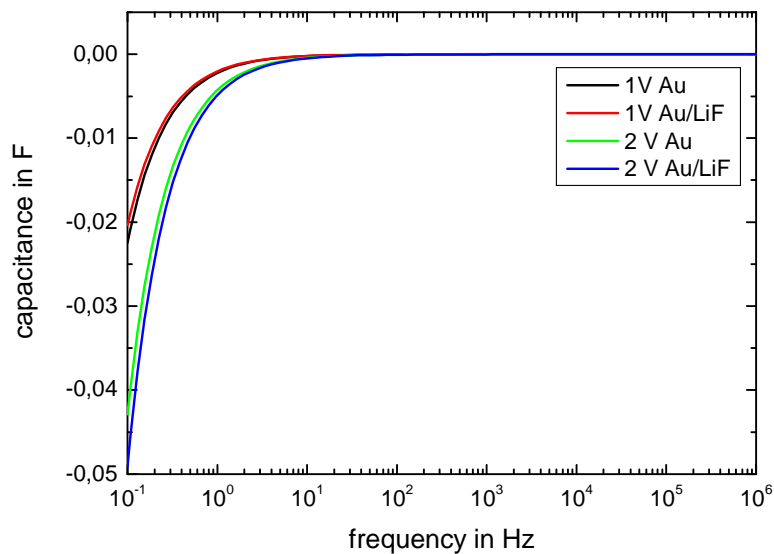
In the following a brief description of the main results is given. The results for temperature dependent measurements and the dependency on active layer thickness is shown in the report of Roland Rösch, while here I will focus on the influence of electrode work function and replacement of the active layer by an insulator.

### 3.1 Cathode work function dependence of negative capacitance

To investigate NC-dependence of work function of top electrode material, we prepared BHSCs described in chapter 2.1 by using Gold and Gold/LiF as top electrode material. The choice of these two electrodes should help directly to discriminate on the influence of charge injection levels. Figure 2 and Figure 3 show dark I-V-characteristics and frequency response of capacitance respectively.



**Figure 2: Dark I-V-characteristics of BHSC with Au or Au/LiF top electrode.**

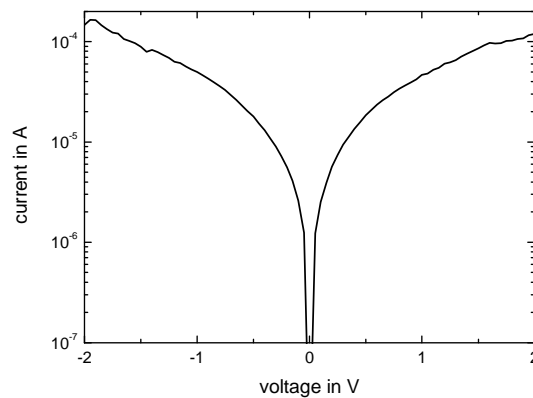


**Figure 3: Frequency response of capacitance for BHSC for Au or Au/LiF top electrode for two different forward biases.**

From the IV-characteristics we observed only a minor influence of the insertion of LiF between the active layer and the gold electrode – the forward currents deviate from each other slightly within the 0.2-1.4 Volts range. However, for larger forward currents the curves coincide again and the resulting negative capacitances appear to be very similar for 1 and 2 Volts forward bias. Therefore the main controlling factor seems to be the forward dc-current.

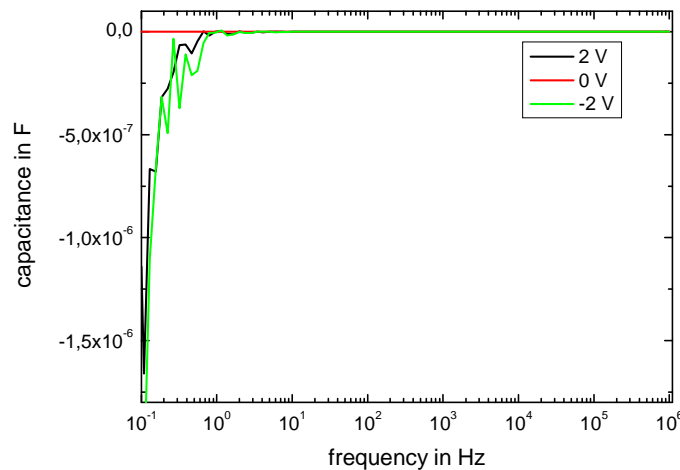
### 3.2 Replacement of active layer

In order to further investigate the effect of the kind of charge carrier recombination on negative capacitance, we replaced the active layer (P3HT/PCBM) by Polystyrene (PS). The resulting sample structure is ITO/PS(140 nm)/Al – a simple MIM-type of a device. Figure 4 shows its dark I-V-characteristics. It is clearly visible that there is no diode behaviour anymore but the device behaves as a simple resistor (16 k $\Omega$ ).



**Figure 4: Dark I-V-characteristics for Polystyrene.**

Surprisingly this sample shows negative capacitance as well (compare Figure 5). But this device shows negative capacitance in forward and reverse bias, in contrast to the bulk heterojunction solar cells, which never showed negative capacitance in reverse bias. It should be noted here, that with a parallel resistance of 16k $\Omega$  and an inductance of the wires of only 0.5  $\mu$ H no negative capacitance due to them is expected [5].



**Figure 5: Frequency response of capacitance for ITO/PS/Al for different forward biases.**

## 4 Future collaboration and projected publications

In agreement with Prof. Sariciftci in Linz, we plan to continue our collaboration also in the future based on a project application to a national Austrian funding agency. In the mean time the publication of one or two papers is projected. All of the collected data from the visit shall enter a larger overview and we may publish in addition some minor aspects separately, for example the temperature dependency of the negative capacitance within the solar cell devices.

### References

- 
- [1] S. Berleb and W. Brütting, “Dispersive electron transport in tris(8-hydroxyquinoline) aluminum (Alq(3)) probed by impedance spectroscopy”, *Phys. Rev. Lett.* 89, 286601 (2002)
- [2] R. Kassing, “Calculation of frequency-dependence of admittance of selc diodes”, *Phys. Stat. Sol. (a)* 28, 107 (1975)
- [3] H.C.F. Martens, H.B. Brom and P.W.M. Blom, “Frequency-dependent electrical response of holes in poly(p-phenylene vinylene)”, *Phys. Rev. B* 60, R8489 (1999)
- [4] E. Ehrenfreund, C. Lungenschmied, G. Dennler, H. Neugebauer and N.S. Sariciftci, “Negative capacitance in organic semiconductor devices: Bipolar injection and charge recombination mechanism”, *Applied Physics Letters* 91, 012112 (2007)
- [5] K. S. A. Butcher, T. L. Tansley, and D. Alexiev, “An instrumental solution to the phenomenon of negative capacitances in semiconductors”, *Solid State Electronics* 39, 333 (1996)