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Contact effects in organic thin-film transistor sensors

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ABSTRACT

Contact effects in organic thin-film transistors (OTFTs) sensors are here investigated specifically respect to the gate field-induced sensitivity enhancement of more than three orders of magnitude seen in a DHα6T OTFT sensor exposed to 1-butanol vapors. This study shows that such a sensitivity enhancement effect is largely ascribable to changes occurring to the transistor channel resistance. Effects, such as the changes in contact resistance, are seen to influence the low gate voltage regime where the sensitivity is much lower.

1. Introduction

The scientific and technological driving force towards the development of performing conducting polymer (CP) based solid state sensors is still very strong despite this field has been initiated more than 30 years ago [1]. Recently, organic thin-film transistor (OTFT) sensors have risen the interest of the scientific community for their enhanced level of performance [2–6]. In this configuration, highly repeatable responses were measured by properly gate biasing the device [2,3] whereas broad chemical selectivity was conferred either by covalently bound side groups [7] or by means of CP blends [8]. Besides, an important assessment of their selectivity capabilities was achieved with a chiral OTFT, that exhibited field-effect amplified sensitivity allowing detection of optical isomers in the tens part-per-million (ppm) concentration range [9], *i.e.* with a three order of magnitude sensitivity improvement [10,11].

This report aims to demonstrate that the sensing process, in particular the field-induced sensitivity enhancement, can be largely ascribed to changes of the channel resistance R_{ch}, eventually ruling out dominating contributions from of the contact resistance (R_c) or leakage current variations. The results reported can also shed light on the origin of the contact resistance in OTFTs.

2. Experimental methods

2.1. Organic thin-film transistors fabrication

The transistors used for this study have a bottom-gate structure and consist of a highly *n*-doped silicon wafer

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(resistivity: 0.02–1 Ω/cm) coated by a 300 nm thick SiO_2 thermal oxide (dielectric capacitance per unit area: C_i = 10 nF cm^2). Each sample was fabricated on a cleaved wafer piece of *ca.* 2 cm^2. The silicon substrate with a gold pad acts as the gate contact (G) while the silicon dioxide is the gate dielectric. The SiO_2 surface was alkyl functionalized by treatment in 1,1,1,3,3,3-hexamethyldisilazane saturated vapors for 24 h. The dielectric surface was covered by a α,ω-dihexyl-hexathiophene (DHα6T) thin-film deposited by thermal evaporation at a base pressure of 8×10^{-7} with the substrate kept at room temperature. A series of 30 gold source (S) and drain (D) contacts were defined, by thermal evaporation through a shadow mask, directly on the organic films. Before the measurements, the OTFTs were annealed under a vacuum of 10^{-5} Torr at 100 °C for 30 min. Transistors were produced with different channel lengths (distance between the two probed pads), namely: L = 0.2 mm, 0.6 mm and 1 mm, while the channel width (the pads' longer dimension, W), was kept constant at 4 mm. The sensors were fabricated and measured in a standard laboratory environment and operated at room temperature. The synthetic approach for preparing the α,ω-dihexylsexithiophene comprised a Stille coupling between the 5,5′-bis-trimethylstannyl-2,2′-bithiophene and the 5-bromo-5′-hexyl-2,2′-bithiophene. The product precipitated from the reaction medium as a red powder and was purified from soluble byproducts by subsequent Soxhlet washing with methanol, chloroform, acetone and *n*-hexane.

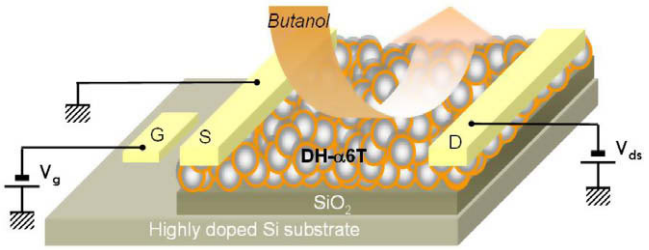
2.2. Sensing measurements

The analyte, in a nitrogen stream and at a controlled concentration, was delivered through a nozzle (positioned at a fixed distance of few mm from the device channel surface) directly onto the active layer surface, as depicted in Scheme 1. The I_{ds}–V_g transfer characteristics were measured by biasing the device in a common source configuration by sweeping V_g (from positive to negative potentials) at a fixed V_{ds}, namely −50 V. The current, I_{ds}, flowing in the channel region was measured in nitrogen and in a flux of controlled butanol concentration in N_2, obtained through a system of computer controlled flow meters. The response measurements were performed at relatively high analyte concentrations (3750–11,250 ppm) as this condition allowed to better discriminate the effects of the contact resistance variation. Both the transfer characteristics (measured in N_2 and in the analyte atmosphere), lasted for 45 s with a total flux of 200 ml/min. Before starting each run the unbiased device was conditioned by exposure to the analyte atmosphere for 45 s.

3. Results and discussion

The system investigated is a α,ω-dihexylsexithiophene (DHα6T) OTFT with a bottom-gate top contact configuration (Scheme 1). Such a device has been widely investigated for 15 years now [12–17] and can, in many respects, be taken as a model system. The DHα6T thin-film, exhibiting a morphology formed of a three dimensional percolation-type network, with nano-sized crystalline domains separated by voids of comparable size [18], acts both as transistor channel material and as sensing layer. In agreement to what already reported for OTFTs exposed to volatile organic compounds, changes in the drifting source-drain current were seen upon exposure of the DHα6T OTFT to 1-butanol and the response and recovery times were generally quite short, falling in the 10–100 s of seconds range at most [2,3]. Weak chemical interactions are likely to occur between the DHα6T thin-film and the alcohol molecules, the latter being eventually partitioned between the solid (the DHα6T thin-film) and the gaseous phase. Since diffusion of the molecules into the crystalline grains is unlikely, such molecules largely percolate through the voids around the grains till the interface with the dielectric is reached. The analyte molecules are physisorbed at the grains surface and this can enhance the potential barriers at the boundaries [19], generating also charge trapping effects. The degree of physisorption is a function of the chemical affinity between the active layer and the analyte [7], and it occurs in the DHα6T bulk, as well as at the interface with the dielectric, were the two-dimensional transport takes place.

Typical DHα6T OTFT current–voltage characteristics in the inert N_2 atmosphere are reported in Fig. 1a. Here, the source-drain current (I_{ds}) is reported as a function of the source-drain bias (V_{ds}) for different gate biases (V_g). As DHα6T is a p-type semiconductor, negative values of V_{ds} and V_g ($|V_g| > |V_t|$) drive the device in the *on-state* (accumulation mode), while V_g values below the threshold voltage, V_t, generate a regime of charge depletion (*off-state* or depletion mode) [2]. The field-effect mobility (μ) and the threshold voltage, V_t, are graphically extracted from the relevant square root of I_{ds} *vs.* V_g plot (Fig. 1b) resulting in μ = 0.1 cm^2/Vs, V_t below −2 V while a current amplification of 10^4 can be achieved. These figures of merit are state of the art values for DHα6T [12–15], although best mobility



Scheme 1. DHα6T thin-film transistor sensor structure upon exposure to 1-butanol vapors along with biasing details.