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The organic transistor: State-of-the-art and outlook

Gilles Horowitz

ITODYS, Université Paris Diderot, 15 rue Jean-Antoine de Baif, 75205 Paris, France

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Abstract Since their first appearance at the end of the 1980's, organic transistors have been experiencing a growing interest from both academic and industrial institutions. In this short review, we address the current state of the art of this new kind of electronic device. In particular, we try to define what characterizes an organic semiconductor, and in what it differs from its inorganic counterpart. As far as the applications are concerned, we show that the organic transistor must not be viewed as a direct competitor to silicon; instead, its future lies in the opportunity to implement new low-cost fabrications techniques, and in the possibility to realize flexible devices on polymer substrates.

PACS. 72.80.Le organic semiconductors – 85.30.Tv field-effect devices – 64.75.Yz self assembly

1 Introduction

Although they have been identified as early as 1948 [1], organic semiconductors have not been used in practical devices until the middle of the 1980's [2,3]. During fifteen years, electronic organics remained a confidential field of research where only a small handful of academic teams were involved. Since the outset of the 21st century, it has experienced a tremendous development in both academic and industrial institutions. Up to now, this growth was mainly related to the organic light-emitting diodes, with the advent of several commercial devices as early as 1999. However, the organic transistor is now also entering the market with the launch, expected next year, of an electronic paper by the company Plastic Logic.

The short review that follows aims at showing why a certain category of organic solids does behave as semiconductors that can be used as the active element of field-effect transistors. We will focus on what these organic compounds differ from their inorganic counterparts, and in which kinds of application they can be more advantageous than the conventional silicon transistors.

2 Organic semiconductors

The major event that marked the birth of organic semiconductors is most probably the unveiling of conducting polymers in 1977 [4]. It was actually at this time that it became possible to envision the use of organic materials for the fabrication of devices in which an electrical signal is modulated.

Organic semiconductors are organic solids made of conjugated molecules characterized by an alternation between

Figure 1. Representative examples of conjugated polymers (left) and short molecules (right).

singly and doubly bound carbon atoms. In these unsaturated molecules, the presence of pi-orbitals offer the availability of electrons that can involve in charge transport mechanisms. In the beginning, conducting polymers were foreseen as potential substitutes for metals with the major advantages of light weight and easy processing. Actually, the serendipitous discovery of electrically driven light emission in poly-para-phenylene-vinylene (PPV) [5] moved the interest of conducting polymers to organic electronic devices. The family of organic conjugated materials comprises several conjugated polymers, but also short molecules that can be either oligomers (short polymers with a well-defined number of monomers in their backbone) or specific molecules like phthalocyanines. Representative examples are given in Figure 1.

Figure 2. Diagram of the thin-film transistor (TFT) architecture. S: source; D: drain; G: gate; Top down and from left to right: bottom gate, bottom contact; bottom gate, top contacts; top gate, bottom contacts; top gate, top contacts.

3 Organic transistors

3.1 Structure and operating mode

The most widespread structure for organic transistors is the so-called thin-film architecture (TFT) widely used in the active matrix of flat panel displays. The structure with its various alternatives is shown in Figure 2.

The organic TFT (OTFT) behaves as a capacitance where one of the plates is constituted by the gate electrode, while the second plate is made of an organic semiconductor layer. In turn, this layer is equipped with two additional electrodes, the source and the drain, placed at a small distance of each other and connected to the external circuit. The space between the source and the drain is called the channel; its length L (the distance between the source and the drain electrodes) and width W represent the basic geometrical dimensions of the device.

Polarizing the gate against the source by a bias V_G induces a charging of the capacitance, which in turn leads to the formation of a conducting channel between the source and the drain electrodes. The conductivity of this channel is controlled by the gate voltage, which in turn modulates the current flowing between source and drain.

In practice, there exist two operating regimes of the transistor. At low drain voltage V_D , the device works in the linear mode; the current I_D that flows between source and drain is given by:

$$I_D = \frac{W}{L} \mu C_i \left(V_G - V_T - \frac{V_D}{2} \right) V_D, \quad (1)$$

where μ is the mobility of the charge carriers (electrons or hole, depending on the sign of the charges that are injected at the source), C_i the capacitance of the gate insulator (per unit area) and V_T the threshold voltage.

When $V_D > V_G - V_T$, the device enters the saturation mode. In this regime, the current no longer depends on the drain voltage:

$$I_{Dsat} = \frac{W}{2L} \mu C_i (V_G - V_T)^2. \quad (2)$$

3.2 Charge transport

As shown by Equations (1) and (2), the mobility of the charge carriers is a crucial factor of merit of the transistor.

Figure 3. Improvement of the mobility for three organic semiconductors used in organic transistors, one polymer (polythiophene) and two small molecules (pentacene and rubrene). Data on rubrene pertains to single crystals.

Accordingly, the search for high mobility materials is still very active. However, the mobility is not only dictated by the nature of the organic semiconductor; it also strongly depends on other parameters such as the crystal structure and the quality of the various interfaces that intervene in the device: interfaces between the insulator and the semiconductor and between the electrodes and the semiconductor. Figure 3 shows that impressive improvements have been gained with time by working on these structural aspects.

Data in Figure 3 relates to one polymer – polythiophene – and two small molecules – pentacene and rubrene [6,7]. The best performance is produced by small molecules, with values in excess of $10 \text{ cm}^2/\text{V.s}$ on single crystals that offer both high purity and low level of structural defects. Mobility up to $6 \text{ cm}^2/\text{V.s}$ has been reported for polycrystalline pentacene [8]. Polymers provide are more easily processable than single molecules. However, their mobility is in average ten times lower than that achieved with small molecules.

All the materials reported in Figure 3 are said to be p-type because the carriers injected in the conducting channel are positively charged holes. n-type organic transistors, where the injected charges are negatively charged electrons, have also been identified. However, these compounds are often oxygen and/or water sensitive, so they suffer degradations when exposed to the ambient. For this reason, care must be taken during the fabrication of n-channel organic transistors to avoid exposure to air. However, we note that more recently, strategies have been developed to synthesize n-type compounds that also offer good air stability [9].

3.3 Role of interfaces

A remarkable feature in Figure 3 is the evolution of the mobility measured on the same compound, which indicates that charge transport mechanisms are not only material, but also device dependent. Such a behavior clearly

shows the crucial role played by interfaces in the operation of the transistors. There are two kinds of these interfaces in the device: That between the gate insulator and the semiconductor, and that between the source and drain electrodes and the semiconductor.

3.3.1 The insulator-semiconductor interface

A transistor is constructed by piling up very thin (a few tens of nanometers) layers of different natures – insulators, conductors and semiconductors – on top of a thicker (neutral) substrate. Figure 2 shows the various architectures that the device can adopt, dependent of the order after which the layers are deposited on the substrate. The bottom gate structures are the most common ones. They are characterized by the fact that the semiconductor is deposited on top of the insulator. The most widespread deposition techniques are physical vapor deposition for small molecules and spin-coating for polymers. In both cases, the nature of the surface of the insulator plays a decisive role in the quality of the interface.

Ever since the 1990's, professor Jackson's group at the University of Pennsylvania [10] has established that some specific surface treatments of the insulator could induce a major improvement of the performance of the device. In these early organic transistors, the insulator was made of silicon oxide SiO_2 thermally grown on a heavily doped silicon wafer that served as the gate electrode. Such a basic structure, which comes from the conventional microelectronics technology, is still widely used, although polymeric insulators are gradually gaining the preference. However, it is now well established that SiO_2 is not well suited to organic devices, because it contains functional groups that are susceptible to act as traps for the charge carriers [11]. An elegant way to neutralize these functional groups is to modify the surface of the oxide with a self-assembled monolayer (SAM) that spontaneously forms when dipping the substrate in a solution containing a reactive molecule susceptible to chemisorb on the surface. In the case of SiO_2 , the reactive molecules are made of alkyl-silanes (e.g., octadecyl-trichlorosilane OTS). The formation of the SAM is a two-step process, with first a fast adsorption of the reactive group, followed by a slow rearrangement of the molecules that lead to a quasi bidimensional crystal structure. Such an organisation is the result of an interplay between adsorption and the van der Waals interactions between molecules [12].

An alternative solution to passivate the surface of the oxide is the deposition of an ultra-thin polymer film like polystyrene [8]. As noted above, the current trend is to replace to inorganic oxide by a full polymer layer as the gate insulator, which presents the advantage of being compatible with fabrication techniques derived from the printing technology (e.g., ink-jet printing). In this case, a specific surface treatment of the gate insulator is no longer required.

Figure 4. Illustration of the Transfer Line Method for various gate voltages.

3.3.2 The interface with electrodes

As the performance of the organic transistor is improving, limitations due to the contact resistance at source and drain electrodes are becoming a major limitation to further improvements. A first requisite was to find a simple and reliable way to estimate the contact resistance. Today, one of the most widespread method is the so-called Transfer Line Method (TLM), a technique originally developed for the hydrogenated amorphous silicon transistor [13] that consists of measuring the resistance of devices produced in the same run with various channel lengths. From Equation (1) and $V_D \ll V_G - V_T$ the total resistance R (channel resistance plus contact resistance R_c) between source and drain contacts writes:

$$R \times W = R_c \times W + \frac{L}{\mu C_i (V_G - V_T)}. \quad (3)$$

Thus, plotting the resistance measured at low drain bias (linear regime) as a function of channel length would give a straight line, the extrapolation of which to zero length yields the contact resistance. Figure 4 illustrates the method in the case of pentacene with gold source and drain electrodes.

The contact resistance in organic transistors originates from the mechanisms of charge injection from a metal to an organic semiconductor. The key parameter in that instance is the height of the energy barrier that forms when the metal and the organic semiconductor are put in close contact. In its simplest description, the height is given by the difference between the work function of the metal and the electron affinity of the semiconductor for the injection of electrons, or the ionization potential for the injection of holes. This is illustrated in the central diagram of Figure 5. The key energy levels are the metal Fermi level E_F and the semiconductor highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), i.e., the hole and electron transport levels, respectively.

However, real interfaces often show a downward or upward shift of the levels, which substantially alters the in-

Figure 5. Energy diagram of the metal-organic semiconductor interface. Center: no interface dipole (vacuum level alignment). Left and right: Upon formation of an interface dipole Δ , the energy levels shift, thus inducing a change of the injection barriers. HOMO and LUMO stand for Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital; E_F is the metal Fermi level.

Figure 6. Gate voltage dependent contact resistance as measured by TLM on bottom gate, bottom contact organic transistors with pentacene semiconductor and gold source and drain electrodes. The gold electrodes were modified with various thiol-based SAMs bearing various dipole moments.

jection barrier heights. The shift is attributed to an interface dipole Δ , which generally originates from interface gap states [14,15]. This usually detrimental effect can be turned to beneficial by purposely introducing an interface dipole between the electrode and the semiconductor layer, which can be achieved by using SAMs made of molecules bearing the appropriate dipole moment. For hole injection, fluorinated molecules appear to be the good choice, as shown by the results recently obtained in our group [16] and illustrated in Figure 6. The transistors have bottom, bottom contact architecture; the semiconductor is pentacene and the source and drain electrodes are made of gold. The figure shows the gate voltage dependent contact resistance as estimated by TLM for various treatments of the electrodes. As compared with bare gold, we note an increase of the contact resistance with decanethiol (DT), and a decrease with the fluorinated molecule (PFDT). A further improvement is obtained with a fluorinated hexanethiol, which we attribute to the shorter length of the molecule.

These results are in good agreement with the reported direction of the dipole moment of the respective molecules

[17], and also with the measured work function of the modified gold electrodes as estimated from UV photoelectron spectroscopy (UPS) [16].

4 Fabrication techniques

Because of the limited mobility and speed in organic semiconductors, organic transistors are not expected to compete with conventional silicon transistors. Their interest resides in their ability to be easily fabricated at low temperature, on flexible (plastic) substrates and from solutions. The envisaged fabrication techniques are drastically different from those of the microelectronic world. Undoubtedly, the most promising techniques are those derived from the printing technology. This can be envisioned because organic semiconductors can be made soluble to formulate inks. Ink-jet and roll-to-roll printing have already been reported [18]. They would lead to low-cost and easily processable devices.

5 Conclusion

Organic transistors have now entered their industrial age. Although their performance in terms of mobility and switching speed remains lower than that of the silicon transistor, applications can be envisioned in domains where low fabrication cost, flexible substrates and large areas are required. Besides the search of organic compounds with efficient electrical transport and good air stability, decisive advances in the quality of the interfaces considerably helped in improving the performance and reaching the threshold for practical applications.

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