Chapter 1

Introduction

The basic building block for solid-state electronics is the field-effect transistor (FET). The basic layout is presented in Fig. 1.1a. A field-effect transistor is a three terminal electrical switch where two contacts, the source and the drain, are separated by a semiconductor. The third contact, the gate is used to modulate the conductivity of the semiconductor. Current modulation is achieved by applying a bias on the gate with respect to the source. Charge carriers are electrostatically accumulated or depleted at the semiconductor dielectric interface, modifying the conductivity. This device was first suggested in 1928 by Lilienfield (Fig. 1.1b). The first prototype of a working transistor was only achieved in 1947 by Bardeen, Brattain and Shockley (Fig. 1.1c). Integration where several transistors were combined in a single integrated circuit was demonstrated in 1960. Transistors realized at that time were based on $n$-type doped semiconduc-

Figure 1.1: a) typical layout of field-effect transistor, consisting of a source and drain electrode, a gate, a gate dielectric and a semiconductor. b) the first report of a field-effect transistor by Lilienfield. c) the first prototype of a working field-effect transistor demonstrated by Bell labs.
tors \(e.g.\) where the transport is governed by electrons. Such transistors allow for the fabrication of \(n\)-type logic referred to as NMOS, still reliability and power dissipation were poor. A breakthrough was the development of \(p\)-type doped silicon (PMOS) where the transport is governed by holes. Now complementary (CMOS) logic with improved performance and reliability could be realized.\(^4\) Since then the number of transistors integrated on a single chip has grown to the hundreds of millions with typical feature sizes of 45 nanometers.\(^5\) Silicon technology has been the dominant force in integrated device manufacturing and will retain this position in the foreseeable future.

![Examples of organic electronics](image)

**Figure 1.2:** Examples of organic electronics a) a flexible CMOS-like organic circuit, b) flexible PMOS organic circuits, c) radius flexible display with organic backplane from Polymervision.

On the other hand, ‘plastic transistors’, \(e.g.\) transistors in which an organic material is used as the active semiconductor,\(^6\) may form the basis of a new low-cost microelectronic technology on flexible substrates (Fig. 1.2b).\(^7\) The use of organic materials has a number of important advantages over conventional techniques using mainly inorganic materials, like amorphous silicon. The low process temperature, typically less than 150 °C, creates the possibility to use a wide range of plastic substrates instead of glass. Furthermore, the (thermo)mechanical properties of organic semiconductors are compatible with plastic substrates. Innovative products enabled by organic transistors are contactless radio frequent identification (RFID) tags and flexible displays. In RFID systems the reader sends electromagnetic waves that are captured by the antenna on the label. Using this energy a rectifier provides the DC power needed to read an identification code stored in the label memory. The code is send back to the reader using the same radio link used to send power.\(^8\) The application for RFID
tags is on improved logistics by item-level identification of goods. A huge market is foreseen for ultra low cost printed labels, or so-called electronic barcodes. The second emerging application of organic transistors is as pixel engine and driver of flexible displays. The first consumer bendable and rollable electrophoretic displays with an organic active-matrix backplane have been announced for 2009 by at least two companies, Polymervision\textsuperscript{9} (Fig. 1.2c) and Plasticlogic.\textsuperscript{10}

1.1 Fabrication methods for organic transistors

The organic semiconductor can be applied by vapor deposition or by solution processing. A vapor deposited organic semiconductor generally yields higher thin-film transistor performance. However, solution processing is preferred for high-volume, low-cost production. It simplifies the manufacturing process compared to the conventional chemical vapor deposition techniques, especially for large areas and it allows for high-throughput. Preferably all layers, and not only the semiconductor, are processed from solution.\textsuperscript{11–15} Because the processing is done at ambient temperature, organic electronics can be produced on basically any substrate, including cheap and flexible films. Next to the deposition, solution processing opens a plethora of alternative patterning technologies such as printing,\textsuperscript{16,17} stamping,\textsuperscript{18} selective dewetting\textsuperscript{19} and inkjet printing.\textsuperscript{14} The ultimate goal is a roll-to-roll solution-based process leading to ultra-low cost electronics. Organic transistor research in the last 15 years has been mainly focused on the development of new \textit{p}-type semiconductors to improve environmental stability and charge carrier mobility. As witnessed in many overviews of the field, for polymeric \textit{p}-type semiconductors the mobility has improved more than four orders of magnitude, from values in the order of $10^{-5}$ cm$^2$/Vs before the 90’s to values just below unity nowadays. Small molecule organic semiconductors have improved in a similar way, from the typical mobility of $10^{-3}$ cm$^2$/Vs of the early 90’s to values surpassing 1 cm$^2$/Vs nowadays. Processing and deposition techniques still play a significant role to determine the mobility of the semiconductor films. Depending on the degree of internal ordering, on the presence of traps and on the properties of the semiconductor/insulator interface, the mobility of a given material can vary in a transistor by more than one order of magnitude.

\textit{P}-type organic transistors have been combined into logic gates such as in-
verters and NAND gates. A major bottleneck for digital PMOS circuits is the design of logic gates with enough noise margin and low enough noise margin variability. The noise margin, ‘the maximum allowable spurious signal that can be accepted by a logic gate while still giving correct operation’ can be optimized by minimizing the parameter spread of discrete transistors. This has resulted in digital PMOS integrated circuits in which hundreds of transistors have been combined. To improve noise margin of logic gates and to improve the clock frequency of integrated circuits, complimentary logic is indicated for which n-type semiconductors are required. Traditionally n-type materials have exhibited extremely poor performance as well as limited environmental stability. Recent research, though, shows promising improvements. For instance, a cyanated perylene carboxylic diimide derivative with an initial mobility of 0.12 cm²/Vs is reported. The mobility of this n-type material degrades by one order of magnitude after about 400 days storage in ambient conditions. State of the art mobility in n-type materials reaches values around 1 cm²/Vs and can be reasonably air-stable. For the same reason there is a growing interest in ambipolar transistors. Ambipolar semiconductors support both hole and electron accumulation. The transistors can operate in either p-type or n-type

![Diagram](image.png)

**Figure 1.3:** Different approaches towards ambipolar field-effect transistors. In a) a blend of two semiconductors is applied. Electrons are injected in the LUMO of the acceptor and holes into the HOMO of the donor. In b) a single material is used. The small bandgap allows injection of both holes and electrons from similar contacts. In c) a wide bandgap and dissimilar electrodes are used where the low work function electrode injects electrons and the high work function electrode injects holes.
mode or in a mode where both hole and electron accumulations co-exist. The
dual nature of ambipolar transistors have allowed integration into CMOS-like
logic gates and integrated circuits. The power dissipation is not less than that
of PMOS circuits but the noise margin has improved dramatically. Three types
of organic ambipolar transistors have been investigated to date: those based on
a bilayer of an electron donor (n-type) and an electron acceptor (p-type) mate-
rial, those based on a blend of the two types of material, and single-component
ambipolar FETs.\textsuperscript{26} Furthermore ambipolar transport in single materials can be
induced by using electrodes with different work function such that one electrode
inject holes and the other electrons. The operation mechanism is schematically
depicted in Fig. 1.3. Although the bilayer approach is interesting from a scien-
tific point of view and yielded notable hole and electron mobilities of up to 0.04
$\text{cm}^2\text{Vs}^{-1}$,\textsuperscript{26,28} its main technological drawback is the need to deposit two semicon-
ductor layers on top of each other. With this respect, blend systems and single
compounds are preferred since they can be deposited in one single processing
step. Though, a major bottleneck of blends is the morphology which strongly
affects the device performance. Hence, a single ambipolar compound, often a
small bandgap semiconductor, is preferred. Decreasing the bandgap facilitates
injection of both charge carriers using similar electrodes. This is technologically
crucial. The main advantage of ambipolar transistors can be demonstrated by
making CMOS-like integrated circuits without any increase in fabrication com-
plicity. An interesting feature of ambipolar transistors is the observation of light
emission upon charge recombination. This requires a thorough understanding of
the charge transport of both carriers. Knowledge about the charge transport of
ambipolar materials in field-effect transistors is still in its infancy.

The ultimate fabrication technology for organic electronics is by self-assembly.
Self-assembly is the autonomous organization of components into patterns and
structures without human interference. Using such processes nanostructures
can be fabricated with a near atomic precision over large areas. This bottom-
up approach for molecular electronics had already been proposed in the 70’s.\textsuperscript{29}
The slow advances in the field reflect the difficulties encountered to fabricate
self-assembled electronics. Self-assembled electronics can be realized in different
device geometries \textit{e.g.} two and three terminal device layout. Two terminal diode
devices consist of a SAM sandwiched in between two electrodes. This is realized by self-assembling molecules onto an electrode, typically a thiol gold system is used. A major bottleneck in molecular diode systems is the fabrication of the second electrode due to the formation of shorts. For integrated circuits a three terminal device based on self-assembly is imperative. In this case a self-assembled monolayer field-effect transistor (SAMFET) is indicated. This device is obtained when the semiconducting self-assembled monolayer is spontaneously formed onto the gate dielectric. However, the fabrication of SAMFETs has proven to be a historical challenge. Issues are long-range order in the SAM, as well as contacting the SAM.

1.2 Organic semiconductors used in this thesis

Materials are classified according to their electrical conductivity in three categories; conductors, semiconductors and insulators. Generally carbon based molecules and polymers are insulating.

![Figure 1.4: a) The chemical structure of polyacetylene b) Schematic representation of the electronic structure of polyacetylene.](image)

When double carbon bonds are alternated with single carbon bonds, conjugation is obtained. The carbon atoms attached in the double bond configuration are sp$^2$-hybridized with 3 coplanar electron orbitals and one remaining $p_z$-orbital perpendicular to the plane. The highly localised electron density in the overlapping sp$^2$ hybridised orbitals form $\sigma$-bonds making up the coplanar backbone. The delocalised electron in the $p_z$ orbital forms upon conjugation an extended $\pi$-orbital. Charges in these delocalised $\pi$-orbital are predominantly responsible
for the electrical as well as the optical properties. A well known conjugated polymer is poly(acetylene) (see Fig. 1.4). Ideally the conjugation in the molecules results in two long range delocalised bands referred to as the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) separated by the bandgap.\textsuperscript{30} In practice disorder in the polymer causes charges to hop through localized states.\textsuperscript{31} For poly(acetylene) high conductivities were obtained after doping the polymer with iodine. This finding was rewarded in 2000 with the Nobel Prize in chemistry. Since then a lot of work has been put into improving the properties organic semiconductors. Numerous classes of organic semiconductors can be distinguished depending on their chemical backbone. In this thesis only a limited amount of organic semiconductors are used. Poly(triarylamine) (PTAA) and a quinquethiophene (T5) derivative are used as $p$-type organic semiconductors (see Fig. 1.5a/b). PTAA is used in chapter 3 as a amorphous air-stable organic $p$-type semiconductor. The T5 derivative is used to fabricate SAMFETs described in chapter 8. Commercial available small bandgap dyes, nickel dithiolene (NiDT) and a squarylium dye (SQ1) were used as single component ambipolar organic semiconductors (see Fig. 1.5c/d). The model compound NiDT was used to make air-stable ambipolar field-effect transistors as presented in chapter 2, 3, 5 and 6. SQ1 was used to fabricate light-emitting ambipolar organic field-effect transistors (LEOFET) as described in chapter 4.

1.3 Outline of the thesis

This thesis focuses on two topics. The first topic addresses ambipolar field-effect transistors, which allow to fabricate CMOS like logic and light emitting transistors via a simple fabrication process. A thorough experimental and theoretical investigation on the charge transport of ambipolar materials in field-effect transistors is presented. The work serves as a basis to understand the operating mechanisms of organic ambipolar field-effect transistors. The second part discusses self-assembled electronics, as the ultimate form to fabricate complex device structures via autonomous self-organization. Two different device architectures, \textit{e.g.} a molecular diode and a self-assembled monolayer field-effect transistor, are fabricated based on the process of self-assembly.
A detailed overview of the experimental methods, device fabrication, technological details and device characterisation is presented in each chapter separately. The work is divided in the following sections.

In chapter 2, a model is used to describe charge transport in disordered ambipolar organic field-effect transistors. The basis of this model was developed for disordered unipolar organic transistors. This model is extended to calculate all regimes in unipolar as well as ambipolar organic transistors. By applying it to experimental data obtained from ambipolar organic transistors based on a narrow-gap organic molecule excellent fits were obtained.

In chapter 3, a unified model is given describing the current-voltage characteristics and the potential profiles. The model is derived for unipolar field-effect transistors as well as ambipolar field-effect transistors. By performing scanning Kelvin probe measurements the validity of the models was benchmarked. Finally the potential profile of ambipolar field-effect transistors allows to visualize the recombination zone.

In chapter 4, radiative recombination was investigated in ambipolar near-infrared light-emitting organic field-effect transistors. Using the model developed
in chapter 2, the emission could be accurately described. A first tentative approximation of the width of the recombination zone is given.

In chapter 5, we extend the model used in the previous chapters by including a finite recombination rate. An analytical model is presented for the width of the recombination zone in ambipolar organic field-effect transistors. Numerical calculations validate the model. Surface potential and light-emission profiles of an actual ambipolar devices are in good agreement with the calculations.

In chapter 6, the feasibility of flexible CMOS-like logic is demonstrated by fabricating ambipolar field-effect transistors on foil. Using an air-stable ambipolar semiconductor, logic gate and ring oscillators were demonstrated to function in air and light over an extended period of time.

In chapter 7, alkanethiols on gold are used to fabricate two terminal molecular junctions. By structuring the devices and applying PEDOT:PSS as a top contact a yield of unity is obtained. For the first time integration and upscaling of molecular junctions is demonstrated based on a 150 mm wafer process technology.

In chapter 8, fabrication of self-assembled monolayer field-effect transistors (SAMFETs), a historical challenge, is demonstrated. By using molecules with a semiconducting core and a silane anchor group, densely packed monolayers on silicon dioxide are spontaneously formed. The SAMFETs exhibit large On/Off currents, high reproducibility and mobilities. A functional integrated circuit, in which hundreds of discrete transistors are addressed simultaneously, is demonstrated.

1.4 References

1. Lilienfeld, Device for controlling electric current, *US patent 1900018* (1928)


9. see http://www.polymervision.com

10. see http://www.plasticlogic.com


