Detection of explosive vapors using organic thin-film transistors

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Abstract
Field effect transistors (FETs) based on organic materials were investigated as sensors for detecting 2,4,6-trinitrotoluene (TNT) vapors. Several FET devices were fabricated using two types of semiconducting organic materials, solution processed polymers deposited by spin coating and, oligomers (or small molecules) deposited by vacuum sublimation. When vapors of nitroaromatic compounds bind to thin films of organic materials which form the transistor channel, the conductivity of the thin film increases and changes the transistor electrical characteristic.

The use of the amplifying properties of the transistor represents a major advantage over conventional techniques based on simple changes of resistance in polymers frequently used in electronic noses.

Keywords
Gas sensor, organic transistor.

INTRODUCTION

Organic semiconductors have been used to fabricate field – effect transistors for application in polymer integrated circuits. Applications have been demonstrated in research environment, like pixel switches, drivers for displays, and integrated circuits [1]. Other emerging application area of organic transistors (OTFTs) is that of sensors. Polymeric and oligomeric semiconductors can be tailor-made to optimize their responsiveness towards specific chemical agents and may form the basis for new approaches to chemical sensing. Organic semiconductors are also suited for printing techniques like ink-jet printing, micro-contact printing, offset and gravure printing. In this way it will be possible to fabricate low cost, low weight and very large surface area sensors, a decisive element that discerns organic electronics from production technologies based on organic semiconductors like silicon.

Several gas sensors based on organic transistors have been reported in the literature [2]. OTFTs employing alkoxy-substituted polytertiophene thin films have been demonstrated to wok as alcohol sensors with sensitivities as good as 0.7 ng/ppm [3]. The same group has also reported a humidity sensor based in 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA) [4]. The published work shows that the use of a transistor configuration exhibits superior performance with respect to simple resistor [5]. This is due to the amplifying properties of a field effect device; a further advantage is that the FETs can provide more measuring parameters, such as threshold voltage changes, mobility variations, as well as a change in the device current.

Conducting polymers have also been used for detecting vapours of nitro-aromatic compounds [6]. In this case the polymer is not used in a transistor device but in a optical technique. Nitroaromatic compounds are strong acceptors when they bind to a fluorescent conducting polymer trap states are created. These traps provide recombination centers, which reduce the fluorescence yield.

In this article the high reduction potential of the TNT molecules are used in a similar way. However in this case the interaction between the strong acceptor and the p-type polymer creates electronic states, which changes the electrical properties of a field effect transistor.

EXPERIMENTAL

A typical organic TFT device is shown in Fig. 1. A heavily n-doped silicon wafer is used as a substrate, and the gate dielectric is a 200 nm thick (thermally grown) SiO_2 insulating layer (C_{ox} = 19 nFcm^{-2}). Gold source and drain interdigitated electrodes are photolithographically defined on the SiO_2, see Figure 1b.

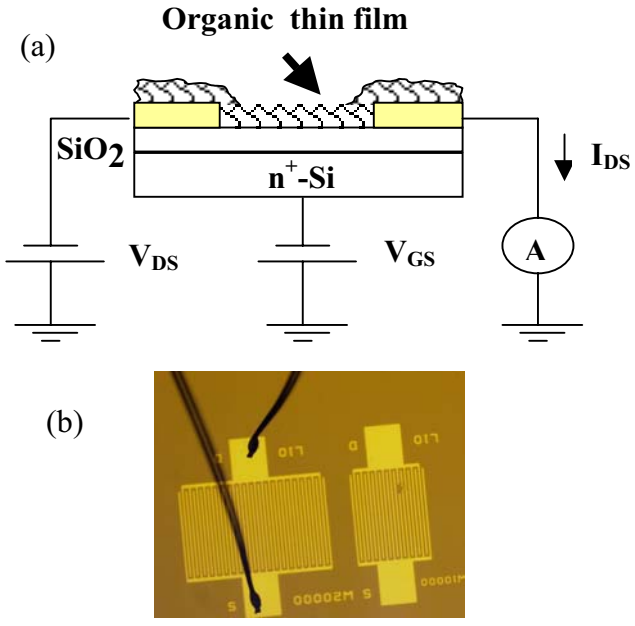
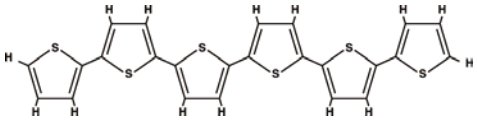


Figure 1. (a) Schematic of an organic thin film transistor structure. (b) Photograph of the interdigitated drain-source electrodes.

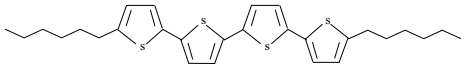
The channel dimensions were *W/L* = 20,000 μm/10 μm. All the electrical measurements were carried out in vacuum (10^{-6} mBar).

The chemical structure of the organic semiconductors used is represented in Figure 2. The α-sexithiophene (α-T6) thin films were deposited by thermal sublimation in a ultra-high vacuum organic molecular beam deposition apparatus (base pressure (10^{-9} mBar) onto pre-formed TFT test substrates. During the deposition, the sample substrate was held at 150ºC.

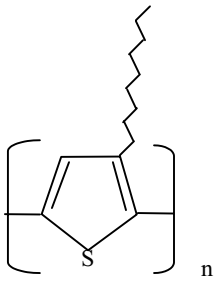
Poly-3-hexythiophene and Dihexylquarterthiophene (DH4T) are soluble materials and the have been deposited by spin coating.



sexithiophene



Dihexylquarterthiophene (DH4T)



poly-3-hexythiophene

Figure 2. The molecular structure of same active materials used in this work.

The transistors used in this study exhibit good characteristics with a low off current and field effect mobility in the order of 10^{-2} cm^2/Vs. The output characteristics (I_{DS}-V_{DS}) show current saturation as well as negligible contact resistance (see Fig. 3.)

RESULTS

Figure 4, shows the response of sexithiophene transistor to an exposure of 4-nitrotoluene vapor. The transistor was polarized with a small voltage between drain and source (V_{DS} = –0.5 V) while the gate is periodically pulsed from +5V (depletion) to –10V (accumulation). Under these bias conditions the FET operates in what it is call linear region. These conditions were selected to minimize stressing effects, which cause metastable changes in the device properties. When the device is driven in pulsed mode it is observed a saw wave type response visible in Fig 4. This behaviour it is not fully explained yet. We believe that is related a build up of space charge in trap states located in the accumulation channel.

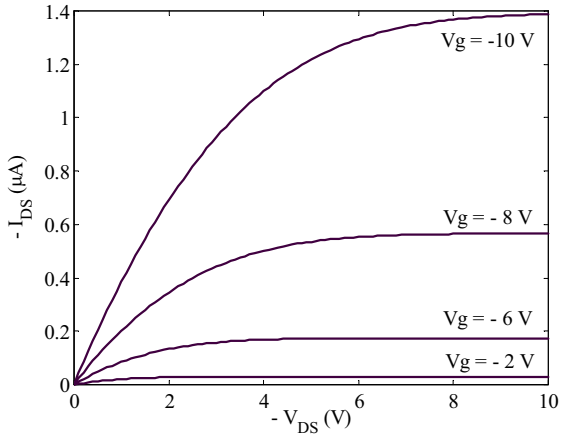


Figure 3. I-V characteristics of a sexithiophene transistor.

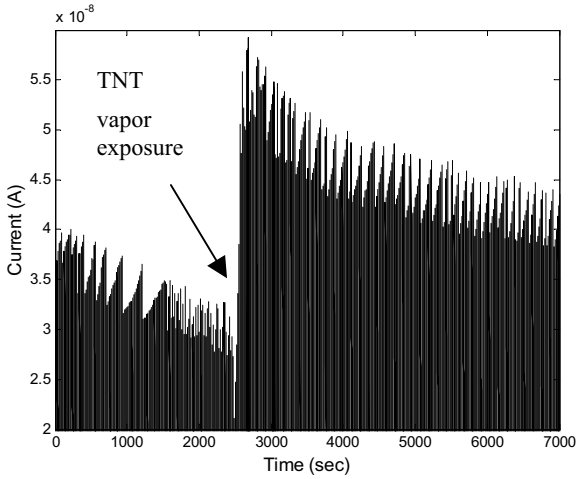


Figure 4. Response of a sexithiophene thin film transistor to a TNT vapor.

When the transistor is exposed to 4-nitrotoluene vapors, the (I_{DS}) current increases quite rapidly and reaches a final value that is more than double the initial current magnitude. It was also observed the changes are irreversible even upon vacuum pumping. Also the devices remain insensitive to

any further exposures to TNT vapors. This confirms that TNT molecules interact strongly and in a permanent way with the organic layer. This is in contrast with the effects of moisture and oxygen as reported [7].

Transistors using thin layers of poly3-hexythiophene did not show measurable changes when exposed to TNT vapors.

The transistors used are normally off, that means there is no conduction channel for zero bias in the gate. In the other side the TNT molecules behave as strong acceptors, acting as effective dopants. Therefore, even without gate bias, the transistor should be sensitive to a TNT exposure. An accumulation channel should start to appear when the TNT molecules start to interact with the thin active organic layer. The advantage of not using the gate bias is to eliminate the stress induced changes, and the additional complications of driving the device under pulsed mode.

A transistor where the active layer was a soluble form of sexithiophene, the Dihexylquarterthiophene (DH4T) was tested under zero gate bias conditions. At a drain-source bias of –10 V and zero gate bias the device current is below micro Amps. Figure 5 shows the TNT vapor induced changes in the transistor off current. The device the current, exhibit almost step-like response to the TNT exposure. The induced changes in the current magnitude are also quite significant from 0.5 μA to almost 3 μA.

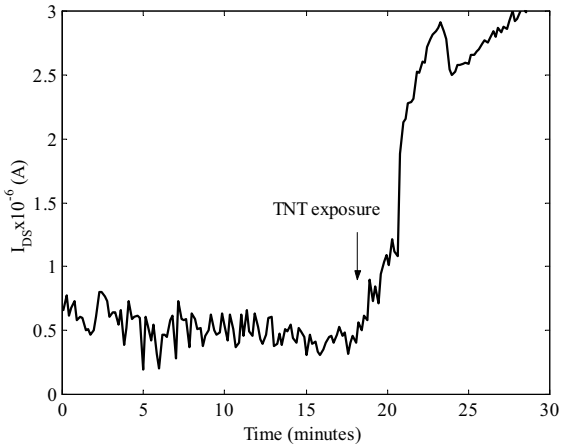


Figure 5. Response of a dihexylquarterthiophene (DH4T) thin film transistor to a TNT vapor.

DISCUSSION

MOSFET devices have been employed as gas sensing devices for long time; in these devices the gas molecules interact with a sensitive gate inducing a change of the work function of the gate that results in a shift of the threshold voltage. The organic transistor operates in a different way, the organic active layer is itself the sensitive region, and therefore minute changes in this active layer should induce major changes in the transistor electrical characteristics. Without gate bias applied, the transistor should operate as a normal chemiresistor sensor where all the variations are only due to a changes in the electrical conductivity.

TNT molecules are strong acceptors, and when they reach the surface of the organic film they should interact with the polymer by removing an electron and leaving behind a hole, which can act as a free charge carrier. The question is, does the TNT diffuse into the polymer? The time response observed in Figure 4 and Figure 5 is to fast for a diffusion mechanism. We believe that in first instance the effect is only in the surface. Probable all the TNT molecules attach to the surface and they create a space charge layer which temporally disturbs the FET accumulation. Later, some TNT molecules may diffuse into the polymer and may act as dopants.

It is also well know that oxygen also acts as a dopant for p-type organic semiconductors [7]. Fortunately, the response to oxygen is much slower and weaker and the one observed. Hence the organic layer responds preferentially to TNT.

We observe some degradation in the transistor electrical properties when exposed for longer periods of time (months) to air, however in spite of this, sexithiophene transistors can still respond to TNT vapours.

CONCLUSIONS

The prototype sensor described in this paper responds to nitroaromatic compounds of the type present for instance in the chemical signature emanating from a landmine.

Improvements in the sensor design should push the minimum detection limit of the sensor and improve the low term stability in atmospheric environment.

It is likely that the concentration of TNT present in the air over a landmine is in the femtograms per ml of air. It is not possible yet to reach this sensitivity. However if one thinks that these devices can be produced at low cost in flexible substrates with enormous active areas, they maybe reach the sensitivity to detect buried landamines. The sensor may be as well adapted to field screening of other substances including pesticides, and other substances of environmental interest.

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