Organic thin-film phototransistors based on poly(3-hexylthiophene)

G Scarpa, E Martin, S Locci, B Fabel and P Lugli

Institute for Nanoelectronics, Technische Universität München, D-80333 Munich, Germany

E-mail: scarpa@tum.de

Abstract. We investigated visible and UV light response of OTFTs based on the solution processable poly(3-hexylthiophene) (P3HT) semiconducting polymer. The transistors show a photoresponse in channel current under white and UV light illumination. Stabilization time after illumination and recovery time after turning off the light sources are also studied. A transport analysis based on a modified drift-diffusion model is presented.

1. Introduction

Organic phototransistors (OPTs) are one of the best feasible applications of organic thin film transistors (OTFTs) because of the large absorption and the excellent photocurrent generation efficiency of organic semiconductors both in the ultraviolet (UV) and visible range [1]. Solution-processable OPTs [2] can be easily integrated in smart clothes, packages, and biological systems as light sensors, biosensors and/or multifunctional sensors. OPTs fabricated by thermal evaporation of some oligomers as pentacene [3] and rubrene [4] have been found to have a very high photoresponse. Also solution processible OPTs based on conjugated polymers, such as poly(9,9-dioctylfluorene-co-bithiophene) [5] and methano [6,6]-phenyl C61-butyric acid methyl ester (PCBM) [6] have been reported.

Poly(3-hexylthiophene) (P3HT) is a solution processable semiconducting polymer, which is suitable for roll-to-roll process applications. It has reported field effect mobility up to ~0.1 cm²/V s [7], close to the value of amorphous silicon and it is one of the most promising materials for applications in OTFTs and solar cells [8, 9]. However, the use of P3HT for phototransistor applications is only reported in combination with other compounds. Meixner et. al. reported the use of dye-doped P3HT OPTs using dyes for wavelength selection [10], while Mok et. al. adopted P3HT in composite form combined with TiO₂ nanoparticles demonstrating good photocurrent generation under white light illumination [11]. Finally, the UV light sensitivity of OTFTs based on P3HT has not yet been analyzed.

In this work, a good photosensitive behavior due to response to UV and white light is reported for OTFTs based on P3HT processed from solution without any further treatment. The results show a fast response of transistors under light illumination, constituting a promising performance for further application of OPTs.
2. P3HT-transistor

2.1. Device fabrication
Bottom-gate OTFTs on boron-doped silicon wafers (p+-Si) as substrate were fabricated. The doping level is around 10^{18} cm^{-3} and the conductivity is equal to 10,000 S/m (purchased from Si-Mat, Landsberg). On top of the p+-Si surface an 80 nm thick silicon dioxide (SiO_2) layer was grown in a dry oxidation process at 1000ºC. This insulator separates the p+-Si gate and the contact electrodes titanium/gold (2 nm Ti, 45 nm Au), patterned by lift-off in an optical lithographic step. The channel has a large cross-section area (W/L) because of the interdigitated electrode structure used for the contacts [12]. In the inset of Figure 1 (left), a schematic cross-section of the transistor structure is shown. The values for the channel length (L) were chosen between 10 µm and 100 µm. In particular, three transistor structures with 10 µm, 50 µm and 100 µm channel lengths are investigated here. The conducting polymer (regio-regular poly-3-hexyl-thiophene, rr-P3HT, Sigma-Aldrich) was used as received and dissolved in toluene solvent with a mass relation of 1 to 100. The active layer was deposited by spin coating (1000 rpm for 20 s) under nitrogen atmosphere. The polymer and the dielectric surface were not modified. A semiconductor characterization system (Keithley 4200-SCS) was used for all measurements. The analysis has been carried out at room temperature under ambient conditions.

2.2. Device physics and simulations
Our simulation is based on the drift-diffusion approach implemented in the commercial software tool SENTAURUS\textsuperscript{TM}, which is a widely used and well-known software package designed for inorganic semiconductors [13]. When the organic phototransistor is illuminated, excitons are generated in the semiconductor [14]. Those excitons which do not recombine lead to an electron-hole pair. In the device, these carriers, as well as the others that are injected by the contacts, will move according to the drift-diffusion model, which means that they will drift, driven by an applied electric field, or diffuse, due to the presence of a gradient of the carrier density [15]. Although we were unable to simulate the dynamics of exciton generation and recombination, we simulated the phototransistors using the SENTAURUS drift-diffusion simulator adding an optical generation term. Optical generation is considered by adding a generation rate \( G(r,t) \) to the continuity equations (1):

\[
\begin{align*}
\nabla \cdot J_n &= -qG(r,t) + \frac{\partial n}{\partial t}, \\
\nabla \cdot J_p &= -qG(r,t) + \frac{\partial p}{\partial t}
\end{align*}
\]

where \( P_0(r,t) \) is the incident power of the wave beam in the position \( r \) at the time \( t \), \( E_{ph} \) is the photon energy and \( \alpha \) is the absorption coefficient. We assume a constant light absorption throughout the entire device. In this framework excitons are not considered and the photons directly generate an electron-hole pair. P3HT parameters used for the simulations are electron mobility \( \mu_e = 1 \cdot 10^{-6} \text{ cm}^2/\text{V}s \), hole mobility \( \mu_h = 1.28 \cdot 10^{-3} \text{ cm}^2/\text{V}s \), band gap 2.13 eV, electron affinity 3.2 eV, dielectric permittivity 3 and density of states \( N_c = N_v = 2 \cdot 10^{21} \text{ cm}^{-3} \).

2.3. Electrical characteristics
Figure 1 (left) shows the measured and simulated output characteristics under dark conditions of a sample device with 20 µm channel length and a W/L = 13,350. As the surface of the silicon dioxide was not treated separately, nearly all transistors showed a positive threshold voltage of about +5 V, thus displaying a clearly conducting channel already at a zero gate voltage, as can be seen from the picture. The field-effect mobility extracted from the transfer characteristics of the transistors was in the order of 10^{-4} cm²/Vs, which was consistent with previous findings and experiments [12]. Figure 1
(right) shows the space charge distribution in the device. The transverse (gate induced) electric field attracts holes at the interface forming a layer of charges that acts as the channel.

**Figure 1.** Left: Measured (circles) and simulated (lines) output characteristics of an OFET with P3HT spun out of toluene with a channel length of 20 µm and W/L = 13,350 on 80 nm silicon dioxide. Inset: schematic picture of the transistor structure (cross-section) adopted in our studies. Right: Space charge distribution at V_g = -10V, V_d = -15V

### 3. Photoresponse of the devices

Several measurements for evaluating the photoresponse of the transistors to white and UV light were performed. A white light source with an intensity of 7.9 mW/cm² and a UV diode arrays-source with an intensity of 8.6 mW/cm² (with a peak wavelength of 375 nm) has been used. All experiments were done with the light illuminating the entire surface of the transistors. The distance between the focus and the sample for white light was fixed at 10 cm and for the UV measurements 2 cm was used. A fast response under illumination and the capability of the transistors to recover to the initial state are important factors for further applications of OPTs. Therefore, measurements of the channel current, under light illumination, versus time have been performed. Figure 2 shows a channel current change of 1 µA and 0.8 µA under UV and white light illumination, respectively; by fixed values for V_ds (-15 V) and V_g (-10 V). In spite of the small values, this current increment could be high enough for photosensors applications. The recovery time after turning off the light, is about 90 s, comparable with recovery times reported for phototransistors [1]. However, it is so far a quite high value and constitutes an important disadvantage.

**Figure 2.** Channel current responses under white and UV light illumination is presented. 30 s UV and 30 s white light has been applied. V_ds = -15 V, V_g = -10 V.

The simulated response to the illumination shows that the generated carriers determine a space charge distribution which is almost uniform along the channel, except for the vicinity of the contacts. The potential being also uniformly flat in the device (most of the voltage drop occurs in the vicinity of the
source contact), very long times are required to relax the exceeding carriers once the light is turned off, because both the electric field and the carrier gradient are low. The proposed simulation (Figure 3 left) qualitatively agrees with the experimental data, but still exciton dynamics should be included to provide a better fitting.

![Figure 3. Left: Simulated response to illumination. Right: Space charge under illumination.](image)

4. Conclusion

The photosensitivity of OTFTs based on solution-processable P3HT p-type organic semiconductor has been tested. All measurements were done at room temperature ambient conditions and the polymer was used as received. The transistors show a good response to white and a higher one to UV light. The time analysis shows a fast response after the illumination and a slow recovery time after turning off the light source. This delay for recovering the initial value in channel current is a big disadvantage of the phototransistors. The recovery time depends also on the measurement starting point. In other words, the initial polarization state and the density of charges trapped are important factors before starting the measurement. Here, the gate voltage plays an important role for controlling the initial conditions. Despite these disadvantages, low-cost, large-area applications of solution-processable P3HT-based phototransistors are feasible.

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