Organic field-effect transistors for sensing applications

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Summary

The discovery that organic polymers have the ability to function as conductors and semiconductors has opened a new field of possibilities in electronics. Although organic electronics will probably never be able to compete with inorganic semiconductor electronics in terms of charge carrier mobility, operation speed and miniaturization, it can provide cheap, easy processable, flexible devices for low-end applications in electronics, such as white light illumination, flexible displays, solar cells, RFID-tags and sensors. Semiconducting polymers are a special group of plastics, which differentiates itself from 'common' non-conducting plastics by the fact that they possess a conjugated backbone, i.e. alternating single and double bonds. The conjugation allows electrons and holes in the π-molecular orbitals to be delocalized along the conjugated segments of the molecule. However, since the conjugation is often broken by defects and twisting of the polymer chain, the charge carriers are localized within the conjugated segments. From this disorder in conjugation length, the HOMO and LUMO levels in organic semiconductors are not well defined but they have a Gaussian spread. The main transport mechanism in semiconducting polymers is dominated by hopping transport, which is strongly dependent on the energetic and structural disorder in the polymer.

Sensors, devices which have a response to a physical entity and convert the response into an analyzable signal, are becoming steadily one of the most important and investigated applications in organic electronics. Of special interest is the use of organic field-effect transistors (OFETs) as sensors or as core component thereof. A particular type of sensor is the biosensor, a sensor that contains a biological molecule or even cell as part of the detection mechanism. The use of biological molecules or cells as detection unit has the great advantage of enhancing the selectivity of the sensor, since biological molecules have so evolved to react very specifically only with few selected compounds.

This thesis focuses on the study of organic field effect transistors and their usefulness for (bio)sensing applications. The research is more focused toward fundamental understanding of the use of the OFET as a sensor or biosensor rather than realization of the sensors itself, although a prototype biosensor based upon dual-gate structure has been shown.

In *Chapter 2* the materials used throughout this Thesis have been discussed and the design of the devices and the experimental procedures for fabrication and characterization were described.

In *Chapter 3* the device operation of organic dual-gate field-effect transistors (DG-OFET), fabricated by solution processing, is characterized. It is shown that by sweeping the bottom gate bias of the devices and keeping the top gate bias constant, the threshold voltage of the bottom gate of the devices depends on the top gate bias with two linear relationships for two different regimes, assuming that the mobilities of the top and bottom channels have similar magnitudes, and that the capacitance of the semiconductor layer is not negligible. The first regime is observed when one gate is positive, hence the respective channel is in depletion and no gate screening will occur, while the other gate is in accumulation regime, the field of the positive gate will penetrate to such a large extent that the channel in accumulation will be affected by both gates. The second regime is observed when both channels are in accumulation, the charges present in the channels will screen the respective gate potentials, hence both channels will operate individually and no mutual influences are observed. Moreover, it is observed that a direct effect of the shielding of the gate bias by the accumulated charge carriers at the interface is clearly marked by a drop in the transconductance of the dual-gate transistors between the two regimes.

The DG-OFET also stands as theoretical model for the operation of the biosensor described in *Chapter 4*, the Bio-FET. The Bio-FET is an organic FET transducer with a DG-OFET structure where an integrated sulphate-binding protein (SBP) layer replaces the top gate electrode. SBP was genetically engineered to contain a thiol group for surface-anchoring without affecting its binding activity. The modified receptor was covalently coupled to a maleimide-functionalized polystyrene layer spincoated on top of the transistor's surface. Fluorescence spectroscopy and tapping-mode atomic force microscopy were used to confirm the covalent coupling of SBP to the surface of the functionalized polystyrene layer. Measurement of the dissociation constant of SBP after drying and rehydration showed that the protein remains active even after being dried, making it suitable and versatile for sensing purposes. The binding of sulphate ions in dry conditions was detected by a shift in the threshold voltage. Combined with surface density measurements by AFM, an effective charge of –1.7q per protein was found, as expected from the Bio-FET operation model, based on the operation characteristics of the DG-OFET.

Organic field-effect transistors can be also used directly as sensor devices. The most straightforward sensing mechanism is chemical doping of the organic semiconductor itself in the OFET. To build a proper sensor, however one must understand the process and kinetics of doping. In *Chapter 5* the kinetics of

acid doping of regio-regular poly-3-hexylthiophene in field-effect transistors were investigated. The dopand used was a vaporized perfluorinated chloroalkylsilane. The dopant density has been derived from the shift of the pinch-off voltage, as a function of temperature and exposure time. The change in dopand density can phenomenologically be described by stretched exponential time dependence, with a saturation dopant density of $1 \pm 0.5 \times 10^{26}$ m^{-3} and a thermally activated relaxation time with an energy barrier of 0.6 eV, which agrees with reported values for protonation reactions of organic molecules. It was shown that a similar relationship holds for previously reported kinetics of poly-thienylene-vinylene doped with molecular oxygen. The good agreements obtained indicate that the doping kinetics of disordered organic semiconductors follows indeed a stretched exponential time dependence.

An important parameter in organic electronics, as in electronics in general, is the charge carrier mobility in semiconductors. For the response in sensors based upon organic semiconductors it is very important to understand the relationship between the charge carrier density in the device and the mobility of the charge carriers. In *Chapter 6* the charge carrier mobility dependence on the charge carrier density in semiconducting polymers was investigated. Here the mobility of the organic semiconductors was investigated over a carrier densities range from 10^{15} cm^{-3} to 10^{20} cm^{-3} in order to experimentally establish the relation between mobility and carrier density. The mobility at low (10^{15} -10^{16} cm^{-3}) and high (10^{18} - 10^{20} cm^{-3}) carrier density was extracted from undoped hole-only diodes and field-effect transistors, respectively. Intermediate densities were probed using chemically doped Schottky diodes and transistors. It was shown that the mobility is almost constant for carrier densities below 10^{16} cm^{-3} and follows a power law dependence for carrier densities higher than 10^{18} cm^{-3}. In some materials however an anomaly in the intermediate range was observed, characterized by a sharp increase in mobility with the charge carrier density. The anomaly is probably caused by a significant presence of trapping levels, caused either by impurities or disorder, which are filled by the extra charge carriers introduced by doping, resulting in the strong increase of the mobility of the material.

Finally it is important to note that organic electronics, and in particular organic field-effect transistors, is a promising technology for low-cost sensing applications without necessarily sacrificing the selectivity and sensitivity of the sensing devices. The use of OFETs as sensors can be both direct, as through the chemical doping mechanism, or can be integrated with biological molecules, to give rise to biosensors, which would combine the selectivity of the biological molecules with the low-cost fabrication and flexibility of semiconducting polymers.