Low-Cost Chemical Sensing Platform with Organic Polymer Functionalization

Matti Kaisti, Aapo Knuutila, Zhanna Boeva, Carita Kvarnström and Kalle Levon

***Abstract*—The characteristics of an inexpensive transistor based chemical sensing platforms with organic polymer, polyaniline (PANI), was investigated in terms of tranconductance, pH sensitivity and drift properties. The platform consists of a printed circuit board manufactured in a standard manufacturing process and commercial discrete MOSFETs. The platform is funtionalized with PANI by a simple low-cost drop casting. The platform shows low average pH sensitivity of 9.1 mV/pH in the range 4-7 where physiological recognition events take place and as such is a promising candidate for intrinsic charge based biosensing since PANI is able to directly interact with charged macromolecules such as proteins and DNA. Additionally, the PANI functionalized sensors show low non-monotonic drift and only slightly reduced transconductance compared with the MOSFET counterpart.**

***Index Terms*—ISFET, extended gate, polyaniline.**

I. INTRODUCTION

ION sensitive transistor based sensors manufactured in CMOS processes have been used to detect chemical and biological interactions. ISFETs have been realized in both custom and commercially available silicon processes. In the latter, the silicon nitride passivation layer has been successfully used as a pH sensing membrane. These membranes show high pH sensitivity and have yielded success in pH based detection. However, biosensors relying on direct detection of the intrinsic charge of a macromolecule, suffer from the high pH sensitivity. ISFETs manufactured in CMOS processes can be miniaturized to durable structures with high multiplexing capability. However, for applications without such high multiplexing requirement a low cost ISFET platform utilizing a commercial discrete MOSFET has been proposed. [1], [2] By using commercial transistors the main cost in developing active devices can be significantly reduced.

We present a chemical sensing platform which is based on extended gate ISFETs with organic polymer surface functionalization. The organic polymer functionalization provides a simple and low-cost alternative to oxide membranes.

The functionalization by PANI is attractive in biosensing applications due to its redox sensitivity [3], bio-immobilization capability [4] and ability to tune the band gap by protonation [5]. Additionally, the surface of conducting polymers can be covalently functionalized with biomacromolecules, such as proteins and DNA by the use of thiol and glutaraldehyde facile chemistry [6], [7]

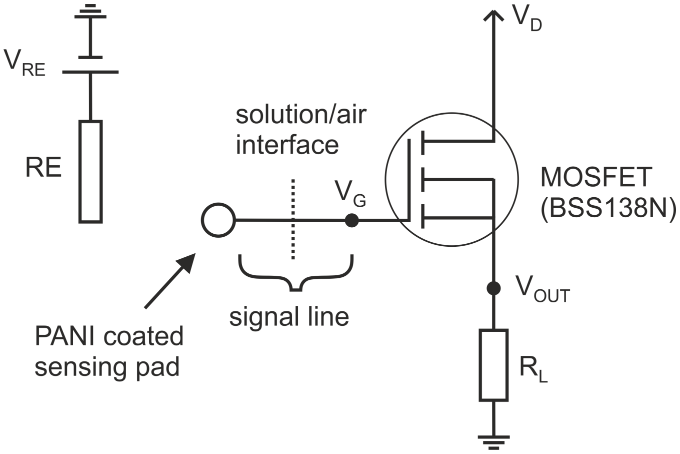

Fig. 1: Circuit presentation of the platform with one sensor. The gate of the MOSFET is connected to the sensing pad via copper trace. Sensing pad is coated with polyaniline (PANI). RE is the reference electrode and the voltage applied to it is V_{RE}, V_G is the voltage at the transistor gate, V_D is the applied drain voltage and V_{OUT} is the output voltage of the sensor that is read out with analog-digital converter (ADC), R_L is the load resistor of the source follower configuration.

II. SENSING PLATFORM

The sensing platform consists of a printed circuit board, nMOS transistors (Infineon BSS138N) and PANI coated sensing pads. A circuit presentation of one sensor in the platform is shown in Fig. 1 and the realization of it, is shown in Fig. 2 The circuit and its realization are explained in figure captions.

*1) **Printed Circuit Board:*** The PCB was manufactured in a standard electronic manufacturing process. The PCB material is a high temperature (150 °C) FR4. The gold surface was patterned by electroless nickel immersion gold (ENIG) surface plating. The traces were encapsulated with liquid photoimageable solder mask. The sensing areas are exposed to have a gold surface prior to the surface functionalization. The transistors were soldered into the platform. The sensing area was 0.79 cm^2.

*2) **Chemicals:*** Aniline (Sigma Aldrich) was purified by distillation under reduced pressure. Ammonium peroxidisulafate (Sigma Aldrich) was used without additional purification. 10 mL of 0.1 M solution of aniline in 1 M HCl was

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Matti Kaisti and Aapo Knuutila, Technology Research Center, University of Turku, 20014 Turun Yliopisto, Finland, e-mail: mkaist@utu.fi.

Zhanna Boeva, Process Chemistry Centre, Department of Chemical Engineering, Åbo Akademi University, 20500 Turku, Finland and Chemistry Department, M.V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.

Carita Kvarnström, Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, 20014 Turun Yliopisto, Finland

Kalle Levon, Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, New York, 11201, United States

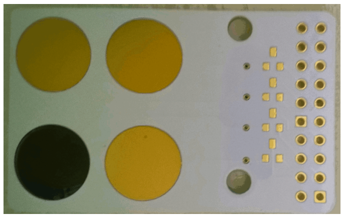


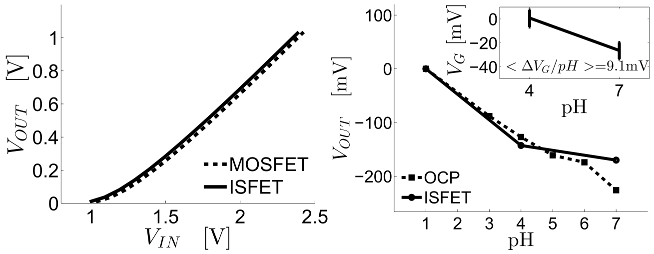
Fig. 2: An example of the sensing platform with one functionalized sensing element. The two rows on the right are through holes for the connector that provides bias for the transistors. Adjacent are the connector soldering pads for four SOT-23 case transistors, one for each sensing element. The independent sensors in the platform all share the same RE.

mixed together with 10 mL of 0.125 M solution of ammonium peroxidisulafate in 1 M HCl. The reaction mixture was briefly stirred and left overnight to complete the polymerization. Then the black-green precipitate was separated by filtration, washed with water and acetone until the washing liquids became colourless afterwhich it was left overnight for deprotonation in a 10 wt.% ammonia water solution. The deprotonated PANI (in emeraldine base form) was again washed with acetone and dried in air. The dried sample was dissolved in N-methylpyrrolidone to produce 7 wt.% solution of emeraldine base of PANI. [8]

The used buffer solutions were pH 7 phosphate buffer and pH 4 citrate buffer purchased from FF-Chemicals. The pH 1 (1 M HCl) was prepared by dilution of concentrated hydrochloric acid. Surfaces were washed with deionized water between measurements.

*3) **Surface Functionalization**:* The prepared solution of emeraldine base of PANI in N-methylpyrrolidone was drop-casted onto to the gold surface of the sensing pad and dried in the air for 2 days. In open circuit potential (OCP) comparison measurements PANI solution was drop casted onto glassy carbon (GC) electrode and dried in the same way. Subsequently the sensing pads and GC electrode were immersed in 1 M H_3PO_4 overnight for protonation of PANI and converting it into electrically conducting PANI-H_2PO_4, where H_2PO_4 is an anion from phosphoric acid acting as a counterion for the protonated PANI chains to fulfill the electroneutrality.

*4) **Measurement Setup**:* The used discrete nMOS transistor was biased in a source follower configuration with a constant drain voltage of 2 V. The platform was immersed in a solution so that all sensing pads were in it, but the transistors remained in air. The bias voltage was applied using an Ag/AgCl (3 M KCl) reference electrode (RE). The sensor output V_{OUT} was digitized with AD-converter and send to a PC where all data post processing was done. The linearity of the source follower configuration was measured and was used to reduce the sensor output to the MOSFET gate (V_G) to discount any configuration related non-linearity. In pH measurements a constant V_{G0} was substracted in order to shift the output near zero for easier comparison of results. OCP of PANI films were measured for comparison using a Lawson potentiometer in a standard two electrode setup having a GC electrode as a working electrode and an Ag/AgCl (3 M KCl) as an RE.



(a) (b)

Fig. 3: a) The transfer characteristics of the sensor measured from the RE and from the transistor gate. The V_{IN} is V_G for the MOSFET and V_{REF} for the ISFET. b) ISFET pH sensitivity between pH 1 to pH 7 compared to OCP. Inset: Zoom of the ISFET gate voltage variation in pH 4 to pH 7 range. Data set includes five sensors. The gate maximum voltage variations are 22.5 mV and 15.6mV in pH 4 and pH 7 buffer solutions, respectively. The MOSFET typically has similar threshold voltage variations indicating that the functionalization has little or no impact on the threshold variation.

III. RESULTS AND DISCUSSION

A. Voltage Division

In extended gate ISFETs with oxide membranes a capacitor is formed in series with the transistor gate oxide, effectively lowering the device transconductance [9]. PANI-H_2PO_4 has been found to be applicable to OCP measurement without any external potential applied between the electrodes. ISFETs are commonly biased through the RE. This creates a potential difference across the sensor. To verify that the PANI membrane does not suffer from the applied bias we simultaneously probed V_{OUT}, V_G, and V_{RE}. The measurement shown in Fig. 3 a) was made in pH 7. The small difference in the slope of the curves implies small voltage division between the extended gate and the transistor and thus only a slightly reduced transconductance [9]. Similar result was obtained in pH 4.

B. Sensitivity

The OCP of polyaniline is dependent on pH and decreases on the pH increase. The pH sensitivity of polyaniline is affected by the nature of substituent in PANI benzoid rings and the counterions residing on the charged nitrogen atoms of emeraldine salt [3]. In case of full deprotonation the protons are removed from the nitrogen atoms of PANI and the dihydrophosphate counterions are released to the outer solution. PANI-H_2PO_4 exhibits low pH sensitivity in the pH range where most bioassay's operate. In extreme pH values the surface exhibits stronger protonation/deprotonation and thus increased pH sensitivity. At pH values higher than 9 PANI deprotonates strongly leading to unpredictable behavior.

We compared PANI-H_2PO_4 functionalized ISFET pH sensitivity with corresponding OCP measurements. The results are shown in Fig. 3 b). The pH sensitivity in both measurements are in good agreement between pH 1 and pH 4. However,

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the PANI modified ISFETs exhibited a pH sensitivity approximately 7.2 - 13.6 mV/pH between pH 4 and pH 7 (Fig. 3 b) inset). The OCP revealed pH dependency up to 33 mV/pH in the same pH range. We attribute this difference to the different substrate onto which PANI is drop-casted. The work functions of carbon and gold are different making the interfacial behavior between the substrate and PANI different. Thus, PANI pH sensitivity alters in OCP and ISFET measurements. Additionally PANI adhesion properties on different surfaces are not fully known, possibly contributing to the pH sensitivity.

The thickness in the drop-casted membranes can not be precisely controlled. However, it has been shown previously that the pH sensitivity in electropolymerized PANI(Cl) has only a slight dependence on the film thickness [3] and thus we expect the small variations in the film thickness to have only a minor impact on the sensitivity.

C. pH time response

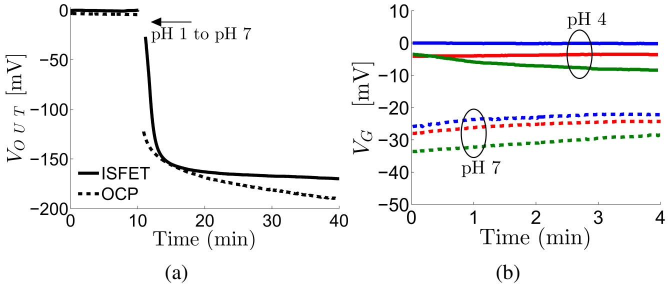
We investigated the pH time response of the PANI functionalized sensor. First the output of a sensor was recorded in pH 1 (1 M HCl) solution for 10 minutes. Then the pH 1 solution is changed to pH 7 0.05 M phosphate buffer solution. The gap in the recorded signals is due to the requirement to remove the solution entirely when it is changed. Consequently, the surface responds to the changed pH by deprotonation which is seen as a decreased output voltage. The pH response of the surface is fast and in the ISFET measurement the potential decays to its e^{-1} value within 2 minutes and the overall response is slightly less than 170 mV. The most significant surface potential change occurs at the low pH values where the pH sensitivity is high. The OCP measurement reveals very similar behavior as shown in Fig. 4 a). The ISFET exhibits fast response after which the surface potential is only slightly decreasing. The OCP measurement reveals two distinct responses, a fast response and a slow response. The fast response is practically identical to the one obtained with ISFET. However, the surface potential continues to decrease whereas the ISFET is quite stable. This results in a larger potential change in the OCP measurement upon changed pH. The increased pH sensitivity was also observed in Fig. 3 b).

D. Drift

We investigated the initial sensor drift in pH 4 and pH 7 buffer solutions. Neutral state PANI sensing pads were immersed in a buffer solution and the first few minutes of the output of a platform with three functionalized pads were monitored. This was repeated for pH 4 and pH 7 buffer solutions. The recording is shown in Fig 4 b). The results reveal no systematic response as small drifts in either direction or no drift is observed during the first few minutes. Similar small drift properties for N-PANI have been reported in [10].

IV. CONCLUSIONS

An organic polymer functionalized extended gate ISFET based platform manufactured in standard electronic process with discrete components was presented. The results revealed the applicability of organic electronics in extended gate ISFETs. The sensors utilize PANI that can interact with biological macromolecules and have low average pH sensitivity where biological recogniton events take place, thus rendering them as promising candidates for intrinsic charge based biosensors.



(a) (b)

Fig. 4: a) ISFET response to pH change compared to OCP. V_{OUT} is the open circuit potential for the OCP measurement and V_G for the ISFET measurement. Both are normalized to zero voltage initial condition. b) Time recordings of a platform with three functionalized sensing areas in pH 4 and pH 7 buffers solutions.

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