1 Introduction

1.1 Organic Electronics

Electronics play an indispensible role in our daily lives. Due to the continuous evolution in materials processing technologies it became possible to imagine taking advantage of electronics in different areas and to find innovative applications. The most impressive and practical developments are seen in computers and microelectronics. The invention of metal-oxide-semiconductor field-effect transistor (MOSFET) in 1960 opened a new era in electronics, rendering today's computer technology possible, which still has not come to an end following the pace giving "Moore's Law" [1, 2]. Computing and data saving ability of computers increased rapidly. Today, billions of MOSFETs are a part of our every day lives; in our computers, cellular phones, cars, aerospace, medical systems, home entertainment and many other microelectronic devices. These successful implementations are based on the continuous improvement in the handling of the famous semiconductor, silicon.

Besides the high-performance applications, the knowledge gained from semiconductor technology triggered the research on new large-area and low-cost applications. An important example is the development of thin-film transistor (TFT) made of hydrogenated amorphous silicon. Amorphous silicon does not reach the performance of single crystal silicon due to their lower charge carrier mobility. They found applications in low-performance devices, e.g. display applications, where single crystal silicon can not be utilized [3]. Today, TFTs are the basic structures of active-matrix liquid crystal displays, which are replacing the classical displays and televisions. Another celebrated application of silicon is the solar cell. Solar energy gained a large amount of attention in the recent energy crisis and mass production of solar panels launched in industrial countries. Solar cells require large areas to benefit from sun light. Low-cost, low-performance silicon devices are therefore crucial to produce large area devices.

While the evolution in electronics was the main focus of interest, a new field of electronics was silently being launched in 1970s: the discovery and development of electrically conducting polymers [4]. These materials exhibit much lower charge carrier mobility compared to silicon, which results in a large response time and low switching speed, e.g. in a logic circuit. Organic semiconductors offer different, interesting properties that made them attractive for researchers. These materials are light, mechanically flexible, they can be synthesized at much lower temperatures, and they can be dissolved in organic solvents so that thin-films can be deposited by spin-coating or printing techniques.

Although conductivity was readily observed in various organic materials, it took about 10 years for the researchers to understand the properties of these materials and their appropriate preparation. First field-effect device based on electrochemically grown polythiophene film was presented in 1986 [5, 6]. Since then, a wide variety of new organic materials, both small molecules (oligomers) and polymers have been synthesized and investigated for their electrical properties [7-11]. Field-effect devices with mobility values higher than those of amorphous silicon were presented already in 1997 [12]. With their overall properties conducting polymers impressed the researchers. A new vision of producing low-cost electronic devices on flexible, inexpensive plastic substrates with fast and simple processing techniques was born. Within the last two decades, applications like RF-ID devices [13], electronic paper [14], active-matrix displays with organic light-emitting diodes (OLED) [14, 15], integrated circuits [16], chemical vapor sensors [17], electrochromic windows [18] and organic solar cells [19] are demonstrated. Most of these applications would not be realized with inorganic semiconductors. Moreover, simple applications that use printed organic devices, like electronic card games, are already in the market [20].

"Organic electronics" has become one of the most popular research fields today, being explored by interdisciplinary research groups and institutions [21]. Applications like RF-ID tags, OLED displays and organic solar cells gained much attention since the potential applications have large markets that offer the potential of very high volume production. Therefore, the main driving force of this field is the manufacturing of low-cost products by using, e.g., large-area printing techniques. A forecast made by IDTechEx, a consulting company specialized on electronics, recently reported about a business size of around $250 billion by 2025 [22].

Printed RFID tags find different applications like product identification, brand protection, electronic tickets, etc. These applications belong to the group also named as "disposable electronics" or "one-way electronics", and require extremely low-cost processing techniques. Today the RFID technology is being used in pallet-level tagging in logistics where the costs of used silicon chips are over $0.20. The idea of replacing even the optical bar codes on every product with RFID tags seems to be possible provided that the chips cost less than $0.01, which can be realized by large-area printing techniques [23].

Similarly flexible displays have attractive applications like wearable lightweight information displays and wall-size displays like wallpapers. Several companies have already demonstrated prototypes of flexible organic displays [24-26]. Another very interesting application, organic solar cells, attracted serious attention after the recent improvements in conversion efficiency [19]. Although presented efficiency values are lower than that of silicon-based devices and the organic materials exhibit a limited lifetime, organic solar cells offer exciting capabilities. Since they are transparent and flexible, they can easily be applied over windows of high buildings enabling every building to produce its own electricity. Also the lower manufacturing costs offer the opportunity to cover very large areas with solar cells and produce remarkable amount of electricity. Considering the wide range of applications including flexible lightweight batteries, organic logic memories, corrosion protective coatings, etc., it can be concluded that organic electronics surely is one of today's most interesting research topics, and will be future's one of the most exciting technologies.

However, to achieve more complex applications like RF-ID tags, performance of devices needs to be further improved. Since large-area processing of multilayer structures brings significant limits to materials and configuration, performance of the devices does not reach the level of laboratory test devices. The challenges to overcome towards the commercialization of organic devices determine the direction of research in this field. They can be summarized together with their consequences as follows:

- Low charge carrier mobility → high operating voltages, low switching speed
- Sensitivity of organic materials to atmospheric conditions → short life time
- Difficulties in low-cost processing of functional films with fine structures → high operating voltages
- Reproducibility

Accordingly, research on OFETs can basically be classified into three groups, which have to be considered in close correlation. These groups with their respective research area can be listed as follows:

- Materials and interfaces → performance (mobility), reproducibility, chemical stability
- Device physics → determination of material requirements
- Processing technology → fine electrode structures, reproducibility

This thesis elaborates on organic field-effect transistors (OFET), which are the basic structural units in organic electronic devices (RFIDs, displays, memory devices, etc). Possibilities to improve device performance and to decrease the processing temperatures were investigated. Especially materials aspects are examined in details. New materials are introduced and organic devices with novel gate insulators are presented. The next section briefly introduces challenges and actual topics in OFET research to give a motivation about this study, whereas detailed information on the development of OFET research can be found in chapter 2.

1.2 Scope of thesis

Organic field-effect transistors are among the most intensively studied organic devices. Since their introduction in 1986, electrical performance of organic field-effect transistors increased continuously. Improving the performance of OFETs by optimizing organic semiconductor and dielectric materials is known to be an effective and useful route towards low-cost solution-processed devices. Electrical performance of discrete films of semiconductor and dielectric, as well as their cooperation at the interface is the key to improved properties, such as charge carrier mobility and threshold behavior. Downsizing the device dimensions, such as channel length L and width W; or introducing very high performance inorganic layers also improve the device performance and help discovering the limits of organic devices. But the applicability of downsizing in low-cost, large-area devices is questionable. Therefore solution-processed systems, using low temperature and simple processing techniques are selected for this study.

<u>Semiconductors</u>

It is known that small molecule semiconductors, like pentacene, exhibit higher performance compared to soluble polymers. Due to the small molecule size, crystal grain sizes in range of micrometers can be reached, which enhances the charge transport. However small molecules require vacuum evaporation methods for the film deposition, which are more complex, slow and expensive (see chapter 2). One very promising group of semiconducting polymers come from polythiophenes; poly(3-alkylthiophene) (P3AT). P3ATs offer high field-effect mobility due to their ordering properties and the possibility of wet chemical processing. This group of polymers has been applied in OFETs since 1996 and their properties were readily explored to a certain extent when this study has started (see chapter 2). Therefore a member of this polymer family was chosen for this research, which is **poly(3-hexylthiophene) (P3HT)**. Organic transistors with inorganic and organic dielectric materials were investigated. Effects of material purity, interfaces, processing solvents, annealing conditions and interaction with the atmosphere on charge carrier mobility and device characteristics are the subjects covered in this study.

Gate insulators

Earlier studies on organic transistors focused almost exclusively on the performance of organic semiconductors. Results pushed the performance of organic devices into the range of amorphous silicon TFTs [12, 27]. Due to the advancement in the understanding of charge transport and charge injection, the research was extended to materials for source and drain contacts and substrate surfaces [28]. There were only several publications concentrating on polymeric gate insulators until the early 2000s. Most of these reports were limited to demonstration of novel devices. Comprehensive research and insight about the influence of dielectric materials were not addressed (see ch. 2). Additionally, from the wide variety of polymers, a limited number of materials were investigated as gate insulators. The studies generally did not focus on a detailed materials selection, but the reported materials were used because they were well established or reported before. However, perhaps the material with the greatest effect on device and semiconductor performance is the gate dielectric. Many years of intensive research was necessary until this became clear and many research groups concentrated on gate insulators [28-31]. Detailed information about recent developments and influence of dielectrics on device performance is discussed in chapter 2.

The extent of studies and reports on gate insulators were very limited when this research has started. This was the driving factor to focus on gate insulators and materials related aspects of OFETs. The method of systematic materials selection and design was followed to improve the electrical performance of devices and to understand solvent and interface related phenomena in OFETs [31, 32]. The innovative scientific achievement established within this study is the introduction of novel insulating materials including thermosetting thin-films as well as ferroelectric, high-*k* nanocomposites to OFET research. The work addresses the requirements for a gate insulator in a bottom-gate transistor and corresponding materials selection process. The application of selected insulators in OFETs by optimizing film-processing conditions and investigation of interface issues conclude this work.

Another remarkable accomplishment achieved within this work is the participation of the Hamburg University of Technology (TUHH) in a large scale scientific industrial project, “MaDriX”, under The Federal Ministry of Education and Research (BMBF – Bundesministerium für Bildung und Forschung). The research on new printable materials and devices leaded to results that were interesting for industrial institutions working on printed electronics. As a consequence, the Institute of Optical and Electronic Materials of TUHH now participates in a € 15 million project as a sub-contractor of Elantas Beck, together with other industrial companies and universities [33].

The main research topics this study aims to cover are:

- Understanding the device physics and improvement of the performance of hybrid transistors by the optimization of semiconductor processing and dielectric/semiconductor interface
- Systematic selection of new materials for simple solution-processed gate insulators
- Exploring the electrical insulation performance, size limits and surface properties of the selected insulators and their optimization for the selected OFET configuration
- Investigation and comparison of device performance based on material properties, surfaces, solvents and processing parameters
- Preparation and modification of new high-*k* nanocomposite materials for the reduction of operating voltages
- Demonstration of an all-polymer field-effect transistor by the selected materials
- Demonstration of memory retention and hysteresis behavior in solution-processed ferroelectric OFETs

1.3 Structure of thesis

This thesis is composed of six chapters. First chapter is an introduction on organic electronics and organic field-effect devices. Second chapter gives the theoretical background on conducting polymers and the technology of organic field-effect transistors. It also includes parameter extraction in organic field-effect devices. Chapters 3, 4 and 5 are about the main experimental work realized in this research. In chapter 3 hybrid devices are discussed where the electrical properties of semiconductor P3HT were characterized. Influence of purity, annealing conditions and processing solvents are investigated. Chapter 4 deals with gate insulators, including materials selection and electrical characterization of both the insulation layers and OFETs with these insulators. Importance of semiconductor/dielectric interface is addressed. In chapter 5 solution-processed ferroelectric functionalized OFETs are presented. Ferroelectric poly(vinylidene fluoride) based copolymer was blended with barium titanate nanopowder to reach high dielectric permittivity values, which helps sinking the operating voltages without disturbing the ferroelectric functionality. The final chapter concludes the work and addresses further suggestions for the future work.