

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 [2, 4] 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 [1], by attributing this phenomenon to electron-hole recombination.

The main purpose of this Exchange Grant was to get a deeper understanding of negative capacitance. To reach this aim several organic solar cells were built and impedance spectroscopy was carried out on these cells.

The work carried out during the visit at the Linz Institute for Organic Solar Cells will be explained in detail, followed by some main results.

2. Experimental

A. Device Preparation

As mentioned above, first of all some devices are needed to carry out impedance spectroscopy. The organic semiconductor thin film devices studied herein were prepared in sandwich geometry (see figure 1). Substrates for these devices were 1.5 cm x 1.5 cm large glass sheets covered with indiumtinoxide (ITO, purchased from Merck, Inc.). To ensure secure connection of the metal top electrode without risking the connector tip to punch 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 ($\text{HCl conc} : \text{HNO}_3 \text{ conc} : \text{H}_2\text{O} = 4.6 : 0.4 : 5$) for 20 minutes. The part where ITO should remain was coated with scotch tape to protect it from the acid. For thorough cleaning the substrates subsequently underwent 20 minutes in a acetone and/or isopropanol bath in supersonic bath. After drying, the substrates were covered with PEDOT:PSS or directly with the organic semiconductor layer, depending on the desired device structure.

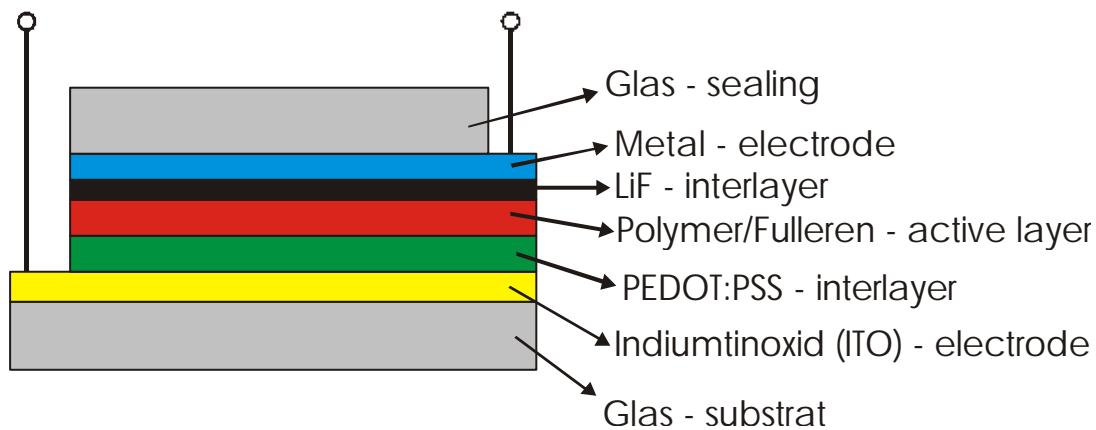


Fig. 1: Common design for an organic solar cell.

Active layers made from poly(3-hexylthiophene-2,5-diyl) (P3HT, purchased from Rieke, Inc.) and (1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C₆₀) (PCBM, purchased from Nano-C, Inc.) in different mixing ratios were 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 thicknesses.

The top electrodes were applied by thermal deposition through a shadow mask in vacuum better than 10^{-5} mbar. Tungsten boats, covered with aluminumoxid were used as source. Although thin interfacial layers of Lithiumfluorid (LiF) are known to improve electron injection from the Al into the typical π -conjugated polymers such as P3HT, no LiF was used.

Last but not least, all samples were heat treatet (120°C , 5 minutes), in order to reach better diode performance.

In detail, three different samples, with the following parameters were used:

Name	PEDOT:PSS (approx. 50nm thick)	Active layer material	Active layer thickness	Top electrode material	Top electrode thickness
16-3	yes	P3HT:PCBM 2:1 1,2% wt. in CB	100 nm	Al	250 nm
18-2	yes	P3HT:PCBM 2:1 1,2% wt. in CB	100 nm	Al	70 nm
2-3	no	P3HT:PCBM 1:1 2% wt. in CF	500 nm	Al	100 nm

Table 1: Investigated samples (in order of appearance).

B. Experimental Methods

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

Impedance spectroscopy was either carried out with a Hewlett Packard HP 4284A Precision LCR-Meter (range: 20 Hz till 1 MHz) or with a novocontrol Technologies Alpha-A High Performance Frequency Analyzer (range: 3 μHz till 20 MHz) under dark conditions for different forward biases. In order to carry out temperature dependent impedance spectroscopy the test devices were put into a cryostat from Oxford Instruments and cooled down with liquid nitrogen. A temperature range from 77 K to 280 K was obtained. Taking into account both

working close to equilibrium as possible and reaching a good signal to noise ratio the AC signal amplitude of 50 mV was chosen.

3. Results

The main results obtained during the exchange will be presented in the following chapter. Please take into account, that these results are not fully interpreted and discussed until now.

A. Negative Capacitance – A True Phenomenon

The phenomenon of negative capacitance seems to be not a real physical phenomenon but more an artifact from the measurement, if someone is not familiar with impedance spectroscopy. Even experts argue against this phenomenon with parasitic series inductance, low device conductances or large device leakage current (e.g. [7]). Taking into account these doubts the first task was to proof the negative capacitance in the low frequency regime. For these purposes two different plots are show. In figure 2 one can see the impedance spectra of an organic solar cell (sample “16-3”) connected in series with a known parasitic inductance of various values.

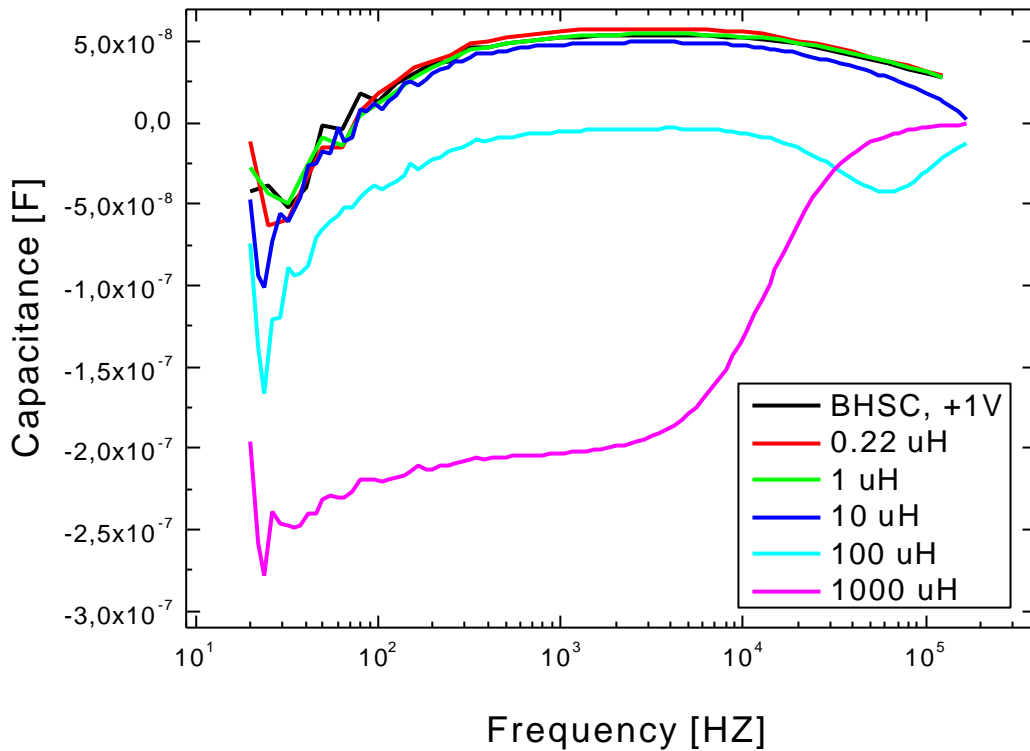


Fig. 2: Impedance spectra of an bulk heterojunction solar cell (BHSC) at room temperature.

Parameters: 50 mV AC, +1 V DC, 20 Hz – 1 MHz

From figure 2 one can derive, that parasitic inductances of 10 μH or less do not change the behavior of our spectra. Taking into account, that the parasitic inductance of 1 m of BNC-cable is 250 nH and the inductance of our device under test (DUT) can be neglected, a parasitic inductance can not be the reason for the measured negative capacitance at low frequencies.

Figure 3 shows the Cole-Cole plot of another BHSC (sample “18-2”).

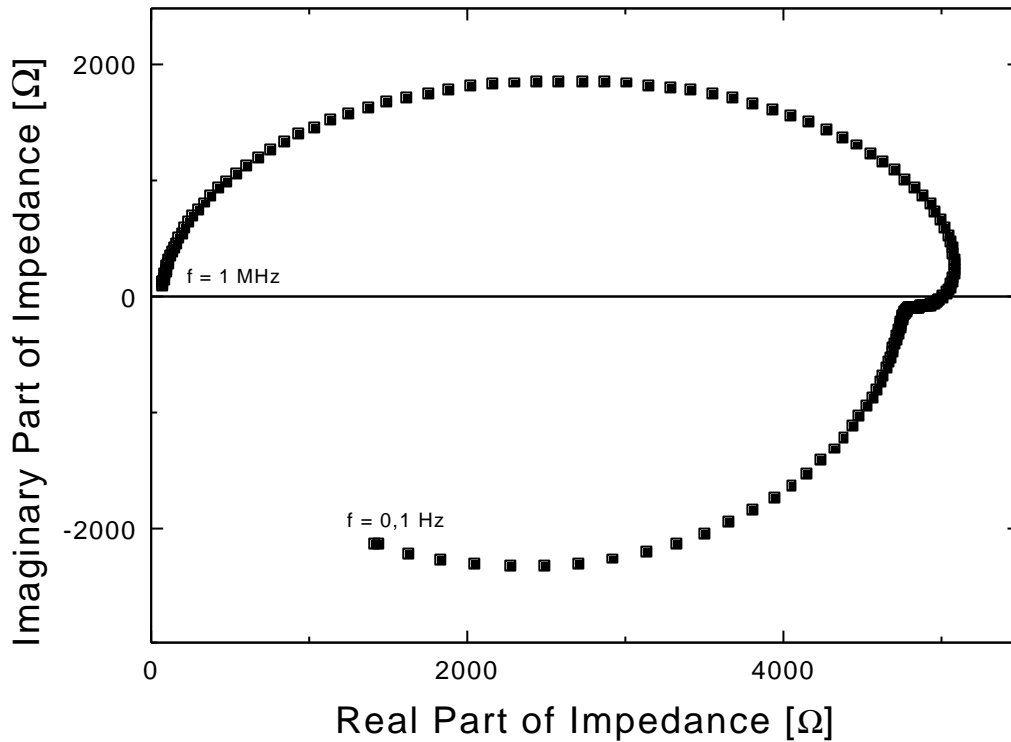


Fig. 3: Cole-Cole of a BHSC. Parameters: 50 mV AC, 2 V DC, 123 K, 0,1 Hz – 1 MHz

The Cole-Cole plot of sample “18-2” at 123 K is another strong proof, that the measured negative capacitance is a real physical phenomenon. The data-points run counter-clockwise through the graph. Only a capacitance behaves in this way (an inductance would run clockwise) [5, 6]. The reason for the negative value of the capacitance is a loss in phase-correlation of the instrument due to physical effects of the active layer at low frequencies.

B. Temperature Dependent Impedance Spectroscopy

Temperature dependent impedance spectroscopy allows to get a deeper understanding of the negative capacitance. But before forward biases are applied one should have a closer look on temperature dependence at 0 V DC. Figure 4 shows the impedance spectra of another BHSC (sample “2-3”) at different temperatures.

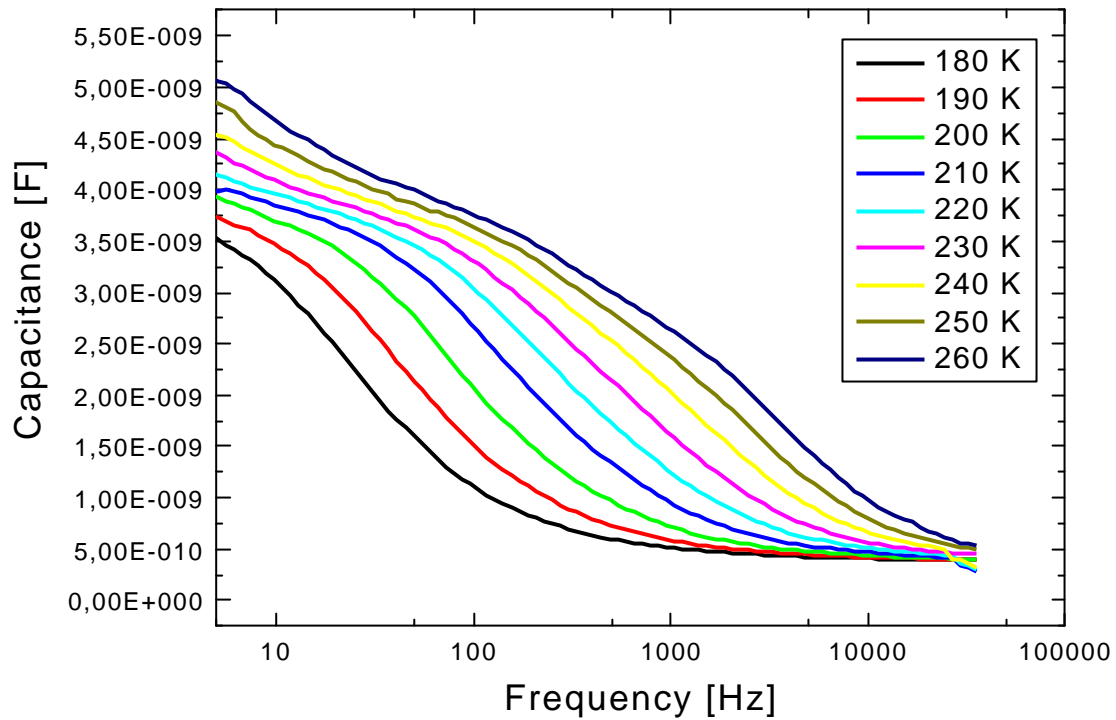


Fig. 4: Temperature dependent impedance spectra of a BHSC. Parameter: 50 mV AC, 0 V DC, Temperature range: 180 K – 260 K, Frequency Range: 5 Hz – 36 kHz

As one can see the capacitance increases as expected with lower frequencies starting from the value of the geometric capacitance at higher frequencies (with an active area of 6 mm² the geometric capacitance is estimated to 400 pF).

At low temperatures (till 200 K) only one slope is present. Going to higher temperatures a second slope appears (see figure 5). This feature is not fully understood until now and subject of further investigation.

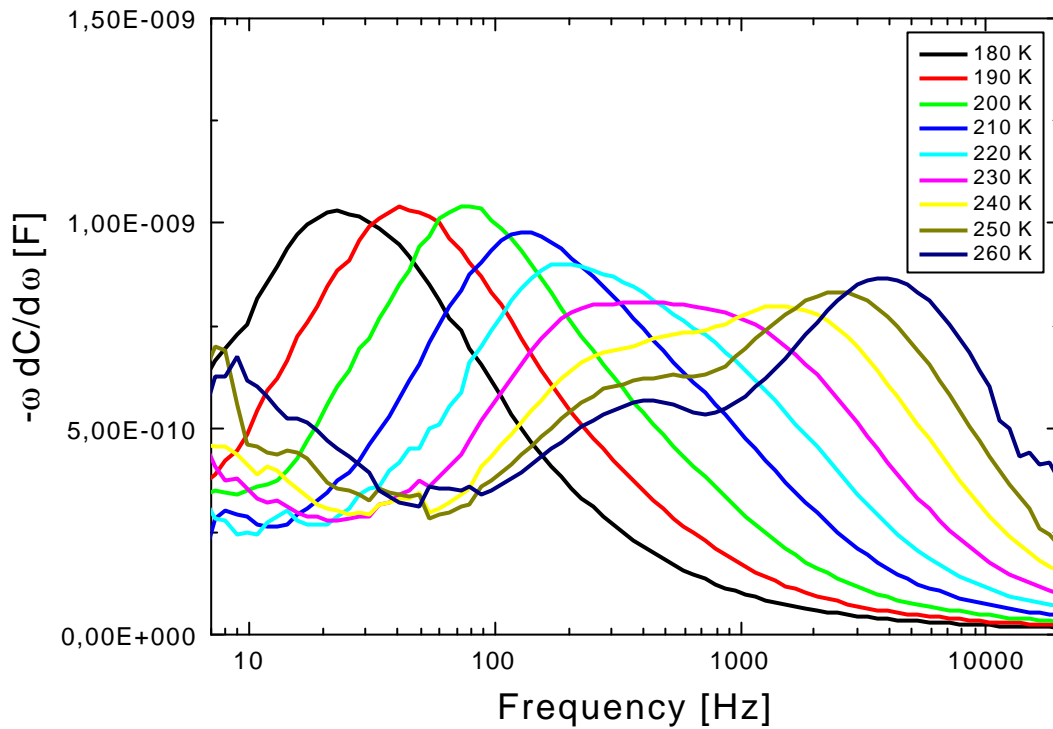


Fig. 5: First derivative of impedance spectra from figure 4.

C. Temperature Dependent Negative Capacitance

After carrying out temperature dependent impedance spectroscopy at 0 V DC, one can apply a forward bias to investigate negative capacitance. The following figures show the temperature dependent impedance spectra for a BHSC (sample “18-2”) at several forward biases. The geometric capacitance of this sample (active area of 6 mm²) is estimated to 1,5 nF.

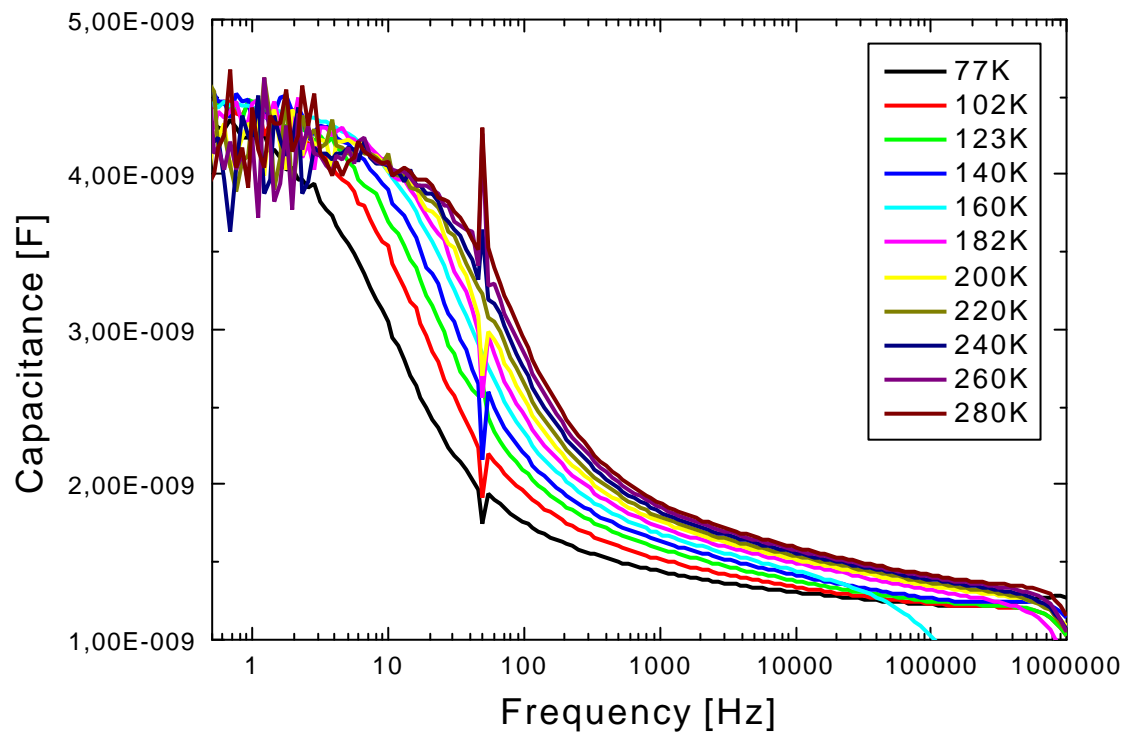


Fig. 6: 0 V DC

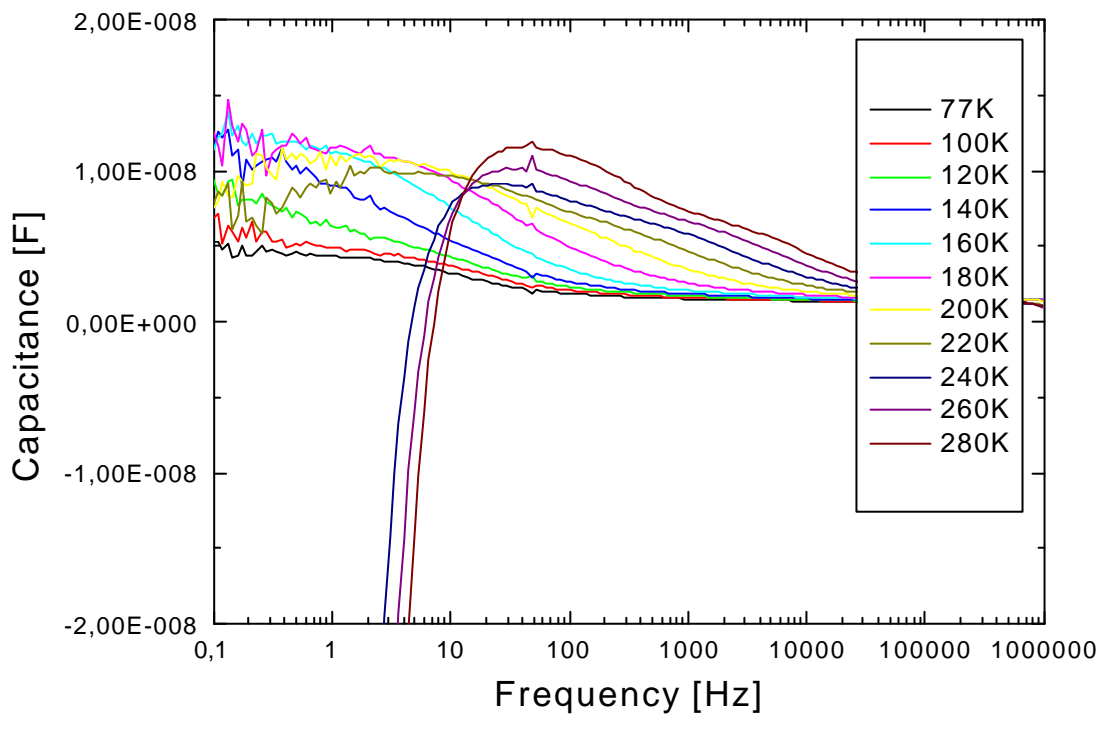


Fig.7: 0,5 V DC

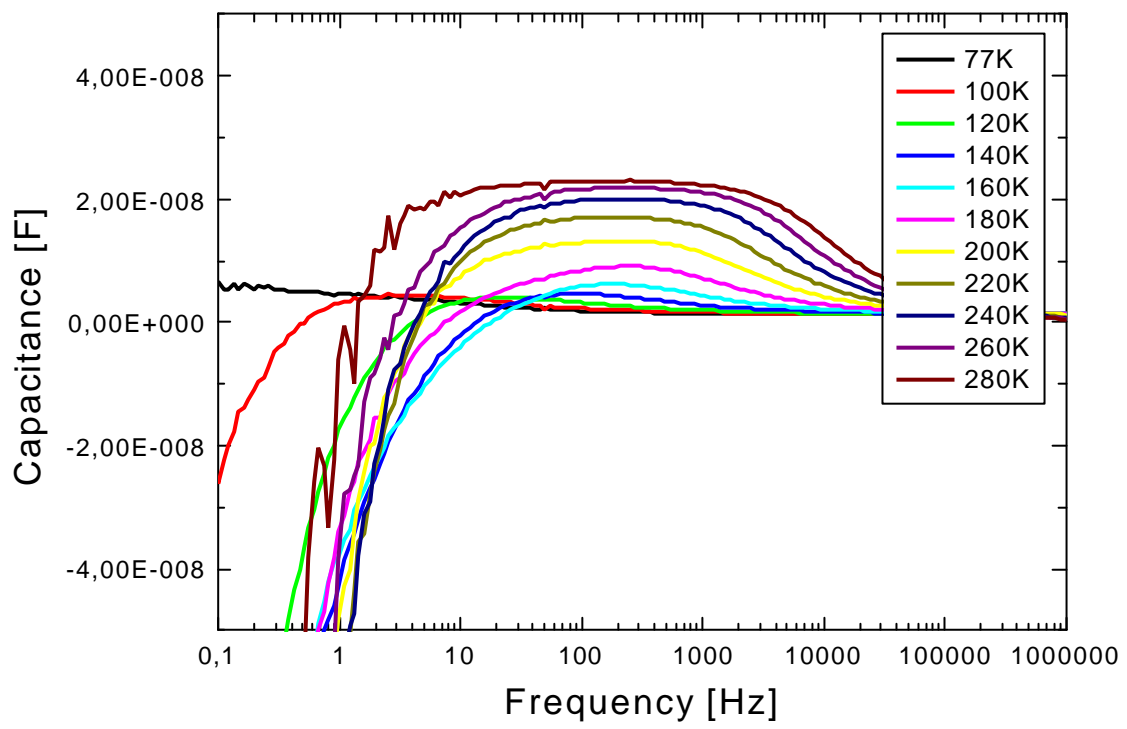


Fig. 8: 1 V DC

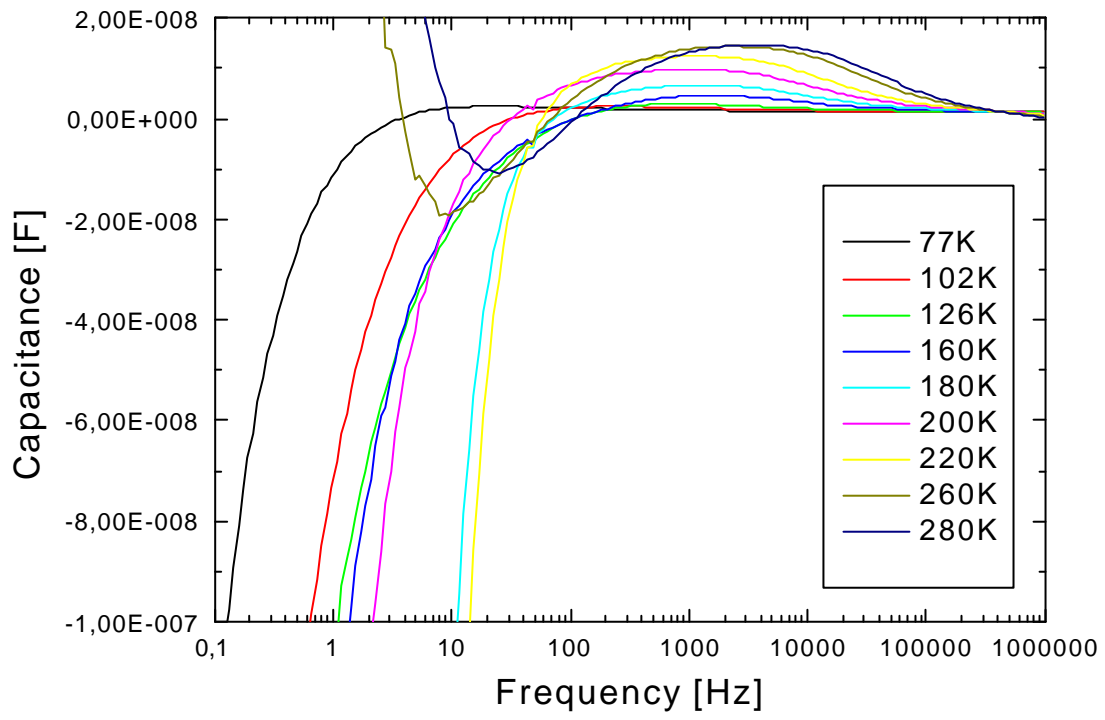


Fig. 9: 1,55 V DC

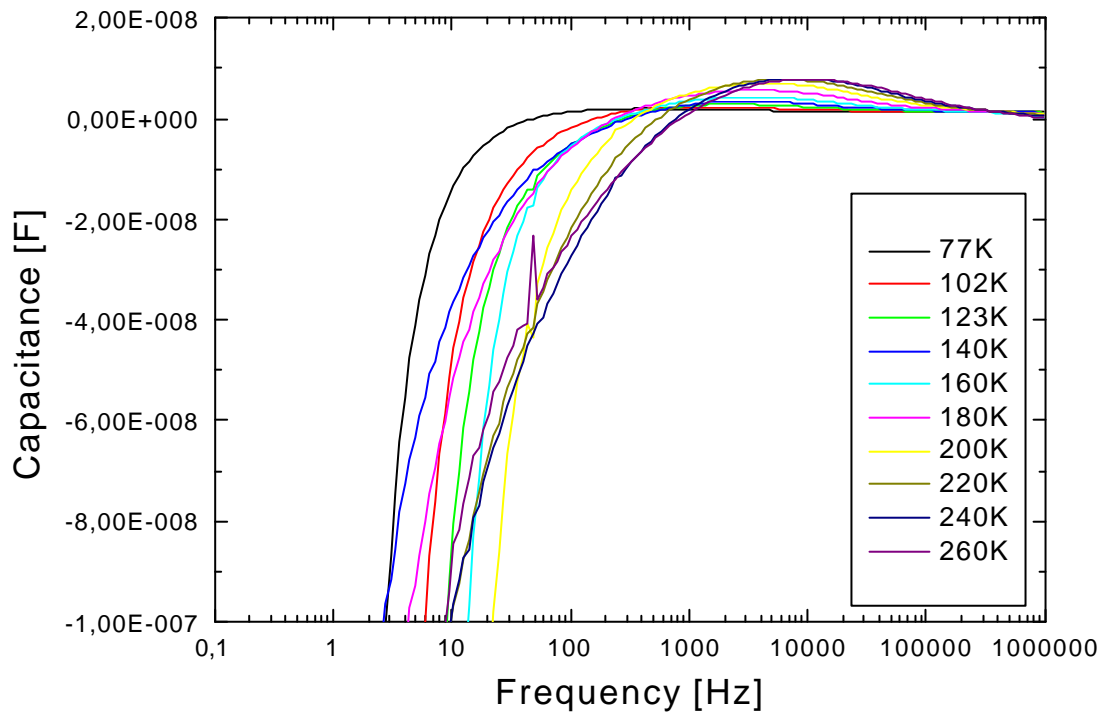


Fig. 10: 2 V DC

Figures 6 till 10 show a clear temperature dependence of the negative capacitance. These data are subject of interpretation and discussion which will result in a publication when all doubts are resolved.

References

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Future Collaboration with Host Institution / Projected Publications

It is planned to publish all data shown above in a learned journal, when all details are discussed. Professor Niyazi Serdar Sariciftci, Eitan Ehrenfreund, Almantas Pivrikas and Christoph Lungenschmied will be involved in the publishing process.

Until now no official future collaboration between the LIOS and the TU Ilmenau is planned.

Acknowledgement

I want to thank all members of the LIOS for their helpfulness and kindness. Special thanks go to Almantas Pivrikas, my local supervisor, Christoph Lungenschied (Konarka, Inc.) for fruitful discussions and his hints, Eitan Ehrenfreund (Technion-Israel Institute of Technolgy) for his theoretical work (without him we would be in the dark) and last but not least thanks to my host Professor Niyazi Serdar Sariciftci, who allowed me to work in his labs.