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Low-voltage printable OFETs for sub-ppm detection of ammonia under humid conditions

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Abstract

This report describes the development of a gas sensor platform based on all solution-processed bottom-gate bottom-contact organic field-effect transistors that operate at ≤ -2 V. The sensor was able to detect ammonia as low as 600 ppb under high relative humidity (RH=80%).

Keywords: Organic Filed-effect Transistors, Inkjet Printing, Bilayer Dielectric, Sensor Array, Ammonia Detection

Introduction

Ammonia (NH_3) sensing is of great interest due to its relevance to environmental and health monitoring applications. Nevertheless, current ammonia sensing technologies have their own limitations; e.g., metal oxide gas sensors require high temperatures (between 200 and 300 °C) in order to operate, which hinders their integration on to low-cost plastic substrates. Moreover, they are susceptible to interference from water vapor [1]. Conducting polymers such as polyaniline show room temperature sensitivity towards low concentrations of ammonia, but suffer from slow recovery rate. Therefore, heating is often required to enhance their reversibility, which adversely increases power consumption [2].

Recently, organic field-effect transistors (OFETs) have attracted considerable attention due to their customizability through chemical structure tailoring, low-temperature processing, intrinsic mechanical flexibility, and compatibility with large area manufacturing [3-5]. These features together with multiparametric data acquisition and signal processing provide OFETs with great potential as low-cost yet reliable gas sensors [6-7]. However, achieving high performance OFET devices operating at low voltages (compatible with low power, battery-operated devices) using only solution processes proves to be challenging. Faraji and co-workers reported OFETs operating at <1.5 V developed using solution-processed bilayer dielectrics with high capacitance values [8-9]. The dielectric is comprised of a high-*k* organic/inorganic hybrid nanocomposite, capped with a thermally crosslinked poly(4-vinyl phenol) (PVP). Herein, we report an all-polymeric bilayer dielectric to achieve low-voltage operation.

One of the major issues affecting performance and yield of devices with stacked layers (i.e., capacitors, OFETs, etc.) is the non-uniform cross-section profile of inkjet-printed electrodes due to the coffee-ring effect [10]. In order to suppress these non-uniformities in the printed silver gate electrode, we modified the plastic substrate surface using a crosslinked polymeric buffer layer prior to inkjet printing metallic electrodes.

Low-voltage bottom-gate bottom-contact (BGBC) OFET-based sensing platform was fabricated using only solution processing techniques. The room temperature response of the sensor towards various concentrations of ammonia under dry and humid conditions was evaluated.

Experimental

A 125 µm polyethylene naphtalate (PEN; Teonex Q65FA, Teijin Dupont Films, Japan) was used as the substrate. PEN surface was briefly treated with O_2 Plasma and spin-coated with an aqueous polymeric solution. The substrate buffer layer was then thermally crosslinked at 120 °C for 1 hr. Gate electrodes (width 250 µm) were patterned from a commercial silver nanoparticle-based ink (DGP 40LT-15C, Advanced Nano Product, South Korea) using a Fujifilm Dimatix DMP-2831 inkjet printer, and sintered at 140 °C for 30 min. Smooth silver tracks (thickness ~120 nm) were obtained with a resistivity of 18 µΩ cm. A bilayer of a high-*k* polymer capped with a UV curable polymer, processed from orthogonal solvents, was used as the gate dielectric. Total thickness of the bilayer was 440 nm. Source and drain silver electrodes were then inkjet-printed using the same process for the gate electrodes, defining channel length and width of 100 µm and 2 mm, respectively.

Poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene) (DPPTTT) was prepared according to procedures reported elsewhere [5] and used as the organic semiconductor (OSC). Following 5 min perfluorobenzenethiol (PFBT) treatment of source and drain electrodes, DPPTTT was spin-coated from a 1,2-dichlorobenzene solution.

Gas sensing was conducted using an automatic vapor generating system (AVGS) to generate the desired ammonia vapor concentrations as described previously [11]. The system was equipped with two sources of ammonia: a cylinder of compressed anhydrous ammonia in air at a concentration of

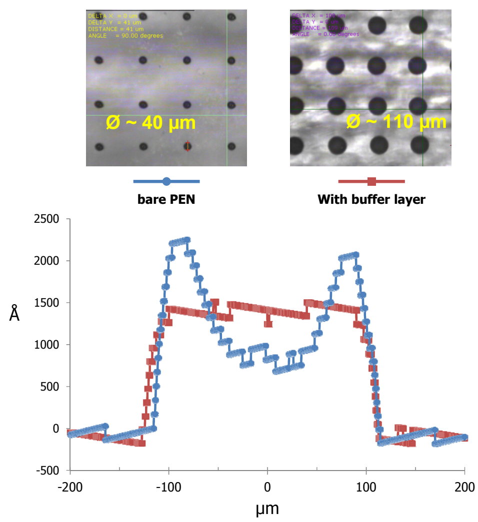

***Figure 1.** Images of an array of inkjet-printed Ag dots on bare PEN (left) and PEN with buffer layer (right). The surface profiles of printed silver tracks, measured by a Dektak profilometer, are also shown. The Dimatix platen was kept at 60 ºC during printing in all cases.*

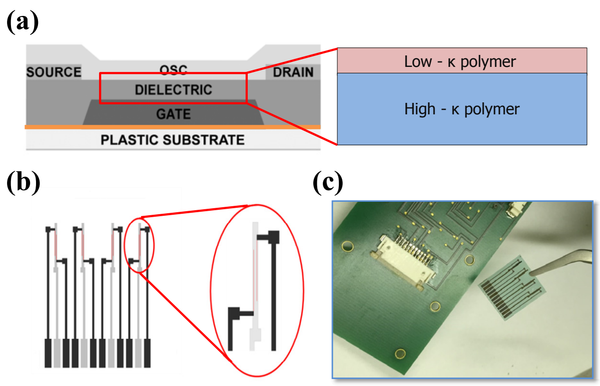

Figure 2. *a) and b) Schematics showing single OFET device and array structures used in this study, respectively. c) Final fabricated array (consisting of 4 OFETs) coated with the OSC layer.*

1000 ppm (BOC, UK) was used to generate ppm levels of ammonia vapor concentrations; sub-ppm concentrations were produced using an Owlstone vapor generator loaded with a pre-calibrated permeation tube (Owlstone Ltd., UK). A humidifier was utilized to produce a flow of air with controlled levels of humidity. A series of mass flow controllers (MFCs) and solenoid valves were employed to control the flow rates and the mixing of the vapor streams in order to achieve an output of desired NH_3 concentration and humidity.

FET CP16 (JLM Innovation GmbH, Germany) was used to record sensor signal at 500 ms intervals. The response of the sensor was measured as the change in the OFET's source-drain current (I_D at a constant V_G and V_{DS}) upon exposure to various concentrations of ammonia.

Results and Discussion

The polymeric buffer layer provides a smooth surface with a measured root-mean-square (RMS) roughness of about 0.3 nm. The hydrophilic nature of the polymer allowed improved wetting and spreading of the Ag ink on the substrate. The size of a single silver dot increased from 40 µm on bare PEN substrate to 110 µm for PEN coated with the buffer layer (Figure 1). This leads to smooth and uniform silver tracks with no bulges or coffee rings. Moreover, the thickness of the printed gate

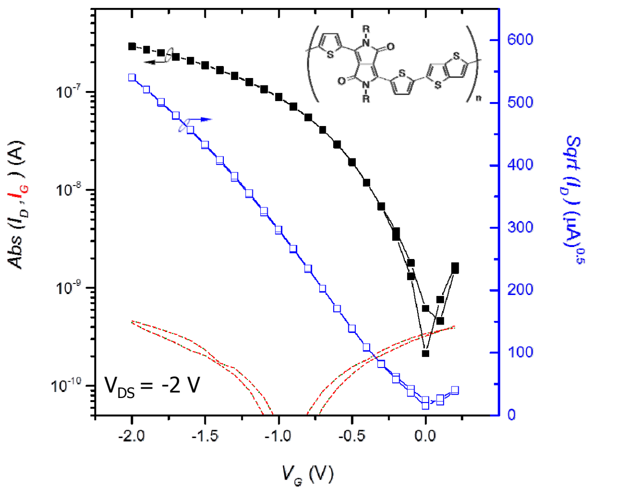

Figure 3. *The representative transfer characteristic (I_D–V_G) of the fabricated transistor measured by an Agilent semiconductor device parameter analyzer. Leakage current is shown in red dashed line. Inset depicts the molecular structure of DPPTTT.*

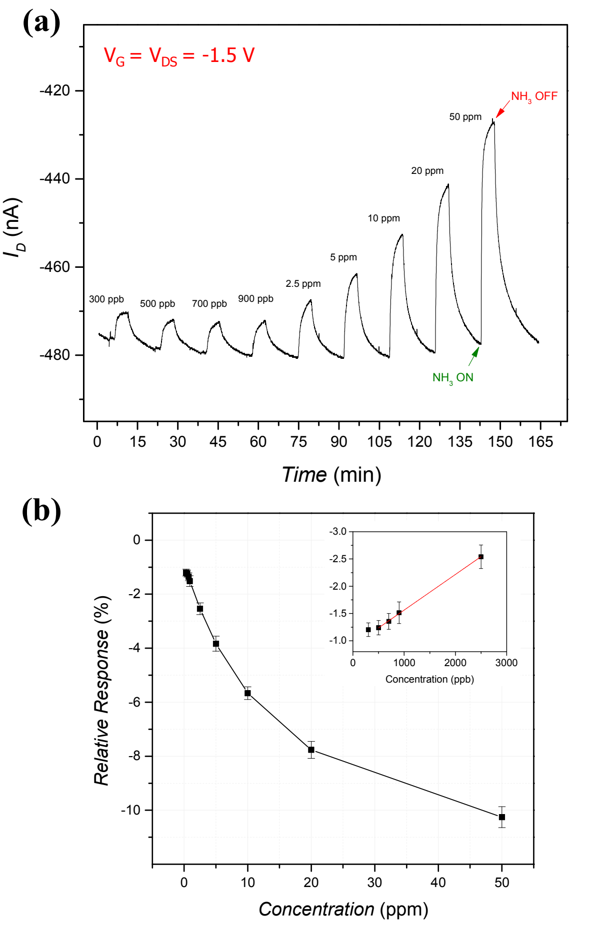

Figure 4. *a) Room temperature transient sensor response upon exposure to sequential ammonia concentrations from 300 ppb to 50 ppm at RH80%. b) Corresponding sensor calibration curve. The error bars represent standard deviation over 15 measurements; inset shows the linear fit to response at lower concentration regime.*

electrode decreased on the substrate buffer layer, which effectively decreased the thickness of the gate insulator required. Figure 2.a shows BGBC OFET structure with the bilayer gate dielectric. This bilayer was employed in order to achieve high areal capacitance (~140 nF/cm^2) as well as smooth, trap-free interface between dielectric and organic semiconductor. The OFET array platform's schematic and the actual fabricated device are shown in Figure 1.b and c, respectively.

Transfer characteristic of the fabricated DPPTTT-based OFET is demonstrated in Figure 3. Correspondingly, the following OFET's figures of merit were extracted:

µ (cm^2/Vs)	I_{on}/I_{off}	V_{Th} (V)	SS (mV/dec)
0.3	10^3	0.15	230

where µ is mobility, I_{on}/I_{off} is the ON/OFF ratio at V_{DS} = -2 V, V_{Th} is the threshold voltage and SS is the subthreshold swing. Using bilayer dielectric resulted in low operating voltage devices with small gate leakage current and negligible hysteresis.

The OFET sensor was exposed to sequential concentrations of ammonia under dry and humid conditions produced by the AVGS. Figure 4.a shows the transient change of the I_D upon exposure to 300 ppb to 50 ppm ammonia vapor in air with 80% relative humidity (RH). The exposure and recovery times were 5

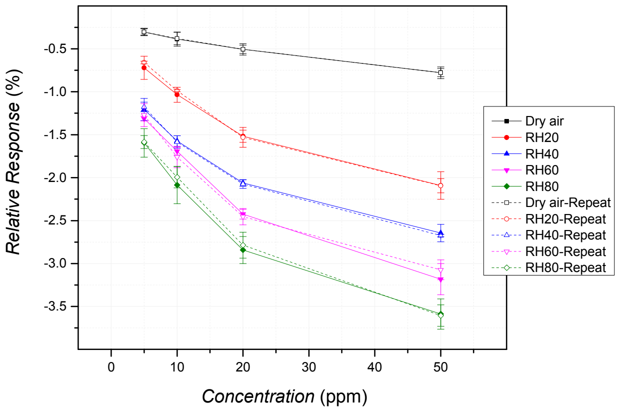

Figure 5. *Sensor calibration curve under different humidity conditions. Dotted lines are results of the repeat measurements after 2 weeks. Error bars represent standard deviation over 4 measurements.*

and 10 min, respectively. NH_3 is a reducing gas and it is believed to decrease the number of charge carriers (holes) at the p-type semiconductor-dielectric interface, thereby decreasing OFET's I_D at a constant bias. Response of the sensor was calculated using Equation 1:

$$\text{Relative Response} = (I_{D\,max} - I_{D\,b})/I_{D\,b}\,.100\% \qquad (1)$$

where $I_{D\,max}$ is the source-drain current value after exposure to ammonia and $I_{D\,b}$ is the baseline value, immediately before exposure. Based on the corresponding calibration curve (Figure 4.b), the theoretical lower limit of detection (LOD) was estimated to be ~600 ppb. LOD was calculated as the ammonia concentration to which the sensor signal is at least 3 times the noise value.

It is of crucial importance for practical applications to evaluate the effect of humidity on sensor performance. Response of the sensor is compared at different RH values: 0 (dry air), 20, 40, 60 and 80% (Figure 5). Ammonia can interact with water to form ammonium hydroxide (Equation 2):

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (2)$$

As the humidity increases, Equation 2 shifts towards the right and the concentration of hydroxyl groups increases. This further reduces the number of holes in the channel, hence improving the response magnitude. The same exposures were repeated after 2 weeks (dotted lines in Figure 5). These results demonstrate that sensor behavior remained almost unchanged over this period, which confirms the short-term stability of the sensor under ambient conditions.

Although, in this work, the array is coated with a single OSC, suitable patterning techniques can be adopted in order to deposit different semiconductors on the same platform to realize a multisensor array for detection of multiple analytes and gas mixtures.

Conclusions

Fully solution-processed bottom-gate bottom-contact OFET sensors with ≤ -2 V operating voltages were successfully fabricated. DPPTTT-based sensor showed rapid, sensitive and reversible room temperature response to ammonia vapor under dry and humid air conditions over the concentration range studied. Such OFET arrays can be used in novel printed electronics applications, such as low-cost and low-power flexible sensors.

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Ehsan Danesh received his MSc degree in polymer engineering from the Amirkabir University of Technology (2008), and his PhD in chemical engineering & analytical science from the University of Manchester (2014). His PhD focused on the fabrication of gas sensors for smart food packaging. He is currently a PDRA at the Organic Materials Innovation Centre (OMIC). His work has focused on the development of novel printable OFETs for gas sensing applications.