

Scientific Report

about an

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1 Introduction

Thin films of polymeric semiconducting materials have been used to realize several types of electrical devices, such as solar cells, light emitting diodes and transistors. As compared to inorganic semiconductors they exhibit many potential advantages in the production process, for example low processing temperatures, low unit costs and high manufacturing throughput by employing well established printing technologies.

These advantages come at the expense of a generally reduced performance as compared to the well established crystalline inorganic semiconductor technology. For instance, low electron and hole mobilities and pronounced charge carrier recombination are problems related to disordered organic systems. Among others these issues prevented organic photovoltaic devices –up to now– reaching power conversion efficiencies as high as reported for their inorganic counterparts.

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) 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, not well understood feature, which has recently received considerable attention, 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.

Main purpose of this Short Visit Grant was to get a deeper understanding of negative capacitance in bulk heterojunction solar cells by analyzing the influence of different parameters, like film thickness, work function of top electrode, operating temperature, and replacement of the active layer by an insulator.

2 Experimental

2.1 Device Preparation

Organic semiconductor thin film devices studied herein are prepared in sandwich geometry (see Figure 1). Substrates for these devices are 1.5 x 1.5 cm large glass sheets covered with ITO, purchased from Merck, KGaA. 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 is removed by chemical wet etching. This is done by exposing the surface to a strong acid (HCl conc : HNO₃ conc: H₂O = 4.6 : 0.4 : 5) for 20 minutes. To protect the part of the substrate where ITO should remain free from acid, it was coated with scotch tape. For thorough cleaning substrates subsequently undergo 20 minutes in acetone and/or isopropanol supersonic bath. After drying, the substrates are covered with PEDOT:PSS by spin coating or directly with the organic semiconductor layer, depending on the desired device structure.

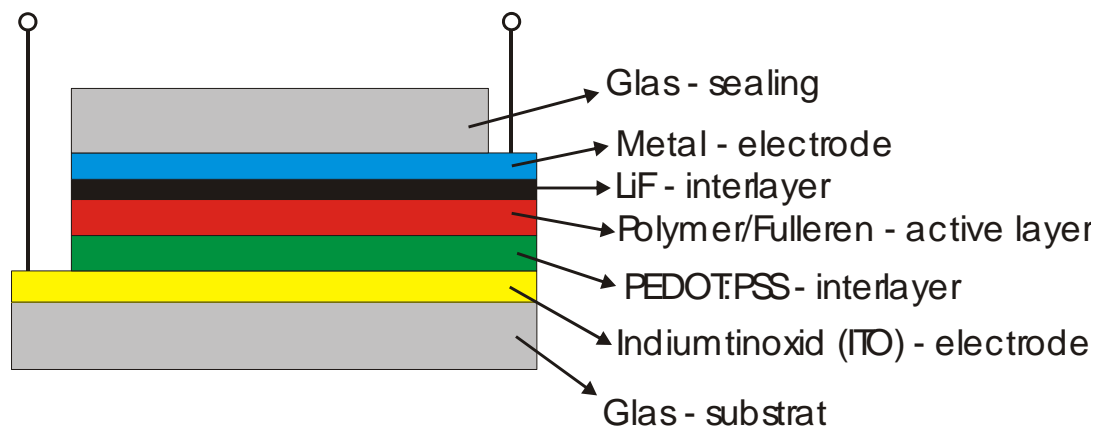


Figure 1: Common design for an organic solar cell.

Active layers made from poly(3-hexylthiophene-2,5-diyl) (P3HT, purchased from Rieke Metals, Inc.) and (1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C₆₀) (PCBM, purchased from Solenne) in different mixing ratios are either spin cast from a solution in chlorobenzene (CB) or coated by using the doctor blade technique from a solution in chloroform (CF), in order to achieve different larger thicknesses.

Top electrodes are applied by thermal deposition through a shadow mask in vacuum better than 5×10^{-6} mbar. Tungsten boats are used as source. Last but not least, all samples are heat treated (120°C, 5 minutes), in order to reach better diode performance.

2.2 Experimental Methods

After device preparation I-V-curves of all organic solar cells are determined by using a sourcemeter (Keithley), in order to select best cells for further investigation as well as for determine DC-behaviour of the cells.

Impedance spectroscopy is carried out with “novoccontrol Technologies Alpha-A High Performance Frequency Analyzer” (range: 3 μ Hz till 20 MHz) under dark conditions for different forward biases. In order to carry out temperature dependent impedance spectroscopy test devices were put into a cryostat from Oxford Instruments and are cooled down with liquid nitrogen. A temperature range from 77 K to 280 K was obtained. 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

Main results obtained during the exchange will be presented in this chapter, except for results on the insulating layer and the variation of the top cathode.

3.1 Temperature Dependent Measurements

Temperature dependent measurements are carried out on a bulk heterojunction solar cell described in chapter 2.1 but without LiF between active layer and top electrode. A temperature range from 77 K up to RT is covered in the measurements. In Figure 2 dark I-V-curves are shown. As one can see, current through the device is reduced with lower temperature in both directions (forward and reverse bias), but decreases faster in forward bias, which leads to smaller rectification for lower temperatures. Furthermore the exponential region in forward bias shifts to higher voltages and has a smaller slope with lower temperatures. I-V-curves for RT show an interesting detail, the current in forward bias is higher for the measurement after the cooling procedure.

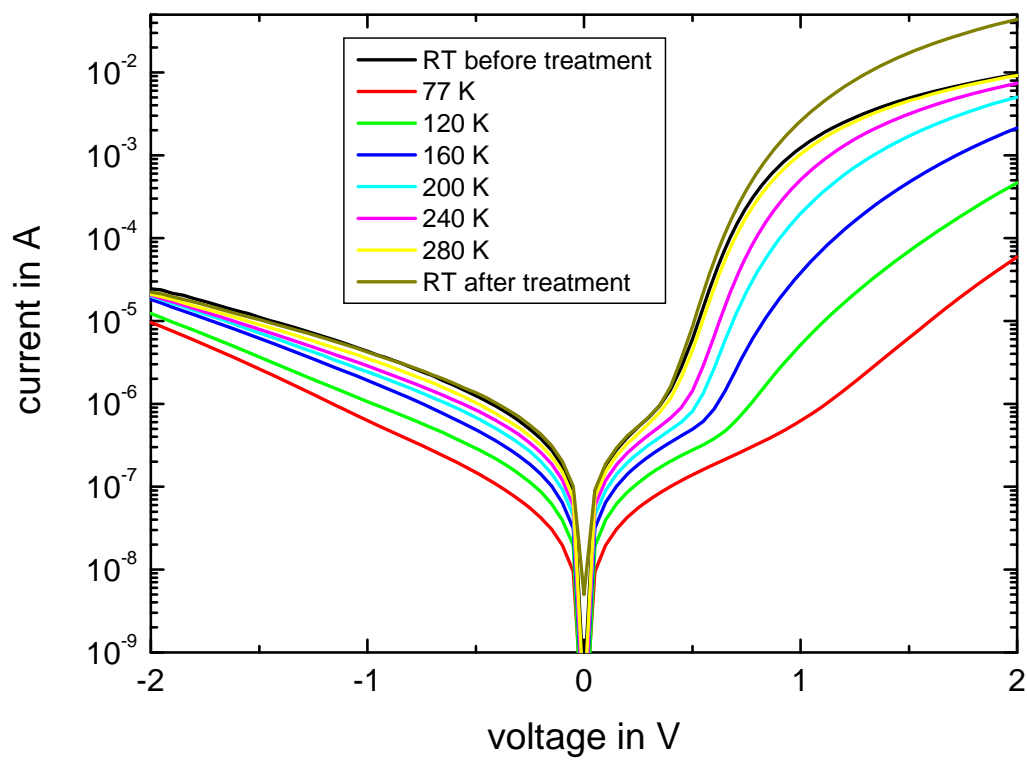


Figure 2: Dark I-V-curves for P3HT/PCBM-based BHSC for different temperatures from 77 K up to RT. RT-measurement was carried out before cooling down to 77 K and after heating up to RT again.

Figure 3 and Figure 4 show the frequency response of capacitance for this BHSC for two different forward biases and temperatures from 77 K till 280 K. The absolute value of negative capacitance increases with forward bias and temperature for a certain frequency. At 1 V forward bias and 77 K negative capacitance is almost “frozen out”.

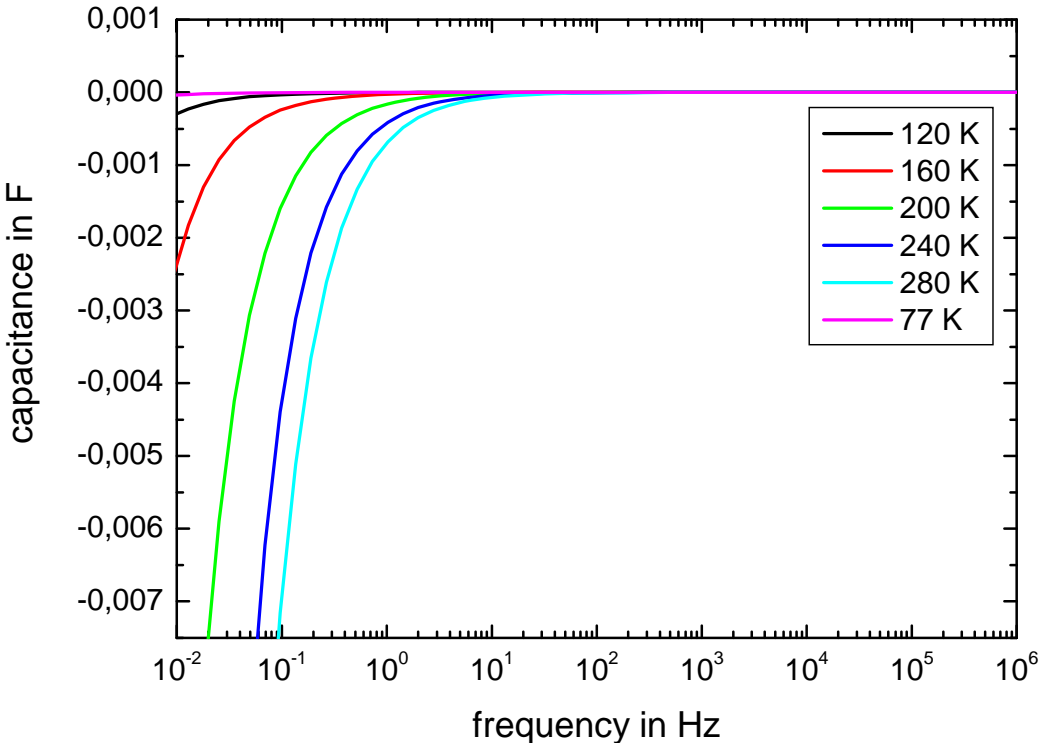


Figure 3: Frequency response of capacitance for BHSC for different temperatures at 1 V forward bias.

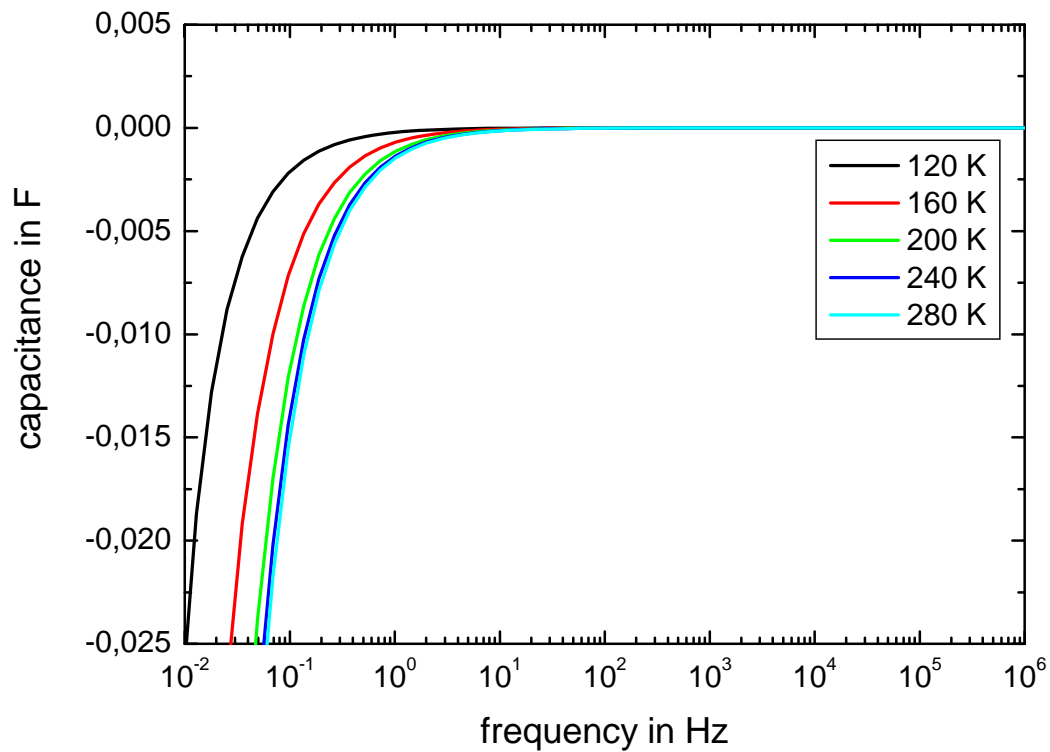


Figure 4: Frequency response of capacitance for BHSC for different temperatures at 2 V forward bias.

3.2 Film thickness dependence of NC

Next parameter to vary is film thickness of the active layer. We use doctor blade technique to get three different values (400 nm, 800 nm and 1500 nm) by applying it one, two and three times on three different substrates. Figure 5 shows frequency response of capacitance for 2 V forward bias and Figure 6 shows I-V-curves of these three samples. Absolute value of negative capacitance increases with decreasing film thickness like current for DC-measurement (see Figure 6, please note, that there was some light shining on the sample).

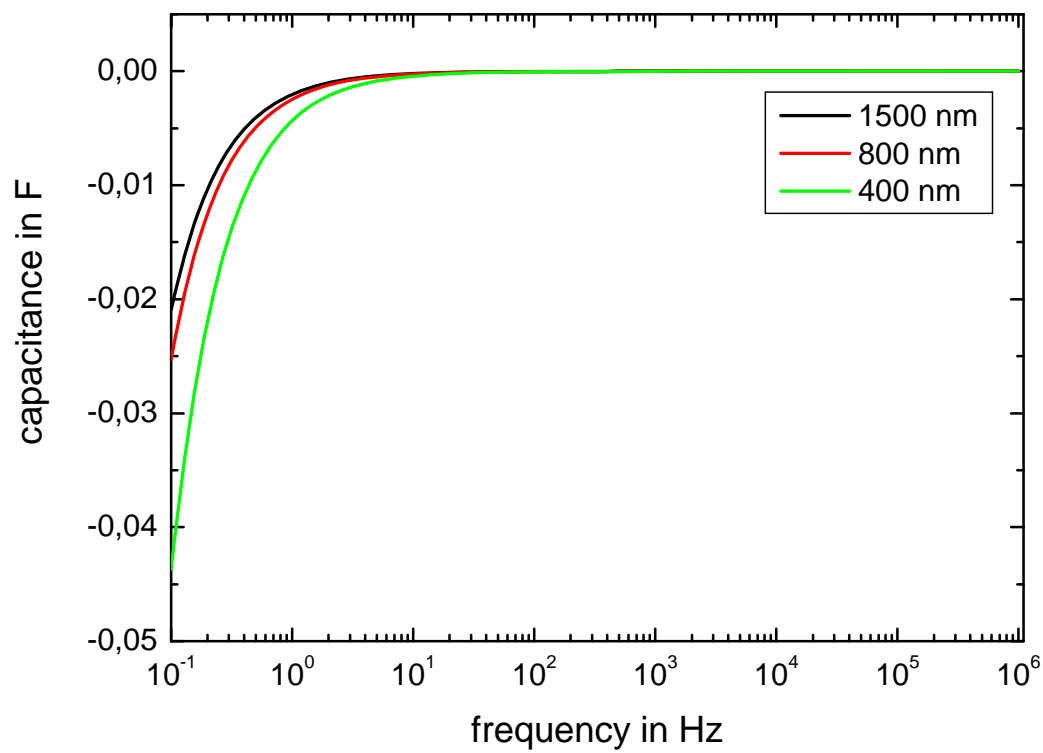


Figure 5: Frequency response of capacitance for BHSC for different film thicknesses at 2 V forward bias.

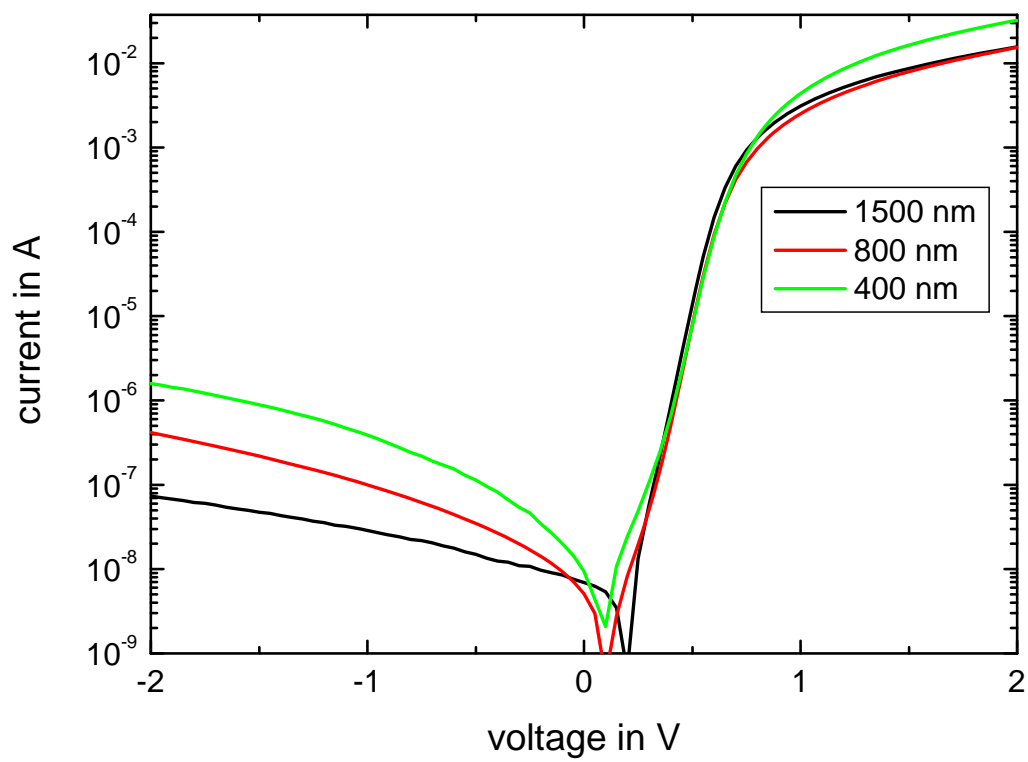


Figure 6: Dark I-V-curves for BHSC for different film thicknesses.

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

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