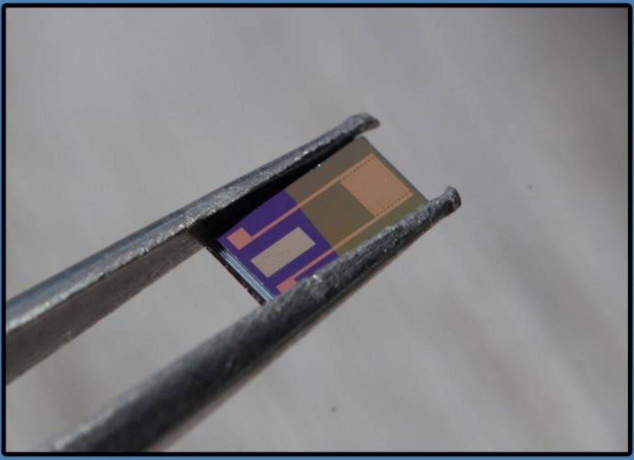
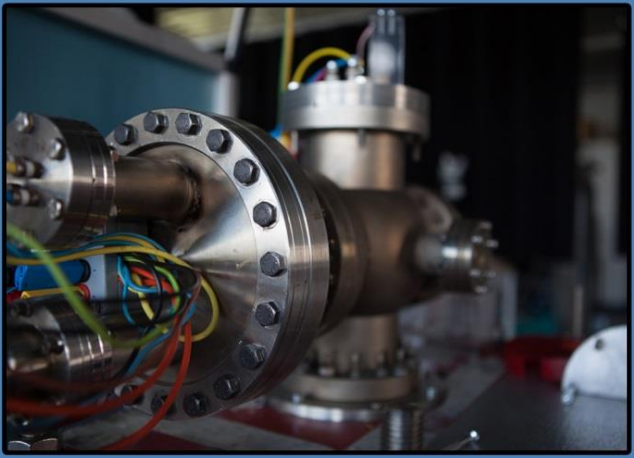
LIGHT SENSORS BASED ON ORGANIC PHOTOTRANSISTORS





Bachelor thesis in Mechatronics

NanoSYD

Mads Clausen Institute

University of Southern Denmark

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June 3rd 2013

Preface

This report is written as a summery for the work done in the bachelor project made by myself; sixth semester student Jens Lausen. All work described in this report has been done by me including the report itself.

The project is done for- and in collaboration with NanoSYD and is investigating a field of their interest, as well as my own. The goal in this project is to investigate organic semi-conductors in a so called organic field effect transistor configuration, OFET for Short, and its optoelectronic properties. At NanoSYD work has recently started with OFETs. This is due to the fact that the organic materials used can be more or less “tailored” to a desired property and the organic semi-conductors are, potentially cheaper to produce. The OFETs can function as photo transistors, in which the electrical characteristics of the transistor change when the transistor is illuminated, i.e. such a component can serve as a light sensor. In this project the Optoelectronic characteristic of such OFETs will be investigated.

Besides the supervisor, I would like to give special thanks to André Luis Fernandes Cauduro and Luciana Tavares for helping with the cleanroom fabrication, organic molecular beam deposition and test measuring set-up.

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Jens Larsen Lausen

Abstract

Since there is a large interest in semi-conductors applications the purpose of this project has been to cover the characteristics of such devices. The Organic semi-conductors were produced in the Organic field effect transistor (OFET) configuration. Photolithography and organic molecular beam deposition was involved in the production method. The characterization of the OFETs was measured electronically, by sweeping the biasing for the drain and gate. Measurements were made both under white light exposure and darkness as well as with a controlled wavelength; to further investigate how and when the OFET reacts to different photon energies. An optical test for the organic materials used was also made to validate the absorption of the materials. The materials used were α-6T and NaT2.

Results for the electronic measurements show a change in photocurrent and the responsivity of the OFETs when changing bias for drain and gate, light intensity and wavelength. The results of the optical measurements show the absorption spectrum of the materials. Results of the electronic measurements are comparable with the results optical measurements.

Evidence found in this project indicates that the OFETs used have optoelectronic abilities and can be used as a photo sensor. The OFET does change characteristic over time of operation though.

Table of Contents

Preface 2

Abstract 3

1 Project Formulation 6

1.1 Project background 6

1.2 Problem Formulation 6

1.3 Objectives 7

1.4 Problem Delimitation 7

2 Theory 8

2.1 Physical Principal of OFET 8

2.2 Absorption and emission of light 9

2.3 Photocurrent 10

2.4 Responsivity 10

3 Fabrication 12

3.1 Recipe for fabrication of OFETs 12

3.2 Architecture of OFETs 12

3.3 Production of OFETs 14

4 Experimental Details 15

4.1 Pretests 15

4.1.1 Testing equipment setup 15

4.1.2 Test of set-up with standard transistor 17

4.1.3 Initial test of organic transistor substrate 17

4.1.4 Organic Photo transistor testing with white light 18

4.2 Absorption measurements of organic materials 19

4.2.1 Testing equipment setup 19

4.3 Final Test 21

4.3.1 Testing equipment setup 21

4.3.2 Organic Photo transistor testing with variable wavelength 21

5 Results/discussion 23

5.1 Pretests 23

5.1.2 Initial test of organic transistor substrate 23

5.1.3 Organic Photo transistor testing with white light 24

5.2 Absorption measurements of organic materials 27
5.2.1 α-6T 27
5.2.2 NaT2 28
5.3 Final Test 29
6 Conclusion and Outlook 34
7 Bibliography 35
Appendix 36
A: Work plan 37
B: Individual study in quantum mechanics 40
C: Theory of organic optoelectronic semi-conductors 44
D: Recipe for cleanroom 51
E: Recipe for lab 57

1 Project Formulation

A work plan has been made as a means to structure this project the best way possible; this can be found in appendix A: Work plan.

1.1 Project background

This project serves as bachelor project for the student Jens Lausen. The project has been developed on the NanoSYD research center at the University of Southern Denmark. The project is concerned with optoelectronic properties of organic transistors. A research theme which is still ongoing within the group, since the characteristic has not fully been determined for these devices, further explanation will follow in the problem formulation.

The student has completed 5 semesters at MCI Sønderborg and will work on this project on the sixth semester, which will conclude the bachelor thesis.

1.2 Problem Formulation

The group at NanoSyd has recently started working on organic optoelectronic devices. Optoelectronics is defined as electronic devices which interact with light, e.g. detection and radiation of light. The reason for the use of organic materials is due to the fact that organic components are easier to manufacture to achieve different electrical and optical properties; by replacing their chemical radicals[1]. The production method of the organic devices also holds a potential of lower price.

The scientists at NanoSyd recently produced some organic field-effect transistors, or OFETs, which showed sensitivity to light. This means that the OFETs changed their characteristics when exposed to light, affecting the conductivity along the channel. Preliminary results, made by Xuhai Liu showed that the devices made promising photoconductive effects; however the underlying mechanisms are still unclear[2].

The purpose of this project is to investigate the properties, functionalities and potentially to optimize the OFETs mainly by selection of material. The results will also be compared to other experiments done with organic devices. For the project description formulated by supervisor Jakob Kjelstrup-Hansen look in the CD Annex Project formulation from Jakob Kjelstrup-Hansen.

1.3 Objectives

The objectives of this project are:

- To produce such OFETs at the facilities at Alsion.
- To demonstrate the photocurrent effect in OFET devices.
- To determine their characteristics. Namely investigate the effect at different wavelengths and intensities.
- To compare with other experiments with organic devices.
- To theoretically create a describing model with respects to absorption spectra.

Parallel to this project the student has also been doing an individual course in quantum mechanics calculation. The calculations and simulations for this course are made in a program called Arguslab. These sorts of calculations are quite relevant for the theoretical part of this project and some of the work done in this course is featured as appendix in this report, see appendix B: Individual study in quantum mechanics.

1.4 Problem Delimitation

As mentioned in the project formulation, some calculations and simulations will be done in a program, which can handle the advanced quantum mechanical calculations better. This is not directly part of this project and it will not be thoroughly explained except in the appendix, as mentioned above. Furthermore the theory and model for the characteristics may be somewhat limited since it may be quite substantial to make a model which can include all physical parameters. Hence the main focus will be to model the characteristics as a function of the absorbed light.

2 Theory

In the early stages of this project a report, which focused on the physical operational principal of field effect transistors, was made. This chapter will cover this issue, however, a more in-depth discussion of the basic physics can be found in appendix C: Theory of organic optoelectronic semiconductors.

2.1 Physical Principal of OFET

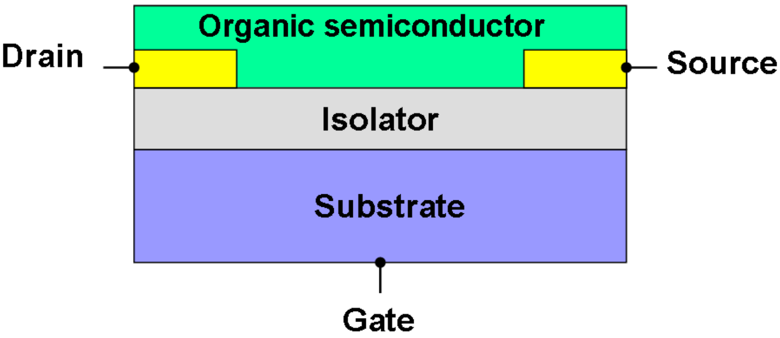

Figure 1 – Side view of typical OFET[8]

Much like an inorganic field effect transistors the organic counterpart is a device with three electrodes. Figure 1 shows a schematic of an organic semiconductor transistor on a back gate configuration. The OFET (Organic Field effect Transistor) is composed by a source and a drain which are responsible for conducting the current throughout the device. The third electrode, the gate, will control the current magnitude. In between the source and drain electrodes is the organic semi-conductor; which will not conduct automatically. In contrast to the inorganic counterpart, this is not due to the fact that there are two opposite oriented diodes, or that the semi-conducting material in-between cannot conduct on its own. But rather due to the fact that the organic materials' HOMO and LUMO energies do not align closely enough with the energies levels of the electrode metals. To consider the example, which is also the used design for the OFETs in this project, of two similar electrode metals; The HOMO energy, LUMO energy or both energies must be close to the work function of the electrodes. Then a potential must be created between the electrodes to make a conduction path. The biased electrode will be charged and thereby there is a potential drop between them. The electrode which is biased, drain, will generate an electric field. Since this field is the differential of the expression for the voltage drop over the OFET, the electric field will decay over the OFET and be zero at the other electrode.

This will insure that the lines for the HOMO and LUMO energies are sloped. For this to properly function the holes, which are the carrier charges for α-6T and NaT2, must have reduced the potential they need to overcome even more. This is achieved by inducing an electric field by biasing the gate electrode. The electric field will move the HOMO and LUMO energies up or down, depending on if it is positive or negative. Applying a negative field will raise them both and vice versa. See figure 2 for a depiction of this concept. Note that this setup will conduct through the movement of holes; the electrons cannot be injected from their electrode. This means that this setup is monopolar. The biasing on the drain will attract holes and the push away electrons, since they are negative.

The organic materials are able to conduct due to the fact that they are built up by carbon rings with aromatic bonds, meaning that the electrons in these bonds have their wave functions distributed on the entire molecule. The LUMO orbital are π-conjugated orbital, meaning that they can interact with the molecular orbitals of neighboring molecules.

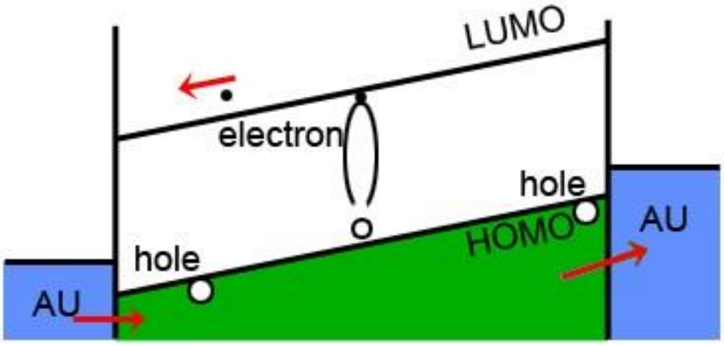

Figure 2 – Principal of p-type Transistor

The OFET is also optoelectronic, which means that it can absorb- and emit light. If a photon with the right energy hits a molecule, an electron can be excited from one of the occupied lower molecular orbitals to an unoccupied higher molecular orbital. I.e. there will be a hole in the HOMO band and an electron in the LUMO band, which is also called an electron-hole pair. They will then start moving in opposite directions; which creates an excess current.

Relevant source material[3];[1].

2.2 Absorption and emission of light

Electromagnetic radiation can be absorbed and emitted by matter. This happens when a photon excites an electron from one orbital to a higher one. In the same manner an electron can jump from a high orbital to a low and emit a photon, see figure 3 for a demonstration of these principles.

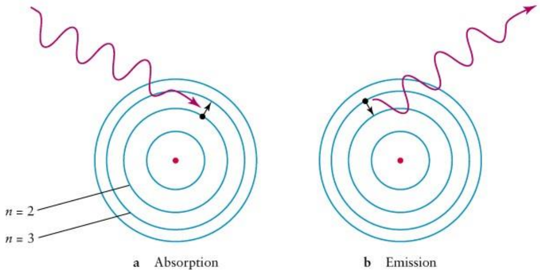

Figure 3 – Absorption and emission of a photon[9]

All materials are capable of absorbing incoming electromagnetic radiation to some extent. Not all are capable of emitting them, though, when considering electron shifts under biasing. Even though a material can absorb it; it is not all that can generate a current with it. Almost everything absorbs infrared light, but this is not the absorption of interest either. The infrared photons are absorbed by the atoms or molecules themselves and affect the vibration of these. That is why infrared light generates heat.

The study of interest here is when electrons shift states under biasing. The momentum for the electron in its current state must be the same as the moment for the electron when it has shifted states. This is necessary in order to be able to generate a photon when shifting states and is also known as direct band gap. Otherwise the energy will be lost to heat instead.

Small molecules are able to absorb and emit photons, as well, as they are comparable in size to atoms and thereby have similar energies in their molecular orbitals as the atoms have in theirs. For the visible light, an organic material will start absorbing when the photon energy reaches the band gap. This will generate electron hole pairs which then can then be detected.

The list of organic materials that can be synthesized is theoretically infinite, hence the organic materials has the possibility of being “tailored” exactly for a purpose; in this case making it conducting, optoelectronic and specifying the absorption wavelength.

2.3 Photocurrent

Photocurrent is the current that is created by incident light. The photons will excite electrons, creating electron hole pairs and a charge will build up. If the charge has a potential drop, then there will be a current. In an inorganic photodiode, for example, this is detected as a current. The current is then an indication of light. The photodiode is operated at zero bias or reverse bias, for a larger depletion zone; meaning that there is no current flowing when it is not exposed to light.

When operating an OFET, it must operate with a current flow to be properly used. An OFET can be operated in off-state, no V_{DS}, but this will not be investigated in this project. Hence in this regard the photocurrent of an OFET is given by the current when exposed to light minus the current in darkness:

$$PC = I_{D;\,illuminated} - I_{D;\,Dark}$$

Relevant source material[4].

2.4 Responsivity

The responsivity is a characteristic used to determine how much the given material responds to the incoming light. As mentioned before incoming light can create electron hole pairs, which can be observed as a current. The responsivity describes how much current is generated by the power. In other words which amount of photocurrent is created by which amount of incoming power. To calculate this for an OFET, the active region must be known. That is the region where the current runs in the semi-conductor, which is also where the incoming light is absorbed. This is also a way of assessing the sensitivity of the OFET. The more current created by the incoming light power the higher responsivity and thereby sensitivity of the device. The responsivity is calculated by dividing the photocurrent by the product of the incoming intensity and the area of the active region:

$$R = \frac{PC}{Int * A}$$

Relevant source material[4](same as 2.3 photocurrent).

3 Fabrication

The substrate that the OFETs are based on in this project is a standard substrate used by NanoSY. The details of the substrate will be displayed in the architecture sub-chapter.

3.1 Recipe for fabrication of OFETs

The substrate base for the OFET was created in the cleanroom at Alsion, where photolithography is used. After this the substrate was taken to the Lab at NanoSYD where the organic molecular beam deposition of the organic material was done. Look in the appendix D: Recipe for cleanroom for a walkthrough instruction of the process in the cleanroom and look in appendix E: Recipe for lab for a walkthrough instruction of the process in the Lab. Once the OFETs where done they were stored in a glove box at the lab. The glove box is filled with nitrogen which should prevent degradation as a result from oxygen exposure. Furthermore the container for the OFETs was wrapped in aluminum foil to protect them from UV- light exposure.

3.2 Architecture of OFETs

The substrates for the OFETs are mainly the target of interest when talking about the architecture for them. As long as the organic material is deposited on top of the active region it will function. There are, however, also architectural options with the organic material itself. If produced under a higher ambient temperature the small organic molecules may arrange in fibers. A fiber can conduct even better than a film due to the fact that the molecules are even more packed. With a fiber the orientation and position suddenly becomes relevant and hence there are optimization options in this. Fibers will not be considered in this project however.

For a schematic of the architecture of the substrates for the OFETs look at figure 4. This is a figure of the mask outlining used in the lithography process. There are two electrodes which weave together. This is in order to make a larger active area for the organic material to conduct on; the larger the contact area thy have the better. The two electrodes weaved together are the source and drain electrodes. Since the drain is per definition the biased electrode, and the two electrodes are identical, the electrodes just function as the opposite of the other. The source and drain are placed on top of the

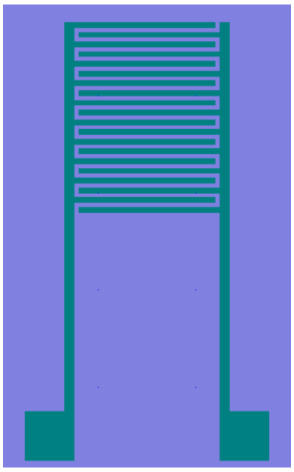
Figure 4 – OFET Substrate

oxide layer which means that they are electrically insulated from the doped silicon base. The gate electrode is the one in the middle. This one is in contact with the base of the substrate and since the substrate is so heavily doped that it is conductive the entire base will serve as the gate capacitor.

On figure 5 more than one transistor substrate is displayed. The mask produces six different substrates defined by their difference in distance between their "fingers". The distances are: 50 [µm], 25 [µm], 10 [µm], 5 [µm], 2,5 [µm] and 1 [µm]. The produced substrates does not yield good results for the 1 and 2,5 [µm] distances; which are either fully or partially short circuited. In this project only the substrates with 5 and 10 [µm] will be used. The dimensions for a 5 [µm] substrate are displayed under here, look at figure 6 for a zoomed in version of the 5 [µm] editions as well:

- Channel length: 5 [µm]
- Channel width (Same as the length of a finger): 1400 [µm]
- Finger width: 50 [µm]
- Distance from finger end to electrode base: 50 [µm]
- Electrode base width: 100 [µm]

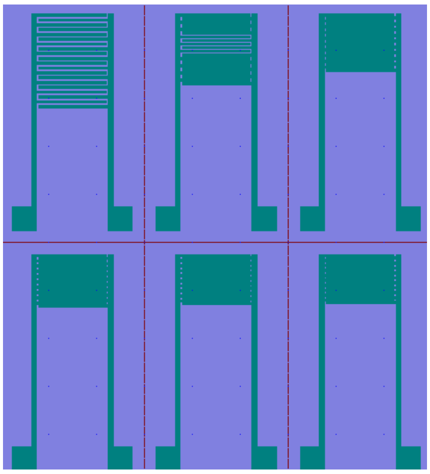

Figure 5 – Mask design including six different OFET substrates

The dimensions are used to calculate the area between the fingers like this:

19 gaps of 1400 [µm] = 26600 [µm].

Total area = 26600 [µm] * 5 [µm] = 133000 [μm^2] = 1,33*10^{-7} [m^2]

Figure 6 – Magnification of substrate architecture

The area between the "fingers" is the area of interest; the rest is disregarded, including the area between the "finger" ends. The organic material will rise in resistance with the distance, which is why only the short distance between the fingers is regarded. This area calculation will be used in chapter 4 Experimental details.

3.3 Production of OFETs

In this project a total of four batches of transistors where produced. The batched were produced chronologically. It turned out that the transistors from batch one and two where defective and could not be used for testing; this is specified in chapter 4.1.3 Initial test of organic transistor substrate. The substrates used for these batches were from the same production in the cleanroom, which bears evidence to the faulty part being the substrate itself. Since the defect was a short circuit, the substrates have most likely had small holes in the oxide layer leading to small connections being made between the gold electrodes and the substrate base. This suggests that at least one of the masks used for the photolithography has been dirty.

For the third batch some substrates were donated by Luciana Tavares, who is also mentioned in the preface. The substrates where identical to the ones produced by the student, except for the defection, and could therefore be used instead. Batch three has α-6T deposited as the organic film and batch four has NaT2 deposited as the organic film.

4 Experimental Details

This chapter holds the details on how the experiments and tests were carried out. Further details on the results and evaluation of the experiments can be found in chapter 5: Results and Discussion.

4.1 Pretests

The pretests for this project had the role of showing the characteristics of the OFETs and to compare the characteristics for the OFETs produced in this project to each other and other tests with OFETs. This is to further validate the optoelectronic effects found in Xuhai's PhD Thesis[2].

The light intensity of the microscope lamp used has been found and calculated, chapter 4.1.4 organic photo transistor testing with white light, but the spectrum is unknown. Furthermore there is no guarantee that the spot of the light is uniform. Hence this values for the responsivity and photocurrent is not completely exact, but still serves as demonstration of the effect.

4.1.1 Testing equipment setup

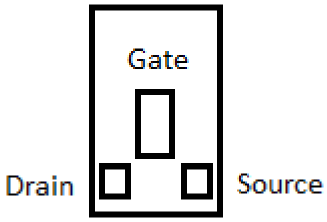

Figure 7 – Orientation of OFET during testing

The pretests were conducted at the lab at Alsion. The testing was carried out in the same manner for all the pretests. The samples were placed under a microscope, which served as aid to place the probes and supplied the light source.

Once placed the probes were attached, it does not matter which is drain and which is source; but for the sake of argument the source and drain were always placed on the same electrodes, see figure 7. The gate and drain probes are connected to one amplifier each which is connected to an output from the computer. The source is connected to a current to voltage signal converter which then sends a signal to the computer. The equipment is listed here:

- Probes: XYZ-manipulators with tungsten tips
- Gate amplifier: Falco Systems WMA-02 amplifier
- Drain amplifier: Falco Systems WMA-300 amplifier
- Source Converter: SR570 current amplifier
- Labview : NI PCI6229 DAQ

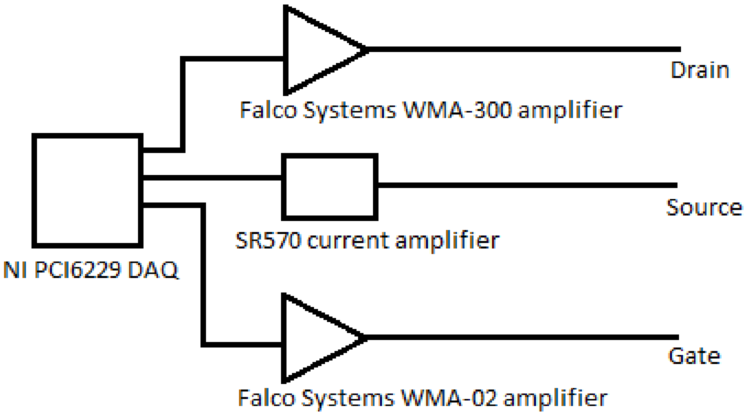

Figure 8 – Diagram of test set-up of the equipment

See figure 8 for a diagram of the setup. The Amplifier for the gate has a high output impedance, 50 [kΩ], but this does not matter since the current running to the gate/base capacitor is not important. The amplifier for the drain is also high compared to what would be used had this been an ordinary MOSFET. But the impedance in the organic transistor is several orders of magnitude larger than it would be in a MOSFET, therefore the impedance in the amplifier had almost no effect. The current to voltage signal converter can be adjusted to send signals in the range from 1[V/pa] to 1 [V/mA]. The ratio should be as low as possible, due to the fact that the noise will always be, more or less, in the same voltage range. This means that if one wants to measure low currents at a high ratio; the small currents will be indistinguishable from noise. The ratio cannot be too small though; since the input to the Labview program can max be five volts. The Labview program used is called: “Advanced I-V sweep with gate by H3 and JKH v2,31beta_jkh” and was created by Jakob kjelstrup-Hansen and Henrik Henrichsen. The light source used is a built in microscope lamp. Its spectrum is unknown but its intensity has been measured which can be viewed in chapter 4.1.4 Organic Photo transistor testing with white light. The measurements were done in a “black box” were the measurements can be shielded from the ambient light. All measurements are hence made in darkness or only in light exposure from the desired light source.

4.1.2 Test of set-up with standard transistor

The first test that was done was with a standard inorganic N-type transistor. This was to test if the functionality of the test setup was as expected. The transistor was of the type: JFET bf 245c. It was mounted to the probe station like described in the sub chapter above, though this was a little more challenging than mounting the flat organic transistor. The test sweep was for the V_{DS} and the test parameters for the test were:

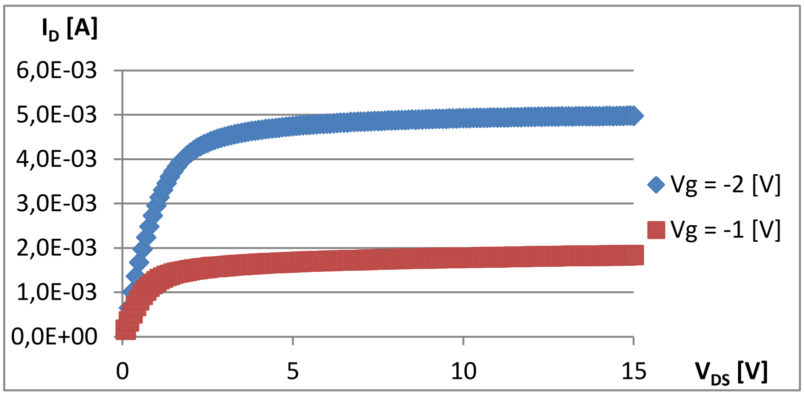

Figure 9 – I_D Characteristic as function of V_{DS} for JFET bf 245c

- Sweeping V_{DS} from 0 to 15 to 0
- V_G= -3 ; -2
- Step: 0,1V
- Slew rate: 10 V/s
- Step Settling delay: 0s
- Sensitivity: 1 mA/V
- Compliance: 5,00E-3

Since this transistor is not light sensitive; only a test- without light, was done. A graph was made from the result which is displayed in figure 9. The result clearly shows a transistor characteristic, although the settling value for the current is only one third of the value found in the datasheet. This can be due to uncertainties with this particular design of transistors.

4.1.3 Initial test of organic transistor substrate

For the first tests, using organic transistors, the transistors from batch one and two where used. Description on the different batches can be seen in chapter 3 Fabrication. Unfortunately the transistors of these two first production batches where not functioning correct, which is described in the respective chapter. This resulted in the first couple of tests being inconclusive and the data not suitable for further evaluation.

4.1.4 Organic Photo transistor testing with white light

The transistors produced in batch three would show more satisfactory results. Before the final, organic, layer was deposited on the transistors, they were measured in the test set up to check for short circuits. The transistors functioned as expected, like a capacitor, for the Vg voltage and hence the final deposit was made.

This test with the transistors from the 3rd batch was done with four transistors; two of a 5 [µm] gap and two of a 10 [µm] gap. In this test it was transistor 1 and 2(5 [µm]) and 6 and 7(10 [µm]) from the respective batch. The organic material is α-6t. The test parameters for the test were as following for the V_{DS} Sweeps:

- Light intensities: 0%; 25%; 50%; 75%; 100%
- Sweeping VDS from 0 to -30 to 0
- VG= 0 ; -10; -20; -30
- Step: 0,2V
- Slew rate: 0,1 V/s
- Step Settling delay: 5s
- Sensitivity: 10 µA/V
- Compliance 50,0E-6

The Test parameter for the V_G sweeps where:

- Light intensities: 0%; 100%
- Sweeping VG from 0 to -30 to 0
- VDS= 0; -10; -20; -30
- Step: 0,2V
- Slew rate: 0,1 V/s
- Step Settling delay: 5s
- Sensitivity: 10 µA/V
- Compliance 50,0E-6

The shifting in intensity is only made in the V_{DS} Sweep. Each test was repeated to validate the results.

The photocurrent and responsivity were also of interest in the pretest. The substrates were exposed with light from a white light source. To calculate the intensity for the light source, the power output of all the emitted light was measured with a Vega-Oplair power sensor. To do this the microscope lamp was removed from its holder and held up closely to the sensor. The measured power of the emitted light was: 0,286 [W]. After the measurement the lamp was re attached to its holder and the spot size it generated was measured, since the lamp was pointing at an angle it was an ellipse. The area of the spot was calculated as following:

$$A = a * b * \pi$$

$$A = 0{,}045 * 0{,}042 * \pi$$

$$A = 0{,}005938\ [m^2]$$

Thus the intensity is:

$$In = \frac{P}{A}$$

$$In = \frac{0{,}286}{0{,}005938}$$

$$In = 48\ [\frac{W}{m^2}]$$

The spot is assumed to be homogenous and the power sensor was last calibrated three years ago. Therefore the values cannot be expected to be exact and will only serve as an indication of the effects. Exposing the transistors with light increases the current; for further explanation on the results see the results and discussion chapter.

4.2 Absorption measurements of organic materials

The Absorption properties of the organic materials can be measured in numerous ways. While the absorption should be evident from the photocurrent produced by light at a given wavelength in the transistor, it is a good idea to have several indicators of the absorption properties of the material. These following measurements have been made to probe and verify the absorption spectra of the materials. The test measures the amount of light intensity transmitted through the thin film of the materials. The materials of study are α-6T and NaT2.

4.2.1 Testing equipment setup

For the test two small pieces of glass were exposed to organic molecular beam deposition with the given material. These pieces were placed, one at a time, in the testing equipment which has a broad wavelength source. Before the deposited pieces were measured a reference piece had been used which was just pure glass, this is to account for the small amount of intensity that is lost in the glass itself and the small reflection. Light is then transmitted through the sample and picked up by a sensor, all the data is sent to the computer program which automatically corrects for the reference piece and background light source noise, figure 10 displays a diagram for the set-up. The equipment used was:

- Spectroscopic Ellipsometer SE200BM-M300 configured for Photometry Transmission Measurement

The measurements have been made with a sample time of 100 [ms] and 512 samples made for each measurement. Except for α-6T which had one measurement from 400 to 700 [nm] made with a total of 768 samples. This measurement has the same resolution as the 400 to 600 [nm] resolution made for the NaT2.

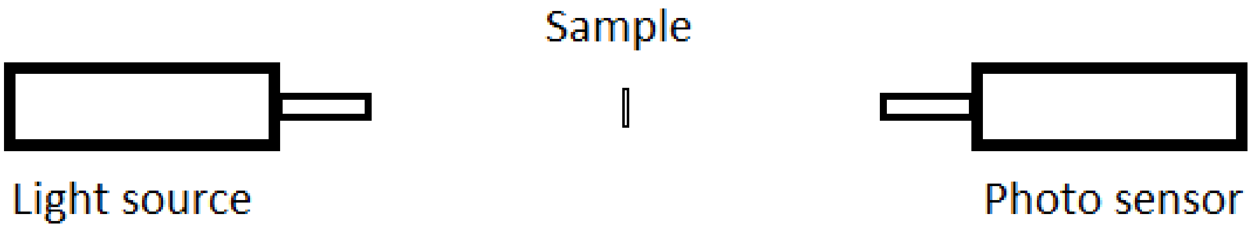

Figure 10 – Diagram of test set-up of the equipment

4.3 Final Test

The final test will further investigate the optoelectronic properties of the OFETs. This time the light source will be delivered from a monochromator, where the wavelength and the power will be known. The characteristics of the OFETs will be investigated as functions of the wavelength.

4.3.1 Testing equipment setup

The tests were conducted at the lab at Alsion. The testing equipment and set-up for the electronic measurements are similar to that of the pretest, for details see chapter 4.1.1 testing equipment setup. The rest of the setup consists of a fluorescence microscope, a monochromator and a lamping house which produces white light. The lamp produces white light, the monochromator selects a wavelength which is send to the fluorescence microscope, which focuses it down and exposes the sample through a 5x objective. Figure 11 displays a diagram for this set-up. The equipment used was:

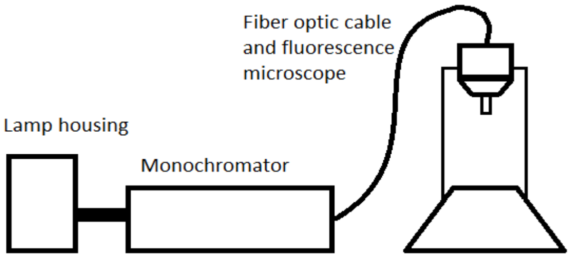

Figure 11 – Diagram of test set-up of the equipment

- Newport 67005 Lamp system with 150 W Xe ozone free bulb
- Cornerstone™ 260 1/4 m Monochromator
- Mitutoyo FS70 Fluorescence Microscope

The spectrum of the light source is known for the range 450 to 700 [nm]. Since the device has been calibrated, the power for a given wavelength has been found and through this the intensity is known since the area of the calibrated photocell is known. The calibration was done in collaboration between Jens Lausen and André Luis Fernandes Cauduro and is estimated to have no more than a 5% error, specifications for the calibration may be found in the CD Annex Summary of Photocurrent experiments.

4.3.2 Organic Photo transistor testing with variable wavelength

The OFETs used are those from batch three, which was also used in the pretest, and those from batch four. The measurements were therefore conducted for OFETs both deposited with α-6T and NaT2. The measurement itself will be a V_G sweep like in the pretest, the test parameters were as following for α-6T:

- Light From 700 to 450 [nm] in steps of 10 [nm]
- Sweeping VG from 0 to -30 to 0
- VDS= -30 V
- Step: 0,2V

- Slew rate: 0,1 V/s
- Step Settling delay: 5s
- Sensitivity: 10 µA/V
- Compliance 50,0E-6

The Test parameters were as following for NaT2:

- Light From 700 to 450 [nm] in steps of 10 [nm]
- Sweeping VG from 0 to -30 to 0
- VDS= 0; -10; -20; -30
- Step: 0,2V
- Slew rate: 0,1 V/s
- Step Settling delay: 5s
- Sensitivity
    - 100 nA/V for: 700 – 490 [nm]
    - 1 µA/V for: 480 – 470 [nm]
    - 10 µA/V for: 460 – 450 [nm]
- Compliance 50,0E-6
    - 500,0E-9 for: 700 – 490 [nm]
    - 5,0E-6 for: 480 – 470 [nm]
    - 50,0E-6 for: 460 – 450 [nm]

The OFETs used for this test were transistor four from batch three and transistor one from batch four, both of them with a 5 [µm]channel length.

Before and after the measurements with light exposure a measurement was made in darkness as a reference for calculating photocurrent. The reason for making both one before and after is to check for current drifting and investigate how much the characteristic might change.

The results were normalized in regards to the known spectrum from the light source and the results can be seen in results and discussion section. The light spot hitting the sample is assumed to be uniform. This is of cause not a completely accurate assumption, but the fact that the light beam has crossed several objectives to be focused should mean that it is quite homogeneous. The time between each sweep was approximately 40 [s] and the exposure time was approximately 15 [s] prior to the V_G sweep and of cause during the sweep.

5 Results/discussion

For details on the experimental details view the respective chapter.

5.1 Pretests

5.1.2 Initial test of organic transistor substrate

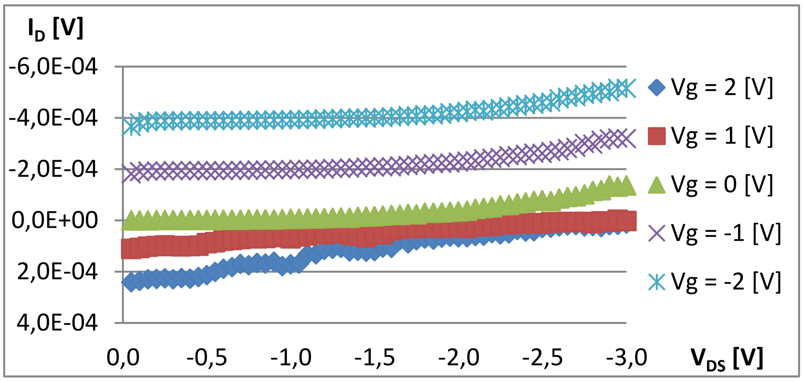

Figure 12 – I_D Characteristic as function of V_{DS}

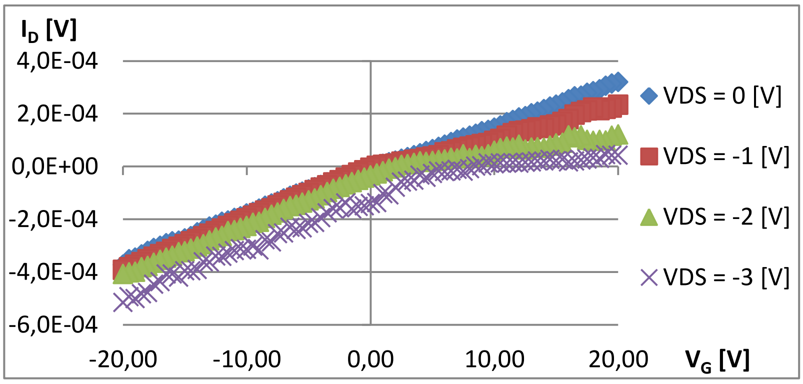

Figure 13 – I_D Characteristic as function of V_G

The two first batches of OFETs produced were not functioning correctly and cannot be used for the characterization. Displayed on figures 12 and 13 are the results generated in this test. Clearly they are not that of a typical transistor characteristic. Further investigation shows that the transistor has a short circuit between the gate and the drain electrodes; causing a current to run even at zero V_{DS} for any V_G. Calculations show that the conductor between the two has a resistance in the vicinity of 62 k Ω which is quite close to the 50 kΩ of the gate amplifier plus a little extra resistance in the short circuit. This is demonstrated in one of the tests shown in figure 13. Here it can be observed that, at V_{DS} equal to zero, the transistor behaves as a linier resistor. Hence the substrate of these transistors was faulty.

5.1.3 Organic Photo transistor testing with white light

For the tests two type of transistor substrates where used, one with a channel distance of 5 [µm] and one with 10 [µm].The organic material used was α-6T. It was to be expected that the ones with the smallest channel distances would lead the highest current as the semi conduction layer is thinner. In the test two of each transistor was tested and the highest values of current for the first measurement at -30 VDS -30VG and no light exposure, for them were as following:

- Transistor 1; 5 µm: -5,91 [µA]
- Transistor 2; 5 µm: -13,22 [µA]
- Transistor 6; 10 µm: -6,28 [µA]
- Transistor 7; 10 µm: -1,44 [µA]

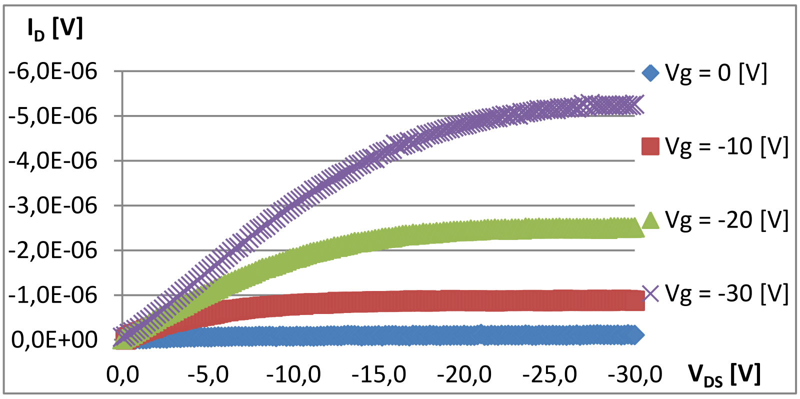

Figure 12 – I_D Characteristic as function of V_{DS}

This indicates that the assumption cannot be made directly in these measurements. The physical connection is still there but it is clear that there are other, high influencing, factors involved in the conductivity other than the channel length.

In all test it shows that there is some hysteresis in the results; meaning that the current when sweeping up, is not the same as the current when sweeping down. The current is usually of higher magnitude when sweeping up, but some few incidents it was the other way around. There was no defined distinguishable pattern in this behavior and the reasons for the change in current are not well understood. This phenomenon will not be studied further in this thesis and all results in this report are from the sweep from 0 to -30 volts, both for the V_{DS} and the V_G. Atypical result for the V_{DS} and the V_G sweep is displayed in figures 14 and 15, where the transistor characteristic is evident.

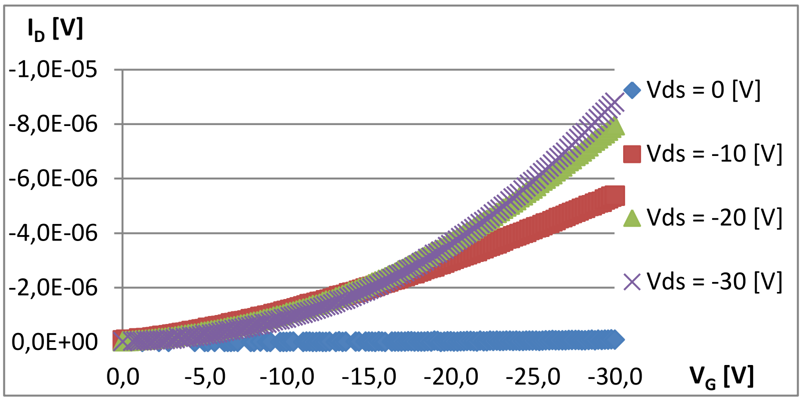

Figure 13 – I_D Characteristic as function of V_G

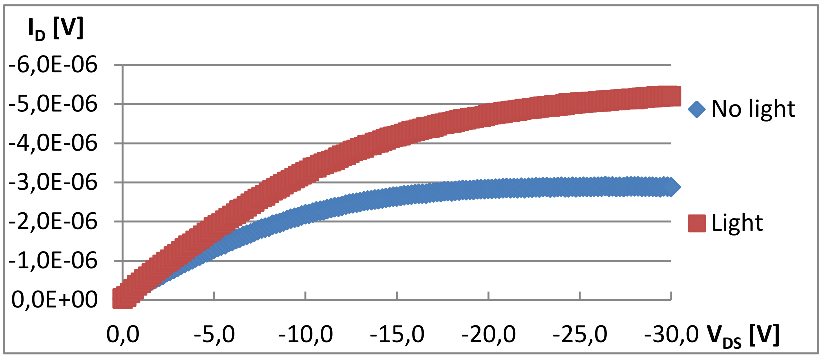

Figure 14 – I_D Characteristic as function of V_G with and without light

When investigating the light sensitivity it is evident that the transistors are defiantly sensitive to light. Figure 16 show Transistor 1 at full light exposure and at no light exposure; at V_G equal to -20 [V]. It is clear that the transistor responds to the incoming light. Furthermore the saturation point is reached at lower V_{DS} value for the sweep without light. Hence its characteristic has changes both in which current runs through it and at which voltage it is reached.

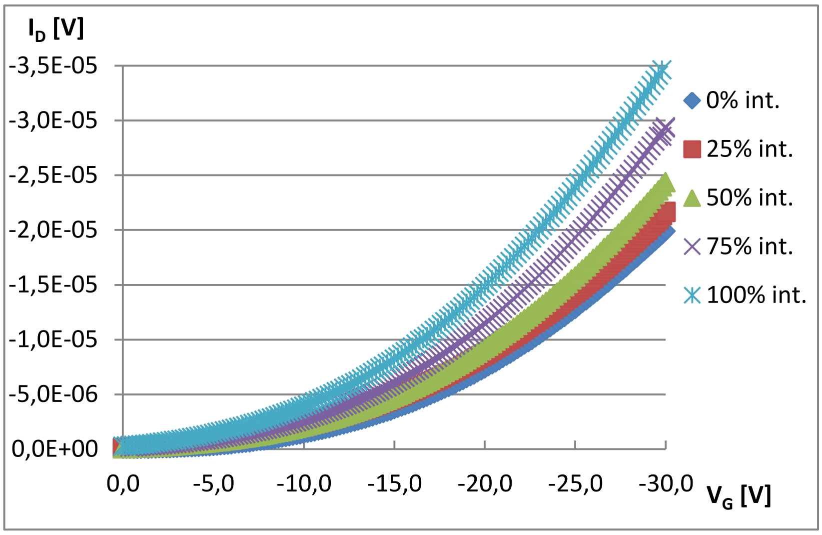

Figure 16 – I_D Characteristic as function of V_G at four different intensities

Figure 17 shows transistor 2 at four different light intensities for V_{DS} equal to -30 [V]. Once again it is evident that the transistor is sensitive to light. Note that the no light current at -30 VDS and -30 VG for the VG sweep , figure 17, is -19,9 [µA] and the first measurement at -30 VDS and -30 VG, mentioned as the no light exposure above, is -13,22 [µA]. These values should in theory be the same, but they are not close enough in value to be just an uncertainty. It is caused by the fact that the V_G sweep was made after the VDS sweep and the organic material has most likely been charged after this. When exposed to light an excess current is created called the photocurrent. The photocurrent has been calculated for the transistor as following:

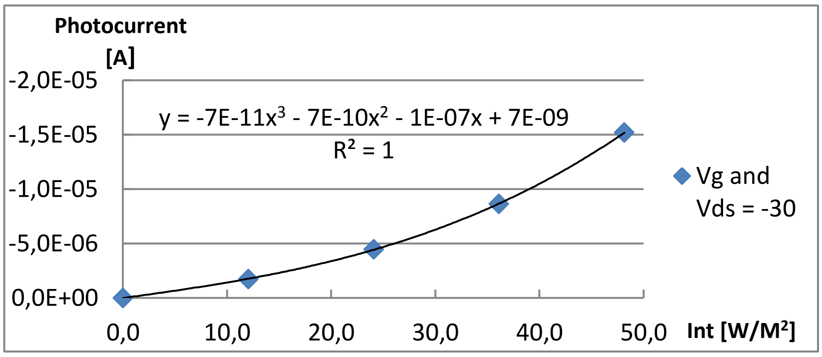

Figure 15 – Photocurrent as a function of intensity

$$PC = I_{D;\,illuminated} - I_{D;\,Dark}$$

$$PC = -35{,}1 - -19{,}9$$

$$PC = -15{,}2\ [\mu A]$$

This is the photocurrent for the maximum intensity look at figure 18 for a graph of the photocurrent as a function of intensity for transistor 2. The photocurrent seems to rise as a polynomial equation, which increases with the intensity. It fits perfectly with a 3rd order polynomial equation, meaning that the photocurrent rises potentially with the intensity. This, however, is different for similar results obtained by other investigations of organic transistors. Compared with the test in Journal of Materials Chemistry[4], the fit is linear rising for small intensities and logarithmically going to an asymptote for the higher intensities. The parameters of the two measurements are within range of each other's values both for intensity, V_{DS} and V_G so the only other option must be difference in architecture and material.

The material responds to the incoming light and creates extra electron hole pairs, which are then observed as photocurrent. How much the OFET responds is called the responsivity.

The responsivity of the transistor has been calculated as following:

$$R = \frac{PC}{Int * A}$$

Int. is the intensity of the incoming light and A is the area of the active region in the transistor. Figure 19 shows a graph for the responsivity of different intensities. The measurements used are the same as for the results of the photocurrent.

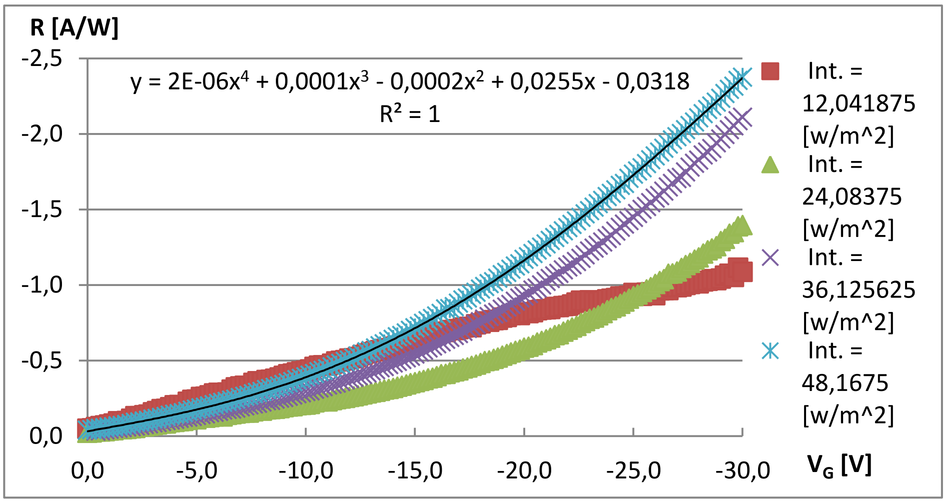

Figure 17 – Responsivity as a function of V_G

The graph in figure 19 shows how the Responsivity increases for higher gate voltages for transistor 2, the V_{DS} is constant at -30 V. Meaning that the higher the gate voltage is the higher the amount of current gained from the incoming power is. A trend line has been added to the highest intensity, which shows that the responsivity raises as a 4th order polynomial equation with respects to V_G. When comparing this to the results of Journal of Materials Chemistry[4] the results bear some similarity, but it seems that their graph, once again, is split into two; one for lower V_G and one for higher V_G. It seems that the responsivity ends out as a 1st order polynomial equation. Once again this is most likely due to difference in architecture and material. The responsivity showed by them has a higher value, but this is likely due to the fact that they used higher intensity. They have shown a responsivity of 3 [A/W] at 12 [W/m^2] and 6 [A/W] at 23 [W/m^2], though their values and the ones used here are still within range of each other and neither of the two spectra is known.

The responsivities found in Xuhai's PhD thesis[2] are much lower than the ones found here, but the dimensions for the transistors are different and the results here are for α-6T where his are for NaT2.

The Responsivity curves behaves similarly, except for the one with the intensity of 12 [W/m^2]. This is most likely due to the fact that the full effect of the light exposure cannot be obtained at such small intensities. Furthermore the values for the responsivity seem to be higher, for small V_G values, for the lowest intensity. This could be due to degradation of the organic material, since this measurement was made as the first one.

5.2 Absorption measurements of organic materials

The two absorption spectra obtained from the measurements, have been investigated to find the band gap values for the materials. The absorption spectra for the materials will also be used for comparison to the electrical measurements in the next sub chapter.

5.2.1 α-6T

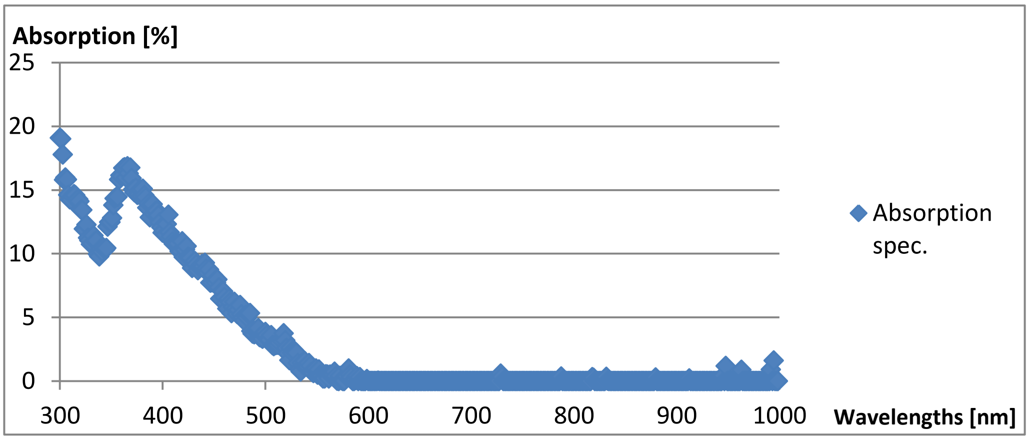

Figure 18 – Absorption spectrum for α-6T

The measurement yields a transmission spectrum for the sample; the spectrum is inverted to an absorption spectrum and plotted as seen in figure 20. This is a measurement for the full spectrum from 300 to 1000 [nm]. The spectrum was also done for a smaller area of 400 to 700 [nm] for a finer resolution.

Figure 21 shows the spectrum for 400 to 700 [nm], zoomed a bit in to the relevant area, for α-6T. The measurement has been made for wavelength 400 to 700 [nm] with 768 points. A trend line has been made for the absorption limit to evaluate the energy for the band gap. The values used for this line have been marked red. The values for the zero absorption are marked green. An average has been calculated for the zero absorption. Of cause this value should, in theory, had been zero; but noise and default absorption has made it a bit higher. The average zero absorption is: 0,27 [%] and is represented by the horizontal line in the graph. The points in between the red and the green are a transition zone between the absorption limit and the zero absorption and there values are disregarded. The trend line for the absorption limit hits the average at the wavelength: 562,5 [nm], which corresponds to 2,2 [eV]. From other sources, Solar Energy Materials & Solar Cells[5], it is established that the band gap for α-6T is 2,2 [eV], so this result fits fine with that of others.

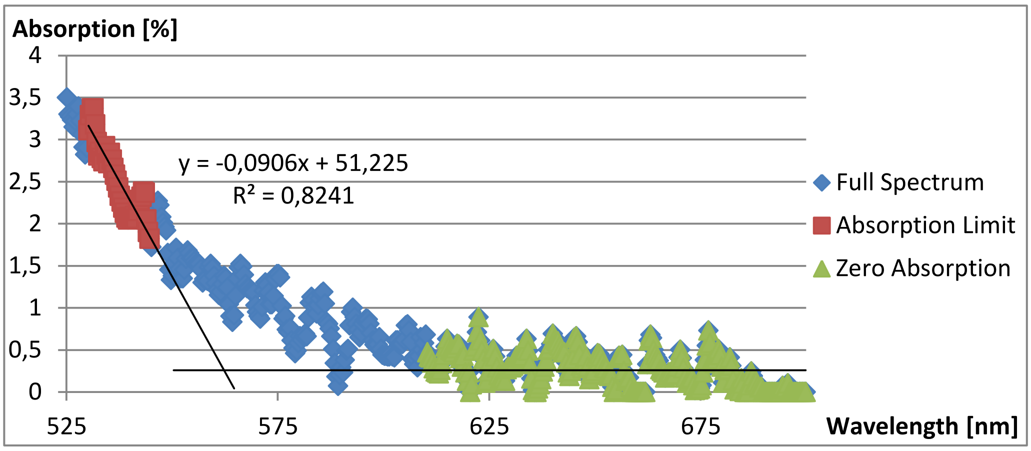

Figure 19 – Absorption Spectrum showing were the absorption is considered zero and the wavelength limit for the absorption for α-6T

5.2.2 NaT2

The measurement yields a transmission spectrum for the sample; the transmission spectrum is inverted to an absorption spectrum and plotted as displayed in figure 22. This is a measurement for the full spectrum from 300 to 1000 [nm]. The spectrum was also done for a smaller area of 400 to 600 [nm] for a finer resolution.

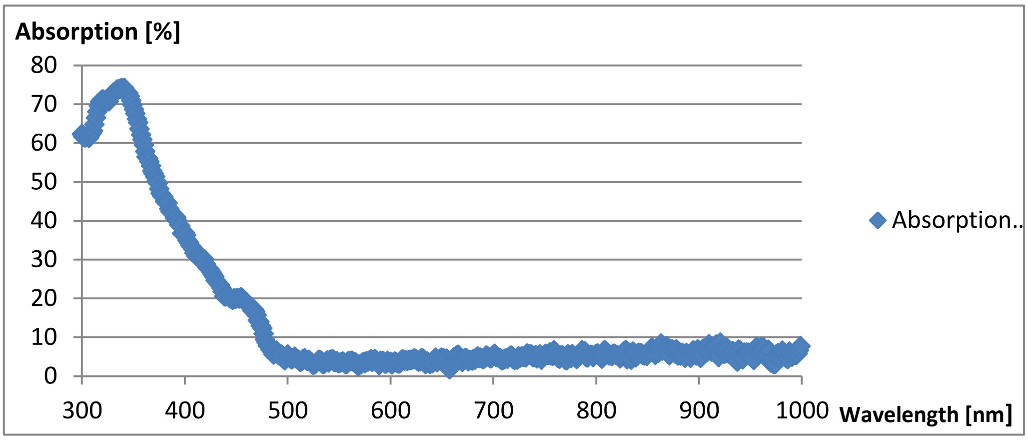

Figure 20 – Absorption spectrum for NaT2

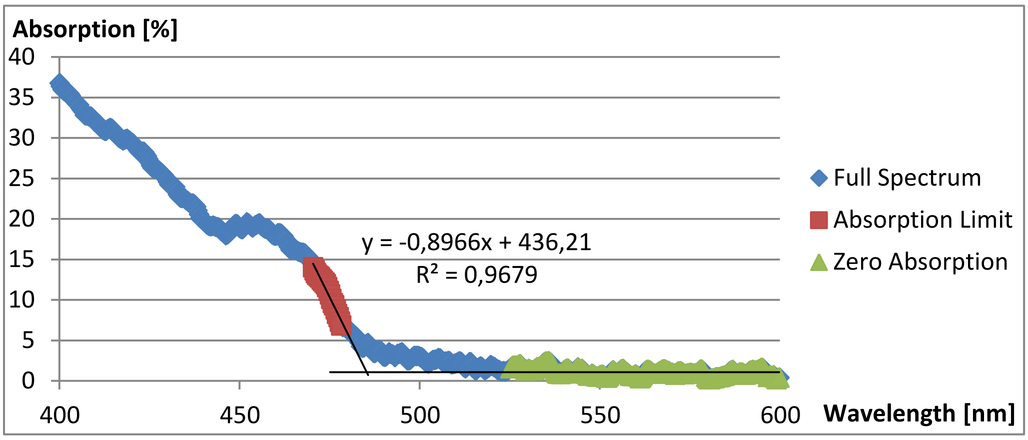

Figure 21 – Absorption Spectrum showing were the absorption is considered zero and the wavelength limit for the absorption for NaT2

Figure 23 shows the spectrum from 400 to 600 [nm]. This measurement was made from 400 to 600 [nm] with 512 points. As with the one for α-6T a trend line has been made for the absorption limit and an average has been made for the zero absorption, which is: 0,27 [%], see figure 23. The band gap has, again, been evaluated in the same way and the wavelength found is: 485,3 [nm], which corresponds to 2,6 [eV]. Comparing this with 2,5 [eV] in Advanced functional materials[6] it can be concluded that this measurement is quite accurate.

5.3 Final Test

In this final test, the responsivity and photocurrent may finally be investigated as functions of wavelength. Furthermore two different types of material for the semi-conductor will be investigated, α-6T and NaT2.

The current in dark was measured for both transistors before and after the sweep of wavelength. Ideally the current would be the same before and after but this was not the case. It is to be expected, however, organic semi-conductors proves to be quite unstable when having charged up in some manner. This can also be observed with the quite noticeable hysteresis that shows when sweeping the voltages up and down. This is likely to be caused by some charge traps in the material, though this phenomenon is not well understood. The current measurements were as following for α-6T:

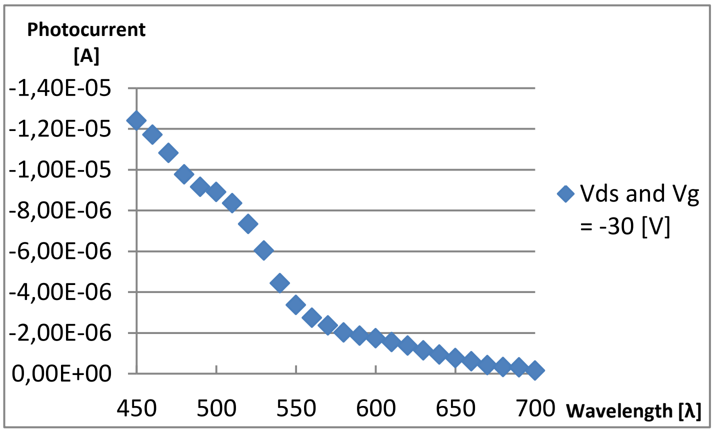

Figure 22 – Photocurrent as a function of wavelength for α-6T

- Before: -8,39 [μA]
- After: -16,37 [μA]
- Difference: 7,98 [μA]

The current measurements were as following for NaT2:

- Before: -60,23 [nA]
- After: -74,83 [nA]
- Difference: 14,56 [nA]

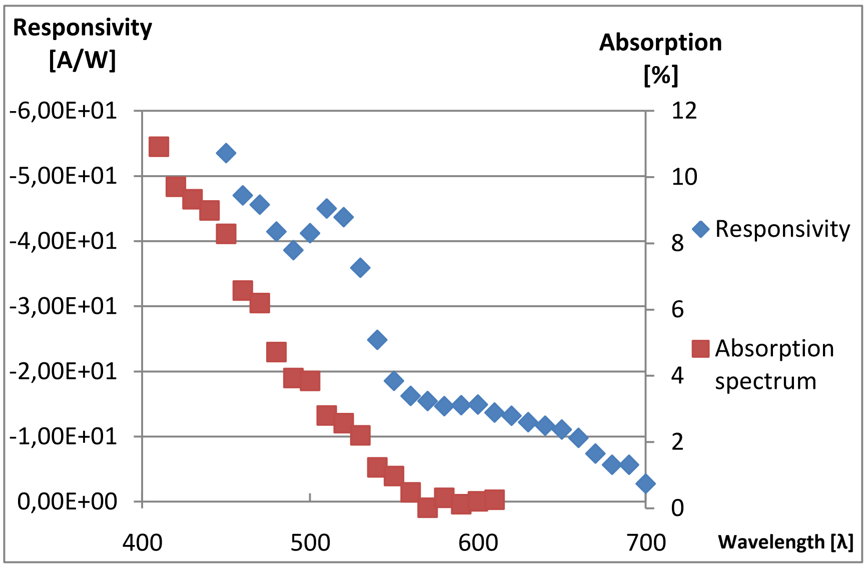

Figure 23 – Responsivity as a function of wavelength compared with absorption as a function of wavelength for α-6T

The plots which will be shown in this section are only for the final values of the voltages; the sweep of the voltage was made anyway to make the tests as comparable as possible to the others. Figures 24 and 25 show the photocurrent and responsivity for the α-6T OFET at V_{DS} and V_G equal to -30 [V]. In figure 25 the responsivity is compared directly with the absorption spectrum from chapter 5.2 Absorption measurements of organic materials. Furthermore the intensity used for the responsivity is varying in accordance with the calibration made; see chapter 4.3.1 testing equipment setup. This means that in its formula, which is given by:

$$R = \frac{PC}{Int * A}$$

The intensity is not constant but follows the spectrum of the light source.

The Figure for the photocurrent shows an increase in current as the wavelength decreases which is to be expected as the photon energy reaches the band gap. The band gap energy is at wavelength 562 [nm] and a sudden increase in current can be observed there. There is, however, photocurrent before that point. This might be a source error due to charging of the organic material.

The responsivity is increasing as expected and is following the absorption spectrum quite well. As with the photocurrent there is some responsivity before the energy for the band gap is reached; for reasons similar to that of the photocurrent, since the responsivity is proportional with it. At this point is pure speculation and should be investigated further.

The responsivity starts rising drastically more or less at the same point as the absorption. There is a sudden drop in the responsivity, though, which is not visible in the absorption spectrum, not even with higher resolution and zoomed into this point. This behavior is not really consistent with charge traps or other phenomena that could cause a decrease in current, since the effect should be consistent; the measurements were all taken with approximately the same time interval. It could be some sort of source error, so more investigation in this area is advisable.

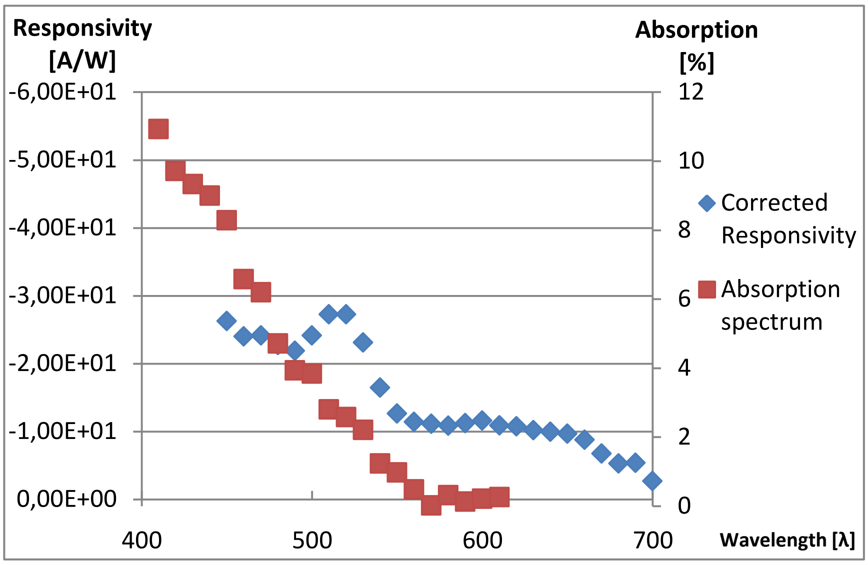

Figure 24 – Corrected responsivity as a function of wavelength compared with absorption as a function of wavelength for α-6T

As mentioned earlier the dark current from before the measurements and after was quite different. This may to some extend be represented in the results. Hence an interpolation has been made for the ratio, of the currents before and after, as a function of the wavelength. This expression has been multiplied to the responsivity in order to try to compensate for the charging of the material. Figure 26 shows the same graph as figure 25, but this time the responsivity is corrected for the charging. The shape of the corrected responsivity looks similar to that of the original responsivity, but the corrected responsivity does not rise after its sudden decrease. It is at this point not possible to say if this is a viable way to correct for the charging. Two things are assumed in this way of compensating. First; it is assumed that the charging effect of the material is directly proportional to the wavelength, but it is probably more likely that the proportionality is more complex than that and may even include more factors. Secondly; even if the proportionality is relatively simple, it is probably still not linear, which this interpolation is.

The results for the measurements done with the NaT2 OFETs are made in the same way. Figures 27 and 28 display the photocurrent and the responsivity compared with absorption. Like with the α-6T the photocurrent increases when the energy for the band gap is

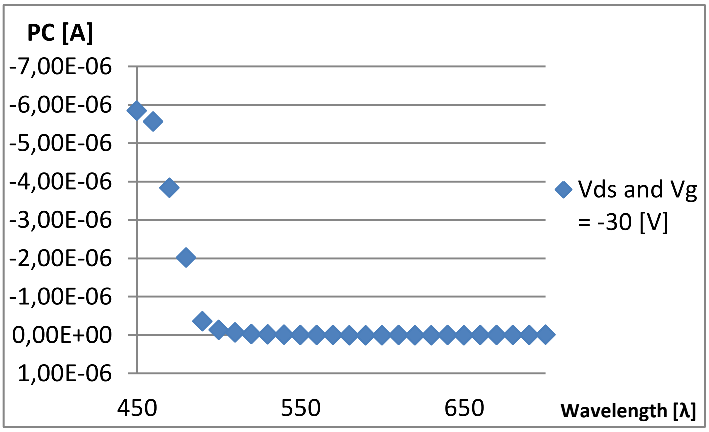

Figure 25 – Photocurrent as a function of wavelength for NaT2

reached but for the NaT2 this is an even more drastic increase. Furthermore the current values are quite low before the band gap, almost negligible. For the wavelengths 700 to 540 [nm] the photo current only changes from -3,32 to -3,62 [nA]. In between this interval the current were sometimes even lower than the initial -60,3 [nA] for the dark current; which resulted in a positive photocurrent. This means that the material does not respond within this wavelength at this range of the wavelengths and that the difference observed in current is noise.

The current raises several magnitudes of power once it has reached the band gap. This is why the compliance for the program had to be changed when doing this measurement. It indicates that the relative response to incoming light as a function of wavelength is large than that of α-6T.

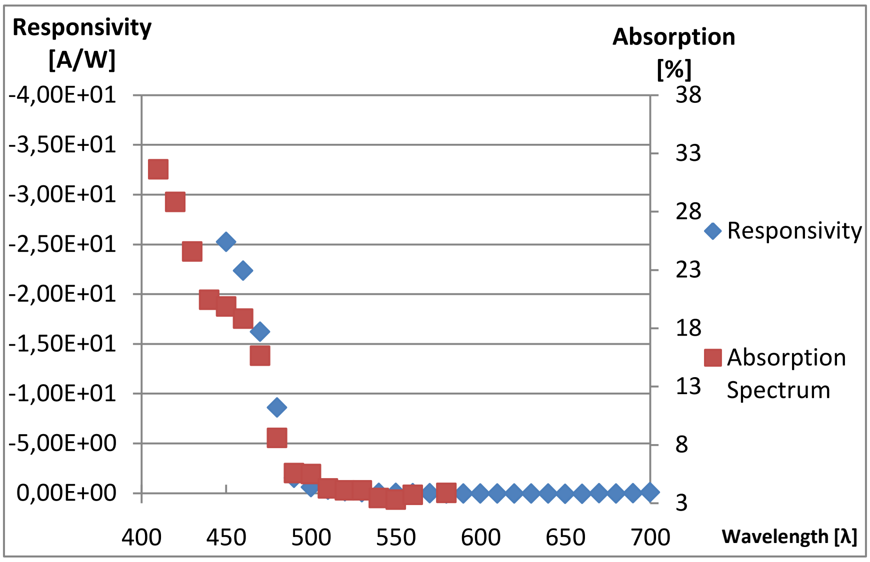

Figure 27 – Responsivity as a function of wavelength compared with absorption as a function of wavelength for NaT2

The responsivity of the NaT2 OFET is also increasing rapidly when the band gap energy is reached. It once again goes from almost no value to a value almost as high as that for the α-6T increasing several magnitudes of power. It follows the absorption spectrum quite well except for a small deviance where the spectrums slope stalls a bit and the responsivity does not. This could very well be due to charging of the material or uncertainty.

The Difference in the dark current before and after is not as severe as with the α-6T but it is still present. Figure 29 shows a graph where the responsivity, once again, has been corrected with an expression for the ratio. This correction has been carried out in the same way as for the α-6T. This time the responsivity holds the same shape though and only differs in magnitude.

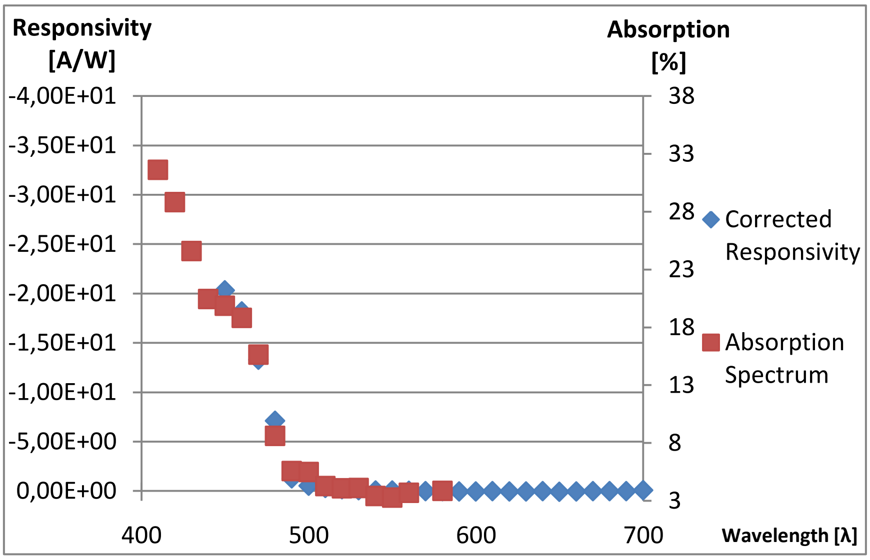

Figure 26 – Corrected responsivity as a function of wavelength compared with absorption as a function of wavelength for NaT2

The max responsivities of the OFETs are quite high with the uncompensated responsivities being:

- α-6T: -53,5 [A/W]
- NaT2: -25,2 [A/W]

And for the compensated responsivities:

- α-6T: -26,2 [A/W]
- NaT2: -20,3 [A/W]

These values are very high especially compared to those obtained in Xuhai liu PhD thesis[2], but responsivities in this range wave been obtained by others and comparing with Applied physics letter[7] these results are not unrealistic. These results are measured under other parameters and cannot serve as a direct comparison, but it demonstrates that very high responsivities have been obtained. In the given source a responsivity as high as 82 [W/A] has been reported for an organic device.

Though there is a need for some sort of expression for the current drift due to the likely charging of the material; there is still no solid evidence that the compensation used here is the right way to do it. In the contrary this compensation technique is likely not sufficient. When these results were found from the measurements; the initial plan was to further investigate if time allowed it, mainly by assessing the dark current between every shift in wavelength, but unfortunately the measuring equipment broke and the test could not be done.

6 Conclusion and Outlook

It can be concluded that the magnitude of the current cannot be directly based on the architecture of the substrate alone, though the design of the OFETs is indisputably functioning. It seems that there are other factors determining the current than the channel length of the substrate. Such things as the homogeneity and purity of the organic film could be having an impact.

The results for the characteristics of the OFETs have been satisfactory. With very high responsivities it is safe to conclude that the OFET configuration can be used as a photo sensor. Even more so; the responsivity will increase potentially with the gate voltage and thereby give option to adjust sensitivity of the device. As a future outlook this could yield an easy option to adjust and calibrate a device; and thereby more than make up for the fact that the device current can vary quite a lot from device to device.

The OFETs seem to be in accordance with the absorption spectrum for the organic materials, though for future outlook this effect could be even further validated and for an even wider range of wavelengths.

The OFETs do have the tendency to drift in the current after longtime exposure and operation. This gives uncertainty as to how accurate the measured currents are. Before a proper application of the OFET configuration can be utilized, it will be necessary to investigate further. The effects that cause these phenomena are definitely a study of interest for the further development of organic semi-conductors. For a future outlook on this; a test similar to the final test in this project could be done with the dark current being measured between every step, so as to get an expression for the effect. This could be the first step in a deeper understanding of the phenomenon.

The absorption of α-6T has proven to be much lower at its max value than that of NaT2. The dark current is several orders of magnitude smaller for NaT2 than α-6T though, but when they both start to absorb, they are more within range of each other, both in current and responsivity. This means; that while α-6T conducts better, NaT2 has a higher relative Responsivity and is therefore very useful as a sensor since its range can be distinguished easier. In a future outlook for this- it could proof fruitful to investigate the applications with some of NaT2s sister molecules such as NaT, NaT3, NaT4 and so one. As the chain lengths change so does the band gap energy; therefor other sensor ranges can be utilized.

The testing in this project has shown a potential increase in current when an electric field is applied, in this case from the gate voltage. Future options for this might be numerous. If the efficiency of photon absorption is increased by the electric field then this could be used in other organic semi-conductor devices apart from photo sensors, so as to increase the efficiency of components current- or power production.

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[15] “http://www.chemicalbook.com/ChemicalProductProperty_EN_CB0750598.htm.” .

Appendix

In the back of this report a CD is featured. In addition to a digital copy of the report it holds the appendixes and annexes which has not been printed out and included in the report.

A: Work plan

In order to structure the work which needs to be done in this project a work plan been made. The work plan is divided up into a work method and a work schedule, or time plan. The method is structured as a flow card and is coherent with the scientific method.

Flow card for work method

For The flow card will be divided into steps; each step describes what should be done at this point. The steps may be repeated if necessary.

1. **Research**

   The first thing to do in this project is to acquire knowledge. Hence the first part of the project will be oriented towards doing theoretic research in the area and acquiring theoretic knowledge. It is also necessary to acquire basic knowledge about transistors, organic transistors, micro fabrication and electro physics.

   The knowledge that has been acquired during this process will be explained and accounted for in the theory part of the report.
2. **Micro Fabrication**

   Once a basic understanding of the theory has been established, it is times to move on to the fabrication of the organic devices. It will be necessary to have a basic knowledge of micro fabrication for this step. Once some devices has been made; they will be examined and evaluated.
3. **Functionality testing**

   In extension of step two, the parts which are produced will be used in a functionality test. This is in order to test if the produced transistors are working correctly and are yielding a recognizable transistor characteristic. At the same time this will test the functionality of the setup itself. A test on an inorganic transistor will also be conducted.
4. **Preliminary testing**

   These pretests are mainly to demonstrated and document the principle of the light sensitive OFETs. These tests will be replicated out from the tests already done by NanoSyd and will, presumably, yield similar results. The characterization will happen by measuring the current with and without light exposure. In this preliminary test a non-specialized light source will be used.

5. **Testing optic measurement of absorption**

   Measurements will be made on the organic materials used in the OFETs to determine their absorption characteristics.

6. **Final testing**

   If more devices are needed, the fabrication part in step two will be repeated. With the arrival of new testing equipment, hopefully, the OFETs will now be measured while exposed to a light sweep of different wavelengths. From this characterization can once again be made; this time with a higher accuracy on the intensity and as a function of wavelength. The results will be compared to results in step five.

7. **Evaluation of model and results**

   All test results from step four to six will be evaluated and composed to a model for the characteristics of the OFET. The focus will especially be on five and six to investigate whether the absorption spectrum and the measured Photocurrent are comparable. A hypothesis can, hopefully, be formulated on this and show the connection.

In accordance with this flow card for the project a time table has been made to best perform the work and plan when to do it. See next section

Timetable

The timetable is made in accordance with the work method; look in the CD Appendix Management. Furthermore some milestones have been made to guide the project. The milestones can be seen beneath or in the CD Appendix Management.

Milestone	
#	Description
M1	Report on basic functionality of Transistors and optoelectronic devices
M2	Demonstrate Transistor characteristic on inorganic transistor as Set-up test
M3	Successfully fabricate Standard OFETs using the facilities at Alsion
M4	Validate functionality of produced Transistors
M5	Validate Characteristics of the OFETs for the pretests
M6	Determine the absorption spectrum for the organic materials optically
M7	Map the characteristic for the final test including functionality of wavelength for light

Risk assessment

The timetable is made in accordance with the work method

The risk assessment has been made in accordance with the milestones. For every milestone there is a risk. For the risk assessment with consequence and reaction to failure (Plan B) see the CD Appendix Management.

Comments on work

This project was originally intended to count for 20 ECTS points. The project was originally planned to have a theoretical quantum mechanics part as well. Therefore the original work plan, timetable, milestones and risks were quite different than the once featured now. The request for the extension to 20 ECTS points was denied half way into the project and therefore changes were made.

B: Individual study in quantum mechanics

This report will focus on quantum mechanical calculations for small organic molecules. The calculations will focus on finding the band gap value between the highest unoccupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Through this it will be possible to determine at what photonic energy the molecule will start to absorb incoming light. Furthermore the absorption spectra can be assessed when the allowed electron excitations and their energies have been found.

To do this assignment the computer program Arguslab will be utilized. The program will be used for the simulations of the individual molecules and to calculate the values for them.

Introduction

Quantum mechanical calculations are usually so complex that they cannot be solved analytically. If the calculations are concerned with systems that are more complex than a hydrogen atom; then some sort of numerical method must be used. This is due to the fact that the orbital cloud, that describes the position for the electron, is affected by other electrons. Furthermore it is relatively simple to calculate the wave function for a simple 3D energy well, such as the single point that the hydrogen core is. It is something else, entirely, to do it for several wells such as a larger atom core, or even several atoms like in molecule.

This is where a computer comes in handy. It would be extremely time consuming for a human to do even the simplest numerical calculations. In this report the used program for this will be Arguslab, which is a simulation program for quantum mechanical calculations. The program has a design feature capable of designing more or less whatever molecule one can think of. It is also able to calculate the most correct position of the atoms which is put in the molecule. After this the wave functions for the orbitals and the absorption spectrum for the molecule can be determined.

Semi-empirical methods

When calculating quantum mechanics in a molecule, the general concerned is usually with finding the wave function of an electron. The wave function is given by Ψ(x,y,z,t), which is a function the position and the time. To find this wave function the Schrödinger's equation must be used:

$$i\hbar\frac{\partial\Psi}{\partial \mathrm{t}} = H\Psi$$

Solving this equation can prof rather difficult as mentioned and this is where the program Arguslab uses a semi-imperial method called Zindo which stands for: "Zerner's Intermediate Neglect of Differential Overlap".

Since the method is semi-empirical it both uses a mathematical model and fits the model on known parameters. These known parameters come from systems already known by experimental investigation. So the mathematical model will try to fit whatever results it gets to known results from systems that bear some similarity. This means that the computing process does not need to be extremely precise. If the mathematical model was the only thing the program had to work with, it would consume extreme amounts of time and require a powerful computer. Adding the empirical data to fit the parameters to makes the computing much faster while still maintaining a realistic result.

The mathematical model makes some, not completely correctly, assumptions. First of all it assumes that the atoms in a molecule does not move and are completely stationary. The energy potential around the points, which are the atoms, is now constant. Secondly when calculating the wave function for one electron, one position is assumed for the rest of them, so that the repelling force can be calculated. This is of cause not a correct way to do it, but once it has calculated the wave function for all the electrons it can start converging. This means that it will calculate it for all the electrons again, this time reacting to the wave function of each other. Through iteration of this step it will correct the wave functions and converge closer and closer to the real result. The most correct result is that where the energy for the stages is lowest since this is a thermodynamic rule.

Model simulations

To demonstrate the functionality of Arguslab; two examples has been made in the program that will now be demonstrated. The two materials of study are α-6T and NaT2.

α-6T

On figure 1 a picture of α-6T is displayed, the picture is taken directly from Arguslab.
The molecule is built out of six aromatic rings consisting of four carbon, three hydrogen and one sulfur. The rings are bound together by single covalent bonds.

The first thing done to this molecule once it has been composed is to find the right geometry for the atoms; which is done with the function: “settings for a geometry optimization calculation”. Once these settings have been selected the program must do the calculation with the function: “Run a calculation”. The program will now optimize the position of the atoms in the molecule.

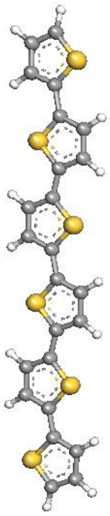
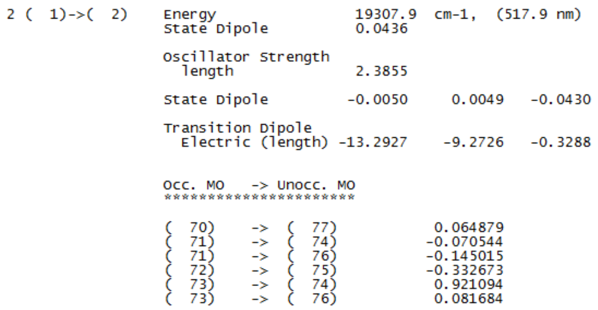


Figure 1 - α-6T molecule

To calculate the absorption spectrum for the molecule the function: “Calculate the electronic absorption spectrum” must be used. Once the settings have been confirmed the function: “Run a calculation” is used again. The program will now return a text file with the data. In figure 2 an example of how this data looks is displayed. This data shows which shift in orbitals has the right energy to absorb a photon with wavelength 517,9 [nm]. The oscillator strength length tells how likely it is, hence it is relatively proportional with the amount of intensity absorbed.



```
2 (  1)->(  2)    Energy                  19307.9  cm-1,  (517.9 nm)
                  State Dipole            0.0436

                  Oscillator Strength
                    length                2.3855

                  State Dipole           -0.0050     0.0049   -0.0430

                  Transition Dipole
                    Electric (length) -13.2927    -9.2726   -0.3288


                  Occ. MO   -> Unocc. MO
                  **********************

                  (  70)    ->  (  77)          0.064879
                  (  71)    ->  (  74)         -0.070544
                  (  71)    ->  (  76)         -0.145015
                  (  72)    ->  (  75)         -0.332673
                  (  73)    ->  (  74)          0.921094
                  (  73)    ->  (  76)          0.081684
```

Figure 2 - Arguslab return data

Figure 3 shows an optical measurement of α-6T. Compared with the absorption found in Arguslab, the 517,9 [nm] is pretty close to the one found in the experiment. The absorption starts at this wavelength and is hence an expression for the band gap. This is also evident since the orbital shift 73 to 74 is, respectively, HOMO and LUMO. The simulation is, however not completely accurate since, when investigating the graph further, the absorption starts at 562,4 [nm]. This means a difference in energy for the band gap: from the experimental 2,2 [eV] to the Simulated 2,4 [eV].

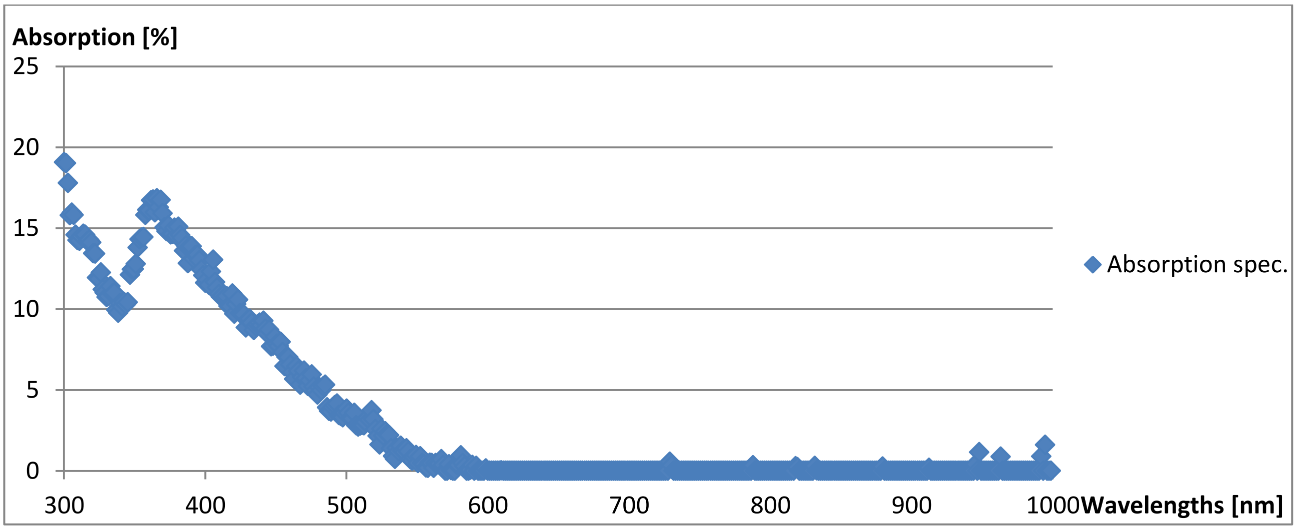


Figure 3 - Optically measured absorption spectrum for α-6T

NaT2

On figure 4 a picture of NaT2 is displayed, the picture is also taken directly from Arguslab. This molecule is made from two of the same sort of aromatic rings as in α-6T, which are flanked by two double benzene rings.

The procedure for the calculation is exactly the same as with α-6T. The calculated absorption for the NaT2 molecule is 428,5 [nm]. Figure 5 shows a graph of an experimental measurement of NaT2. Once again the experimentally found spectrum is displayed. The wavelength found in Arguslab is once again the one for the band gap since it has the HOMO LUMO shift from orbital 71 to orbital 72. Though the value from Arguslab is in the right range, it is not completely accurate. The wavelength from the graph is 485,3 [nm], this means a difference in energy for the band gap: from the experimental 2,6 [eV] to the Simulated 2,9 [eV].

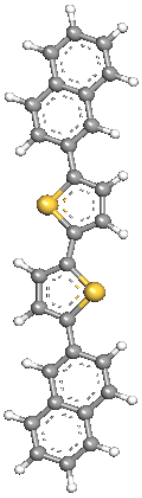


Figure 4 - NaT2 molecule

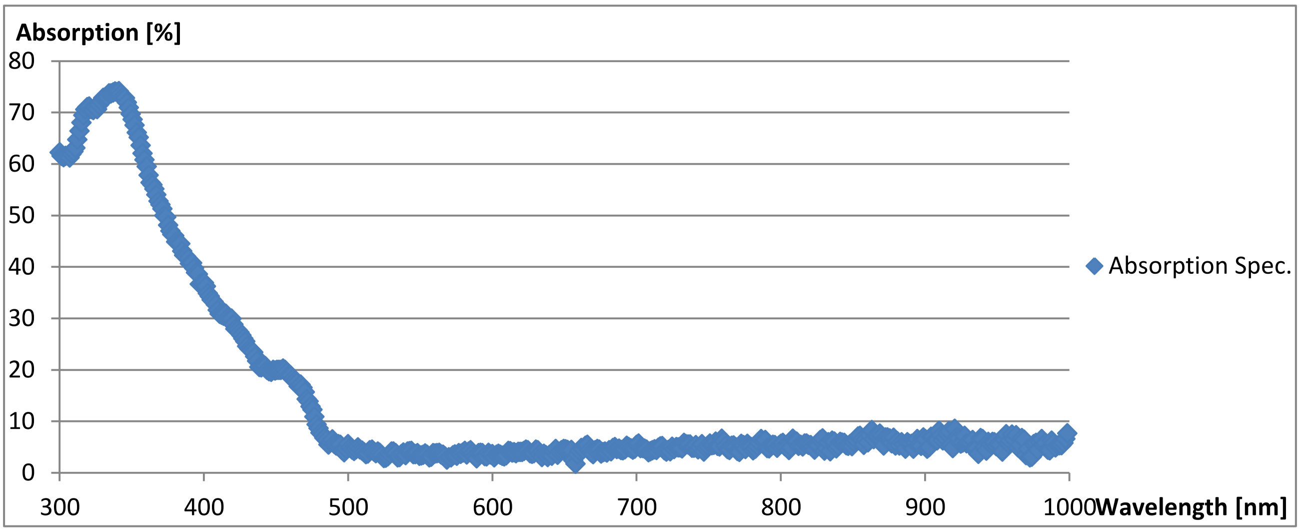


Figure 5 - Optically measured absorption spectrum for NaT2

Conclusion

The Arguslab simulations are a usable tool for indicating the band gap values and absorption spectrum of a molecule. Though it is not completely correct in its value and can therefore only be used as a hint in the value range. The values are approximately 5 to 15% larger than they are in real life. This remain a viable tool if the task at hand is to design an entirely new molecule and one would like to have some indication of its absorption properties and band gap.

C: Theory of organic optoelectronic semi-conductors

In this report the functionality of an optoelectronic OFET will be described. But in order to reach a satisfactory description of such a device, it is necessary to describe other devices, and the physics behind them, first. Initially; the inorganic semi-conductor will be described first, with its applications as diode and transistor. After that the focus will be shifted to the organic semi-conductor.

Conductors, semi-conductors and insulators

In electronics; there are generally three different types of materials in terms of electrical properties. The material is either a conductor, a semi-conductor or an insulator. A conductor will always conduct if biased whereas the Semi-conductor and the insulator will not. This is due to electronic structure of the different materials. For a conductor there will always be electrons which are not locked in the chemical bond between the different atoms, these electrons are said to be in the conduction band. Conducting materials are usually metals which are known to have free electrons in the outer orbitals due to the metal bond the atoms make. Whereas a material such as silicon; makes covalent bonds instead, where the electrons are not free. Silicon is a semi-conductor.

Figure 1 displays how the conduction band and the valence band are placed in the different materials. Both the conduction band and the valance band has multiple allowed states in them, that is why the bands have a height and thereby states along the increasing energy. As it can be seen there are no allowed states in the band gap for semi-conductors and insulators. This means that the electrons are in the valence band and cannot shift to the conduction band, not without a work being done to them. This of cause makes sense since all the electrons in silicon are used for the covalent bonds. The only difference between a semi-conductor and an insulator is the band gap.

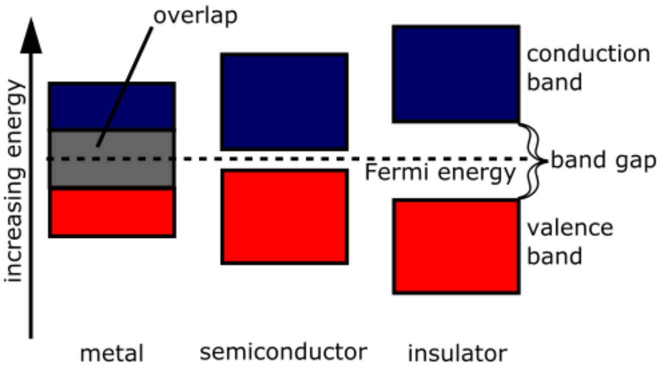


Figure 1 - Conduction band and valence band for metal (conductor), semi-conductor and insulator.[10]

As mentioned the electrons in silicon cannot go to the conduction band, reach a higher and "free" orbital, without a work being done to them. In the metal this is not the case, since these two bands overlap. This also means that the Fermi energy level is in the conduction band. The Fermi energy level must be close to the conduction band to in order for the material to conduct electrons.

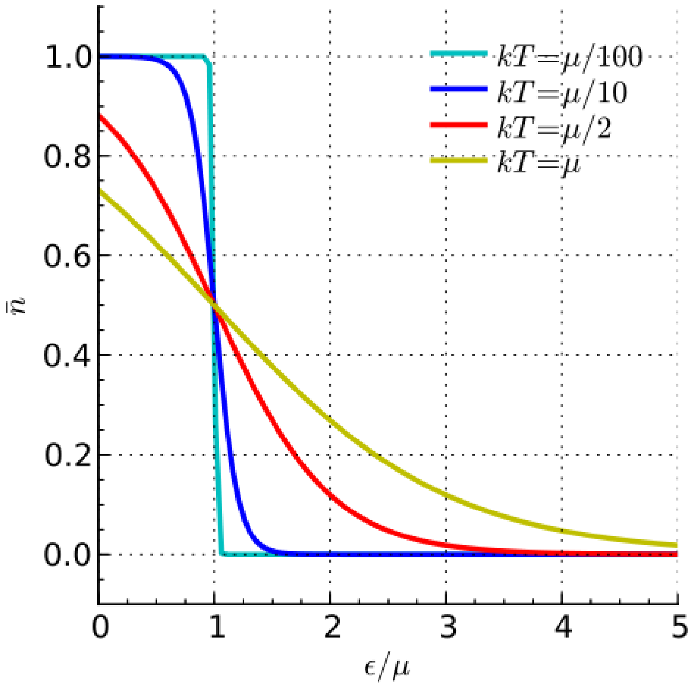


Figure 2 - Fermi-Dirac Distribution – x-axis is the energy of a state compared with the Fermi energy and y-axis is the probability that a state is filled by an electron. The graph shows hoe the probability changes as the temperature rises.[11]

Look at figure 2. This is a graph describing the importance of the Fermi energy level. As is can be observed; the probability to find an electron in a state above the Fermi energy is zero, though this changes if the material is not at absolute zero, as shown by the other lines. This means that there might be some electrons in the conduction band of a semi-conductor at room temperature, but not enough to lead any significant current. The Fermi level is placed in the middle of the band gap and thereby, if the temperature is non-absolute zero, the chance of finding an electron at this state is 50%, with the probability decreasing with the increase in energy. But the electron cannot be at a state that is not allowed so the chance is of cause zero, and the Fermi energy level merely shows that this would be where a 50% chance was, if it was possible. As for the metal; the Fermi energy level is in the conduction band, and thereby there are states that the electrons can be in. This is why metal will conduct, in its solid stat, at any temperature.

Inorganic semi-conductors

Doping

In order to make a semi-conductor conduct at room temperatures, Doping of the given material is necessary. The doping processes apply impurities in the lattice in the form of other atoms. For expel; Silicon has four valence electrons and makes four covalent bonds with four other silicon atoms. But if some of the other atoms are substituted by Phosphorus which has 5 valence electrons; then after the covalent bonds has been satisfied there will be one surplus electron. Even though the bonds that have been made by the other electrons are not metal bonds, the surplus electron will still be in the conduction band, since it cannot be part of a covalent bond itself. So effectively, what the doping does in this case is to push the Fermi Energy level up, the chance of finding an electron in a higher state is higher. This is called negative (n) doping and can be done with atoms from the 5th main group. If done heavily enough; the Fermi energy level does not only rise towards the conduction band, but starts to have so many electrons in the, otherwise depleted, band gap that the material starts to conduct. Another form of doping also exists; this one is called positive (p) doping and applies impurities from the 3rd main group instead. This means that there will be a deficit of electrons in the valence band. If done heavily enough the same will happen as for the (n) doping but towards the valence band instead the material will also be able to conduct. This time with "holes" instead of electrons though. This means that the valence band can actually conduct, or just above the valence band in the newly created state, but through the fact that there are an electrons missing in the bonds between the atoms, hence this conduction is of the positive charge carrier called a "hole".

P-n Junction

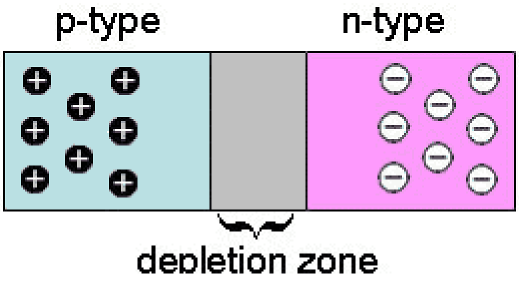


Figure 4 - p-n junction with depletion zone[13]

Although silicon can be doped so much that it can conduct to some extend this is not necessarily desired. Silicon can be used in semi-conductor electronics, without being able to conduct by itself. A good example is the p-n junction, where there are two silicon parts; one n-doped and one p-doped. These two are put together, which results in an almost instant depletion zone being created between them, figure 3. This is due to the fact that there is an energy difference between the two Fermi energy levels. For this to stabilize there is a current of "holes" from p to n and a current of electrons from n to p for a short time until the levels have merged and the depletion zone has been created. The conduction band and valence band for this condition can be seen in figure 4. To induce a current it is necessary to bias the p-n junction, but it is important that the cathode is on the n-type and the anode on the p-type, since this will inject the right charges and "squeeze" the depletion zone together.

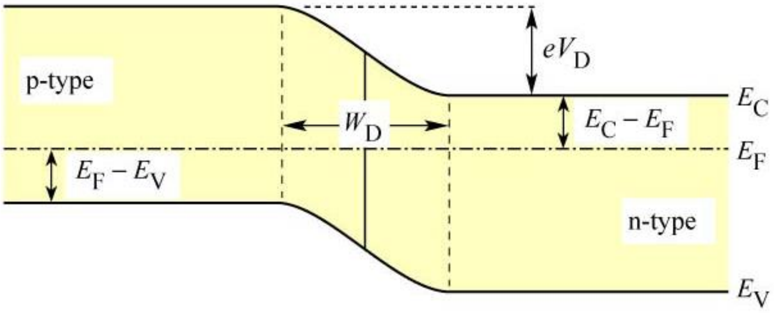


Figure 3 - p-n junction in zero bias[12]

Figure 5 displays a p-n junction under a forward bias. Under forward bias the energy between the bands are closer, Hence "holes" and electrons can easer diffuse into the depletion

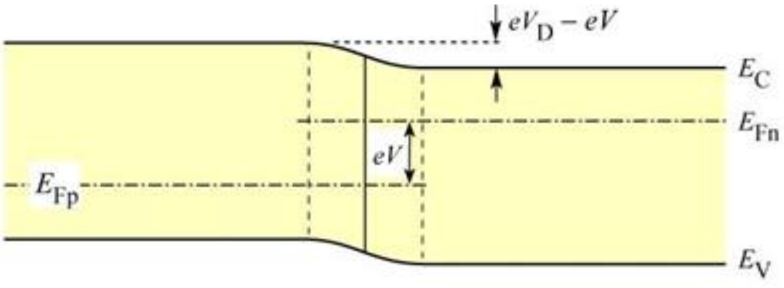


Figure 5 - p-n junction under forward bias[12]

zone, which is smaller. The two Fermi energy levels are no longer at the same level, hence there will be a higher diffusion into the depletion zone to try and make it lager and leveling out the Fermi energy levels. Charges and holes recombine in the depletion zone and are ever replaced by new ones. This will continue as far as there is a bias. Though the voltage of the bias has to be high enough for the electrons to have the right amount of energy corresponding to the difference between the conduction band and valence band, which is why a diode must have a minimum bias to function. The energy that the electron must lose to recombine with the "hole" is used to emit a photon. It should, however, be mentioned that this only happens if the electron can jump to an empty state with the same momentum as its former state. If not; no emission is made and the energy is lost to heat instead. If the empty state and the former state have the same momentum the device is an optoelectronic device. The device can also be applied as a photo detector operating at zero bias or reverse bias (to increase the depletion zone). When operating like this, an incoming photon may be absorbed by an electron in the valence band which then jumps to the conduction band. The photon must have the exact amount of energy needed for this jump, once this happens a hole will be left in the valence band and an electron in the conduction band, which leads to a current being created. The p-n junction device is a simple diode

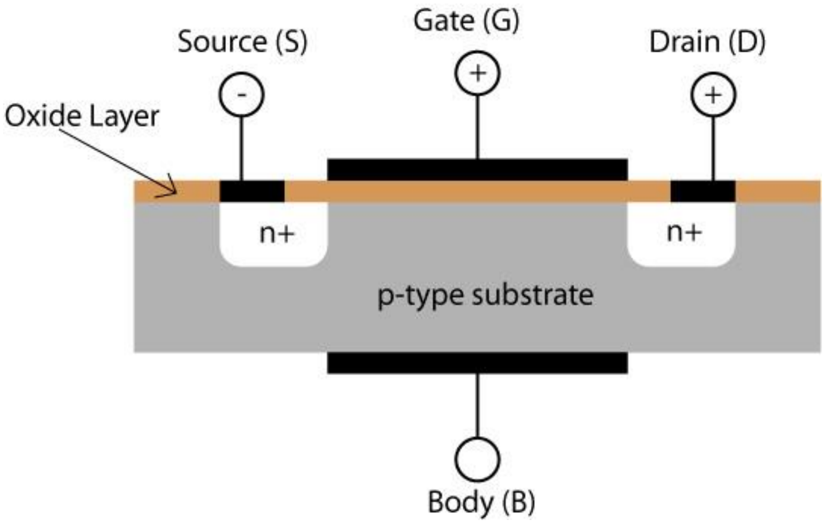


Figure 6 - n-type MOSFET[14]

Field Effect transistor (FET)

The Inorganic FET is built of the same parts as the diode; it just has one more junction. It is set up in two different configurations; pnp and npn (also called p-type and n-type respectively). Look at figure 6 for the architecture of an n-type FET. The Device has two p-n junctions, each pointing in different directions, which means that the device cannot conduct, even under forward bias. Hence the device has a third electrode, the gate electrode. By applying a positive voltage on the gate it will function as a capacitor between the gate electrode and the body. This will attract a lot of negative charges close to the oxide p-type interface, which can then conduct a current, under a positive voltage from drain to source. This will once again push the conduction band and valence band of the different parts closer together, but the device is still two opposite diodes so the current does not run under the same circumstances as in the diode. Instead the current runs only in the conduction band and is only carried by electrons. This means that the drain and source electrodes must be made of a metal which is roughly comparable to the Fermi Energy level of the conduction band of the n-doped silicon. The current, in an n-type FET, runs from drain to source (since the electrons run the other way). A p-type FET functions in the same way but here the current is conducted in the valence band, must have a negative voltage on the gate and the current runs from source to drain. Due to the fact that the current only runs in one band, an inorganic FET cannot function as an optoelectronic device.

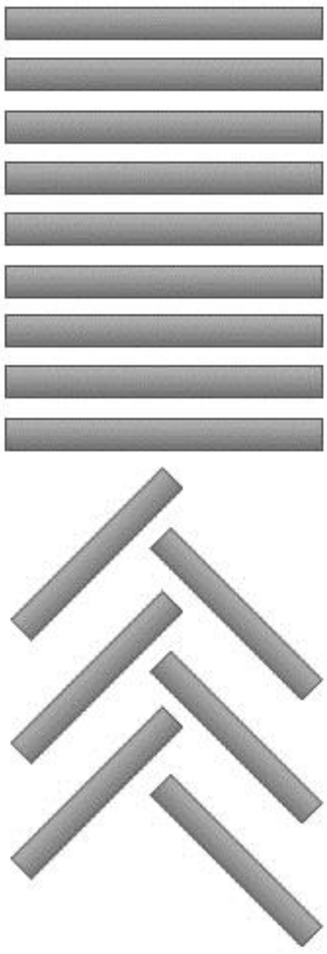


Figure 8 - π–orbitals in a molecule (top) and σ-orbitals in a molecule (bottom)

Organic Optoelectronic devices

In organic semi-conducting devices; the semi-conducting material is not a doped silicon crystal but rather small organic molecules or polymers in a solid-state structure. The molecules in this structure link together not by covalent bonds like the silicon atoms, but the weaker van der Waals force and dipole–dipole interactions that exists between molecules. Needless to say; there isn't any conduction band and valence band between the molecules, since this is a concept between atoms. Instead there are the lowest unoccupied molecular orbital (LUMO) analogues to the conduction band and the highest occupied molecular orbital (HOMO) analogues to valence band. These are results of the covalent bonds between the atoms in the molecules; where, since the molecule is small, the electron cloud covers the entire molecule. For an organic semi-conductor it is important that the higher orbitals of the molecule are π–conjugated. This means that the electron cloud extends far out normal from the molecular plane, which is useful to create contact between molecules, a so called π– π stacking. This is quite similar to the atoms in the silicon where states in the conduction band made it possible for an electron to be shared between atoms. If a molecular orbital is of σ-type, then it is much more confined to the plane of the molecule, and will be insulating instead, See figure 7. So a solid state structure with a lot of molecules with π-orbitals can conduct current if the molecules are closely enough packed and are packed the right way. There are two ways of packing which are doable; the "herringbone" and the coplanar

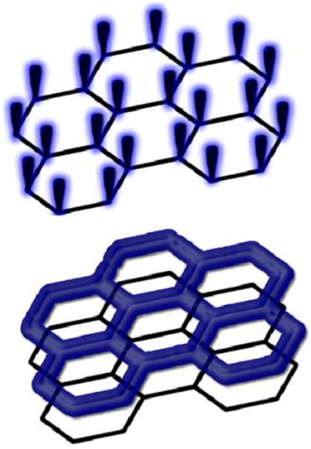


Figure 7 - Coplanar packing (Top) and "Herringbone" packing (bottom)

see figure 8. The long rectangular planes in figure 8 represent a molecule. Another important factor for a molecule is that it is not twisted. The molecules used in organic semi-conductors are usually mode from rings, for example benzene rings, which means that in order to have the best π–conjugation the rings of the molecule must be, roughly, in plane with each other. A typical molecule used is the thiophene group oligomere, look at figure 9 for a variation of it, the sexithiophene (T6). In contrast to the inorganic semi-conductor a molecule, such as T6, can conduct by itself, but its conducting abilities are enhanced by introducing a variant, but this time in the molecule. One of the molecule rings may be substituted with another ring to either make the molecule electron donating or electron withdrawing. This can be compared with raising and lowing of the Fermi energy level, but the substitution of an electron donating ring will raise both the HOMO and LUMO energies, whereas the substitution of an electron withdrawing ring will lower them both. Hence this can be used to adjust the HOMO and LUMO energies; so that they fit the Fermi level of the electrode metals better. So until now the similarities in functionality are quite similar for organic and inorganic, but there are differences. The operation itself for the transistor differs. In contrary to the ordinary FET the Organic FET (OFET) can function as an optoelectronic device. Look at figure 10 for the architecture of a typical OFET.

An OFET will normally have its gate at the bottom and then either the organic film with the electrodes on top or, as in figure 10 the electrode with the film on top. The key difference from an ordinary FET is that there is only one type of material in the Organic semi-conductor.

Figure 9 - Sexithiophene (α-6T)[15]

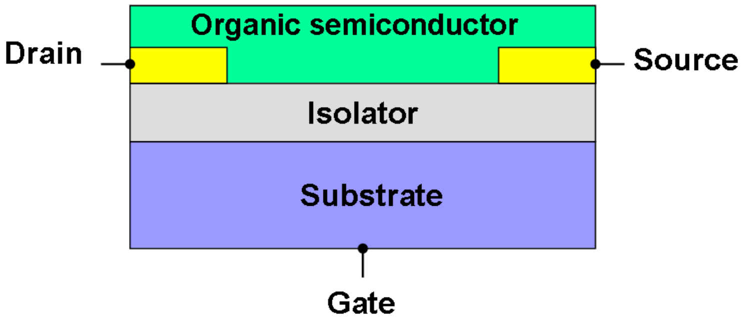


Figure 10 - OFET[8]

This is because the substituted molecules are in all the organic material. They are still not numerous enough to lead a current but if a gate voltage is applied the capacitance will; once again, populate the isolator organic interface with charges which can conduct a current. This means that the OFET can function as an Ordinary FET would. There is the opportunity to run it as an optoelectronic device as well. This means that the transistor must run as an ambipolar OFET. First of all the organic material must have substitutes of both kinds, so that both “holes” and electrons can be conducted. Furthermore the drain and source must not be of the same conducting material. The Drain should be made of a material which will be good injecting “holes”, such as ITO, and the source should be good at injecting electrons, such as Ca. The reaction, see figure 11, can happen under a forward bias by itself, since the device is comparable to a diode, though without depletion zone. Or it can happen if the material is affected by an electric field. Both can serve to bend the HOMO and LUMO energies and thereby make both “hole” and electron injection possible. Hence recombination is possible in the substrate, which will generate a current. In a transistor operated in this manner a current will already run, so it is the change in current which is the means to detection.

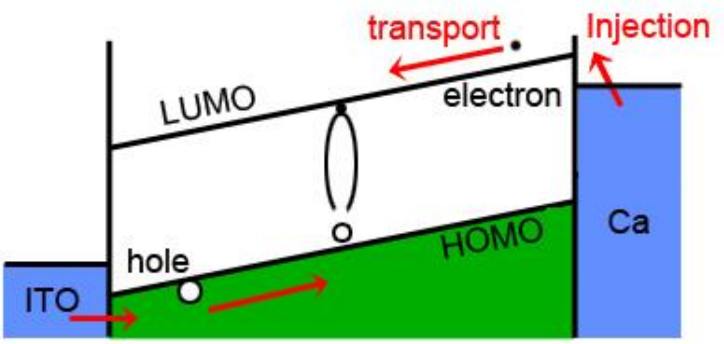
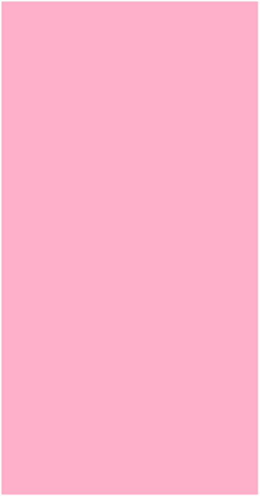
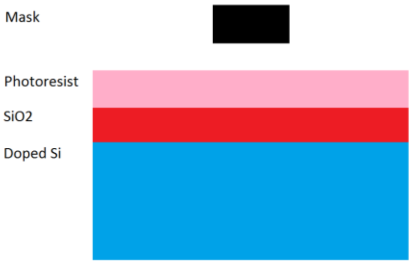
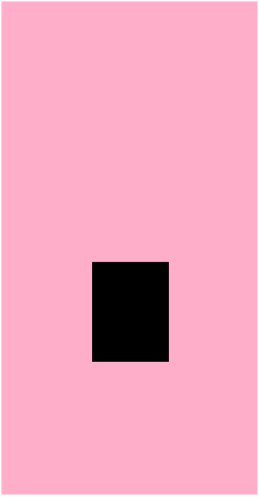
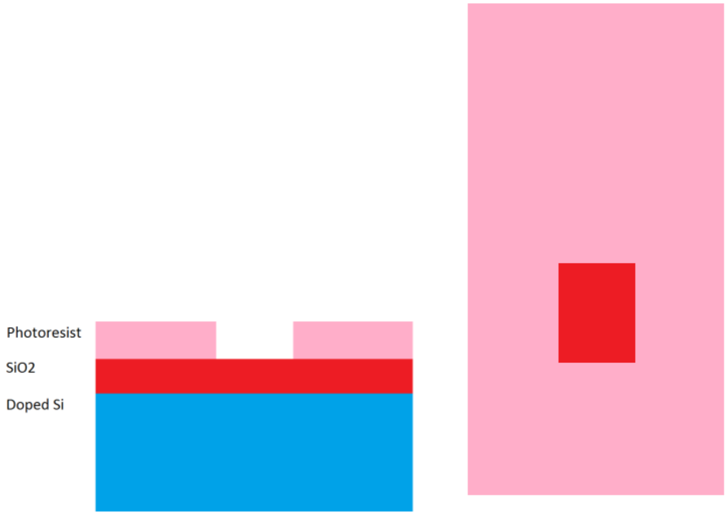
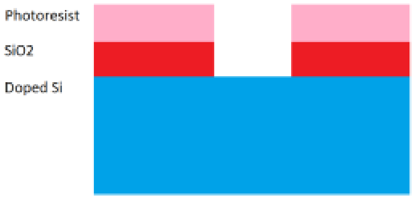
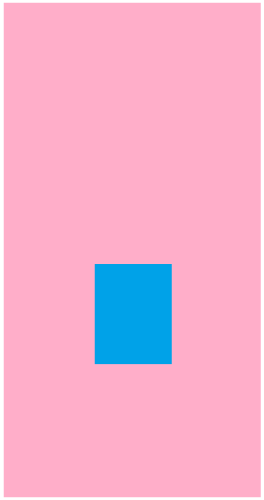
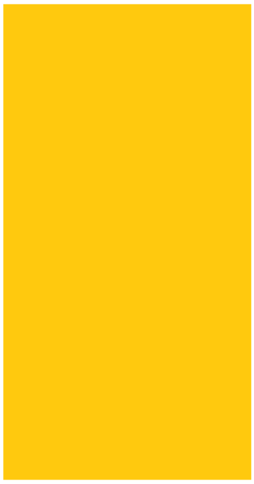


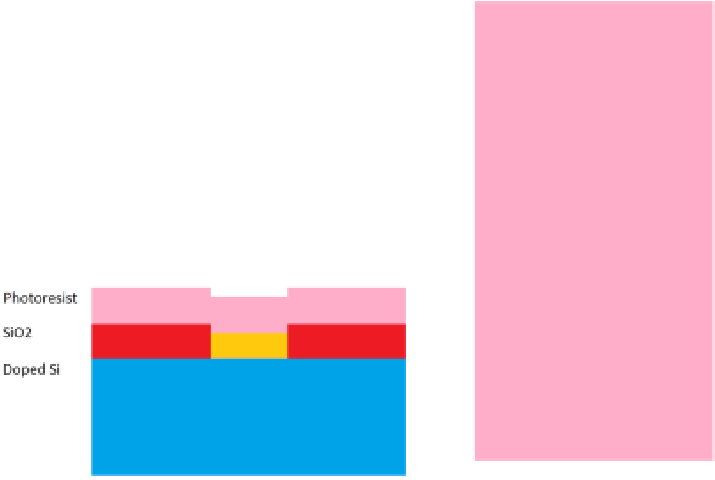
Figure 11 - Operation of an optoelectronic device

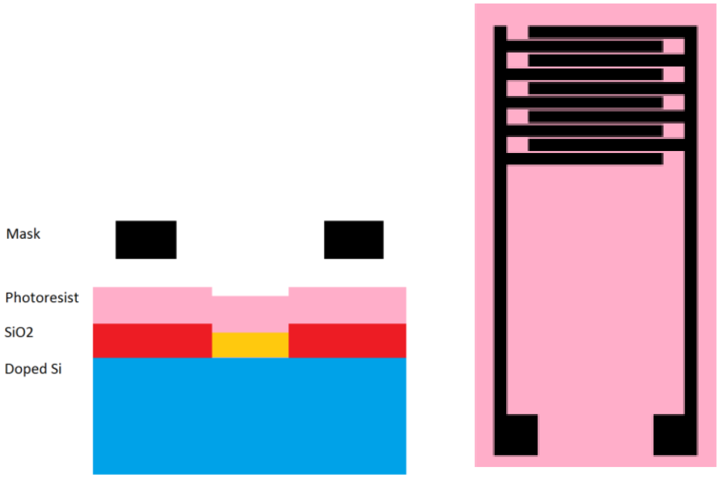
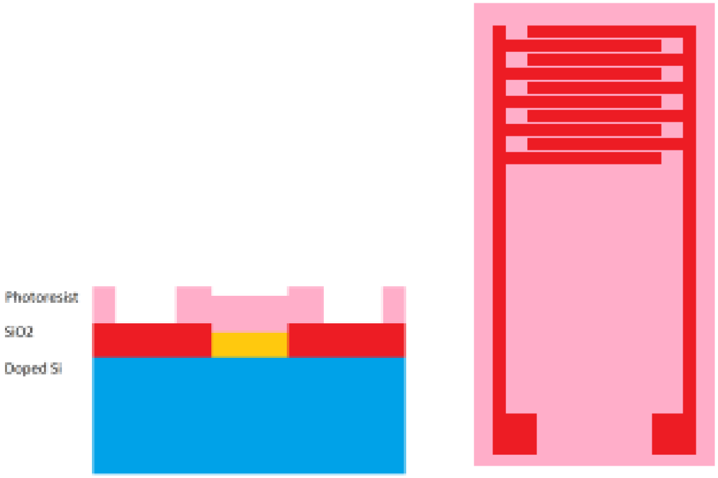
D: Recipe for cleanroom

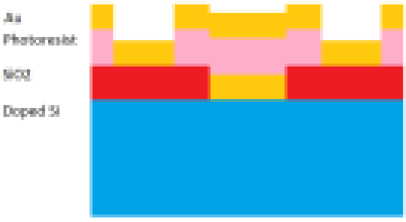
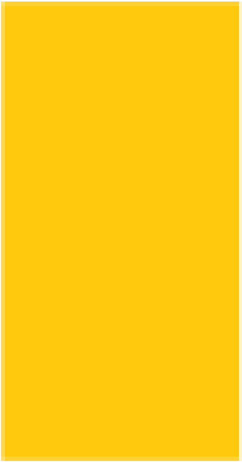
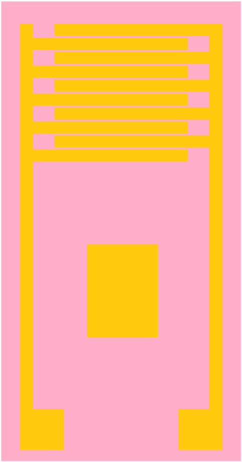
Step 1: Applying a layer HMDS (Adhesion Promoter)	
Step 2: Apply Photoresist to the wafer: 1. Automatic resist dispense 2. Spin at 500 [rpm] for 5 [s] 3. Spin at 4000 [rpm] for 30 [s] Photoresist: AZ5214E Layer Thickness: 1,4 [µm]	 
Step 3: Prebake the photoresist on hotplate for 60 [s] at 90 [°C]	
Step 4: Apply mask 1 (Gate electrode mask)	 
Step 5: Expose with UV-light for 2 [s]	

Step 6: Inversion bake the photoresist on hotplate for 100 [s] at 130 [°C]. After this make a flood exposure with UV-light for 25 [s] without the mask	The Exposed part becomes cross-linked after inversion bake. After the flood exposure the rest of the photoresist becomes dissolvable.
Step 6: Inversion bake the photoresist on hotplate for 100 [s] at 130 [°C]. After this make a flood exposure with UV-light for 25 [s] without the mask	The Exposed part becomes cross-linked after inversion bake. After the flood exposure the rest of the photoresist becomes dissolvable.
Step 7: Put the wafer in developer bath, with the developer AZ351B, for 60 [s]. Shake the wafer during the process.	
Step 8: Rinse wafer in rough rinse bath and then fine rinse bath.	
Step 9: Spin drying. Use Predefined program for the spin drying machine in the cleanroom.	

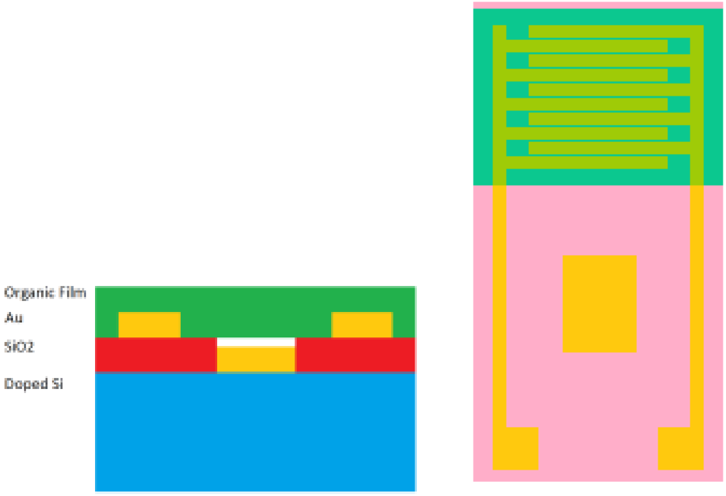
Step 10: Put the wafer in Etching bath with HF for 6 [min]	 
Step 11: Rinse wafer in rough rinse bath and then fine rinse bath.	
Step 12: Spin drying. Use Predefined program for the spin drying machine in the cleanroom.	
Step 13: Place wafer in Cryofox Vapor deposition machine. Use e-Beam physical vapor deposition program. Deposit 2 [nm] titanium, for better grip to substrate, and 30 [nm] gold as the electrode metal.	 

Step 14: Put wafer in acetone bath to all photoresist and thereby removing the metal placed on top of the resist (Lift-off)	
Step 15: Rinse wafer in rough rinse bath and then fine rinse bath.	
Step 16: Spin drying. Use Predefined program for the spin drying machine in the cleanroom.	
Step 17: Applying a layer HMDS (Adhesion Promoter)	
Step 18: Apply Photoresist to the wafer: 1. Automatic resist dispense 2. Spin at 500 [rpm] for 5 [s] 3. Spin at 4000 [rpm] for 30 [s] Photoresist: AZ5214E Layer Thickness: 1,4 [µm]	
Step 19: Prebake the photoresist on hotplate for 60 [s] at 90 [°C]	

Step 20: Apply mask 2 (source/Drain electrode mask)	
Step 21: Expose with UV-light for 2 [s]	
Step 22: Inversion bake the photoresist on hotplate for 100 [s] at 130 [°C]. After this make a flood exposure with UV-light for 25 [s] without the mask	The Exposed part becomes cross-linked after inversion bake. After the flood exposure the rest of the photoresist becomes dissolvable.
Step 23: Put the wafer in developer bath, with the developer AZ351B, for 60 [s]. Shake the wafer during the process.	
Step 24: Rinse wafer in rough rinse bath and then fine rinse bath.	

Step 25: Spin drying. Use Predefined program for the spin drying machine in the cleanroom.	
Step 26: Place wafer in Cryofox Vapor deposition machine. Use e-Beam physical vapor deposition program. Deposit 2 [nm] titanium, for better grip to substrate, and 30 [nm] gold as the electrode metal.	 
Step 27: Put wafer in acetone bath to all photoresist and thereby removing the metal placed on top of the resist (Lift-off)	 
Step 28: Rinse wafer in rough rinse bath and then fine rinse bath.	
Step 29: Spin drying. Use Predefined program for the spin drying machine in the cleanroom.	

E: Recipe for lab

Step 1: Mount the substrates on holder and apply a shadow mask to limit the depositing area. Place the holder in the chamber.	
Step 2: Pump vacuum in the chamber. Value should be below 5 [µTorr].	
Step 3: Warm the organic material up to the evaporation temperature. 290 [°C] for α-6T and ??? [°C] for NaT2	
Step 4: Open shutter and do the organic molecular beam deposition Film thickness: 30 [nm]	
Step 5: Close shutter	
Step 6: Vent with argon	