Gas-Dependent Field Effect Transistor with an Electrodeposited Conducting Polymer Gate Contact

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Field effect transistor structures with a conducting polymer gate contact have been realized. An electrodeposition technique, suitable for a wide range of conducting polymers, was used. This is illustrated with the deposition of two different types of polypyrroles. The sensors show responses to organic vapors due to partial charge transfer between the sorbed vapor and the conducting polymer, and can be used for electronic nose applications. Due to the measuring principle, based on work function instead of resistance changes, this sensor is also believed to be useful for fundamental research on gas-polymer interactions. © 1999 The Electrochemical Society. S1099-0062(98)10-110-4. All rights reserved.

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Because conducting polymers interact with a wide range of gases,¹ they can be used as nonspecific gas sensors. These sensors are frequently used in electronic noses. The changes in the polymer resistance, which are generally used to transduce the gas interaction do, for certain applications, produce satisfying results.² For many other applications, drift problems are encountered.³ The origin of these problems may involve processes like oxidation or relaxation of the polymer, but are still rather poorly understood. It is especially difficult to distinguish the drift contribution of the polymer molecules from drift caused by unstable charge-transfer properties like the contact resistance and the charge transfer between the individual polymer chains.^{4,5} Work function measurements can, in contrast to conductivity measurements, be performed with only a negligible current passing through the film. This allows the intrinsic electronic properties of the conducting polymer to be measured, without interference from charge-transfer processes like chain hopping and contact resistance. Separating the different contributions to the polymer resistance would help to understand the mechanisms involved and so might help to locate the origin of some of the drift problems.

The Kelvin probe^{6,7} is the classical method for work function measurements. However, the insulated gate field effect transistor (IGFET) is much more convenient. The threshold voltage of this device is dependent on the work function of the gate contact material.^{6,8} When a conducting polymer is used as a gate contact, the threshold voltage becomes gas dependent. Such devices are generally known as gas-dependent field effect transistors (GASFETs). Because most conducting polymers are poorly solvable,⁶ GASFETs are generally realized by spin coating or gas-phase deposition of conducting polymers on field effect transistor (FET) substrates.^{6,10-14} However, this greatly limits the range of polymers that can be used.

In the area of chemoresistors,² a large range of available polymers with advantageous gas sensing properties are normally obtained by electrodeposition of different polymers. This paper describes a technique allowing the fabrication of the GASFETs by electrodeposition.

Experimental

GASFETs having the structure shown in Fig. 1 were realized. They consisted of a FET without a gate contact, but with the gate area surrounded by a Pt electrode. The same type of structure was used before as an integrated sensor actuator system, where the Pt film was used as a pH actuator. Details of the fabrication can be found in papers related to this structure.¹⁵ The gate area of the FET is 15 μ m long and 500 μ m wide. The surrounding Pt electrode has a 20 μ m wide slot which leaves the gate exposed.

The structures were mounted on a printed circuit board, wirebonded and encapsulated with epoxy resin. Conducting polymers



Figure 1. Schematic diagram of the GASFET. (For clarity, the polymer is not shown in the plan.)

were electrochemically deposited over the gate area. Before each deposition, the platinum electrodes were pretreated by cyclic voltammetry in 1.0 M H₂SO₄ as follows: four sweeps at 100 mV/s, with the first and the last being over the range -0.2 to 1.2 V vs. SCE, while for the middle two the anodic limit was increased to 2.0 V. Pyrrole was purified by passage down a neutral aluminum oxide column immediately before use. Polypyrrole (PPy) films were electrodeposited from 0.1 M pyrrole monomer dissolved in either a 0.1 M aqueous butane sulfonic acid (BSA) solution or in acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate (TEATFB). The deposition was performed using a potentiostatic pulse train. The nonaqueous electrolyte consisted of 2 s long 1.5 V vs. standard calomel electrode pulses, separated by 5 s at 0.0 V, while the pulses in the aqueous electrolyte were 0.5 s at 1.1 V separated by 5 s at 0.0 V. The pulse train was applied until the required charge was passed, which was 8 mC for BSA and 6 mC for TEATFB doping. All chemicals used were obtained from Aldrich. The threshold voltage of the finished devices was measured with an FET amplifier.

Resulting Structures

The BSA-doped films displayed good adhesion, while the TEATFB-doped films showed a limited adhesion to the underlying metal; with carefull handling they could also be used for gas measurements. No effort has yet been made to optimize the adhesion, but it is believed that adhesion can be improved by, for example, modification of the metal surface or of the pulse sequence.

Figure 2 shows a scanning electron microscope (SEM) picture of a finished device having a BSA-doped film. In Fig. 3, which is a zoom on the top end of the gate area, it can be observed that the polymer not only deposits on the metal electrode, but also spreads out and completely covers the gate area.

The lateral growth, which is essential to obtain functioning structures, can also be observed clearly in Fig. 4. This SEM image shows a magnification of the edge of the platinum electrode. On the right side, the lateral distribution of the PPy on the substrate can be observed. After deposition of the polymer, a stable threshold voltage representative for the polymer work function could be measured, indicating the proper functioning of the polymer film as a gate contact. In contrast, before deposition of the polypyrrole, the feedback loop of the FET amplifier did not stabilize, which shows that the Pt

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Figure 2. SEM photograph of the active area of a finished structure.



Figure 3. SEM photograph showing the edge of the gate. The different layers of the transistor passivation outside the transistor gate and the metal electrode are clearly visible.

electrode is sufficiently far from the gate area to prevent interference with the work function measurement.

Gas Response

The obtained GASFETs were tested with various organic vapors in a flow system, and significant gas responses could be measured.¹⁶ Figure 5 shows an example for various concentrations of isopropanol vapor to illustrate the different vapor responses of the two types of polymers used. This proves the functionality of the polymer and illustrates the possibility of the realization of differently behaving gas sensors.

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Figure 4. An enlargement of the edge of the polymer coverage on the edge of the metal electrode.



Figure 5. Response peaks obtained from 300 s exposures to various concentrations of isopropanol for (top) BSA-doped PPy and (bottom) TEATFBdoped PPy. The vapor concentrations in mmol/L are marked on the graph.

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