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Interfaces analysis by impedance spectroscopy and transient current spectroscopy on semiconducting polymers based metal–insulator–semiconductor capacitors

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ABSTRACT

Impedance and transient current measurements on metal–insulator–semiconductor (MIS) capacitors are used as tools to thoroughly investigate the bulk and interface electronic transport properties of semiconducting polymers, i.e. poly(3-hexylthiophene) (P3HT). Distinct features were observed at both interfaces, i.e. metal–semiconductor and semiconductor–insulator. The results revealed a dispersive transport in the bulk due to the band tail of the localized states, presence of interface states at the interface between the insulator and the semiconductor and formation of a less conductive small layer at the interface semiconductor–metal contact due to intrusions of sputtered Au particles. Effects of self-assembled monolayers (SAMs) treatments of the gate insulating dielectric were investigated showing that treating the gate dielectric with either ozone or hexamethyldisilazane (HMDS) or octyltrichlorosilane (OTS) alter not only the interface semiconductor–insulator but the bulk properties as well. An exponential density of states with a width parameter of 38–58 meV depending on the surface treatment was found to be representative of the band tail of P3HT. Though both OTS and HMDS treatments slightly increase the density of interface states, only OTS treated samples showed a decrease in disorder parameter of the bulk. The latter fact can be attributed to an increase of the grain size due to a favored π-π stacking film growth. An outcome explaining the already reported increase of the lateral mobility and decrease of the vertical mobility observed upon OTS treatment of the gate insulating dielectric in poly(3-hexylthiophene) based devices.

1. Introduction

In recent years, the field of organic electronics has made a tremendous step when it comes to performances and manufacturing technologies. Organic field effect transistors (OFETs) with field effect mobilities ($10\,cm^2/Vs$) exceeding those of thin-film amorphous silicon devices have been reported [1,2]. Hence, the first applications in e-paper displays, simple integrated circuits, and chemical and biological sensors have been demonstrated [2–4]. Despite the improvements cited above, better microscopic understanding and control of the charge transport required for more demanding applications are still lacking.

One of the main issues on the road to fully understand and control the charge transport in organic semiconductor based devices is the role of traps both at the interface and in the bulk. In fact charge transport in OFETs takes place in a thin accumulation layer buried at the interface between the organic semiconductor and the insulating gate dielectric [5]. Hence, it is not surprising that charge transport in the OFET channels is influenced by the interface [6] and the bulk [7]. OFETs are not the only devices of interest in organic electronics, organic diodes have also attracted a lot of interest as light emitting diodes or solar cells. That is why, the metal contact-semiconductor interface is of high interest. It is well known that the metal deposition for top contacts of diodes can crucially alter the performance of organic diodes [8,9]. Therefore a prosperous future for organic electronics requires firstly tools to analyze interfaces and bulk charge transport properties and secondly ways to control interfaces and bulk charge transport properties.

Recent studies showed substantial improvements of device performance upon surface treatment [10–12]. However the physical reasons behind the experimentally observed performance improvements are still an issue. A commonly seen trend is the improvements of the OFETs performance with more hydrophobic dielectric surfaces [13]. Several device properties improvements are all entangled together: the grain size in the bulk, the surface energy, the surface roughness and the interface states at the

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interface gate dielectric-semiconductor. Hence isolated origins of the observed effects upon surface treatments are still an issue for further improvements. In order to obtain relevant properties of the bulk and the interfaces, we use impedance spectroscopy (IS). Impedance spectroscopy on MIS capacitors offer several advantages from the simplicity of the measurements to the wide range of accessed information on both the interface and the bulk. The use of MIS capacitors is of great interest as MIS capacitors mimics perfectly the interface of the charge transporting channel of OFETs. A light free version of transient current measurements on MIS capacitors is used complementary to the impedance measurements.

In this paper, we provide a full description of impedance measurements carried out on organic semiconductor based MIS capacitors. Analysis of the obtained data is then used to explain the effect of various gate insulating dielectric surface treatments. In addition, the impedance model allows to simulate successfully the transient current data. Section 2 describes the experimental details. In Section 3 we provide a proper equivalent circuit for the impedance measurements analysis. In Section 4 we present the experimental results according to the theoretical background developed in Section 3. Additionally, we compare and discuss results obtained for different surface treatments. Furthermore, the data are compared against transient current experiments.

2. Experiment

The MIS capacitors (as sketched in Fig. 1(b)) were prepared on highly n-doped silicon (Si) wafers (resistivity = 2 mΩcm) with a 100 nm thick thermally grown silicon oxide (SiO_2). The highly n-doped Si acts as the gate and the SiO_2 as the insulating gate dielectric. Three different types of surface treatments were used prior to the deposition of the semiconductor. All the substrates were wet chemically cleaned in an ultrasonic bath with solvents (acetone, isopropylacetate) and exposed to an oxygen plasma for 10 min. One of the substrates was not further modified (O_3 sample) hence serving as a reference and the other two were used for silanization. One of the two remaining samples was exposed to a HMDS saturated atmosphere for 14 h (HMDS sample) and the other one was immersed for 20 h in a 2 wt.% OTS in ethanol solution (OTS sample). Afterwards, the latter two samples were rinsed with acetone and deionized water. The values of the contact angles are summarized in Table 1, and are in the range of reported literature values [14]. A poly(3-hexylthiophene) (P3HT) (Sepiolid-P100, Rieke Metals, regioregularity ~95%, average molecular weight $M_w = 5 \cdot 10^4$ g/mol) layer was spin coated from a 1.5 wt.% chloroform solution for a final thickness of ~170 nm. The MIS capacitors were completed by sputtering (with a rate of 25 nm/min and at a pressure of $5 \cdot 10^{-3}$ mbar) a 100 nm thick top ohmic gold contact onto the semiconductor.

The impedance measurements were made using an Agilent E4980A Precision LCR meter. The signal amplitude was 100 mV in order to assure a low signal-to-noise ratio and the linearity of the system response.

The transient current measurements setup is shown in Fig. 1(c). A packet of charge carrier is created by a step bias function (Fig. 1(a)). The created packet of carriers moves across the sample inducing a time dependent current (Fig. 1(d)). This current is measured through the load resistance (R_{Load}) by a digital oscilloscope. In order to extend the measurements time range, the load resistance was increased from 10 Ω to 100 *k*Ω. A time span of 10 ns–100 ms could be obtained. The step function was generated by a Keithley 3390 function generator. 64 pulses were averaged to increase the 12-bit resolution of the oscilloscope. Before each series of pulses, the background current was recorded and then subtracted from the obtained transient current. The time interval between two successive pulses was set to 10 s.

Temperature dependence measurements were made with the sample mounted in vacuum on a cold-finger cryostat and cooled down with a closed loop liquid Helium supply.

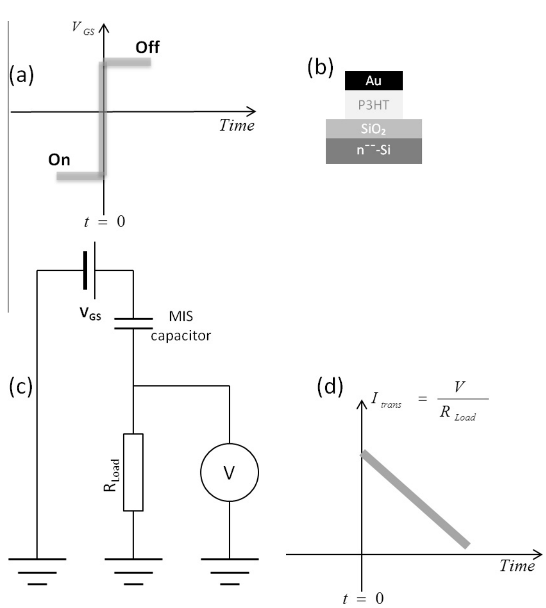

Fig. 1. The setup used for transient current measurements (c) shows the step function applied at the sample (a) and the current measured across the load resistance (d). (b) Device structure of the used MIS capacitor ($A = 3 \times 3$ mm).

3. Theoretical description

3.1. Ideal MIS capacitor

Impedance spectroscopy measurements consists of the response of a given device upon applying an AC voltage which oscillates the Fermi level difference across the device at a given frequency. The impedance is extracted from the phase shift and amplitude of the obtained response current. The response of a MIS capacitor can be obtained from the equivalent circuits in Fig. 2 [15–17].

The admittance of the equivalent circuit for different frequencies (ω) can be represented as

$$Y = G_p + i\omega C_p, \tag{1}$$

where G_p and C_p are the parallel conductance and parallel capacitance of the measured device, respectively. While, the admittance of a MIS capacitor biased in accumulation ($X_D = 0$) is given by (Fig. 2(a))

$$Y = \left[\frac{1}{i\omega C_I} + \frac{R_B}{1 + i\omega C_B R_B} + R_C\right]^{-1}, \tag{2}$$

for the admittance of a MIS capacitor biased in depletion ($X_D > 0$), the additional depletion layer has to be included and the admittance is given by (Fig. 2(b))

$$Y = \left[\frac{1}{i\omega C_I} + \frac{1}{i\omega C_D} + \frac{R_B}{1 + i\omega C_B R_B} + R_C\right]^{-1}, \tag{3}$$

Table 1
Contact angles of water for different types of substrates.

Sample type	O_3 sample	HMDS sample	OTS sample
Contact angle (°)	⩽5	85	96