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Short communication

Effect of passivation on the sensitivity and stability of pentacene transistor sensors in aqueous media

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ABSTRACT

Charge-detecting biosensors have recently become the focal point of biosensor research, especially research onto organic thin-film transistors (OTFTs), which combine compactness, a low cost, and fast and label-free detection to realize simple and stable in vivo diagnostic systems. We fabricated organic pentacene-based bottom-contact thin-film transistors with an ultra-thin insulating layer of a cyclized perfluoro polymer called CYTOP (Asahi Glass Co., Tokyo, Japan) on SiO_2 for operation in aqueous media. The stability and sensitivity of these transistor sensors were examined in aqueous buffer media with solutions of variable pH levels after the passivation of perfluoro polymers with thicknesses ranging from 50 to 300 nm. These transistor sensors were further modified with an ultra-thin film (5 nm) functional layer for selective BSA/antiBSA detection in aqueous buffer media, demonstrating a detection capability as low as 500 nM of concentrated antiBSA. The dissociation constant from the antiBSA detection results was 2.1×10^{-6} M. Thus, this study represents a significant step forward in the development of organic electronics for a disposable and versatile chemical and bio-sensing platform.

1. Introduction

As the demand for diagnostic laboratories continues to increase with increased health care costs, the necessity for rapid and inexpensive medical analyses has become increasingly apparent. The use of optical measurements is predominant, but this method has several limitations due to the required fluorescent dyes and expensive detectors (Neumann et al., 2002). In addition, because optical equipment is not portable, in vivo and in situ measurements are also very difficult. Recent advances in bio-chemical detection research, in part benefiting from the overwhelming progress made in organic electronics, have shown great promise for a viable, low-cost alternative to current optical detection systems (Khan et al., 2010; Roberts et al., 2008).

To date, progress in organic materials has shown a great deal of promise due to the utilization of thin-film and multilayer devices, especially for organic light-emitting diodes (OLEDs) (Friend et al., 1999; Bhansali et al., 2009) and organic solar cells (Wohrle and Meissner, 1991). The rapid progress in this field has been, in part, due to improvements in fabrication processes and the design of new materials, with remarkable upgrading in the electronic properties of semiconducting (Murphy and Fréchet, 2007) and insulating (Klauk et al., 2007; Roberts et al., 2009) materials.

Additionally, micro-biosensors based on OTFTs have recently attracted a considerable amount of attention owing to their potential for miniaturization, standardization, mass-production and a suitable configuration for smart sensor (Khan et al., 2010; Torsi et al., 2008). However, the development of devices based on an air/aqueous stable organic semiconductor still faces many challenges. The open morphology with large clefts between the grains of polycrystalline organic molecules limits the charge transport, which shortens the life of the devices due to degradation of the materials (Dimitrakopoulos and Mascaro, 2001; Zhu et al., 2002; Andraz and Gvido, 2009). Another relevant issue is the method of encapsulation or surface modification, which are both considered to be unfavorable due to solution processing issues (Khan et al., 2010; Sreenivasan and Gleason, 2009).

In this work, we evaluate bottom-contact pentacene transistors as bio-chemical sensors in aqueous media with two different types of top passivation with variable thicknesses, i.e., perfluor-1-3-dimethylcyclohexam (PFDMCH) and/or a cyclized perfluoro polymer called CYTOP by plasma-enhanced chemical vapor depo-

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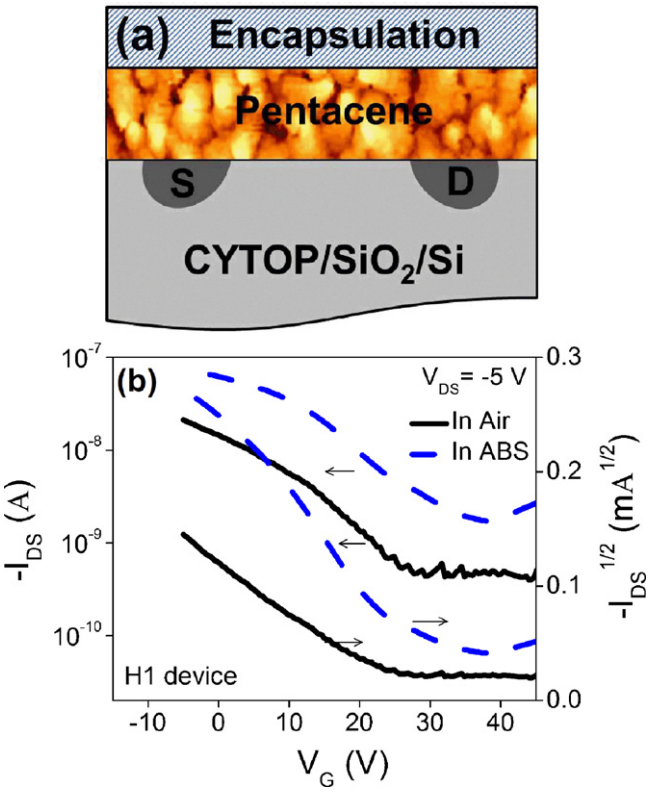

Fig. 1. (a) Schematic representation of the OTFT as a bio-chemical sensor investigated in this study. Fabrication procedure for a bottom contact OTFT with 30 nm pentacene on 15 nm CYTOP/200 nm SiO_2 and source-drain electrodes with a channel W/L of 10. The entire device was passivated with PE-CVD based ppPFDMCH layer and/or spin coated CYTOP layer with variable thickness. (b) [H1-sensor] transfer characteristics (I_{DS} *vs.* V_G) at V_{DS} of −5 V in ambient (solid curves) and in PBS (blue dashed curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

sition (PE-CVD) and/or spin-coating. Since medical analyses are conducted by monitoring the pH variations that occur during various bio-chemical reactions, therefore, we underscore the effect of variable pH levels on these transistor sensors. Additionally, the transistor sensor surfaces were modified with functional layer of maleic anhydride (MA) using PE-CVD and were used to detect BSA/antiBSA immunoassay formation as a model system to demonstrate the resulting detection possibilities.

2. Experimental

All materials were purchased from Aldrich and were used as received without further purification unless otherwise stated. *N*-ethyl-*N*′-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) were purchased from Fluka and rabbit monoclonal antiBSA was obtained from Millipore.

The fabrication of the bottom-contact pentacene transistor is schematically illustrated in Fig. 1a. Additional details pertaining to the fabrication procedure are given in supporting information (SI) section (Khan et al., 2011). The polymerization of perfluor-1-3-dimethylcyclohexam and maleic anhydride was carried out in a custom-built PE-CVD reactor following a well-established procedure in our laboratory (Khan et al., 2010, 2011). Three different thicknesses were used on top of the transistor devices: H1 consisting of 50 nm PE-CVD of PFDMCH polymer, H2 consisting of 300 nm of spin-coated CYTOP polymer, and H3 consisting of 600 nm of spin-coated CYTOP polymer.

For operation in aqueous media for bio-chemical sensing experiments, all bio-chemical molecules were diluted in 10 mM of a freshly prepared concentrated phosphate buffered saline (PBS) solution at pH 7.4. For the pH detection experiments, solutions with different pH levels were prepared using a specific amount of HCl and NaOH depending on the required pH. A custom-built flow cell constructed with Plexiglas was used to confine the buffer and analyte solution to the OTFT channel region, as shown in online SI section, Fig. S1. The contact area was sealed with a Viton O-ring and the flow channel was connected to a peristaltic pump (NovoChem). The peristaltic pump delivered the solution from the solution reservoirs to the sample at a constant rate of 300 μL/min to minimize mass transfer limitations of the analyte to the sensor surface, which has been shown to occur below 20–30 μL/min (Mabeck and Malliaras, 2006).

All electrical and biosensing measurements were performed with a Keithley 4200 semiconductor characterization system in ambient air and in aqueous buffer media.

3. Result and discussion

Details of the device fabrication, functionalization, and experimental conditions used here are described in detail elsewhere and can be found in SI section (Khan et al., 2010, 2011). Briefly, we fabricated a bottom-contact OTFT with 30 nm of pentacene as the active layer on a polymer dielectric with a width (W) of 500 μm and length (L) of 50 μm (Fig. 1a). The transfer and output characteristic in ambient air at drain-source voltage (V_{DS}) = −10 V are featured in online SI, Fig. S2. These devices exhibited an average field-effect mobility of 0.0054 $cm^2/V\,s$ with an on–off ratio of 7×10^4 and a threshold voltage (V_{th}) of −2 V at V_{DS} = −10 V. Moreover, these devices showed no hysteresis due to the CYTOP thin insulation layer on SiO_2 (Jang et al., 2008).

OTFTs with a top passivation layer were further characterized in air and PBS at a low V_{DS} of −5 V,which is necessary for stable operation in aqueous media. The transfer characteristics at V_{DS} = −5 V are shown in Fig. 1b, and Fig. S3 represents the typical behavior of the p-type OTFTs under ambient conditions (greater detail regarding these results are summarized in Table S1). The flow cell was laminated on to the transistor surface with an inlet and outlet opening. After injecting PBS solution, we observed an increase in both the on- and off-current with a small/negligible shift in V_{th}, as illustrated by the blue dashed curve (H1 device, Fig. 1b). The H2 and H3 devices showed an increase in both the on- and off-current with a rather high shift in V_{th}, as shown in SI section, Fig. S3a and b, respectively. The exact mechanisms are still not fully understood at this point, but it is clear that water and (deprotonated) surface hydroxyl groups play a central role by acting as charge carrier traps in polaronic states at the water–semiconductor interface. However, strong dipole fluctuations in the PBS lead to a change in the mobility via thermally activated hopping in the direction parallel to the interface (Tobias et al., 2009; Kumaki et al., 2008; Chua et al., 2005). Nevertheless, these influences were small. Remarkably, the transistors still functioned well in PBS. The output plots are shown in SI, Fig. S4.

To evaluate the implementation of the label-free detection method for monitoring bio-chemical species electronically based on micro-fabricated OTFTs, we used constant bias conditions in which V_G and I_{DS} were set to facilitate the current flow within the channel. The occurrence of a chemical or physical absorption is subsequently converted to the ΔI_{DS} response as a function of time, which ultimately depends on the analyte composition, concentration, and the OTFT bias conditions.

Biosensing experiments, particularly antibody–antigen interactions, depend mainly on the pH of the working solution due to the different isoelectric point (pI) of proteins (Lahiri et al., 1999; Carvalho and Carmona-Ribeiro, 1998). Thus, the sensitivity and