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PRODUCING SMART SENSING FILMS BY MEANS OF ORGANIC FIELD EFFECT TRANSISTORS

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Abstract-- We have fabricated the first example of totally flexible field effect device for chemical detection based on an organic field effect transistor (OFET) made by pentacene films grown on flexible plastic structures. The ion sensitivity is achieved by employing a thin Mylar™ foil as gate dielectric. A sensitivity of the device to the pH of the electrolyte solution has been observed. A similar structure can be used also for detecting mechanical deformations on flexible surfaces. Thanks to the flexibility of the substrate and the low cost of the employed technology, these devices open the way for the production of flexible chemical and strain gauge sensors that can be employed in a variety of innovative applications such as wearable electronics, e-textiles, new man-machine interfaces.

1.INTRODUCTION

Organic materials, based on conjugated organic small molecules and polymers, have paved the way, in the last decade, for the production of devices on large-area, low-cost, plastic substrates[1]. So far, great progress has been made in the field of optoelectronic devices, like Organic Light-Emitting Diodes (OLEDs)[2] and for switching functions by means of Organic Field Effect Transistors (OFETs)[3].

Organic semiconductors offer several advantages due to easy processing, good compatibility with a wide variety of substrates including flexible plastics, and great opportunities in terms of structural modifications. Furthermore, thin films of organic semiconductors are mechanically robust and flexible, and this characteristic offers new possibilities for non-planar flexible electronics. Until now, only few examples of organic semiconductor based field effect sensors have been presented and none of them is fully capable of exploiting the favourable mechanical properties of organic semiconductors[4,5]. Recently, a fully flexible structure for field effect devices has been produced[6]. The main advantage of this structure is that it is assembled starting from a flexible insulating film, but without any substrate. Thanks to this feature, it is possible to expose the gate side of film to an external medium or to apply this flexible structure to whatever kind of substrate; this is normally impossible for structures assembled on a rigid substrate (as, typically, OFETs realized on silicon/silicon dioxide). In this way, it is in principle possible to realize with a fully flexible structure[7]

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a function similar to that of a silicon based Ion Sensitive Field Effect Transistor[8] (ISFET). Ion sensitivity in silicon based FETs results from the presence on the surface of the insulating layer of specific sites for H+ ions in the electrolytic solution[9]. Starting from this principle, several examples of (bio)sensors have been developed, based on the possibility of functionalizing the surface of the insulating layer with molecular layers with specific binding properties for the (bio)molecules dissolved in the medium to monitor[10]. Something similar can be envisaged also for organic field effect sensors, that, in comparison to silicon structures, have several advantages, as the low cost of the technology and the possibility to achieve mechanically flexible structures. Nevertheless, the mobility of organic semiconductors is still low, even if it seems realistic to obtain in a few years devices working at relatively low voltages, comparable with the performances of devices made from amorphous silicon[11,12]. Ion Sensitive Organic FETs (ISOFETs) fabricated on plastic substrates could open the way to the fabrication of flexible devices for solution monitoring and for a number of innovative applications (as, for example, smart food packages, or systems able to be embedded in textiles) that are not possible at present for silicon based devices.

On the other hand, flexible sensors for mechanical deformation and pressure detection have been recently proposed[13] for very innovative applications as artificial skin for robots. In this case, organic thin film transistors are used for assembling a matrix where each transistor addresses a piezo-resistive element that acts as the sensing device. Here, we propose an alternative structure where the organic semiconductor device combines in itself both switching and sensing functions.

II.METHODS AND MATERIALS

Basic structure: A 900 nm-thick Mylar™ sheet (Du Pont), adapted to a plastic frame, works as insulator and, at the same time, as a free-standing surface for device assembling. The Mylar™ sheet has a dielectric constant close to that of silicon dioxide (3.3) and a dielectric rigidity of 10^5 V/cm that allows to apply a gate bias sufficiently high to induce a field-effect in the organic semiconductor. Bottom-contact Au source and drain electrodes have been patterned on one side of the dielectric using a standard photolithographic technique. The basic structure of the device[7] is shown in Figure 1.

Chemical sensor: in this case, one side of the Mylar film is exposed to an electrolytic solution where an Ag/AgCl reference electrode is immersed. Gold source and drain electrodes with W/L = 250 (W and L are the channel width and length, respectively), with L = 25 μm, have been used. Prior to organic deposition, the substrate has been cleaned with acetone, washed with deionized water, and dried with a

Nitrogen flux. Pentacene (Sigma Aldrich) has been used as received. Pentacene films with a nominal thickness of 50 nm have been grown by vacuum-sublimation at a nominal deposition flux of about 1 Å/s.

Measurements of drain-source current (Ids) versus drain-source and gate-source voltages have been carried out at room temperature in air, by means of a HP 4155 Semiconductor Parameter Analyzer. In order to avoid ageing effects, all measurements have been performed immediately after pentacene deposition.

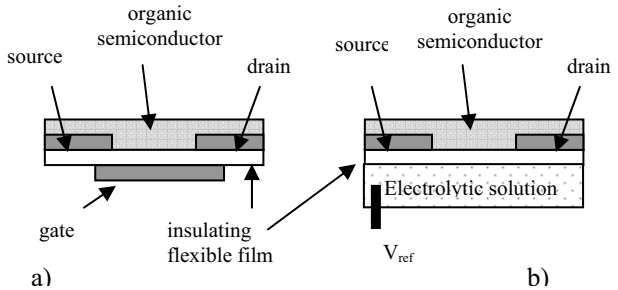

Figure 1. a) basic structure of the transistor; b) the modified chemical sensor device

Mechanical sensor: in this case, the basic structure, provided with a metal gate is so thin and flexible that it can be applied to whatever surface in order to detect, through the variation of the channel current, any mechanical deformation of the surface itself. The device has been glued with the the gate side internally exposed to a suspended stainless steel cantilever. On the opposite extreme of the cantilever different weights are suspended in order to produce a measurable deformation to the cantilever and on the device glued to it. Alternatively, it can be employed as a free standing film, to detect a pressure applied on it through an air flow.

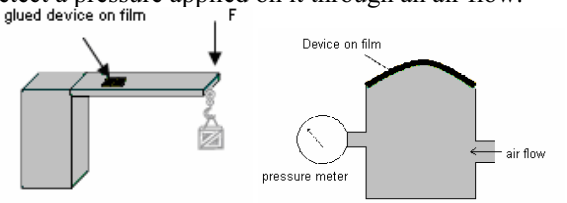

Figure 2. Experimental set-ups for applying a mechanical deformation/pressure.

III. Results and Discussion

Chemical sensor: The basic device for both types of sensors has the typical behavior of organic p-type field effect transistors, working in accumulation mode, with increasing negative values of Ids with increasing negative Vds values and with a clear field effect induced by the Vgs voltage. Present limitations to the performances of such kind of devices are mainly due to the low mobility (currently, typical values for Pentacene are in the range of 10^{-2}-10^{-1} V/cm^{2}s) and the poor time stability of organic semiconductors, due to many different degradation mechanisms that affect the still unclear transport properties of organic compounds. OFET-based sensors can clearly benefit of the continuous progresses obtained in the synthesis of higher mobility and higher stability semiconductors, and also in the comprehension of transport mechanisms in organics. Figure 3 shows the output characteristic of the chemical sensor device. This curve has been registered in presence of an electrolytic solution with a pH of 7 after the reference electrode has been left to stabilize in the same solution for about half an hour. This procedure has been done with the aim of obtaining more stable measurements. As can be seen, $|Ids,sat|$ increases with the increase of $|Vgs|$ similarly to OFETs with a metallic gate. Namely, as can be seen from Figure 4 that shows I_{ds} versus time at different pH values (taken by leaving a 30 minutes hold time after every pH variation; curves are taken at Vds = -90 V, Vgs = -50 V), there is a decrease of the current with basic solutions and an increase with acid solutions that clearly indicate that there is a modulation of the charge at the interface between the insulating layer and the solution (superposed to the underlying degradation mechanism that induces a slow decrease of current also at constant pH).

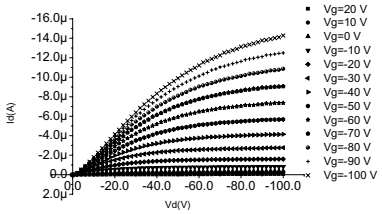

Figure 3.Output characteristic of a device recorded at pH=7

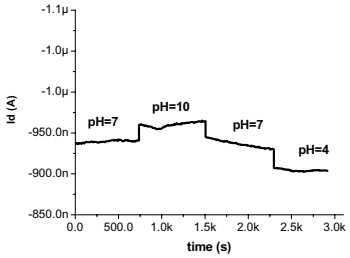

Figure 4. I_{ds} versus time at different pH values (Vds = -90 V, Vgs = -50 V)

When negative charge density is increased in the bulk (and as a consequence, at the insulator/solution interface), as for basic solutions, holes accumulate in the channel in higher density than in the case of neutral or acid solutions. As a consequence, the (negative) current recorded with fixed values of Vds and Vgs is higher. Conversely, in the case of acid solutions, the positive charge accumulated at the insulator/solution interface causes a decrease of the hole density in the channel and a (negative) lower value of Ids.

The dependence of the transistor current on the pH value of the solution must be related to a variation of the threshold voltage of the device due to a charge variation at the solution-insulator interface that can be explained in the frame of the Gouy-Chapman-Stern theory[8] for the behavior

of an interface between a solid surface and an electrolytic solution.

According to this theory, an insulator exposed to an aqueous solution interacts with H+ ions and causes a redistribution of the charge in the solution. When the structure formed by the insulator and the electrolytic solution is completed by a semiconductor layer located at the opposite side of the insulator, as in the case of MOSFET and OFET structures, the charge variation at the insulator/solution interface capacitively induces a redistribution of charge in the semiconductor. In field effect devices, this variation is directly detectable through the variation of the threshold voltage of the device. This working principle is valid both for MOSFETs and OFETs, as already demonstrated by C. Bartic et al.[4], with the obvious differences due to the specific features of organic semiconductor based devices (as low current and high operating voltages).

Mechanical sensor: Figure 5 shows an example of current vs. strain curve. As it can be noticed, within a limited strain range, there is a linear dependence of the drain current with the strain applied to the cantilever that can be interpreted in terms of reorganization of granular domains in the semiconductor layer, induced by the cantilever deflection. Similarly, the current variation with varying pressure levels, according to the experimental setup of fig. 2 (right), as shown in figure 6, can be related to a carrier mobility reduction directly induced by the morphology variation of the semiconducting layer. It is worth noting that the in this case the plastic layer is isotropically deformed while in the case shown in fig. 2 (left) the cantilever bending induces a uniaxial deformation of the device.

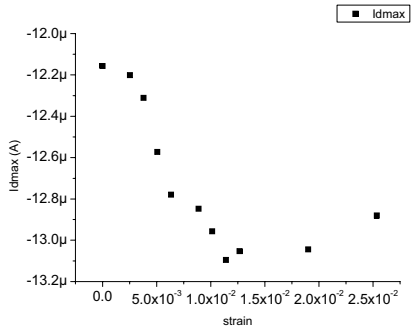

Figure 5 I_{ds} versus strain (bias conditions: Vds = -80 V, Vg= -80 V).

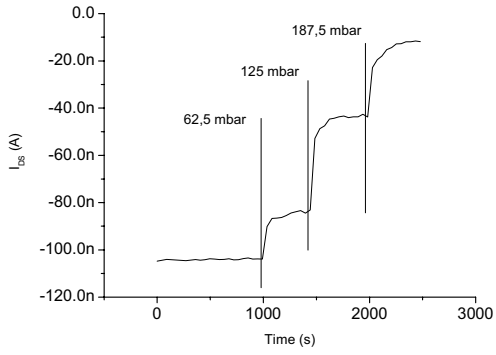

Figure 6 I_{ds} versus time (bias conditions: Vds = -5 V, Vgs = -80 V) with different pressure levels .

IV. Conclusions

In conclusion, for the first time ion sensitive field effect transistors have been produced on fully flexible plastic films. The devices are based on pentacene films grown on bottom-contact Au-patterned on 900 nm-thick Mylar™ gate dielectric. The electrical characteristics indicate that the device behaves as a typical p-channel transistor working in accumulation mode. Output current is modulated by the pH value of an electrolytic solution put in contact with the insulating layer. At present, sensitivity to the presence of ions in the solution has been achieved without any treatment of the insulating layer. Work is in progress for obtaining properties of chemical selectivity to other compounds by a proper functionalization of the insulating layer, with the aim of extending the applicative range of such technology. Furthermore, more complicated structures that include the immobilization of monomolecular layers of pH- and different ion- sensitive compounds are being preliminarly investigated. Also sensors for mechanical deformation have been produced with a similar principle. The preliminar measurements show the sensitivity and the linearity of the device response to the applied mechanical stimulus (deformation or pressure).

Taking advantage of the full mechanical flexibility of the employed insulating sheet, smart electronic films with sensing properties can be produced with this technique. In this way, new possible applications can be envisaged, as, for example, the application of such sensing films to flexible substrate (as textiles) and to 3D surfaces.

References

[1] S. R. Forrest, Nature **428**, 911 (2004).
[2] T. Tsujimura, SID 2003 Technical Digest Vol.XXXIV, Book 1,6 (2003).
[3] C. Dimitrakopoulos, P. R. L. Malenfant, Adv. Mater. **14**, 99 (2002).
[4] C. Bartic, A. Campitelli, S. Borghs, Appl. Phys. Lett. **82**, 475 (2003).
[5] L. Torsi, A. Dodabalapur, L. Sabbatini, P.G. Zambonin, Sensors and Actuators B **67**, 312 (2000)
[6] A. Bonfiglio, F. Mameli, and O. Sanna, Appl. Phys. Lett. **82**, 3550 (2003)..
[7] A. Loi, I. Manunza and A.Bonfiglio, Appl Phys. Lett. **86**,.103512 (2005)
[8] P. Bergveld, Sensors and Actuators B **88** 1-20 2003
[9] M. Grattarola and G. Massobrio "Bioelectronics Handbook: MOSFETs, Biosensors, Neurons" Mc Graw Hill, 1999.
[10] P. Bergveld and A. Sibbald, Analytical and Biomedical Applications of ISFETs (Elsevier, Amsterdam, 1988).
[11] Y. Kato, S. Iba, R. Teramoto, T. Sekitani, T. Someya, H. Kawaguki, T. Sakurai, Appl. Phys. Lett., **84**, 3789 (2004).
[12] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, W. Weber, J. of Appl. Phys., **92**, 5259 (2002).
[13] 13.T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, Proc. Nat. Academy of Sciences USA, . **101**, no. 27, 9966, (2004).