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Cross-linked Polymers as Dielectrics for Organic Field-effect Transistors

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1. Introduction

Organic electronics are getting more and more interest from industrial companies and research groups in the last years since they enable many new applications, which could not be realized by inorganic materials [1–7]. Flexible displays [1], large-area sensors [1], light-emitting large surfaces [8], printable radio-frequency identification tags (RFID) for packaging or logistic industry [2] and many other systems which require flexible, large area and low-cost electronic devices are now developed for the near future or even already commercialized. Organic light-emitting-diode (OLED) displays, for example, are now implemented in portable devices and have higher performance than the traditional LCD displays [9]. OLED displays are self illuminating and do not need back lightening, therefore they have higher brightness, contrast and viewing angle in comparison to LCD displays [9]. Many electronic devices producers implemented OLED displays in their high-end smartphones and SLR cameras [10], and recently LG (a Korean company) introduced a 55-inch OLED television [11]. Large-area solar cells based on organic materials have also found their way to commercialization [12].

All of these innovations were only possible after the introduction of organic conductors and semiconductors. Organic (semi)-conductors have the advantage of their low-cost processing technologies (e.g. printing or spray-coating). However, they have lower electrical conductivity, free charge carriers mobility [13] and packaging density than their inorganic counterparts. Therefore they are normally used in low-cost and low-performance applications, except in the case of OLED where they have clear advantages compared with other technologies.

In order to produce fully flexible devices, elementary devices for electronic circuits (e.g. transistors and diodes) need to be made with flexible materials. The performance of these devices needs to be enhanced and their fabrication processes should be optimized to ensure their commercialization as switching elements in OLED displays or in other circuits. These tasks are principally a material issue, that means new materials with higher performance and easier processability are sought after.

Most of the work done in this direction is devoted to synthesize new semiconducting materials with higher mobility and solution-processability. Parallel to these investigations, new dielectric materials with good dielectric properties even in thin films, solution-processability and good interface properties to the semiconductors should be developed. Cross-linked polymers are advantageous for organic field-effect transistors (OFETs) because of their electrical and chemical properties, specially their high volume resistivity and their stability towards solvents, acids and bases. This work shows that the application of cross-linked materials can also reduce or even eliminate the use of the volatile organic compounds (VOC), for which legal limitations are yearly augmented.

1.1 Scope of the thesis

The main goal of this work is to find new dielectric materials for top-gate OFETs. The top-gate configuration was chosen for its benefits for the production of OFETs (see section 2.1 for more details). The dielectric materials should have the following properties:

- Good electrical properties, in particular high volume resistivity
- Solution-processibility to enable low-cost production of OFETs
- Cross-linking so that another solution-processed layer could be deposited on it
- Fast cross-linking reaction to be suitable for high throughput production technologies (e.g. printing)
- Low-temperature processibility to be usable with flexible substrates based on plastics
- Good interface with the semiconductor to have high-performance transistors
- Low or no use of VOC

1.2 Background and guidelines of the thesis

The importance of developing new cross-linked dielectrics for OFETs was noticed after the participation of the institute of optical and electronic materials (OEM) to a € 15 millions scientific and industrial project, “MaDriX”. The goals of this project were to: develop printed circuits for RFID, ensure reproducibility, develop

techniques for inspection during the production of the circuits and optimize the characterization techniques of printed devices. Different global companies (ELANTAS Beck GmbH, BASF, Evonik Industries AG, PolyIC GmbH & Co. KG and Siemens AG), universities and research institutes with expertise in chemistry, materials for electronics, device development, measurement techniques and in printing were involved in this project. OEM had the task to evaluate dielectric materials developed by ELANTAS Beck GmbH as OFET dielectrics. As other partners were also working on new materials for OFETs, one reference "standard" transistor was needed to compare results. The standard transistor was produced using the same materials and processes by all the partners. The devices were characterized also by standard system using the same measurement parameters, e.g. sweep rates and voltage values. The geometrical structure of the transistors was also standardized. In order to investigate a new dielectric for example, a transistor is fabricated using the new dielectric and the other standard materials in the standard geometry. The fabricated transistor is compared with the standard transistor using the standard characterization system. To be able to directly compare results achieved in different labs, it was necessary to ensure that the different groups measure the same characteristics of the standard transistor in their labs.

In this work, new dielectric material classes, which were not covered by the "MaDriX"-project and which might be fast cross-linked, are investigated. The idea of using a reference transistor was adopted to this study. Uncross-linked polymers were used as comparing reference for the presented materials. The semiconductor used in all the experiments was taken from the same batch to avoid quality fluctuation between different batches. The fabrication process of the devices and the techniques of their characterization are the same for all the devices. Silicon-wafers, functionalized with hexamethyldisilazane, were used as reproducible and reliable substrates.

The characterization of the new cross-linked dielectrics began with the monitoring of their curing reactions, followed by the measurement of their dielectric properties. The study of the interface between the dielectric layer and the semiconductor should be done as part of the selection process. Many classes of materials should be excluded from the selection because of the quality of their interface with the semiconductor, if the low quality of the interface is caused by intrinsic properties of the material. After the characterization of the interface with the semiconductor in a metal-insulator-semiconductor capacitor, transistors were fabricated using the selected dielectric materials.

The characterization of some of the selected and developed dielectric materials were carried by supervised students during their study projects [14, 15] using the previously defined scheme of experiments explained above.

1.3 Structure of the thesis

This work is composed by eight chapters. After the introduction, a theoretical background on OFETs, organic semiconductors and the interfaces between the different layers in OFETs is given. Then, the methods and the experiments used to fabricate and to characterize the devices are shown. The fourth chapter presents the polymers used in this work and their cross-linking mechanisms. In the fifth chapter, dielectric materials based on linear polymers are studied. Then, two different thermally cured polymers were investigated. The seventh chapter deals with photo-curable polymers which were cured very fast and showed good properties in transistors. Conclusions and suggestions for future investigations are presented in the final chapter.

2. Organic field-effect transistors

2.1 Field-effect transistors

A transistor is an elementary electronic device with three electrodes called: gate, source and drain. The current flowing between the source and the drain is controlled by the voltage or current applied to the gate electrode. Therefore, transistors are used in electronic devices as switches or amplifiers. The possibility of miniaturizing solid-state transistors enabled the production of high-density integrated circuits. There are two main classes of transistors: bipolar transistors and field-effect transistors (FETs). The functionality of the latter one will be further explained in this section. There are many possible structures to realize FETs, basically they differ from each other in the way how the controlling electrode (gate electrode) is separated from the semiconductor, for example the gate electrode is separated from the semiconductor by an oxide in metal-oxide-semiconductor FET (MOSFET), by a p-n junction in junction FET and by a Schottky-barrier in metal-semiconductor FET (MESFET). All of these devices are based on crystalline silicon. In 1976, Neudeck *et al.* presented a thin-film transistor (TFT) made with amorphous silicon [16]. The main application of TFTs is as switching elements in active matrix liquid crystal displays. Ten years later, Tsumura *et al.* presented the first polymer-based FET [17]. The presented device consists of a polythiophene electrochemically polymerized between two electrodes. The substrate was a thermally grown SiO_2 on a silicon wafer, the silicon and the oxide play the role of the gate electrode and the insulator. This configuration is widely used to characterize organic semiconductors and to fabricate OFETs.

An OFET can have many possible configurations depending on the order of the deposition of its composing layers. An OFET is called "top-gate" transistor when the dielectric layer is deposited on the semiconductor. Top-contact OFETs have source and drain electrodes deposited on the semiconductor. Fig. 2.1 shows the

four possible configurations of OFETs. Electronic and processing aspects should be taken in account during the choice of the appropriate architecture. In bottom-contact configuration, for example, standard processes of photo-lithography could be used to structure the source and drain contacts. The semiconductor is then not exposed to the developing and stripper solution. In the top-gate configuration the dielectric layer and the gate electrode are covering the sensitive semiconductor and in this way protect it from the environmental degrading species [3]. In addition to that, the gate dielectric does not play the role of a substrate for the semiconductor. Two kinds of insulating materials are needed for this configuration: one material with good dielectric properties and good quality interface to the semiconductor and another material acting as substrate and ensuring good orientation of the semiconductor chains for high free charge carrier mobility. In bottom-gate transistors all of these roles should be ensured by a single material, which limits the choice of appropriate materials. In top-gate configuration the two functionalities could be optimized separately.

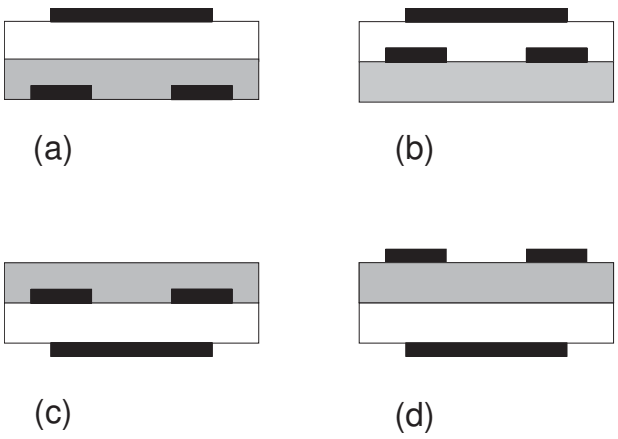

Figure 2.1: Schematics of different OFET configurations (a)top-gate bottom-contacts (TG-BC) (b) TG-TC (c) BG-BC (d) BG-TC. (Metals in black, insulator in white and semiconductor in grey)

The basic principle of function of FETs is that an electrical field can change the density of free charge carriers in the surface of a semiconductor and therefore, also its conductivity. OFETs operate in accumulation regime, it means that the channel induced at the surface of the semiconductor is built with the majority free charge carriers of the semiconductor, i.e. if the semiconductor is p-doped than the channel

is formed by holes. The models and theories adopted for MOSFET, which operates in inversion-regime, still however applicable to OFETs.
The drain current I_d could be described by two equations depending on the operation regime of the FET [18]:

$$- I_{d,lin} = \frac{W}{L} C_i \mu \left(V_{gs} - V_{th} - \frac{V_{ds}}{2} \right) V_{ds} \qquad \text{if } V_{ds} < (V_{gs} - V_{th}) \tag{2.1}$$

$$- I_{d,sat} = \frac{1}{2} \frac{W}{L} C_i \mu \ (V_{gs} - V_{th})^2 \qquad \text{if } V_{ds} > (V_{gs} - V_{th}) \tag{2.2}$$

where $I_{d,lin}$ and $I_{d,sat}$ are the drain current in the linear and saturation regimes respectively, W and L are the channel width and length respectively, μ is the field-effect mobility of the semiconductor, V_{ds} is the drain to source voltage, V_{gs} is the gate to source voltage, V_{th} the threshold voltage and C_i is the capacitance per unit area of the insulator. The transfer characteristic (I_d vs. V_{gs}) is generally used to extract important transistor parameters i.e. field-effect mobility, on/off ratio, V_{th} and sub-threshold swing, as shown in Fig. 2.2. The on/off ratio means the ratio between the currents at the "on" state and the "off" state of the transistor (Fig. 2.2 a). The sub-threshold swing (S) is proportional to the average of the traps at the semiconductor-insulator interface N_{ss}, as shown in the following equation [19]:

$$N_{ss} = \left[\frac{S \ log(e)}{kT/q} - 1 \right] \frac{C_i}{q} \tag{2.3}$$

where e is the Euler's number, k the Boltzmann constant, T the temperature and q the elementary charge. The on/off ratio and the sub-threshold swing could be read from the logarithmic transfer characteristic. The field-effect mobility and the threshold voltage are generally extracted from the slope of the transfer characteristic (I_d vs. V_{gs}) in linear regime or the square rooted transfer characteristic in saturation regime of a FET. However, it was already observed, that the transfer characteristic of amorphous-silicon thin-film-transistors could not be fit with the equations 2.1 and 2.2, because of the dependency of the mobility on the gate voltage [20]. Similar behavior was also observed in OFETs. After Horowitz *et al.* the field-effect mobility could be described by this equation:

$$\mu = \mu_0 \, (V_{gs} - V_{th})^{\gamma} \tag{2.4}$$

where μ_0 and γ are empirical numbers [21]. They mentioned that this power-law dependence could be also derivated from the model presented by Vissenberg and Matters, in which the charge transport is governed by the hopping between exponentially distributed localized states [22].

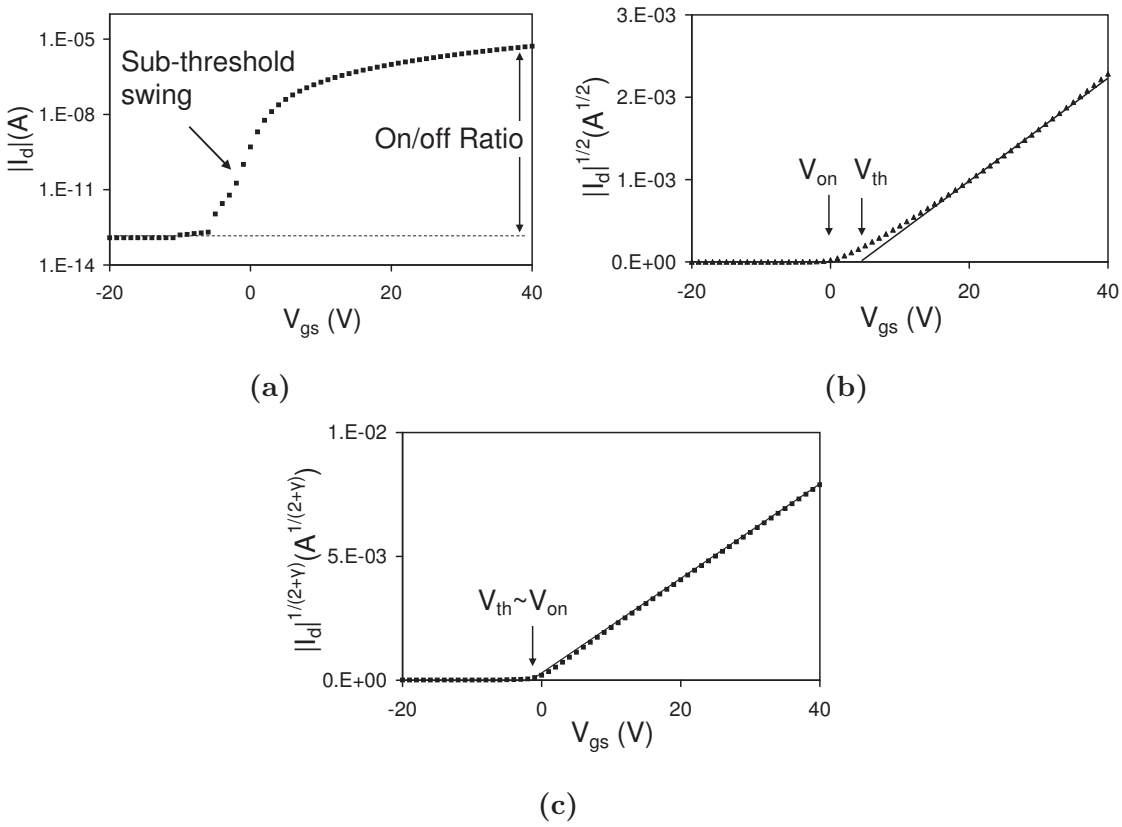

Figure 2.2: (a) logarithmic, (b) square rooted and (c) to $1/(2 + \gamma)$ powered transfer characteristics of an OFET.

In their model, the field-effect mobility is proportional to $(V_{gs} - V_{th})$ raised to $\left(\frac{T_c}{T} - 1\right)$ where T is the temperature and T_c is a parameter indicating the width of the exponential distribution of the states. γ is then a parameter describing the width of this distribution. The drain current in linear regime is then equal to:

$$I_{d,lin} = \frac{W}{L} C_i \mu_0 \left(V_{gs} - V_{th}\right)^{\gamma} \left(V_{gs} - V_{th} - \frac{V_{ds}}{2}\right) V_{ds} \qquad \text{if } V_{ds} < \left(V_{gs} - V_{th}\right) K \quad (2.5)$$

and in saturation regime to:

$$I_{d,sat} = \frac{1}{2+\gamma} \frac{W}{L} C_i \mu_0 \left(V_{gs} - V_{th}\right)^{2+\gamma} \qquad \text{if } V_{ds} > \left(V_{gs} - V_{th}\right) K \quad (2.6)$$

where $K = \left(1 - \sqrt{\frac{\gamma}{2+\gamma}}\right)$. It is noticeable that the value of V_{ds} separating the linear and saturation regimes is changed by the factor $K = \left(1 - \sqrt{\frac{\gamma}{2+\gamma}}\right)$, which means that the transistor is already in saturation regime at drain to source voltages lower than $(V_{gs} - V_{th})$. The drain current should be then raised to $\frac{1}{2+\gamma}$ in order to extract the field effect mobility and the threshold voltage (Fig. 2.2 c). In this curve, the extracted threshold-voltage is near the onset-voltage as in the case of the ideal FET.

2.2 Organic semiconductors

2.2.1 Origin of conductivity in conjugated polymers

Organic materials were introduced first in electronic devices as insulators or as packaging materials, because of their good insulation, processability and mechanical properties. In 1977, it was discovered that an insulating polymer, trans-polyacetylene, with low conductivity ($10^{-3}\ S\,cm^{-1}$) becomes highly conducting after exposure to an oxidizing agent [23]. After this breakthrough in the area of conducting organic materials, other polymers with the same properties were discovered, for example poly(p-phenylene), polypyrrole, polythiophene, polyfuran and their derivatives. Many of these materials are used as semiconductors in the undoped state, for example, the first presented OFET was based on undoped polythiophene [17].

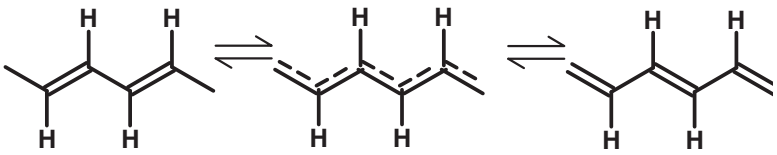

Figure 2.3: The two degenerate A and B phases of *trans*-polyacetylene.

The (semi-)conducting organic materials are based on conjugated systems, that means they contain alternating single and multiple bonds [24]. The "backbone" of the polymer is built by in-plane σ-bonds. Every carbon atom of the conjugated chain still has one unpaired electron (π electron). The orbitals of the π electrons of adjacent carbon atoms overlap and build the π-bond, which leads to an electron delocalization along the polymer. The full bonding orbital (π-bond) and the empty anti-bonding orbital (π^*-bond) correspond to the highest occupied molecular orbital (HOMO) and to the lowest unoccupied molecular orbital (LUMO) respectively. The existence of such bands is one requirement to have electrical conductivity. The other requirement is to have free charge carriers in the material. In inorganic semiconductors, free charge carriers are generated by taking electrons from the valence band (generation of holes) or by donating electrons to the conduction band. The molecular structure of an organic polymer has high interaction with the charge added to it [25]. Because of this interaction, quasi-particles are expected to be responsible for the electric conductivity in organic polymers.

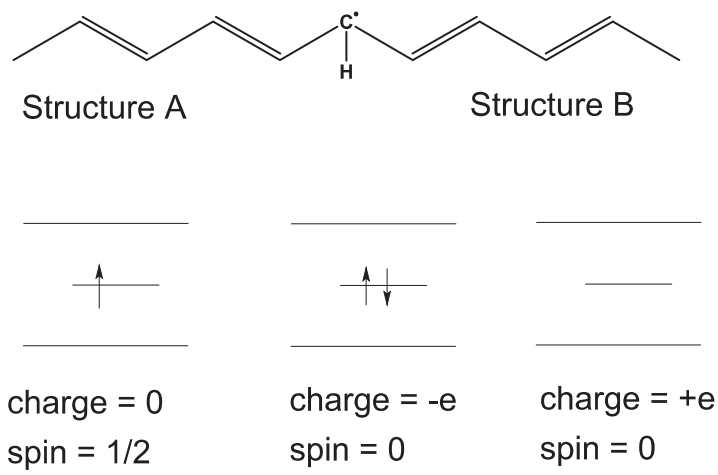

Figure 2.4: Structure of a soliton in a *trans*-polyacetylene and its gap state occupancies in dependence of its charge [24].

The conducting polymers could be divided into two different classes: polymers with degenerate ground state and polymers with non-degenerate ground state. trans-Polyacetylene is a polymer with a degenerate ground state, i.e. it has two geometric structures A and B having the same total energy (see Fig. 2.3) [24]. These two structures, in which the double bonds are shorter than the single bonds, are more stable than the structure with equidistant carbon atoms because of the Peierls instability [24]. When a defect in the bond alternation occurs, a carbon atom would have an unpaired electron and it will separate two branches of the polymer having the two different structures A and B (see Fig. 2.4). These defects are called solitons, the unpaired electron would have a new energy level at the mid gap [24, 26]. The neutral soliton has a spin of 1/2, since the carbon atom is occupied with only one electron. The soliton has no spin when it is positively or negatively charged (see Fig. 2.4) [24].

All the other conjugated systems have non-degenerate ground states [26]. In these polymers, other quasi-particles are responsible for the electrical conductivity: polarons and bipolarons. Polarons could be presented as a neutral soliton associated with a charged soliton, and the bipolarons as the association of two charged solitons [24]. Polythiophenes, for example, are conjugated polymers with a two non-degenerate ground states: an aromatic and a quinoid structures (Fig. 2.5 a,b) [26].