SEMINAR

Organic Semiconductor Thin Film Transistors

Author: Tomaž Mlakar
Adviser: Dr. Gvido Bratina
Nova Gorica Polytechnic

Ljubljana, May 2004
Abstract

In recent years, significant advances have been made in the field of organic semiconductors. These materials are basic building blocks of a number of devices such as organic light-emitting diodes and particularly organic thin film transistors on which this seminar focuses. The fundamental properties of organic semiconductors (materials, bonding and charge transport) are described in the first part. The second part focuses on organic thin film transistors. It describes the basics of transistor operation, the structure and fabrication of organic FETs and its main characteristics. The last part presents the different possible applications of organic transistors and also addresses the main problems that need to be solved in order to utilize the potential that these devices possess.
Contents

1 Introduction 4

2 Organic Semiconductor Fundamental Properties 5
   2.1 Bonding and Structure of OS . . . . . . . . . . . . . . . . . . . . . 5
   2.2 Charge Transport in OS . . . . . . . . . . . . . . . . . . . . . . . . 7

3 Organic Thin Film Transistors 9
   3.1 Structure and fabrication . . . . . . . . . . . . . . . . . . . . . . . . 10
   3.2 Characterization of OTFTs . . . . . . . . . . . . . . . . . . . . . . . 11
   3.3 Applications of OTFTs . . . . . . . . . . . . . . . . . . . . . . . . . 13

4 Conclusion 14

5 References 15
1 Introduction

Transistors that use organic semiconductors (OS) as the active layer are steadily approaching amorphous silicon transistors in terms of performance. These organic devices are presently of great interest because they possess many benefits over their silicon counterparts, including lower cost, greater durability and compatibility with glass and plastic substrates [1]. Organic thin film transistors (OTFTs) have great promise in electronic applications. Perhaps the most attractive application for OTFTs is displays, where they can be used as switching devices for active-matrix flat-panel displays (AMF-PDs) based either on liquid crystals or organic light-emitting diodes (OLEDs). Given their compatibility with polymeric substrates, OTFTs may enable the production of flexible computer screens. Other applications of OTFTs include smart cards and electronic identification tags.

Because of the relatively low mobility of the organic semiconductor layers, OTFTs cannot yet compare to field-effect transistors based on single-crystalline inorganic semiconductors (Si, Ge) in this respect. Consequently, OTFTs are not suitable for use in applications requiring very high switching speeds. The characteristics of OTFTs suggest that they are more suitable for applications requiring large-area coverage, structural flexibility and low-temperature processing [2].

This seminar first describes the basic properties of organic semiconductors which are responsible for the above mentioned characteristics of OTFTs. More information about organic molecular crystals can be found in the seminar by Primož Rebernik. The characteristics of organic semiconductors mainly originate in weak interactions between molecules and in the way charge is transferred. Charge transport in polymers is also discussed in the seminar on OLEDs by Simon Rankel. The next part focuses on the structure and fabrication of OTFTs and the final part describes the characteristics of a typical OTFT.
2 Organic Semiconductor Fundamental Properties

In order to study organic transistors we first describe the properties of the organic layer in these devices. The basic building blocks of organic semiconductors are organic molecular crystals (OMCs). They are formed by molecules which interact with the relatively weak Van der Waals forces. The most common OMCs are polyacenes, perylenes and pyrenes. Another type of organic semiconductors, those based on conjugated polymers has rapidly been developing in recent years. Polymers are very common materials in our every-day lives. From an electrical point of view, polymers have long been considered as insulators. Conducting polymers can be of metallic or semiconductor nature yet keeping the mechanical flexibility and they can be processed with plastic manufacturing techniques.

2.1 Bonding and Structure of OS

Organic molecular crystals and polymer crystal-like structures are formed via three different types of weak Van der Waals interactions [3]: orientational forces between polar molecules, induction forces between neutral and polar molecules and the dispersion forces between neutral molecules. The binding energies of these interactions (\(10^{-3} - 10^{-2} \text{ eV}\)) are significantly smaller than the corresponding energies in covalent crystals (few eV). The bonding energy between two dipoles is:

\[
U_{d-d} = -\frac{2}{3kT} \frac{p_1^2 p_2^2}{r^6},
\]

where \(p_1\) and \(p_2\) are the dipole moments and \(r\) the distance between the dipoles. If a polar molecule with a permanent dipole \(p_1\) induces polarity in a neutral molecule we get a bound state and the mean energy of this interaction is:

\[
U_{ind} = -\frac{2p_1^2 \alpha_2}{r^6},
\]

where \(\alpha_2\) is the polarizability of molecule 2. In order to understand the dispersion interactions between molecules we first have to describe the localization of electrons in a typical molecule of an OS. The simplest example is benzene, which is the basic building block of the above mentioned common OMCs and other polyacenes. Each of the six carbon atoms in a benzene ring forms three coplanar \(sp^2\) orbitals and two of these orbitals form \(\sigma\)-orbitals with the two neighbour carbon atoms. Perpendicular to this plane a \(2p_z\)
orbital is formed. The $2p_z$ orbitals of the six carbon atoms form the $\pi$-orbital (Figure 1). This orbital contains six $\pi$ electrons which are delocalized in the molecule and can thus propagate electrical signals through the molecule [4]. These delocalized electrons can form short-lived multipole moments, which can induce polarity in neighbouring molecules. This phenomena is known as the dispersion interaction and is usually caused by $\pi$ electrons.

![Figure 1: Benzene molecule (a) with the $sp^2$ orbitals (b) and the $2p_z$ orbitals (c).](image)

The other type of material that is used for OS are polymers. Polymers are composed of long chains of monomers, i.e. the molecule units that are linked to each other via carbon bonds. A few examples of these polymers are MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-vinylenephenylene]), CN-PPV Poly[2-(6-cyano-6-methylheptyloxy)-1,4-phenylene]) (Figure 2) and PEDOT (Poly-3,4-Ethynledioxythiophene) (Figure 3).

![Figure 2: CN-PPV polymer.](image)  
![Figure 3: PEDOT polymer.](image)

When the carbon atoms in these polymers have $sp^3$ hybridization, all four valence electrons reside in single bonds and the polymer is an insulator. However, if the carbon atoms possess $sp^2$ hybridization, the fourth electron
occupies the $p_z$ orbital perpendicular to the plane of $sp^2$ orbital and forms the $\pi$-bands. The $\pi$-electron delocalization along the chain determines the electronic properties of the material. The quasi-one-dimensional structure of a polymer is inclined to distort spontaneously, which is known as the Peierls distortion [5]. This in turn lowers the electronic energy and increases the elastic energy of the chain so the system becomes a semiconductor. After the distortion the polymer becomes conjugated (alternation of single and double bonds) which can be seen in the case of polyacetylene (Figure 4).

![Figure 4: Polyacetylene with conjugated bonds.](image)

2.2 Charge Transport in OS

Detectable electrical conductivity can be found mainly in molecular crystals containing molecules with polyconjugated bond system such as aromatic hydrocarbons (benzene) and other conjugated compounds and polymers. The $\pi$ electrons in these compounds are potential sources of free charge carriers.

In inorganic crystalline semiconductors the energy states of charge carriers are described in terms of the valence and conduction band. If a charge is in the conduction band it is virtually free and delocalized. This so-called band model for electron energy states in inorganic crystal lattices is a consequence of the large number of atoms that form the lattice. Each atom contributes its energy states (orbitals) to the lattice but because of their large number, the states overlap and they cannot be distinguished from each other [6].

This is not the case in organic semiconductors. The charge carriers are localized on the molecules (or polymer strings) and have discrete energy states. If we put two $\pi$ electrons in each energy level (Pauli’s principle) from the lowest level up, the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular level (LUMO) corresponds to the semiconductor energy gap. This distance between the valence band and conduction band is much too large to allow for free carriers to be generated at room temperature. For that to happen, an electron would have to acquire huge thermal energy to make the jump to the conduction band. There are still some ways that we can have free carriers in the polymer: injection of
carriers from metallic electrodes or materials with large amounts of free carriers (for example silicon, or a conducting polymer), optical excitation and doping. The levels of the dopant can be much closer to either band and free electrons or free holes are more easily generated even at low temperatures [7]. The doping can be performed by transferring charge by reduction or oxidation. Some examples of dopants are chlorine, bromine, iodine, AsF$_5$ and aqueous acids.

Another consequence of the localization of charge is the charge-lattice interaction. The molecule (or monomer chain) accommodates the introduced charge by adjusting the elastic energy. This deformation of the lattice around the charge is called a polaron and acts as a quasiparticle charge carrier. In conjugated polymers polarons can also form solitons. Solitons are bond alternation domains along the chain with a length of about 15 bonds (Figure 5) and can also act as charge carriers [8].

![Figure 5: Soliton in polyacetylene [8].](image)

Compared to the performance of the inorganic crystalline semiconductors, organic semiconductors have considerably low mobilities (0.1 - 1 cm$^2$/V·s compared to 10 - 100 cm$^2$/V·s for inorganic semiconductors). This is due to the charge-lattice scattering and charge localization. A charge localized on a molecule or polymer chain has to jump from one site to another in order to contribute to the transport. This process is called hopping transport and has not yet been described with complete model, one that would completely explain the phenomena. Two of the simplest models that exist describe hopping as quantum-mechanical tunneling through intermolecular barriers and as thermally activated barrier crossing, respectively. In some cases a transition from hopping to band model was observed at very low temperatures where scattering is virtually non-existent.

An organic semiconductor is a quasi-crystalline structure, i.e. is composed of grains. At the interfaces of the grains, high densities of trap states exist. Traps could be described as ”potential holes” and are mostly formed near impurities or on borders of crystal domains (higher ordering helps to decrease
their number). The trap levels place another restraint on the mobility and most of the time determine the performance limits.

3 Organic Thin Film Transistors

In order to assemble an organic transistor, basic principles of its operation must be known. Almost all organic transistor designs reported in literature are field effect transistor (FET) designs. In contrast to the bipolar n-p-n or p-n-p transistors, FETs are unipolar transistors. Unipolar transistors use only one type of semiconductor channel which is called p-channel or n-channel, depending on the type of majority carriers. The semiconductor layer is placed between or onto two electrodes, the source and drain (Figure 6).

![Figure 6: An example of an OFET. [9].](image.png)

A third electrode, the gate electrode, is used to determine the amount of charge carriers in the semiconductor channel layer via the gate voltage [6]. The gate electrode is separated from the semiconductor by a dielectric. A FET can operate in different regimes; in the depletion regime, a depletion zone is formed near the surface of the semiconductor in which the majority charge carriers are pushed away and only the fixed ions remain. Most organic thin film FETs use the accumulation regime, where the gate voltage is used to lower the energy levels in the organic semiconductor (Figure 7). When the gate voltage is zero, the only charge carriers present in the semiconductor are those injected from the metal electrodes and those that are thermally excited from HOMO to LUMO. The charge carrier density in this case is very small. By raising the gate voltage, the energy levels are lowered below Fermi level. This significantly increases the charge carrier density in the conducting energy states.

When we apply a voltage $V_{SD}$ (typical values are in the order of 10 V) between the source and drain electrodes, a current flows through the semi-
conductor. The voltage on the gate electrode \((V_G)\) in fact determines the conductivity of the semiconductor channel and consequently the source-drain current.

### 3.1 Structure and fabrication

Organic thin film transistors are designed in two major ways \([8]\). Figure 8 shows the schematic view of the top contact and the bottom contact layouts.

For the top contact layout, the semiconductor is deposited on the insulator, then the source and drain contacts are placed. The semiconductor is deposited on the contacts for the bottom contact transistor layout. The
bottom contact device is easier to fabricate, however the device performance is limited due to the poor quality of organic semiconductor film deposited at the interface of the contacts and the channel. The substrate can be rigid like a silicon wafer or glass as well as a flexible material like plastic [8]. In the case of silicon on glass, the gate metal is deposited using lithography. Then insulators such as $\text{SiO}_2$ or similar can be incorporated. For most of the flexible substrates, high temperature processing steps cannot be used. New techniques using conventional printers or photochemical processes were developed to pattern the metal electrodes. The insulating layers can be stamped or spin-coated on flexible substrates.

The way the semiconductor layer is deposited has a major effect on the device performance. The two main deposition methods are [8]:

- **Vacuum deposition**: The materials deposited have good crystalline ordering. The highest mobility reported for an OS employed this technique, which is suitable only for manufacturing small molecule semiconductors. Also, this method requires the necessary equipment as well as the sample preparation steps that are not very compatible with the flexible substrates such as plastic. The temperature at which deposition is performed also has an effect on the ordering of the material.

- **Solution based deposition**: In this case, a solution of the material is transferred to the device structure. Immersing the substrate directly into a solution of indirect methods such as spin-coating, stamping or printing can be used. This deposition technique holds promise for low cost, large area manufacturing of the organic semiconductor based devices. The order of the material is worse compared to the vacuum deposition. This technique is mainly used to produce polymer-based semiconductor layers.

The source and drain electrodes can be patterned with the methods similar to the gate electrode. However, since the semiconductor is sensitive to the solvents used in lithography, the process needs to be modified with the appropriate solvent types. The device might be covered with a protective layer to prevent the degradation of the semiconductor layer due to ambient interaction.

### 3.2 Characterization of OTFTs

Most of the organic thin film transistors reported in the literature are p-channel devices. Transistors with n-channels were found to be unstable when exposed to air because $O_2$ changes the doping in the material [10]. Because of
the low carrier mobility a typical organic transistor is incapable of achieving high switching speeds. Transistor characteristics are broken into two operating regions: the linear regime at low $V_{DS}$ and the saturation regime at higher $V_{DS}$. In the linear region the drain current equals [7]:

$$I_D = \frac{W}{Ld} \varepsilon_i \mu_{eff} (V_G - V_T) V_{DS}$$  \hspace{2cm} (3)$$

where $\varepsilon_i$ is the dielectric constant of the gate insulator, $d$ is its thickness, $V_T$ is the threshold voltage (the voltage at which the channel is opened), $\mu_{eff}$ is the effective carrier mobility, $W$ and $L$ are the channel width and length, respectively (Figure 9). In this region, the transistor functions as an ohmic resistor due to the linear dependence of $I_D$ on the $V_{DS}$.

![Figure 9: Schematic view of an OTFT [12].](image)

When the $V_{DS}$ reaches a certain limit, the semiconductor channel is saturated and an increase in $V_{DS}$ does not result in an increase in drain current. This is due to the fact that for high electric fields, the velocity of the carriers is not proportional to the field, but instead saturates to a certain value [11]. In this case, the transistor operates in the saturation regime [12]:

$$I_{DS} = \frac{W}{2Ld} \varepsilon_i \mu_{eff} (V_G - V_T)^2$$  \hspace{2cm} (4)$$

Compared to the inorganic transistors, the operating voltages of organic FETs are too high for practical low voltage applications. An example of an I-V characteristic is shown in figure 10.

As mentioned before, the biggest problem that OTFTs face is low carrier mobility (0.1 - 1 cm$^2$/Vs). The mobility of charge carriers can be measured
in many ways [7]. The first obvious way is to extract the data from the measured I-V characteristics, providing that the equations for the current accurately describe the material at hand. Another way of measuring the carrier mobility is via the Hall effect. The mobility measured in this way is called the Hall-mobility and can deviate from mobilities measured with other experiments. The most direct way of measuring the velocity and hence the mobility of the carriers is with time-resolved electroluminescence. With an electric pulse, electrons and holes are injected from opposite sides into the active layer. When the carriers meet, somewhere in the active layer, they will recombine and produce light. The time delay to the onset of luminescence directly gives the speed of the fastest carriers, assuming the thickness $d$ of the layer is known:

$$\mu = \frac{\nu}{E} = \frac{d/\Delta t}{(V/d)} = \frac{d^2}{V\Delta t}$$ \hspace{1cm} (5)$$

A similar method is the time of flight (ToF) method, but instead of measuring the light we measure the time-resolved current that injected carriers produce on the other side.

### 3.3 Applications of OTFTs

Organic thin film transistors can provide low cost large area applications which inorganic semiconductor based devices cannot achieve. Low temperature processing and substrates with structural flexibility add multitude of practical possibilities. It is envisioned that identification tags, smart cards,
sensors and flexible displays can be manufactured using the organic TFT technology.

The fact that ambient atmosphere can alter the conduction of an organic semiconductor was utilized to develop an OTFT based odor sensor (Figure 11). The "electronic nose" responded to several vapors by changing its current characteristics. Similar devices can be used for biosensing in water. However, the most promising field for OTFTs still remain low cost and flexible displays.

![OTFT odor sensor](image)

Figure 11: OTFT odor sensor [10].

4 Conclusion

Although the organic transistors attract interest, the work is mostly limited to the research field. So far, there is no commercial product based on organic TFTs. Several issues need to be addressed in order to realize useful applications. One major problem is the low efficiency of these organic devices compared to the inorganic ones, since organic transistors render only low currents despite the large operating voltages. Some of the reasons for this are high trap densities at the grain boundaries and the semiconductor-gate insulator interface. In order to produce high-ordered, high mobility semiconductors new production techniques should be developed. Until then, the organic transistor will remain inferior to its inorganic counterpart.
References


