MASTER

The temporal response of organic photodiodes for imaging applications

Ligthart, A.

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A. Ligthart

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The temporal response of organic photodiodes for imaging applications

Graduation report of
A. Ligthart

Supervisor
Dr. S.C.J. Meskers

Supervising Professor
Prof. Dr. G. Gelinck

Committee members
Dr. M. Creatore
Dr. R.W. van der Heijden

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Molecular Materials and Nanosystems
Department of Applied Physics

Eindhoven University of Technology
Abstract

Organic electronics are a promising new technology with a wide range of applications. Organic photovoltaic devices or photodiodes can for example be used as light detectors in the field of imaging. Organic photodiodes for imaging applications should satisfy three main requirements: low darkcurrent, high quantum efficiency and a fast response time. The aim of this study is to understand and characterize the response time of organic photodiodes using time and frequency dependent measurements.

Impedance spectroscopy allows for simultaneous determination of the (photo) capacitance and (photo) conductance, respectively the reversible and irreversible part of the response. From the simultaneous measurement of the capacitance and conductance a response time can be determined. The measurement results show that the response time is proportional to the light intensity in reverse bias. Close to open circuit voltage the number of the charge carriers in the device is limited by the space charge limit. It is shown that the response time in this limit corresponds to the lifetime of the slowest charge carrier in the device. The lifetime of the slowest charge carrier is dependent on the product of the mobility of the slowest charge carrier and the illumination intensity. Using this relation it is shown that the mobility of the slowest charge carrier can be determined by measuring the capacitance as a function of the applied bias.

By varying illumination intensity, it is shown that the response time of the device depends on the illumination intensity and the applied bias. When the diode is operated close to open circuit conditions, the response time is limited by the lifetime of the slowest charge carrier. Under these conditions the response times determined by varying the light intensity and by varying the applied electrical potential (impedance spectroscopy) are very similar and can be interpreted in terms of the relaxation time of the system. For low light intensities and large applied biases the response time to variations in light intensity is limited by the transit time of charge carriers.

This study shows the importance of balancing the mobility of the charge carriers in the organic photodiode in order to achieve a fast response at low applied bias voltages.
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1 Introduction

Organic electronics have a wide range of possible applications: such as light emitting diodes and organic photovoltaic devices. Organic photovoltaic devices convert light into electricity; solar cells are a well known example. Photovoltaic devices or photodiodes can also be used as light detectors in the field of imaging, optical communications and biomedical sensing. [1], [2]

Organic photodetectors for imaging applications have three main requirements: High quantum efficiency, a low and stable dark current and short response time. A high quantum efficiency increases the sensitivity of the photodiode. The dark current is the current running through the device in the dark. Therefore the dark current determines the lowest light intensity measurable. The short response time is necessary for fast imaging. A long response time will result in a lag in the imaging. [3], [4]

This is study is done in collaboration with the Holst centre. The Holst centre has succeed in developing organic photodiodes with a very low dark current. The photodiode developed by the Holst centre is therefore able to detect low light intensities. This study focuses on characterizing the response time of these organic photodiodes.[5]

1.1 Aim of the study

The aim of this study is to understand and characterize the response time of organic photodiodes using time and frequency dependent measurements. Response time can be defined as the characteristic time with which the photodiode returns to its steady state after a perturbation of either the optical or electrical input.

1.2 Scope of the study

This study consists of three different types of experiments. The first experiment is a steady state measurement of the current as a function of the applied bias in the dark and under illumination. In this experiment the following aspects are studied: The dark current, the transport process and the effect of space charge.

The second experiment is impedance spectroscopy. The following electrical properties are studied by means of impedance spectroscopy; the conductance, capacitance and RC time. These properties are important for charge transport and charge collection in the photodiode.

The last experiment is time dependent photocurrent transient measurements. The photodiode current is measured while illuminated with light pulses.

This report will start with some background information on the working principle of organic photodiodes. In the following paragraphs the theory of the transport process and the built up of space charge in organic photodiodes are discussed. After this introduction, the experimental methods and experimental setups are discussed in chapters 3 and 4. The result of the described experiments will be presented and discussed in chapter 5. Using these results the final conclusions will be made, relating the response time to the light intensity and applied bias.
2 Theory

In this chapter an introduction is given in the working principle of organic photodiodes. This is followed by theoretical description of the transport process in organic photodiodes. In the third section the hopping transport model is introduced. This chapter is concluded with a description of space charge effects in organic photodiodes using the Goodman and Rose model [6].

2.1 Working principle of organic photodiodes

The organic photodiodes (OPD) under study here are based on the bulk hetero junction (BHJ) concept. The diodes consist of two electrodes with an active hetero junction layer in between. A bulk hetero junction is formed when the donor and acceptor materials are mixed throughout the active layer. Usually hole or electron transport layers (HTL, ETL) are added for reducing the dark current injection of charge carriers. In Figure 1 the stacking of the layers is shown.

![Diagram of organic photodiode structure](image)

*Figure 1: The schematic overview of the structure of an organic photodiode. The active layer shows the bulk hetero junction between donor and acceptor.*

When light falls on the OPD it passes through a transparent electrode and is absorbed in the active layer either by the donor or acceptor material. Whether a photon can be absorbed is determined by the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the material, the photon is absorbed when its energy is equal or large than the energy gap. On absorption of a photon by the donor or acceptor material an electron is excited from the HOMO to the LUMO. This results in a bound electron hole pair called an exciton. The lifetime of an exciton is short, in the order of nanoseconds. To prevent losing the electron and the hole they need to be separated. The binding energy of an exciton is approximately 0.5 eV which is 20 times as large as the thermal energy at room temperature. It is therefore nearly impossible for a bound electron hole pair to separate due to thermal energy. To assist charge separation the distance between the electron and the hole needs to be increased. The electron must therefore be transferred from the HOMO of the donor to HOMO of the acceptor; this is called the charge transfer state (CTS). The lifetime of excitons is short and the average diffusion length is only a few nanometers. Consequently only excitons generated near an interface between donor and acceptor material are able to
transfer an electron or hole. This charge transfer happens in < 1ps. The electron and hole pair can be separated and transferred to their respective electrode. To optimize the efficiency of the active layer, the interface between donor and acceptor is maximized. A bulk hetero junction is often used for this. Figure 2 shows the different steps for charge generation in organic photodiodes.

![Figure 2: Sketch of the working principle of an organic photodiode.](image)

For charge transfer a percolating pathway is necessary from the interface to the electrodes. Therefore there is a tradeoff between separation efficiency and transport efficiency. With increased mixing the interface is increased but the number of percolating pathways is decreased. Therefore the transport properties of the active layer are strongly dependent on the manufacturing process.

### 2.2 Charge transport and operating modes of organic photodiodes

After charge separation the hole is located in the HOMO of the donor material and the electron is located in the LUMO of the acceptor material. The electron and hole are transported through the BHJ to the electrodes, resulting in a current. The total current $J_{\text{total}}$ is equal to sum of the hole current $J_{\text{hole}}$ and electron current $J_{\text{el}}$. Charge carriers can be transported either by diffusion or drift type transport. Diffusion transport is driven by gradients in the carrier densities, $\frac{dn}{dx}, \frac{dp}{dx}$ with $n$ the electron density and $p$ the hole density. In drift transport, the charge carriers are driven by the electric field $F$. The field is related to net charge density $(p-n)$ via Poisson's law

$$\frac{dF}{dx} = \frac{\rho}{\varepsilon_0 \varepsilon_r}$$

$$\rho = q(p-n)$$

with $\rho$ the charge density, $q$ the elementary charge, $\varepsilon_0$ the permittivity of free space and $\varepsilon_r$ the relative dielectric. The hole and electron current is given by the following equations
\[ J_{\text{total}} = J_{\text{el}} + J_{\text{hole}} \]
\[ J_{\text{el}} = qn \mu_{\text{el}} F + qD_{\text{el}} \frac{dn}{dx} \]
\[ J_{\text{hole}} = qp \mu_{\text{hole}} F - qD_{\text{hole}} \frac{dp}{dx} \]

with \( \mu_{\text{el/\text{hole}}} \) the electron (hole) mobility and \( D_{\text{el/\text{hole}}} \) the Einstein diffusions constant for electrons (holes). The diffusion constant and mobility are related by the Einstein relation

\[ \frac{\mu}{D} = \frac{q}{k_bT} \]

with \( k_b \) the Boltzmann constant and \( T \) the temperature. Dependent on the applied bias either drift or diffusion transport is dominant.

Organic bulk hetero junction photovoltaics require two contacts with different workfunctions. A contact with a low workfunction for the collection of electrons from the HOMO of the donor material called the anode. For the collection of holes the workfunction of the cathode needs to be matched with the LUMO of the acceptor material. The difference in workfunctions results in potential difference for the contact called the built-in voltage \( V_{\text{bi}} \).

It is possible to distinguish two different operating modes: Forward bias if the potential difference between the cathode and anode is positive and reverse bias if the difference is negative. In Figure 3 the band diagrams in the dark for reverse bias, \( V=0 \), \( V=V_{\text{bi}} \) and forward bias are shown. The device is described as one semiconducting material with the HOMO of the donor material and the LUMO of the acceptor material.

Figure 3: Band diagrams of a diode in reverse and forward bias. The bulk hetero junction is depicted as one semiconducting material with the HOMO of the donor and the LUMO of the acceptor.

In reverse bias charge injection is difficult as the injection barrier is large, thus the current is low. In forward bias charge injection is possible and the charge carriers are transported through the device. Above the built-in voltage drift transport becomes dominant. When the OPD is illuminated charges are generated in the active layer. This means that a photocurrent is measured in reverse bias with drift transport the dominant transport type. The open circuit voltage \( V_{\text{oc}} \) defined as the voltage level at which no current goes through the device is not longer zero but positive and depended on the illumination intensity. Organic photodiodes are usually operated in reverse bias to enhance the extraction of photo-generated charge carriers.
2.3 Hopping transport model and charge trapping

In the previous sections it was suggested that the energy levels in the active layer are well defined. In disordered organic semiconductors electronic states are localized, and the energies of the local HOMO and LUMO levels are localized and statistically distributed. The HOMO and LUMO levels in the active layer have therefore a spread in their energy level. It is often assumed that the density of states (DOS) distribution for the energy levels is a Gaussian

\[ g(E) \propto \exp \left( -\frac{E^2}{2\sigma^2} \right) \]  

(4)

with \( E \) the energy and \( \sigma \) the width of the Gaussian. In Figure 4 the disorder in the energy levels is depicted. The disorder in the energy levels has a significant impact on the transport of carriers. Charges need to be transferred from one energy level to another, this transfer is called hopping. This transfer of charge carrier is described by the Miller Abrahams hopping equation

\[
V_{ij} = \begin{cases}
    v_0 \exp(-2\alpha r_{ij}) \exp \left( -\frac{E_j - E_i}{k_B T} \right), & E_j > E_i \\
    v_0 \exp(-2\alpha r_{ij}), & E_j > E_i
\end{cases}
\]  

(5)

The probability to hop from initial state \( i \) to a new state \( j \) a distance \( r_{ij} \) is dependent on the energy difference between the two states. If the new state is lower in energy the probability is determined by the attempt rate \( v_0 \) and the inverse localization radius \( \alpha \). When the new state is higher in energy a penalty needs to be paid dependent on the energy difference \( E_j - E_i \). Charge carriers will thus relax into the tail of the Gaussian. This can result in charge trapping. For charges located deep in the tail of the Gaussian all neighboring states will be higher in energy as the probability of finding a state lower in energy close by is very small. The charge needs to hop therefore to a higher a energy level but due to the energy difference the probability of a successful hop is small the charge. Consequently the charge carrier will be trapped for a long period of time. Part of the generated charges will get trapped and will remain in the device for a long period of time. In this study it is assumed that the thermal relaxation of charge carriers is negligible and the mobility is time independent.

![Figure 4: A schematic depiction of the hopping transport model.](image)

Figure 4: A schematic depiction of the hopping transport model.
2.4 Photo induced space charge in organic photodiodes

When illuminating the OPD, charge carriers are generated in the device as is discussed in paragraph 02.1. The efficiency of photo generated current is dependent on the balance between charge generation, recombination and transport. In this section a special situation of this balance is discussed: Due to the built up of charge in the system called space charge, the current can be limited by the charge in the device.

In forward bias, injection of charge carriers is possible. An ohmic contact is able to inject an infinite number of charges in the device resulting in an infinite current if the system was not limited in some way. The limiting factor is the repulsion between carriers of the same polarity. This limits the amount of charge that is located in the device (space charge) at the same time. The space charge limited current is described by the Mott-Gurney square law:

\[ J_{SCL} = \frac{9}{8} \mu \varepsilon_0 \varepsilon_r \frac{V^2}{L^3} \]  

where \( \mu \) is the mobility of the charge carriers, \( \varepsilon_0, \varepsilon_r \) are respectively the dielectric constant of vacuum and relative dielectric constant, \( V \) is the potential difference between the electrodes and \( L \) is the distance between the electrodes.

Goodman and Rose presented a model which describes the extraction of photo generated charge from a semiconductor with non-injecting contacts \([6]\), in this case the space charge is solely the result of charge generation as there is no dark current injection.

The current saturates when all charge carriers are extracted from the device, without charge recombination. This is the case when the mean drift length \( w_{e(h)} \) of the holes and electrons is longer than the thickness \( L \) of the device.

\[ w_{e(h)} = \mu_{e(h)} \tau_{e(h)} E > L \]  

where \( \tau_{e(h)} \) is the electron (hole) lifetime and is \( E \) is the electric field. Resulting in a saturation photocurrent of

\[ J_{ph}^{sat} = gqL \]  

with \( g \) the charge generation rate. If the mean drift length \( w_{e(h)} \) of either the electrons or holes or both are smaller than \( L \) then charge will accumulate in the device resulting in a space charge built up in the device. Assume a uniform charge generation in the device and an unbalanced transport \( \mu_e \neq \mu_h \). Let’s consider the case \( \mu_e \gg \mu_h, w_e \gg w_h \) assuming an equal lifetime of the carriers. This will result in accumulation of holes in the device. Resulting in an increase of the electric field near the negative electrode; increasing the extraction of holes and decreasing the extraction of the electrons near the positive electrode. In the region near the negative electrode with thickness \( L_1 \) the field changes until a steady state is reached with the external electron current equal to the external hole current. Figure 5 shows a schematic overview of the built up of space charge in the device.
The thickness \( L_1 \) is given by \( w_1 \) as the carrier with smallest mean drift length must be able to escape the region. The average electric field in the space charge zone can be related to the potential difference over the space charge zone \( V_1 \) and the thickness \( L \) by \( E_1 = V_1 / L \). This then implies for the thickness \( L_1 \):

\[
L_1 = \left( \mu_n \tau_n V \right)^{1/2}
\]  

(9)

with \( V_1 \approx V \) as the voltage drops in the region. The current generated in this region is equal to

\[
J = q g L_1 = q g \left( \mu_n \tau_n V \right)^{1/2}
\]  

(10)

Space charge limited current should satisfy equation (6), combining this with equation (10) gives

\[
L_1 = \left( \frac{9 \mu_n \varepsilon_0 \varepsilon_r}{8 q g} \right)^{1/4} V^{1/2}
\]  

(11)

and

\[
J_{ph} = q \left( \frac{9 \varepsilon_0 \varepsilon_r \mu_n}{8 q} \right)^{1/4} \varepsilon_r^3 V^{1/2}
\]  

(12)

The capacitance of the device in the space charge limit can be calculated assuming that the capacitance is equal to the geometrical capacitance of two parallel plates separated by an insulator. The geometrical capacitance is expressed by

\[
C_{geo} = \varepsilon_0 \varepsilon_r \frac{A}{L}
\]  

(13)

with \( A \) the area of the plates and \( L \) the separation distance between the plates. The effective distance between the plates in space charge limit is given by equation (11). This results in the following equation for the capacitance.
The conductance \( G = \frac{I}{V} \) is given by
\[
G = qA \left( \frac{9 \varepsilon_{0} \varepsilon_{r} \mu_{h}}{8q} \right)^{1/4} g^{3/4} V^{-1/2}
\] (15)

The lifetime of the slowest charge carrier can be calculated using equations (11) and (9).
\[
\tau = \left( \frac{8 \varepsilon_{0} \varepsilon_{r}}{9 \mu_{h} g} \right)^{1/2}
\] (16)

The response time of an electrical circuit is given by the RC time \( \tau_{RC} \), with \( R \) the resistance of the circuit and \( C \) the capacitance. For a diode under open circuit conditions \( R \) is equal to internal resistances of the diode. The resistance of the external circuit does not play a role. Using equations (14) and (15) the response time (RC time) of a photodiode in the space charge limit is found to be equal to the lifetime of the slowest charge carrier.
\[
\tau_{RC} = \frac{C}{G} = \tau
\] (17)
3 Methods

In this chapter the experimental methods for studying the response time of OPDs are described. Electrical response measurements can be divided in two categories: Large and small signal response measurements. In large signal response measurements a large perturbation is used to study the electrical response of the device. The device is excited from one steady state to another steady state. In small signal response measurements a small perturbation is used to probe one steady state. In small signal response measurement it is assumed that the electrical response is (pseudo) linear.

3.1 Impedance spectroscopy

Impedance spectroscopy is a characterization tool commonly used for the characterization of a wide range of electrical devices. In the last decade impedance spectroscopy has become one of the most used techniques for studying charge transport properties of photovoltaic devices. [7], [8]

The impedance $Z$ of an electrical circuit is the measure of opposition the circuit asserts to an applied voltage. The inverse of the impedance is the admittance $Y$.

$$Z = 1/Y$$

Impedance spectroscopy is an example of a small signal response measurement technique. A DC bias $V_{DC}$ is applied over the device and on top of that a small AC bias is applied $V_{AC}(t)$ with an amplitude $V_{AC}$ and an AC frequency of $f$, resulting in an applied bias of

$$V(t) = V_{DC} + V_{AC} \sin(2\pi ft).$$

The AC bias amplitude is kept small to keep the device in equilibrium and the response (pseudo) linear. In impedance measurements the impedance $Z$ is measured and is defined as the ratio between the AC bias $V_{AC}(t)$ and the resulting current

$$I(t) = \Delta I \exp^{(2\pi(f+\theta)t)}$$

with $\Delta I$ the current amplitude and $\theta$ the phase difference.

The response to an AC bias differs between the different electrical components. The most commonly known electrical component is the ideal resistor. The ideal resistor with a resistance $R$ satisfies Ohm’s law equation (21) at all currents and voltage levels.

$$R = \frac{V}{I}$$

From Ohm’s law it is clear that the electrical response of an ideal resistor is linear and will be completely in phase with an electrical perturbation. The impedance of an ideal resistor is thus real and equal to $R.$

$$Z_{resistor} = R$$

The ability to store electrical charge in an electrical circuit is called the capacitance of an electrical circuit. The amount of charge $q$ that can be collected per voltage level is given by the capacitance $C$.

$$C = \frac{q}{V}$$
The resulting current is thus:

\[ I(t) = C \frac{dV}{dt} \]  

(24)

The current is 90 degrees out of phase with an electrical perturbation and increases with increasing perturbation frequency. The impedance of a capacitor is thus imaginary and dependent on the angle frequency \( \omega = 2\pi f \),

\[ Z_{\text{Capacitor}} = \frac{1}{i\omega C} \]  

(25)

These two components can be used to describe the charge transport and collection in OPD. In literature this is extensively reported. There are many different reported device models that use a equivalent circuit approach [7], [8].

The experimental setup for the impedance spectroscopy is described in paragraph 4.3 and the result will be presented in paragraph 5.2.

### 3.2 Photocurrent transient measurements

Photocurrent transients can be divided in large signal response measurements and small signal response measurements. Both measurements methods will be performed in this study. The experimental setup will be described in paragraph 4.4.

In large signal photocurrent transient measurements the device is illuminated for a short period of time. The resulting current response is called a photocurrent transient. By studying the rise and fall of the photocurrent transient the formation and decay of the charge carriers in the OPD can be studied.

This measurement method is well documented in literature. The method, also known as time of flight measurements is used to determine the mobility of the charge carriers in different materials [9]. This method is often hampered by the fact that charge transport is often dispersive and dependent on the light intensity.[10][11]

In small signal photocurrent transient measurements the device is brought in steady state using a constant background illumination and the device is perturbed using a second light source with a lower light intensity. By measuring the time the device needs to return to its steady state, the response of the device as a function of the background illumination can be studied.

McNeill et al. did similar experiments on polymer solar cells[12]. They proposed that the decay time of a small signal photocurrent transient is dependent on the trap state density in the active layer. By varying the background illumination intensity the occupation of traps states is varied. According to McNeill et al. this means that above a certain background intensities all charge generated by the perturbation are ‘free’ (unaffected by traps). They showed that decay time of ‘free’ charge carriers is not strongly dependent on the light intensity.

In this study a method to determine the response time quantitatively using a triangular light perturbation, based on the work of Van der Hofstad et al.[13] is used. How to determine a response time from such a perturbation will be explained briefly as it is explained in the work of Van der Hofstad et al.

The photocurrent response of the OPD \( J_{\text{OPD}}(t) \) can be expressed as the convolution of the system response function \( G(t) \) and the time dependent optical light perturbation \( g(t) \).

\[ J_{\text{OPD}}(t) = \int G(t-\tau)g(\tau)d\tau + \ldots \]  

(26)
The response function $G(t)$ is assumed to be exponential $G(t) = \exp\left(-\frac{t}{\tau_{\text{rel}}}\right)$ with $\tau_{\text{rel}}$ the relaxation time of the system. $G(t)$ can be decomposed in a time-even $G_{\text{even}}(t)$ and time-odd $G_{\text{odd}}(t)$ contribution

$$G_{\text{even}}(t) = \frac{G(t) + G(-t)}{2}$$
$$G_{\text{odd}}(t) = \frac{G(t) - G(-t)}{2}$$

(27)

The time-even response describes the irreversible part of the photo response and the time-odd part the reversible part.

If the temporal width of the perturbation is much larger than the relaxation time $\tau_{\text{rel}}$ of the response function, $G(t)$ can be approximated by a rectangular function $\delta$ with width $\tau_{\text{rel}}$. In the limit of an infinitely fast relaxation time, $G(t)$ converges to a delta function. The time-even and time-odd parts of $G(t)$ can also be approximated using delta function

$$G_{\text{even}}(t) \rightarrow L \frac{\delta(t + \tau_{\text{rel}}) + \delta(t - \tau_{\text{rel}})}{2} = L_{\text{even}} \delta(t)$$
$$G_{\text{odd}}(t) \rightarrow L \tau_{\text{rel}} \frac{\delta(t + \tau_{\text{rel}}) - \delta(t - \tau_{\text{rel}})}{2\tau_{\text{rel}}} = L_{\text{odd}} \delta'(t)$$

(28)

with $L$ an phenomenological constant. From equation (28) it is seen that $G_{\text{odd}}(t)$ takes the form of a derivative of the delta function. The response function needs to satisfy causality; there is no response prior to the perturbation. This means that $G(t < 0) = 0$ therefore $G_{\text{even}}(t > 0) = G_{\text{odd}}(t > 0)$ and $|G_{\text{even}}(t)| = |G_{\text{odd}}(t)|$ for all $t$. To satisfy causality $L_{\text{even}}$ and $L_{\text{odd}}$ are related by

$$L_{\text{even}} = \tau_{\text{rel}} L_{\text{odd}}$$

(29)

It is thus found that the time-even $J_{\text{even}}$ and time-odd $J_{\text{odd}}$ part of the current density is given by

$$J_{\text{even}}(t) = L_{\text{even}} g(t)$$
$$J_{\text{odd}}(t) = L_{\text{odd}} \frac{dg(t)}{dt}$$

(30)

The relaxation time $\tau$ can be thus calculated by:

$$\tau_{\text{rel}} = \frac{L_{\text{odd}}}{L_{\text{even}}} = \frac{J_{\text{odd}}}{\frac{dJ_{\text{even}}}{dt}} = \frac{J_{\text{odd}}}{\frac{dg}{dt} \frac{dJ_{\text{even}}}{dt}}$$

(31)

A similar derivation can be done for the impedance spectroscopy. Starting from equation (26) and replacing the light perturbation $g(t)$ with a voltage perturbation $V(t)$. Following the same derivation and making use of equation (21) for $J_{\text{even}}$ and equation (24) for $J_{\text{odd}}$ gives a relaxation time of:
$$\tau_{rel} = \frac{-J_{\text{odd}}}{dV \frac{dJ_{\text{even}}}{dt} dV} = RC$$ (32)
# 4 Experimental setup

The goal of this study is to characterize the response time of the device. In the first paragraph of this chapter the used OPD is described. In the following paragraphs the experimental setups are described for the steady state, photocurrent transient and impedance spectroscopy measurements.

## 4.1 The organic photodiode

The OPDs used in this study were manufactured by the Holst centre. The OPDs consist out of anode (100 nm) of Molybdenum oxide MoO_x with a BHJ active layer (280 nm) of PCBM and P2 and a transparent cathode consisting out of LiF (3 nm), Al and Ag. The fabrication processes as well as the donor material are confidential. In Figure 6 the stacking of the layer is shown.

<table>
<thead>
<tr>
<th>Encapsulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode: LiF/Ag/Al</td>
</tr>
<tr>
<td>Active layer: PCBM:P2</td>
</tr>
<tr>
<td>Anode: MoOx</td>
</tr>
<tr>
<td>Substrate: Glass</td>
</tr>
</tbody>
</table>

![Figure 6: Overview of the layer stacking in the device](image)

To have a better understanding of the device it is important to know the energy levels of the work functions of the respective materials. The work functions are taken from literature[14]. The work functions of the different layers are depicted in Figure 7.
4.2 J-V measurement

To characterize the OPD (semi) steady state J-V measurements were done under different illumination intensities. The OPD is illuminated using a low power HeNe cw-laser (spot size $\phi$ 1 mm $\lambda = 543$ nm $P = 125$ mW). By using neutral optical density filters (O.D. 0.16-4.08); the intensity of the light can be varied. In Figure 8 the calibration of the O.D. filters is shown. The O.D. filters were calibrated using an inorganic (Si) photodiode with a calibrated EQE. It should be noted that in the experiments no corrections were made for the spot size.

The J-V measurements were done using an Agilent 4155C Semiconductor Parameter Analyzer. The current as a function of the voltage was measured in the range -2.5 V to 2 V with a voltage step of 10mV. The current was determined using an integration time of 10ms. The results of this experiment are discussed in paragraph 5.1.
Figure 8: The light intensity as function of the used optical density filter.

4.3 Impedance spectroscopy

Impedance spectroscopy is done using a Solartron SI 1260 Impedance/Gain-Phase Analyzer. This impedance spectroscope is able to apply an AC frequency up to 1MHz. The DC amplitude is varied in the experiment but the AC bias amplitude is kept constant at $V_{ac} = 10mV$. Impedance spectroscopy is done in the dark and under illumination of the laser. The experimental setup is shown in Figure 9.

![Figure 9: Experimental setup for the impedance spectroscopy](image)

4.4 Photocurrent transient

In photocurrent transient measurements, the device is perturbed using a modulated light source and the resulting photocurrent is measured. The results of these experiments are presented and discussed in paragraph 5.3.
4.4.1 Large signal response

In Figure 10 a schematic overview of the experimental setup for measuring the large signal response is depicted. In this experiment the OPD (size 1 mm²) is illuminated by a modulated light source. The light source used is the low power HeNe cw-laser used in the previous experiments. Using O.D. filters the intensity of the light can be varied. A chopper is used to modulate the light beam into a square wave with frequency 173Hz.

![Schematic overview of the experimental setup for measuring the photocurrent transient due to a square wave modulated light source.](image)

The response signal of the OPD is amplified using a current amplifier (Stanford Research systems SR570) with a gain of 1μA/V and a bandwidth of 1-3×10⁴ Hz. This gain is stable up to signals with a frequency of 10⁵ Hz, which is sufficient for this experiment. The resulting signal is measured and recorded using a Tektronix TDS5052B Digital Phosphor Oscilloscope. The output resistance of the current amp and input resistance of the oscilloscope were matched at 50 ohm.

4.4.2 Small signal response

In the small signal response experiment the OPD is continuously illuminated by the laser resulting in a steady state current. A second light source is used to probe the steady state with a modulated light signal. This second light source is an ultrafast LED (Kingbright L-7104VGC-H green) modulated using a function generator (Agilent 33250A 80MHz function/Arbitrary waveform generator). The light intensity of the LED is kept low compared to the illumination intensity of the laser. The LED is modulated into a square wave signal with a maximum intensity of 0.003mW/cm² and a frequency of 173Hz. The photocurrent was measured using the same setup as in the previous experiment. The experimental setup is depicted in Figure 11.
Van der Hofstad et al [13] showed that the relaxation time of charge carriers in solar cells could be probed with a linearly varying voltage pulse. In this experiment the relaxation time is determined by probing the steady state illumination with a linearly varying light pulse. The same experimental setup is used as in the previous experiment, see Figure 11. In contrast to the previous experiment which used a square wave light pulse, a triangular pulse is used. The triangular light pulse has a width of 2.9 ms and a maximum intensity of 0.01mW/cm². A Si photodiode is placed behind the OPD to measure a reference signal profile of the triangular light pulse.

Figure 11: Schematic overview of the small signal response measurement setup. A laser is used to continuously illuminate the OPD. A LED is modulated using a function generator and is used from probing the OPD.
5 Results and discussion

In this chapter the results of the experiment described in the experimental setup are presented. This chapter starts with the steady state measurements, to understand and determine important parameters of the measured device. The results of this experiment will be discussed by applying simple device models. After discussing the steady state measurements the first time dependent measurement will be discussed; Impedance spectroscopy. Using the knowledge gained from the previous experiments the results of the photocurrent transients are discussed.

5.1 Steady state measurements

5.1.1 J-V measurement in the dark

![Graph showing J-V measurement in the dark](image)

Figure 12: J-V measurement in the dark plotted on lin-log scale, the arrows indicate the sweep directions. The inset shows the J-V measurement on a linear scale.

The J-V measurement presented in Figure 12 can be separated into regimes; forward and reverse bias. In reverse bias the current is small. In forward bias the current shows a strong increase with increasing applied bias.

The measured current density consists out of two components; the injection current and the displacement current. The displacement current $J_{\text{dis}}$ is expected to be independent of the bias but is either positive or negative dependent on the sweep direction. The displacement current is given by the following equation

$$J_{\text{dis}} = C \frac{dV}{dt}$$  \hspace{1cm} (33)
with \( C \) the capacitance of the device and \( \frac{dV}{dt} \) the sweep rate. The displacement current is thus positive with increasing voltage and negative with decreasing voltage. The J-V measurement is performed using a voltage step of 10mV and a measurement time of 10ms per step.

Due to the small leakage current \( (8 \times 10^{-7} \text{ mA/cm}^2 \text{ at } -2 \text{ V}) \) the effect of the displacement current is clearly visible in reverse bias in Figure 12, with the sweep direction depicted by the arrows. In reverse bias \( (V < 0) \), for the forward sweep direction \( (dV/dt > 0) \) the absolute current density is lower compared to the backwards sweep. For the forward sweep direction the injection and displacement current have opposite sign in reverse bias. For the reverse sweep direction the two current contributions have the same sign for \( V < 0 \). In high forward bias the displacement current is negligible compared to the injection and the measured current density is practically independent of the sweep direction.

**Reverse bias leakage current**

First the leakage current in reverse bias will be discussed. As this measurement is done in the dark the charge carriers can only be injected from the electrodes. Two textbook models for charge injection from non-ohmic contacts are: Fowler-Nordheim tunneling[15] and thermionic emission[16]. Fowler Nordheim tunneling describes the tunneling of charges trough a barrier. The thermionic emission model is based on the assumption that a charge carrier can be injected due to its thermal energy. For Fowler-Nordheim tunneling the width of the barrier determines the charge carrier injection. The applied biases in this experiment are low therefore the barrier has a large width. It is thus assumed that thermionic emission is the dominant process for charge injection in reverse bias.

The thermionic emission \( J_{th} \) is dependent on the energy barrier \( \varphi \) and the temperature \( T \) as follows

\[
J_{th} = AT^2 \exp[-\frac{q\varphi}{k_b T}], A = \frac{4\pi^2 q m^* k_b^2}{h^3}
\]  \( (34) \)

with \( A \) the Richardson constant, \( q \) is the elementary charge, \( m^* \) is the effective mass of the injected charge carrier, \( k_b \) is the Boltzmann constant and \( h \) is the Planck constant.

The measurement is done at room temperature 295 K, using equation \( (34) \) the energy barrier can be estimated from the measured dark current. The estimated energy barrier is 1.0 eV, using \( m^* = 9.1 \times 10^{-31} \text{ kg} \) as the electron rest mass.

In reverse bias the holes may be injected from the Al/Ag electrode to the HOMO of P2, the electrons may be injected from the MoOx to the LUMO of PCBM. The values of the energy barriers for respectively the holes and electrons are 1.3 eV and 1.7 eV (see Figure 7). The estimated injection barrier of 1eV is significantly lower. Calculating the dark current using the expected energy barriers; results in respectively a hole and electron current in the order of \( 10^{-11} \text{ mA/cm}^2 \) and \( 10^{-19} \text{ mA/cm}^2 \). The calculated currents are orders of magnitude lower than the measured currents.

In Figure 13a the dark current at different temperatures is measured. The figure shows a decrease in the dark current upon lowering of the temperature. As is expected, at lower temperature the chance of injecting a carrier in the device is decreased as the thermal energy of the carriers is decreased. Using equation \( (34) \) an estimation of the barrier height can made if the current is measured as a function of the temperature, see Figure 13b. The barrier height is estimated to be \( 0.70\pm0.03 \text{ eV} \), which is low compared to the expected height from the work functions (Figure 7).
The used device model of thermionic emission is an over simplification of reality. The model does not take into account image charge effects nor disorder. The charges at the electrodes have an image charge in the bulk. These image charges will lower the energy barrier [16]. Disorder causes a spread in the HOMO and LUMO energy levels. It is likely that charge carriers are injected in the low energy levels; the tail of the DOS. These tail states lower the injection barrier[17]. This means that if the dark current of the OPD needs to be lowered, a material with a higher injection barrier should be used and the disorder (the width of the Gaussian, equation(4)) needs to be reduced. To describe the injection of charge carriers accurately more complex models are needed [17], [18].

**Diffusion limited regime**

In the forward bias regime close to $V_{oc}$ it is expected that diffusion transport is dominant as the electric field close to $V_{oc}$ is small. The diffusion limited current can be analyzed using the classical Shockley diode description:

$$J = J_0 \exp \left( \frac{qV}{\eta k_b T} \right) - 1$$  \hspace{1cm} (35)

Where $J_0$ is the saturation current and $\eta$ is the empirical ideality factor. The ideality factor can be determined by taken the derivative of the natural logarithm of the current.

$$\eta = \left( \frac{k_b T}{q} \frac{\partial \ln J}{\partial V} \right)^{-1}$$  \hspace{1cm} (36)

Wetzelaer et al.[19] proposed that a deviation of the ideality factor from unity can be ascribed to the violation of the Einstein relation (equation (3)). This violation is caused by the deeply trapped carriers that are not in thermal equilibrium with the free carriers. The number of deep trap sites can vary between the components in the solar cell therefore the components can have different ideality factors.
Figure 14: The empirical ideality factor plotted as function of the applied bias.

In Figure 14 the empirical ideality factor is plotted as a function of the applied bias. The ideality factor is determined to be 1.3 which corresponds to values reported in literature for devices with PCBM as dominant pathway for charge transport. This is consistent with electrons in the PCBM rich phase having a higher mobility than holes in the polymer phase. [19]

**Space charge limited current regime**

In Figure 12 a J-V measurement up to 4V is shown, in Figure 15 the logarithmic derivative of the current \( \frac{\partial \log J}{\partial \log V} \) is shown as function of the voltage. For large forward bias the current becomes space charge limited. This would be indicated by the fact that the current is proportional to the square of the applied voltage. If the current becomes space charge limited the logarithmic derivative of the current will converge to the value two.
Figure 15 shows that the current becomes space charge limited for a larger forward bias. As the current becomes space charge limited the Mott-Gurney square law can be used to estimate the mobility of the charge carriers. The mobility is estimated from the current at 4V (120±10mA/cm$^2$) to be $1.4 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ (using $\varepsilon_r = 4$). This value of the mobility is in agreement with the electron mobility of pure PCBM >$1 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, the mobility of electrons in PCBM:P3HT is >$1 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$[20]. It should be noted that the measured mobility can be dependent on the manufacturing processes[21], [22].

To study the effect of temperature on charge transport the J-V measurements are done at different temperatures. In Figure 16a the current at 2V is plotted versus the thermal energy. It is assumed that the current is space charge limited at 2V. The space charge limited current is given by equation (6) the only factor that is dependent on the thermal energy is the mobility $\mu(T)$. 
If it is assumed that charge transport is described by the small polaron hopping model, the activation energy would correspond to an energy barrier for hopping. For a charge transfer hop from one molecule to another, polaron energy needs to be paid. This energy results from the reorientation of the molecule that is necessary for the two molecule states (excited and neutral state) to be in equilibrium[23]. From the measurement an activation energy $E_A = 0.13 \pm 0.01 \text{ eV}$ is determined. The reorganization energy can be determined from the activation energy $E_A = \lambda / 4$. From the measurement $\lambda = 0.52 \pm 0.04$ is determined which corresponds to typical values for the reorganization energy in literature[24].

An important parameter in the hopping model is the energy disorder of the energy bands (HOMO and LUMO). In this model the mobility is dependent on the width of the Gaussian as follows

$$
\mu \propto \exp\left[-\left(\frac{C \sigma}{k_b T}\right)^2\right]
$$

where $\sigma$ is the disorder (width of the Gaussian) and $C=0.7$. Assuming that the current is space charge limited the disorder can be determined by plotting the current versus $1/(k_b T)^2$ as is seen in Figure 16b. The disorder is estimated to be $\sigma = 0.038 \text{ eV}$. From the previous measurements it was concluded that electron transport through PCBM was the dominant pathway. Therefore it was expected that the determined disorder was comparable to the disorder expected for PCBM systems. In literature typical values for PCBM are in the order of $0.1 \text{ eV}$[25].
5.1.2 J-V measurements under illumination

![J-V measurement under different illumination intensities.](image)

In Figure 17 multiple J-V measurements are presented for different illumination intensities. Figure 17 shows that the photocurrent in reverse increases with light intensity as well as the $V_{oc}$. The photocurrent is given by equation (8). The generation rate is estimated as follows

$$ g = \frac{J \, EQE}{LE_p} $$

with $E_p$ the photon energy and $EQE$ the external quantum efficiency. The EQE is a measure of the efficiency; it is the fraction of the incident photons which are converted to current. In Figure 18b the increase in intensity at -2 V is plotted in a log-log plot. From the linear fit with a slope of 0.95±0.02 it is conclude that the current density is linear dependent on the intensity. From the slope of the linear fit in Figure 18a the EQE of the OPD can be determined. The slope is 0.087±0.01 A/W multiplying this by the factor $\frac{E_p}{q}$ with $E_p$ the photon energy, results in an $EQE$ of 0.203±0.003.
Koster et al. [26] proposed a model for the light intensity dependence of $V_{oc}$. They based the model on the metal insulator metal picture, assuming a constant quasi Fermi level. It was found that the light dependence of the $V_{oc}$ is expressed by the following equation

$$V_{oc} = \frac{\eta k_B T}{q} \ln\left(\frac{I}{I_0}\right)$$

with $I$ the illumination intensity and $\eta$ the ideality factor.

In Figure 19 the $V_{oc}$ is plotted as a function of the logarithm of the intensity. The linear fit of $V_{oc}$ versus $10 \log(I)$ reveals a slope of $0.060 \pm 0.001$. Using equation (39) $\eta k_B T / q$ is found to be equal to $0.026 \pm 0.001$ eV. Together with $k_B T / q = 0.025 eV$ at room temperature this implies that under illumination the ideality factor is equal to unity; indicating a dominance of bimolecular recombination according to Wetzaelaer et al.[19].

*Figure 18a,b: (a) The current density at -2V as function of the intensity, the slope of the linear fit is $0.087 \pm 0.01$ A/W. (b) Log log plot of the current density at -2V as a function of the illumination intensity, the slope of the linear fit is $0.95 \pm 0.02$.}*
Figure 19: Open circuit voltage as function of the logarithm of the intensity. The slope of the linear fitting is equal to 0.060±0.001.

**Space charge limited current close to open circuit voltage**

Close to open circuit voltage there is minimal electrostatic energy, so it is expected that the current close to $V_{oc}$ is space charge limited. Di Nuzzo et al.[27] showed that the conductance $G$ is proportional to $g^{3/4}$ in a space charge limited system as is expected from the Goodman and Rose model.

By taking the derivative of the current density at $V_{oc}$ from the $J$-$V$ measurements it is possible to determine if the device is space charge limited at $V_{oc}$. In Figure 20 the logarithm of the conductance is plotted versus the logarithm of the illumination intensity. The data points are fitted with a linear fit with a slope of 0.74±0.02 which confirms that the current close to $V_{oc}$ is space charge limited.
Impedance spectroscopy is a commonly used technique for studying transport properties of electrical devices. Impedance spectroscopy probes a steady state using a voltage perturbation. To determine the response time of the device the reversible and irreversible part of the response need to be determined. This is done by measuring the magnitude and the phase angle of the resulting current; an in-phase and out-of-phase current can be determined. The in-phase component corresponds to the irreversible part of the response and the out-of-phase component to the reversible part, as is described in paragraph 3.1.

5.2 Impedance spectroscopy

In Figure 21a the impedance magnitude is plotted as a function of the AC bias frequency (Bode plot) in the dark for different DC bias voltages. The figure shows that the impedance is linearly dependent on the frequency in reverse bias ($V_{\text{applied}} < 0$). Above $V_{\text{oc}}$ the impedance magnitude shows a flat region. At a certain frequency (cut off frequency) the impedance becomes linearly dependent again. With increasing forward bias the impedance of the flat region decreases and the cut off frequency increases.

In Figure 21b the phase angle of the current is measured as function of the frequency. In reverse bias the phase angle is equal to 90 degrees. In forward bias the phase angle converges to zero with decreasing frequency. With increasing forward bias the peak of the phase angle shifts to the higher frequencies.
Figure 21: (a) The impedance magnitude in the dark as function of the AC frequency, with an AC bias of 20mV and varying DC bias. (b) The corresponding phase angle as function of the AC frequency.

In reverse bias injected charge carriers are unable to reach the other electrode as the electric field points in the opposite direction. Only charge built up on the electrodes is possible; the device will therefore function as a capacitor. The amount of charge that will leave the device after half the period of the frequency is thus linear dependent on the frequency. Pure capacitive behavior corresponds to an out of phase current (90 degrees). Figure 21b confirms that the device behaves as capacitor in reverse bias as the phase angle is 90 degrees.

Above $V_{oc}$ charge carrier are injected and are able to pass through the device in half the period of the frequency; an in-phase current is measured. As the frequency increases the fraction of charge carriers that are able to escape the device in half the frequency period decreases, therefore the out of phase component of the current increases relative to the in phase component; increasing the phase angle.

Above 100000Hz the RC time of external components such as the electrical wiring will affect the measurement, preventing charges from reaching the device. This will result in an unreliable measurement, evident by the inflexion point above 100000Hz in Figure 21a,b. Therefore the data above 100000Hz will not be discussed.

The device can be modeled by assuming an equivalent circuit consisting out of a parallel capacitor and resistor, see Figure 22. In the equivalent circuit contact resistance is neglected.

![Equivalent circuit](image)

Figure 22: Equivalent circuit for the device at low frequencies ($f<100000Hz$).

For such a circuit the parallel conductance $G_p$ and parallel capacitance $C_p$ can be determined using the following equations
\[
\frac{1}{Z} = G_p + i\omega C_p
\]

The parallel conductance is the irreversible part of the response and the parallel capacitance the reversible part.

In Figure 23a,b the conductance and capacitance of the device are plotted as function of the frequency.

![Figure 23](image)

Figure 23: The parallel conductance (a) and parallel capacitance (b) using the equivalent circuit for different DC biases in the dark as a function of the AC frequency.

Figure 23b shows the capacitance as function of the frequency. In reverse bias the capacitance is constant. It is assumed that the capacitance of the device is equal to the geometrical capacitance of two parallel plates. Using equation (13) with \( A = 1 \text{ mm}^2 \) and \( L = 280 \text{ nm} \), the relative dielectric constant can be estimated. The measured capacitance is 163±2 pF. Using equation (13) the relative dielectric constant is estimated to be 5.0±0.1. It should be noted that the used dielectric constant is higher than expected for organic semiconductor materials, which are typically 3-4.

From the parallel conductance and parallel capacitance a RC time can be determined. Above the RC time the device shows capacitive behavior. The RC time is related to the transport of the charge carriers. If charge carriers are not able to reach the opposite electrode because the frequency is too high, the device will behave as a capacitor.

In reverse bias the RC time is large because there is no conductance through the device. Above 0 V the device becomes conductive; the charge carriers are able to reach the opposite electrode resulting in a current. The RC time is frequency dependent as the capacitance is frequency dependent. In the following sections the device behavior will be studied in more depth.
Figure 24: RC time determined as function of the applied DC bias at 1000 Hz AC frequency.

5.2.2 Impedance measurement under illumination

To study the effect of the light intensity on the response time of the device, a laser is used to illuminate the device as is described in paragraph 4.3. There are three interesting regimes to study: reverse bias, forward bias and close to $V_{oc}$.

**Reverse bias**

In Figure 25a,b respectively the measured impedance and phase angle at -2 V are plotted. In the dark the impedance is linear dependent on the frequency in reverse bias. When the OPD is illuminated this behavior changes. The flat region that was observed in forward bias in the dark is now also seen in reverse bias. The flat region shows a decrease in impedance magnitude and an increase in cut off frequency with increasing light intensity. The peak of the phase angle shows a shift to the higher frequencies with increasing light intensity, see Figure 25b.
In the dark almost no charge carriers are present in the device because all charge carriers need to be injected from the electrodes. This is not the case anymore when the device is illuminated. When the device is illuminated charge carriers are generated in the active layer. For frequencies above the transit time charge carriers are unable to escape the device and the conductance is thus frequency depended. For lower frequency the generated charge carriers can escape the device, the conductance is determined by the number of charge carriers that are able to escape the device. It is thus expected that the conductance scales with the charge carrier generation $g$.

Using equation (13) the conductance and capacitance can be determined as a function of the illumination intensity, see Figure 26a,b. From the linear fit in Figure 26a it is possible to conclude that the conductance increases linear with the intensity. The capacitance is independent of the light intensity and equal to geometrical capacitance.

Figure 26: The parallel conductance (a) and parallel capacitance (b) as a function of the light intensity determined at $f=1000$ Hz with a DC bias of -2 V. The line indicates the fitting of a power law $g^\alpha$ with $\alpha=1.06\pm0.04$. 

Figure 25: (a) The impedance magnitude and (b) phase angle for different illumination intensities with DC bias of -2 V.
In reverse bias the conductance is linear dependent on the generation rate. The conductance can be estimated using equation (8) and Ohms law (21).

\[ G = \frac{AqgL}{V} \]  

(41)

A light intensity of 51 mW/cm\(^2\) corresponds to a charge carrier generation rate of 5.07\(\times\)10\(^{26}\) m\(^{-3}\)s\(^{-1}\) assuming a EQE of 0.2. The potential \(V\) is assumed to be equal to sum of the \(V_{\text{applied}}\) and \(V_{\text{oc}}\). The estimated conductance is equal to 1.3\(\times\)10\(^{-5}\) S which is an overestimation as the measured conductance is 4.8\(\times\)10\(^{-6}\) S.

As the conductance is linear dependent on the illumination intensity and the capacitance is constant the RC time will be dependent on the inverse of the light intensity, shown in Figure 27. The black line is the fitting of the power law \(\tau_{\text{RC}} \propto G^\alpha\) with \(\alpha=-1.03\pm0.03\).

![Figure 27: \(R_pC_p\) time as function of the illumination intensity measured at -2 V and 1000 Hz. The linear fit has a slope of -1.03±0.03 (black line).](image)

**Forward bias**

Figure 28 shows the conductance as function of the illumination intensity in forward bias (1 V). From the figure it is clear that the conductance is not linear dependent on the illumination intensity, as was the case in the reverse bias (see Figure 26a). In forward bias the conductance is strongly dependent on the charge injection from the electrodes, resulting in a more complex system.
In Figure 29a,b the capacitance is respectively plotted as function of the frequency and the illumination intensity. In Figure 29a it is shown that the capacitance in forward bias is not the geometrical capacitance of two plates separate by the bulk but is dependent on the frequency. The frequency dependency of the capacitance is caused by the injection of charge carriers. In forward bias charge injection from the electrodes is possible effectively decreasing the distance between the plates. The capacitance is therefore determined by how far the injected charge can diffuse in the system, as the applied bias is below the built-in bias. The diffusion length $l_{\text{diff}}$ is given by the following equation

$$l_{\text{diff}} = \sqrt{Dt}$$

with $D$ the Einstein diffusion constant. From equation (13) it is thus expected that the capacitance decreases with increasing frequency as $C \propto f^{-1/2}$. In Figure 29a this relation is indicated by the dashed line. There is no apparent relationship between charge injection and the illumination intensity as is seen in Figure 29b.
Figure 29: (a) The parallel capacitance as function of the frequency for different illumination intensities at 1 V. The dotted line is proportional to the square root of the time. (b) The parallel capacitance at 1000 Hz as function of illumination intensity. The device area is 1 mm².

The RC time at 1V bias is shown in Figure 30. The RC time becomes more complex in the forward bias as was before with the conductance and capacitance. For low light intensities the RC time is constant. With increasing light intensity the conductance increases as is seen in Figure 28. Therefore the RC time will decrease at higher intensities.

Figure 30: The $R_pC_p$ time measured as function of the illumination intensity at 1 V and a frequency of 1000 Hz.
Close to open circuit voltage

In section 5.1.2 it was shown that the current becomes space charge limited near $V_{oc}$, which was indicated by the relation $G \propto g^{3/4}$. In this section the conductance and capacitance close to open circuit voltage is studied. This is done by applying a DC bias level equal to the $V_{oc}$ measured in the J-V measurements for the respective illumination intensities. In Figure 31a,b the conductance and capacitance as function of the illumination intensity are shown.

![Figure 31](image_url)

Figure 31: (a) The parallel conductance as function of illumination intensity. The fit has a slope of 0.73±0.02. (b) The parallel conductance as a function of the illumination intensity, with a slope of 0.26±0.01. The data points are measured with an AC frequency of 1000 Hz at open circuit voltage.

Figure 31a shows the expected relation $G \propto g^{3/4}$, evident by the linear fit which has a slope of 0.73±0.02. Figure 31b demonstrates that the capacitance is dependent on the illumination intensity. From the fitting it is concluded that the capacitance scales as: $C \propto g^{1/4}$.

The measured relation between the capacitance and the illumination intensity can be derived from the Goodmann and Rose model. In equation (11) it was shown that the space charge region scales as $L_{qc} \propto g^{-1/4}$. Using the equation for the geometrical capacitance (13) the measured relation of $C \propto g^{1/4}$ is found.

When the device is operated close to open circuit conditions the capacitance cannot discharge over the external circuit. The response time of the photodiode is thus equal to the $R_p C_p$ time. From the conductance and capacitance it is determined that the RC time would scale as $\tau_{RC} \propto g^{-1/2}$, this is shown in Figure 32. In the Goodman and Rose model this time corresponds to the lifetime of the holes assuming a constant mobility, this is explained in section 2.4.

The lifetime of the holes can be calculated using equation (16). In Figure 32 the dashed line is plotted using a hole mobility of $1.44 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$. This value is a realistic mobility for the used polymer[20]. It can thus be concluded that the Goodman and Rose model gives an excellent prediction of the RC time close to $V_{oc}$. 
Figure 32: The \( R_pC_p \) time as a function of illumination intensity at \( V_{oc} \) condition measured at 1000 Hz. The black line indicates the fitting of a power law \( g^\alpha \) with \( \alpha=0.47\pm0.01 \). The red dashed line is the prediction of the Goodman Rose model equation (16).

5.2.3 Capacitance voltage measurement

Measuring the capacitance as function of the voltage is often done to study the built up of space charge in the system and charge injection.[28][29]

In Figure 33 the C-V measurement is shown for the device under different illumination intensities. Mesta et al.[29] described the capacitance under dark conditions as follows: The capacitance converges to the geometrical capacitance of the device in reverse bias. When the applied bias is close to \( V_{oc} \) charge carriers are able to diffuse into the bulk but they are not able to reach the other electrode, increasing the capacitance. Above \( V_{oc} \) the charge carriers are transported through the bulk to the opposite electrode, reducing the capacitance. By increasing the biases further; more charge carriers are injected and the capacitance increases due to charge trapping in the device.

Under illumination it is assumed that the system behaves similar. A significant difference is seen in the reverse bias. Under illumination the device is not only relying on the charge injection from the electrodes. Close to \( V_{oc} \), the generation of charge carries in the device will result in a built up of space charge, increasing the capacitance in reverse bias. With increasing negative bias the number of charge in the device will decrease consequently the capacitance will decrease with increasing negative bias; converging to the geometrical capacitance.
Inorganic semiconductor diodes are often described using the Mott-Schottky model. This model describes the dependence of the capacitance on the applied bias, resulting in the following equation

$$C^{-2} = \frac{2(V_m - V)}{A^2 q\varepsilon_0 \varepsilon_r N_A}$$

(43)

with $N_A$ the doping concentration in the device. A similar analysis can be done for organic semiconductors. The Mott-Schottky model is often used to determine the doping concentration $N_A$ in inorganic semiconductors a similar analysis can be done for organic semiconductors.

In the previous sections it was shown that close to $V_{oc}$ the device can be described by the Goodman and Rose model. Using the equations for the geometrical capacitance (13) and the equation for the space charge width (11), the capacitance can be expressed as equation (14).

Making use of equation(14) a similar expression as (43) can be found

$$C^{-2} = \left(\frac{9 \mu_h \mu_o}{8 \varepsilon_0 \varepsilon_r \varepsilon_r} \right)^{1/2} \frac{(V_{oc} - V_{applied})^{3/2}}{A^2}.$$

(44)

Figure 34 shows the Mott-Schottky curve for the device using different illumination intensities. The OPD shows no significant effects of space charge in the dark. It is therefore assumed that there is no intrinsic doping concentration. For high intensities the capacitance scales as $C^{-2} \propto V_{applied}$ in the region $-0<V_{applied}<0.5V$. At high intensities there is thus a space charge effect.
Using equation (44) it is possible to determine the mobility of the slowest charge carriers in the device.

![Mott-Schottky curves for different illumination intensities](image)

*Figure 34: Mott-Schottky curves for different illumination intensities. The arrow indicates the $V_{oc}$ for an intensity of 51 mW/cm² as was determined from the J-V measurement.*

By fitting the regions in the Mott-Schottky plots that shows the $C^{-2} \propto V_{applied}$ dependency the hole mobility can be estimated, using equation (44). The generation rate is given by equation (38), the area of the device $A$ is 1 mm² and the relative dielectric constant is estimated to be 5. The hole mobility is estimated to be $\mu_h = (1.5 \pm 0.4) \times 10^{-5}$ cm²V⁻¹s⁻¹. This mobility is consistent with the mobility found from the RC time measurements close to $V_{oc}$. The hole mobility determined does not vary significantly with the light intensity.

It is also possible to estimate the open circuit voltage of the device using equation (44). For an intensity of 51 mW/cm² the Voc is estimated to be 0.52 ± 0.05 V which is in rough agreement with the Voc of 0.60 ± 0.01 V found in the J-V measurement.

5.3 **Photocurrent transients**

In the previous experiment it was shown that the response time of the device was dependent on the illumination intensity and on the applied bias. In this section the transport of charge is studied using photocurrent transients.

In the previous section the device was studied using an electrical perturbation, in this section the device is perturbed by a modulated light source. This paragraph will consist out of two sections: the large signal response measurements and the small signal response measurements. In the large signal response measurements the transition from one steady state
under dark condition to another steady state under illumination is studied. The impedance measurements in the previous section are an example of small signal response measurement. In these measurements the response to a small perturbation is measured. The perturbation is kept small to keep the system in equilibrium (one steady state). This is done by illuminating the device and using a second light source for the perturbation. This second light source is a modulated light source and has a low intensity compared to the first light source. A more in detail description of the measurement setups can be found in paragraph 4.4

5.3.1 Large signal response photocurrent transients

In Figure 35 the photocurrent transients for different light intensities is shown at short circuit conditions. At time zero the device is illuminated resulting in a sharp increase in current density followed by slow increase to a steady state level. After the illumination is switch off after 2.8 ms, the current decreases to zero.

![Figure 35: Photocurrent transients under short circuit conditions. The inset shows the linearity of the maximum current density as function of the light intensity, the fit has a slope of 0.99±0.03.](image)

The steady state value of the current density under illumination is proportional to the illumination intensity, as can be seen in the inset of Figure 35. From the steady state current density the EQE is estimated to be 0.08.

When the illumination is switched off the concentration of charge carriers in the device will decrease to the equilibrium value in the dark: either by bimolecular recombination or by exiting the device through the electrodes. A long tail after switch off is measured up to 100μs or even longer, see Figure 36. In Figure 36a the photocurrent decay is normalized to the maximum
value and plotted on log-linear scale. This allows for a comparison of the amount of extracted charges relative to the steady state current. The figure shows that the decay of the photocurrent is dependent on the light intensity and cannot be described by a single exponential decay.

The tail of the photocurrent decay can be fitted with a single exponential decay to give an estimation of the decay time. In Figure 36b the decay time determined from the fitting of the single exponential decay in Figure 36a is plotted as function of light intensity. At high light intensities the number of trapped charges in the device is relatively small compared to number of the charges unaffected by traps so called ‘free’ charges. The ‘free’ charges have a shorter lifetime consequently the decay time for high light intensities will be short. At very high light intensities the number of trapped charges becomes negligible; the decay rate will therefore become independent of the light intensity. Upon lowering of the light intensity the fraction of trapped charges in the device increases decreasing the decay rate.

Figure 36: (a) The decay of the short circuit photocurrent transient for different light intensities. The current is normalized to the current at 2.8 ms just before the illumination is switched off. (b) Log-linear plot of the decay of the short circuit photocurrent.

By integrating the decay of the photocurrent the number of charges that exit the device through the electrodes can be determined. In Figure 37 the amount of charge that exits the device through the electrodes is plotted as function of the illumination intensity. The number of charges extracted after switch off is but a fraction of the charges generated in the device. From the fitting of the power law \( g^2 \) with \( \alpha = 0.93\pm0.03 \) it is concluded that collected charge increases linear with illumination intensity. It is therefore assumed that bimolecular recombination losses are negligible. If recombination loss would be significant the number of collected charges would show non linear behavior: An increase in light intensity would result in more recombination as the concentration of charge in the device is larger.
Figure 37: The extracted charge density as function of the illumination intensity, determined by integrating the tail of the photocurrent transients. The line indicates the fitting of a power law $g^\alpha$ with $\alpha=0.93\pm0.03$.

5.3.2 Small signal response photocurrent transients

In this experiment the device is continuously illuminated under short circuit conditions to bring it in a steady state. The continuous background illumination is varied in this experiment. A modulated light source is used to perturb the steady state; the intensity of this light source 0.01mW/cm$^2$ is low compared to background illumination. As described in section 4.4.2

In Figure 38 the photocurrent transients induced by the weak probe light are plotted. From the figure it is immediately clear that the amplitude of the transients is dependent on the background illumination. In the inset in Figure 38 the amplitude of the transient is plotted as a function of the background illumination intensity.

The change in EQE with increasing background illumination is in contradiction with previous experiments were it was found that the photocurrent scales linear with the illumination intensity, see Figure 18 and Figure 35. This discrepancy is at this moment not understood.
Figure 38: The small signal photocurrent transients with varying background illumination. The inset shows the maximum photocurrent density as a function of the background illumination.

In the large signal response measurement illustrated in Figure 36, it was found that the photocurrent decay rate was dependent on the illumination intensity. It is thus expected that in the small signal experiment illustrated in Figure 38, the decay rate would be dependent on the background illumination intensity. In Figure 39 the tail of the normalized photocurrent transient is plotted. The decay rate in the tail of the decay can be estimated by fitting a single exponential decay function. In Figure 39b the single exponential decay time is plotted as function of the illumination intensity. The decay time decreases when the background illumination intensity is increased.

By varying the background intensity the occupation of trap sites is varied. At high intensities all traps are filled by the constant background illumination thus the charge carriers generated due to the light pulse are ‘free’ resulting in a fast decay rate. For low background intensities not all traps are filled thus the generated carriers can get trapped resulting in a slower decay rate.

In this experiment only the tail of the photocurrent decay can be studied qualitatively. To study charge transport of the ‘free’ and trapped charges in a more quantitatively manner another experiments is proposed. This experiment will be discussed in the following section.
Figure 39: The decay of the short circuit photocurrent density for small signal response measurements. The tail of the decay is fitted with a single exponential decay. (b) The decay time of the fitted single exponential decay plotted as function of the background illumination intensity.

5.3.3 Quantitative analysis of the relaxation time

In this section a quantitative analysis of the relaxation time of the device is discussed using the formalism presented in paragraph 3.2. The relaxation time is determined using a triangular optical perturbation, as is described in section 4.4.2.

To determine the relaxation time accurately, the perturbation intensity should be small compared to the background illumination. In practice this precludes measurements with very low background intensities and the relaxation time is determined only in a limited range of background illumination intensities. In Figure 40 the photocurrent response is plotted with a background illumination of 0.24 mW/cm² and a light pulse intensity of 0.01 mW/cm².

Figure 40: (a) The pulse profile measured by the Si photodiode and the short circuit photocurrent response of the OPD with a background illumination of 0.24 mW/cm². (b) The even and odd contribution of the short circuit photocurrent response.

The photocurrent response of the OPD is clearly lagging behind the pulse profile. The lag of the photocurrent response is evident from the shift of the peak photocurrent relative to the...
maximum in illumination intensity. Furthermore the photocurrent shows a long-lived tail after the perturbation. The photocurrent response can be separated in an even and odd contribution using equations (27). The even and odd contributions are plotted in Figure 40b. Using the even and odd part of the current density it is possible to determine the relaxation time, using equation (31). Figure 41 shows the determined relaxation time as a function of the pulse profile.

Figure 41: The relaxation time determined using equation (31) as a function of the triangular light pulse profile, under short circuit conditions.

The determined relaxation time profiles show that for a background illumination of 6.6 mW/cm² the relaxation time is practically uniform, adopting a relatively low value of 20 μs. This implies that the response of the diode can be described accurately using a single relaxation time. For lower background illumination intensities the response time increases. Furthermore at the low pulse profile intensities, the relaxation time shows a rapid decrease. This change in relaxation time at low pulse intensities is attributed to trapping of charge carriers in the device.

At high background illumination intensity all the trap states are filled, the generated charge are thus ‘free’ resulting in a uniform relaxation time. For low intensities not all traps are filled by the background illumination. A part of the charge carriers generated by the light pulse will therefore get trapped and will have a longer relaxation time. The ‘free’ charge carriers will have the same relaxation time, evident in the flat region in the relaxation time profile. The relaxation of charge carriers at low light intensities can consequently not be described using one relaxation time. The transport of ‘free’ charges is dependent on the illumination intensity; it decreases with increasing illumination intensity.
Figure 42: (Points) The relaxation time as a function of the background illumination intensity for different electrical bias. The dashed line represents the upper limit of the transit time of the holes. The solid black indicates the lifetime of the slowest charge carrier determined by impedance spectroscopy.

Figure 42 presents the relaxation time of the ‘free’ charge determined from the flat region of the traces in figure 41. The relaxation time is determined at various bias voltages and plotted as a function of the background illumination intensity. The relaxation time decreases with increasing illumination intensity. Upon increasing the applied bias, the relaxation time decreases. The black line indicates the measured response time under open circuit condition using impedance spectroscopy. Under open circuit conditions the response time is equal to the lifetime of slowest charge carrier at $V_{oc}$ according to Goodman and Rose.

At high illumination intensities the relaxation times determined using an optical perturbation approach the lifetime of the slowest carrier when the applied bias is close to $V_{oc}$. According to the Goodman Rose model, the relaxation time is limited by the lifetime of the slowest charge carriers see equation (16).

At low light intensities the relaxation time is much faster than the lifetime of the slowest charge carrier. At lower light intensities the charge generation rate is too low for built up of space charge. Under these conditions the relaxation time of the diode would then not be affected by space charge. The relaxation time of the diode is then expected to be limited by transit time of the slowest charge carriers.

The transit time can be approximated by

$$\tau_{\text{transit}} = \frac{d^2}{|V_{oc}(g) - V_{\text{applied}}| \mu_h}$$  \hspace{1cm} (45)
with \( d \) the distance to the cathode and the open circuit voltage expressed by equation (39). In this device the hole mobility is estimated to be \( 1.44 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \). An upper limit for the transition time can be obtained by taking \( d \) equal to the thickness of the active layer (280nm). The dashed line in Figure 42 represents the upper limited for the transit time thus obtained. In reality the transit time will be lower as the majority of the holes will be generated closer to the cathode.

At sufficiently low intensity for applied bias well below \( V_{oc} \), the estimated transit time is shorter that the lifetime of the slowest carriers at \( V_{oc} \). Under these conditions it is expected that the response time of the diode will be no longer be limited by the prediction from Goodman and Rose model but will instead be limited by the transit time.

This allows us to explain why the relaxation time measured under optical perturbation can be so much lower than the lifetime obtained from the impedance measurements under \( V_{oc} \) conditions.
6 Conclusion

When the organic photodiode is operated close to open circuit conditions it is shown that the time response determined via photocurrent transient and impedance spectroscopy measurements converge. This is attributed to the space charge limitation in the photodiode. Goodman and Rose have shown that in the space charge limit the response time equals the lifetime of the charge carrier with the lowest mobility. They argue that the lifetime of the slowest charge carrier depends on the product of the illumination intensity and the mobility of the slowest carrier.

At sufficiently low light intensity for applied bias well below $V_{oc}$ the space charge limitation is lifted. When the photodiode is not space charge limited the response time is faster than the lifetime of the slowest charge carrier in the space charge limit. Under these conditions the response time of the diode will be no longer limited by the prediction from Goodman and Rose model but will instead be limited by the transit time.

The important characteristics of organic photodiodes for imaging applications are a fast photo response, high sensitivity and a low dark current. This study shows the importance of balancing the mobility of the charge carriers in the organic photodiode in order to achieve a fast response at low applied bias voltages.

In the Goodman and Rose model used in this study, diffusion of photo generated charge carriers is neglected. In the Goodman and Rose model the local electric field driving the current transport has to vanish when the applied bias equals the open circuit voltage. This assumption is questionable as it can be argued that the field is dependent on the sum of the applied bias and the built-in potential.

In the metal-insulator-metal picture there are no charges located in the active layer this implies that the electric field is zero when the applied bias equals the built-in potential. When charges are generated in the device the electric field depends on the charge distribution according to the Poisson equation. At open circuit conditions the current is zero the charges have thus no preference in direction and it can be assumed that the electron and hole density are the same, resulting in no electric field at open circuit voltage.

A more detailed study should involve a calculation or simulation of the local field and charge distribution in the active layer involving both drift and diffusion type transport. In addition, charge carrier mobility may be simulated by a hopping transport model. Such a hopping simulation can be used to determine the effect of charge trapping on the response time.

This study has revealed the importance of space charge in the active layer of organic photodiodes in their temporal response. This has not been explicitly mentioned in previous publications. This study also shows that by exploiting this limitation, the mobility of the slowest charge carrier can be determined from photocapacitance measurements. This method for determining the lowest mobility is not yet extensively used in mobility measurement studies.
7 References


