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Field Effect Devices Based on $SrTiO_3$ Gate Dielectrics for the Investigation of Charge Carrier Mobility in Macromolecular Films

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Summary: Field effect devices (FET) allow an exhaustive investigation of the electronic transport properties of innovative semiconductors of interest for new applications in modern electronics. In this contribution, we report on the fabrication and characterization of FET devices where $SrTiO_3$ (STO) single crystals and organic macromolecular compounds, such as doped and undoped polythiophenes, or poly(N-vinylcarbazole) (PVK), are used as insulating and semiconducting layers, respectively. STO, with ε_r of about 300, offers the possibility to strongly modulate the charge carrier density in the organic films, thus overcoming the limitations related to the use of more conventional oxides.

Keywords: field effect; polythiophenes; PVK; thin films; transport properties

Introduction

Today, organic semiconductors represent a new and very interesting class of materials which are opening the way to the fabrication of innovative devices with exciting application perspectives (ultra-flat panel displays, flexible ''electronic papers'', radio frequency identification tags, innovative sensors).[1]

Despite the large amount of research focused on these materials in the last 15 years, a deep understanding of the basic electrical conduction mechanisms is still lacking. On the other hand, this understanding is a necessary step to optimize the performances of the final devices, overcoming also the relevant degradation problems which can strongly affect their lifetime. Most of these attempts are based on the improvement of the final structural order at inter- and intra-molecular levels, with the aim to find a direct correlation with electronic parameters, taking also into account the presence of trap states both in the material bulk and at the interfaces with other compounds.

In this regard, one of the most interesting physical parameters for the investigation of electrical transport phenomena in organic semiconductors is the charge carrier mobility μ, representing the carrier drift velocity per unit electric field. In particular, in organic compounds, the mobility is strongly dependent on the temperature and the applied electric field. This dependence plays a fundamental role in assessing the conduction mechanisms, and for this reason, is the favorite subject of many investigation efforts.[1,2] Furthermore, mobility strongly affects the performances of devices based on these materials (i.e. switching speed in transistors)[3] and, consequently, many efforts have been carried out to date to synthesize organic compounds with improved mobility performances.

Recently, in the study of charge carrier mobility, field effect devices (FET) proved to be a very simple and powerful investigation tool. The FET basic working element can be represented by the equivalent

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capacitor formed by the semi-conducting channel between two metallic contacts (source and drain) , the insulating layer and the gate metallic contact. By applying an appropriate gate voltage V_G, it is possible to modify in a reversible way the number of carriers in the semi-conducting channel without changing the structural properties.[3] In this way, beyond mobility, many physical properties can be deeply investigated as a function of the electronic doping and relevant information, concerning the organic compounds and the interface quality between organic and inorganic layers can be deduced. From these general considerations, it is also clear that the charge carrier density modulation in the organic layer is strictly dependent on the value of the equivalent capacitor, which in turn, is directly proportional to the dielectric constant ε_r of the insulating layer.

This means that the use of high dielectric constant layers in the fabrication of organic field effect devices (O-FET) allows analyzing the charge carrier mobility in very strong accumulation regimes. From an application point of view, it allows to reduce the operating voltages, a necessary prerequisite to actually make organic devices that are competitive in a market perspective. These considerations explain well why several experiments have been focused on the investigation of the properties of new dielectric layers with high ε_r, suitable to be employed in the fabrication of O-FET.[4,5] However, from a morphological point of view, it is still not clear what impact high dielectric constant layers actually have on the interface quality with the organic compounds and the related mobility performance.[6] In this regard, the debate is open and new experimental investigations are required.

According to these general principles, in our work we have fabricated O-FET utilizing commercial $SrTiO_3$ (STO) substrates with thickness ranging from 100 to 500 μm. This study is aimed at verifying the possibility to modulate the carrier density of various organic materials, amorphous or well structured, which are of interest for different applications and show very different mobility values.

This work has to be considered as a necessary step for the utilization of thinner STO films for O-FET devices, both for applications and basic investigation. Indeed, the use of single crystals as insulating layers should at the least guarantee the absence of interface traps related to the dielectric surface defects, making it possible to evidence only the effects due to the intrinsic properties of the organic compounds.

Similar FET devices based on STO substrates have been recently and successfully fabricated in our group, achieving the field-effect tuning of carrier density with $Nd_{1.2}Ba_{1.8}Cu_3O_y$ thin films [7,8] and with a micrometric array of gold dots.[9]

Field Effect Basic Parameters

Unlike what occurs in FET devices based on crystalline silicon employed in modern integrated electronic circuits, O-FET do not operate in the inversion regime but only in the accumulation or depletion ones. Under some assumptions, usually well respected in the fabricated devices,[10] the dependence of the I_{DS} current between drain and source on V_G and V_{DS} voltages can be described by simple analytical equations. In particular, when ($V_G > V_{DS}$), the device operates in the so-called linear regime and I_{DS} is given by:

$$I_{DS} = \frac{WC_i\mu}{L} * V_{DS}(V_G - V_{th}) \tag{1}$$

In this case, the channel essentially behaves as a variable resistor which can be linearly tuned by V_G. On the other hand, when ($V_G < V_{DS}$), due to the pinch off of the accumulation layer, the FET works in the saturation regime and the linear dependence described by (1) is replaced by a quadratic dependence determined by the following equation:

$$I_{DS} = \frac{WC_i\mu}{2L} * (V_G - V_{th})^2 \tag{2}$$

In these formulas, W and L are respectively the width and length of the semi-

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conducting channel, μ is the mobility, C_i is the capacitance per unit square related to the dielectric barrier and V_{th} is the threshold voltage. By the analysis of the FET characteristics, a lot of information about the electrical properties of the organic semiconductors can be deduced.

From the sign of the gate voltage that induces the accumulation effect of the charge carriers, it is possible to determine their sign, whereas this is not possible to do from resistivity measurements.

By (1) or (2), it is also possible to determine the threshold voltage V_{th} which takes into account the presence of trap states at the interface between the dielectric barrier and organic channel. It is given by:

$$V_{th} = \frac{qNd}{C_i} \tag{3}$$

where N is the trap density, q the elementary charge and d the semiconducting channel thickness.

Another important parameter in characterizing an O-FET, is the ON/OFF ratio (current modulation capability) which represents the ratio of the current in the accumulation mode ($V_G \gg V_{th}$) to the current in the depletion region ($V_G < V_{th}$), for a fixed V_{DS}. The ON/OFF ratio is also related to the power consumption of the device. In this regard, an optimization of the performances requires a very low I_{OFF}. This condition can only be guaranteed by a low conductivity of the employed semiconductor, because of the absence of the inversion phenomenon in an O-FET.

Finally, the charge carrier,mobility can be directly calculated both in the linear and saturation regimes, by rearranging Equations (1) and (2). It is easy to find that in the former case μ can be evaluated by:

$$\mu = \frac{L}{wC_iV_{DS}} * \left.\frac{\partial I_{DS}}{\partial V_G}\right|_{V_{DS}} \tag{4}$$

while in the latter, one has:

$$\mu = \frac{2L}{wC_i} * \left(\frac{\partial\sqrt{I_{DS}}}{\partial V_G}\right)^2 \tag{5}$$

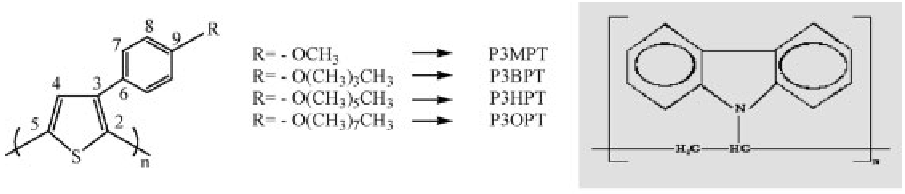
Both formulas are largely employed in organic compound mobility studies, even if it is necessary to remember that some assumptions for their validity, such as a field independent mobility and negligible contact resistances, are not always well verified.

Experimental Results

In our work, we have investigated the electrical properties of some interesting organic semiconductors, focusing our attention in particular on PVK (poly(N-vinylcarbazole)), doped and undoped poly[3-(4-butoxy)phenylthiophene], both deposited by spin coating technique.

PVK is an amorphous compound, widely used in O-LED applications, while poly[3-(4-butoxy)phenylthiophene] is a regioregular material, interesting both for solar cells and, when doped with metals, for O-FET applications.

The chemical structures of the compounds are reported in Figure 1. The film thicknesses are in the range of 1 μm, with a very smooth surface, as shown by AFM investigations. All the details concerning the film structural properties and the deposition process will be reported elsewhere.[11,12]



Poly [3-4'(butoxy) phenylthiophene]

PVK (poly(N-vinylcarbazole))

Figure 1.
Structure of the investigated organic compounds.

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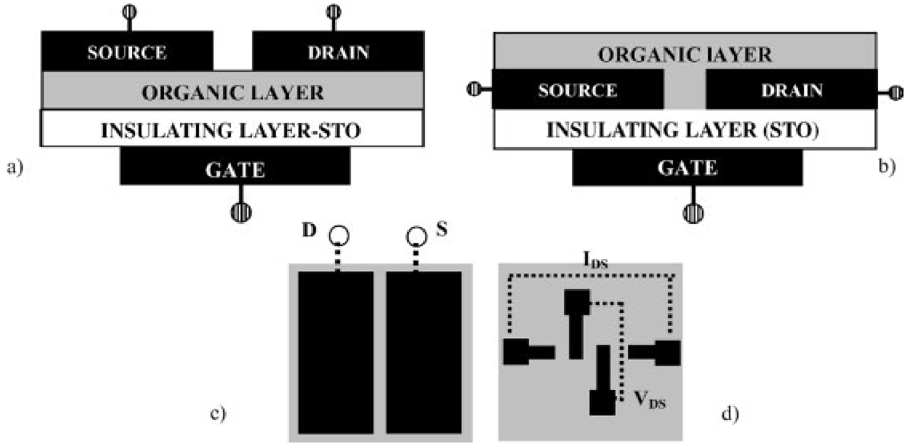

Figure 2.
O-FET configurations: a) Top contact and b) Bottom contact. Top view of field effect devices with two c) and four d) metallic contacts.

Figure 2 shows a schematic view of the fabricated field effect devices. In our work, both the top contact (Figure 2a) and the bottom contact (Figure 2b) configurations have been realized. Similarly, both four (with two current and two voltage pads) and two (same contacts for voltage and current) probe techniques have been adopted. The distance between source and drain in the two contact configuration is usually L = 0.1 mm, while the metallic pads are 9 mm long and 3 mm wide. In the four contact configuration, the distance between the voltage contacts ranges between 0.025 and 0.1 mm. It is important to outline that the four probe technique allows to neglect the contact resistance effect which, for short channels in particular, can strongly affect the measured mobility.[13] In any case, the source and drain contacts are in gold and have been deposited by evaporation, using shadow masks to define correctly the channel size.

Considering the peculiar properties of the materials under investigation, the usual procedures (welding by metals with a low melting point, conducting pastes) for the realization of the external metallic connections to the measuring instruments, can strongly affect the compound properties, both because of their low temperature decomposition and of their easy solubility.

To overcome this limitation, the measurements have been carried out by using a cryogenic probe station, with four metallic probes mounted on micrometric slide plates. Furthermore, in this way, the environmental conditions, where the samples are investigated, can be accurately controlled and this is a fundamental issue to study phenomena such as the stability in air, the influence of light and the possible hydroscopy. The resistivity temperature dependence and I–V current-voltage characteristics have been measured by a standard two probe technique. In the I–V measurements, both the applied voltage and the measured current were controlled by a Keithley 487 picoammeter.

The STO dielectric constant has been experimentally tested by fabricating simple parallel plate capacitors and measuring the corresponding capacitances by using an Hewlett Packard 4108 LCR meter. Experimental measurements of ε_r have been carried out as a function of temperature. At room temperature, a value of about 300 was found, in very good agreement with the data reported in the literature,[14] providing an insulator capacitance C_i per unit area of about 2.5nF/cm^2 when a thickness of 100 μm is considered.

In all investigated compounds, the field effect modulation provides an increase of

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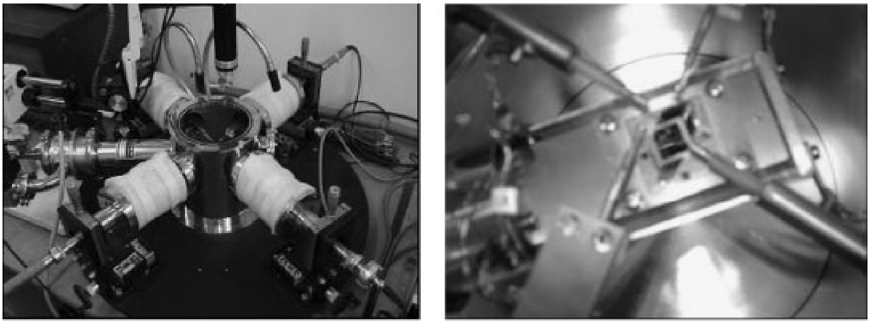

(a)

(b)

Figure 3.
Cryogenic probe station (a) external view and (b) internal view.

the channel resistance R_{sd} for positive gate voltages which is consistent with the fact that the carriers are holes. In Figure 4, for PVK films, some transfer curves (I_{DS} curves as a function of V_G), obtained for different V_{DS} values, are reported. A mobility value of 4.8^*10^{-9} cm^2 V^{-1} sec^{-1} has been estimated by using the formula (5) for the saturation regime. This value of PVK mobility is in good agreement with data reported in the literature and evaluated by means of electrical criteria.

As a further example, we report in Figure 5 two typical transfer curves obtained in the linear region, for FET devices based on 900 nm thick spin coated layers of doped and undoped regio-regular P3BPT. The mobility extracted in the linear regime was $\mu = 2^*10^{-6}$ cm^2/V^*s for the undoped films, showing a negligible field dependence.

Also in this case, the data are in good agreement with those reported in the literature and the quality of the films seems quite good and promising for future investigations. Moreover, by doping the sample with 1% of $FeCl_3$, an increase of the mobility of almost one order of magnitude was obtained.

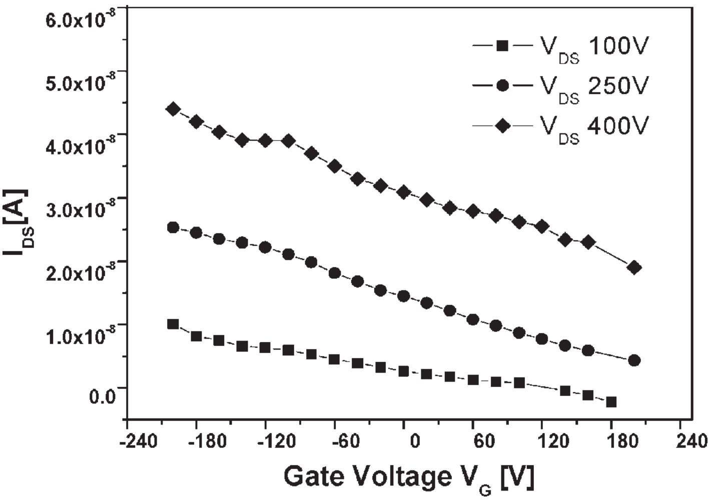

Figure 4.
Transfer-curves for a Field Effect device based on PVK.

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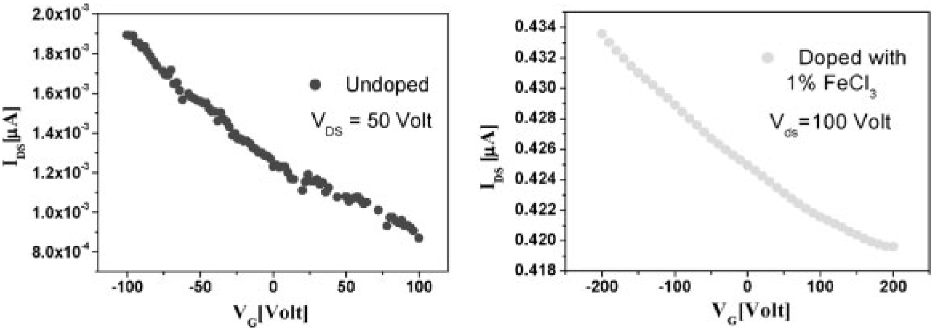

Figure 5.

Transfer curves (I_{DS} vs V_G) for an undoped (a) and $FeCl_3$ doped (b) poly [3-(4-butoxy) phenylthiophene] based FET.

Conclusions

The field effect technique seems to be one of the most suitable tools to investigate the intrinsic electrical properties of organic materials of interest for future applications. In our work, FET devices have been fabricated by combining different organic semiconductors with STO single crystals. Thanks to its high dielectric constant, STO films allow a large modulation of the charge density in the semiconducting channel. Transfer curve measurements have been performed for the fabricated devices and mobility values have been extracted. New device configurations will be analyzed in the near future by reducing the channel length up to the nano-metric scale.

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