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Organic Electronics

Letter

Organic field-effect transistor based sensors with sensitive gate dielectrics used for low-concentration ammonia detection

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ABSTRACT

A novel organic field-effect transistor (OFET)-sensor concept is presented based on the application of an ion-conducting organic dielectric material, which is chemically adapted to change its electronic properties upon contact with an analyte, thereby generating an electrically detectable response. By employing pH-sensitive, ring-opening metathesis polymerized materials as gate dielectrics in bottom-contact OFETs with a meander-shaped top-gate structure, the concept was successfully realized and evaluated with ammonia (NH_3) as gaseous analyte, easily providing distinct sensor response at concentration levels as low as 100 ppm. In addition to current–voltage OFET-analysis, optical spectroscopy and capacitance measurements were used to rationalize the underlying sensor mechanism, which is mainly attributed to a deprotonation of the pH-sensitive groups of the active-sensing dielectrics by NH_3 and a resulting generation of mobile ions, leading to an increase of the charge carrier density within the OFET channel. The proposed concept provides several advantages over existing OFET-sensor detection principles, including the separation of the sensing mechanism from the charge-transport functionality of the semiconductor, inherent protection of the latter against air exposure and increased selectivity by the application of specific dielectric materials. It therefore offers a great deal of promise in contributing to the development of cheap, integrated, smart and flexible (bio)sensor systems.

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1. Introduction

Organic field-effect transistors (OFETs) are promising candidates as smart (disposable) sensor elements in health-, food- and environmental monitoring, diagnostics and control, ranging from light- and chemical vapor sensors to transducers for ions and biological substances [1–4]. Such devices combine the advantages of electroactive organic materials with those associated with field-effect transistors, including applicability of advanced solution-based processing techniques like inkjet printing [5], easy tailorability for enabling sensitivity and selectivity with respect to a target analyte, inherent signal amplification, fast response times, low power consumption, the ability for multi-parameter sensing [6] and the possibility to be integrated into complex circuits with embedded signal processing. So far, several sensors based on organic transistors have been demonstrated or proposed; for instance, gas- or vapor-sensitive OFETs, mainly of bottom-gate type, for gases like N_2 [6], O_2 [6], organic vapors [7,8] or humidity [9,10], with the semiconducting layer as sensing layer, where its conductivity is modulated upon interaction with

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an analyte; pH-sensitive (or ion-sensitive) OFETs [11] based on inorganic dielectrics with an ion-sensitive surface; biochemical OFET-sensors [2,4,11] including specific layers for the detection of e.g. glucose, antigens or DNA. In addition, OFETs using self-assembled monolayers (SAMs) as active-sensing elements [12] and stable OFET-sensor operation in aqueous media have recently been investigated [13,14]. The dielectric strongly affects the device operation of a field-effect transistor [15] and, aside from hysteresis effects [16] and threshold voltage shifts [17] due to space charge polarization, the application of ion-conducting (electrolyte) dielectrics can lead to a strong reduction of the operating voltage by generating large charge carrier densities ($>10^{14}$ cm^{-2}) in an OFET channel through ions moving to the interfaces or even into the semiconductor [18,19]. The corresponding interactions are mainly attributed to the formation of electric double layers at the interfaces (leading to very large capacitance values) or to electrochemical doping (oxidation/reduction processes). Accordingly, by combining the ion-conducting abilities of electrolyte gate dielectrics with an appropriately designed sensing functionality in one layer, the transistor parameters are expected to be easily influenced upon chemical interaction with a specific analyte; this forms the basis of the proposed concept. By separating the sensing mechanism from the charge-transport functionality of the semiconductor, established high-performance semiconductor materials can be used and synthetic effort for optimizing both sensing and charge-transport behavior of a material at the same time is no longer required. In addition, the application of an active-sensing gate dielectric allows for the implementation of device geometries which would be difficult to realize when detecting via the semiconductor. Moreover, in a top-gate architecture the organic semiconductor, which is often sensitive to oxygen and/or moisture [20–22], is largely protected against exposure to ambient atmosphere by the dielectric, enabling the use of less air-stable, but otherwise high-performance materials for the channel layer.

In order to evaluate the proposed OFET-sensor concept, ammonia [23] was chosen as gaseous analyte, which is relevant, e.g. as a marker for fish freshness and meat spoilage and has already been investigated in combination with OFETs by some groups [12,24,25], focusing on the direct or – via integrated reactive SAMs – indirect interaction between NH_3 and the organic semiconductor.

2. Materials and device fabrication

Fig. 1a schematically illustrates the realized OFET-sensor architecture on a Si/SiO$_2$-wafer substrate. The source/drain-electrodes (channel length: 25 μm, channel width: 2.85 mm) were structured via photolithographic lift-off processing, using photoresist (ma-N 1407), developer (ma-D 533/S) and remover (mr-Rem 660) from micro resist technology and including UV-exposure with an EVG-620 mask-aligner as well as thermal evaporation ($p < 5 \times 10^{-6}$ mbar) of a 2 nm chromium adhesive layer and a 50 nm gold layer. As organic semiconductor material, regioregular poly(3-hexylthiophene) (rr-P3HT, $M_n \approx 26,900$ g/mol,

$PDI \approx 1.4$, Fig. 1b) with a layer thickness of ~20 nm was applied via spin-casting in argon atmosphere from a chloroform (CHCl$_3$) solution (2 mg/ml) and annealed in vacuum ($p < 5 \times 10^{-6}$ mbar, 120 °C, 1 h). In order to avoid intermixing of the rr-P3HT film and the active-sensing dielectric layer (both could only be dissolved in organic solvents), a ~700 nm thick polyvinyl alcohol (PVA, Mowiol 5–88, Fig. 1c) intermediate layer was spin-cast from a dialyzed hydrogel (9–10 wt.%) onto the organic semiconductor and dried in argon (110 °C, 1 h) and vacuum ($p < 5 \times 10^{-6}$ mbar, 60 °C, 3 h), providing an ion-conducting, ammonia-insensitive and highly resistant film, which is impermeable to most organic solvents. Afterwards, CHCl$_3$-solutions (60 mg/ml) of the ring-opening metathesis polymerized (ROMP) materials **1a**, **1b** or **1c** (Fig. 1d) were spin-cast and dried (130 °C, 10 min) in argon, leading to a film thickness of ~700 nm. The ROMP-film was in direct contact with the target analyte due to a ~100 nm thick, meander-shaped, thermally evaporated ($p < 5 \times 10^{-6}$ mbar), common top-gate aluminum electrode, so that analyte diffusion through the gate electrode was not required. As for the chemical composition, the applied active-sensing dielectrics **1a** (batch 1: $M_n \approx 35,400$ g/mol, $PDI \approx 1.8$; batch 2: $M_n \approx 44,700$ g/mol, $PDI \approx 1.2$) and **1b** ($M_n \approx 40,800$ g/mol, $PDI \approx 1.1$) consist of xanthene-dye molecules (eosin Y or 2,7-dichlorfluorescein (DCF)), which were connected to a polymerizable norbonene group and co-polymerized with a chemically inert monomer (endo,exo-bicyclo[2.2.1.]hept-2-ene-5,6-dicarboxylic acid dimethylester) as bulk-monomer using ring-opening metathesis polymerization. As non-sensitive reference material, the homopolymer of endo,exo-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid dimethylester (**1c**; batch 1: $M_n \approx 46,100$ g/mol, $PDI \approx 1.1$; batch 2: $M_n \approx 53,400$ g/mol, $PDI \approx 1.1$) was used. Detailed information about synthesis and ROMP in general can be found in literature [26,27]. When exposed to an alkaline analyte such as ammonia, the dye's OH-groups of polymers **1a** and **1b** are deprotonated, thus creating mobile ammonium ions (NH_4^+) and corresponding counter-ions. This ability of the dye-bearing dielectrics to deprotonate and protonate in solid state was verified by a change of the optical properties using UV/VIS- and IR-spectroscopy (see Appendix A and Ref. [26]).

3. Results and discussion

Before evaluating the OFET-sensor concept, each polymer **1a**–**c** (batch 1) was electrically characterized in capacitor structures, consisting of 125 nm thick, structured ITO bottom-electrodes on a glass substrate, a 800–1000 nm thick **1a**-, **1b**- or **1c**-polymer film and ~100 nm thick, thermally evaporated ($p < 5 \times 10^{-6}$ mbar) aluminum comb-shaped top-electrodes. The samples were individually assembled in a custom-made gas-measurement chamber in argon and characterized using an Agilent E4980A LCR meter (test-signal frequency: 1 kHz, test-signal amplitude: 1 V$_{rms}$, interval: 10 s). The impedance (Z) and phase angle (Θ) data of the capacitors were recorded upon exposure to argon and 100% NH_3 and, assuming an equivalent circuit model consisting of a capacitance C_P and a resistance R_P in