SUSPENDED GATE FIELD EFFECT TRANSISTOR MODIFIED WITH POLYPYRROLE AS ALCOHOL SENSOR (U) UNIVERSITY OF SALT LAKE CITY DEPARTMENT OF BIOENGINEERING M. JOSOWICZ ET AL.

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**Title:** Suspended Gate Field Effect Transistor Modified with Polypyrrole as Alcohol Sensor

**Authors:** Mira Josowicz and Jiri Janata

**Performing Organization:**
Department of Bioengineering, University of Utah, Salt Lake City, UT 84112

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**Summary:**
A generic type of new solid state gas sensor is described which uses change of electron work function of a chemically sensitive layer in response to interaction with a gas or a vapor.

**Keywords:** CHEMFET; gas sensors; work function; polypyrrole
ABSTRACT

A generic type of new type of solid state gas sensor is described which uses change of electron work function of a chemically sensitive layer in response to interaction with a gas or vapor. It is shown that if this layer is electrochemically deposited polypyrrole the device responds to lower aliphatic alcohols. The new sensor operates at room temperature and has time response in seconds.
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by
Mira Josowicz and Jiri Janata

Department of Bioengineering, University of Utah
Salt Lake City, Utah 84112

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Mira Josowicz and Jiri Janata

Department of Bioengineering, University of Utah, Salt Lake City, Utah 84112, U.S.A.

* To whom the correspondence regarding this manuscript should be addressed.
INTRODUCTION

Generally, chemically sensitive field effect transistors (CHEMFET) derive their signal from chemical processes which involve ionic species. Thus, direct interaction of ions with the transistor takes place in the ISFET whereas in enzymatically coupled transistor the ions are generated by the enzymatic reaction. On the other hand hydrogen sensitive FET responds to electrically neutral molecular hydrogen [1]. In this device which relies for its operation on solubility of hydrogen in palladium the signal is related to the change of the electron work function of that metal.

It is possible to design transistors in which the response to a general chemical stimulus is based on changes of electron work function. However, there are two requirements which have to be satisfied: First, the chemically sensitive layer must be placed within the transistor structure in such a way that its change of the electron work function does not cancel out. The second is the accessibility of the transistor gate
by the chemical species of interest [2,3]. The subject of this paper is to present the theory, practical implementation and results obtained with such devices.

THEORY

Suspended gate field effect transistor (Fig. 1) can be operated either in the saturation or in the non-saturation region. The two semi-quantitative equations which describe these two modes are:

for non-saturation \((V_D < V_G - V_T)\):

\[
I_D = \frac{\mu_n C_i W V_D}{L} \left( V_G - V_T - \frac{V_D}{2} \right)
\]

(1)

and for saturation \((V_D > V_G - V_T)\):

\[
I_D = \frac{\mu_n C_i W}{2L} \left( V_G - V_T \right)^2
\]

(2)
where $V_T$ is defined as:

$$V_T = \Phi_{ms} + 2\Phi_F - Q_B/C_i - Q_{ss}/C_i \quad (3)$$

The chemical effects discussed in this paper relate to the changes of the electron work function of the electronic conductor adjacent to the gate insulator. The electron work function $\Phi_\alpha$ of phase $\alpha$ consists of two terms: bulk term $\mu_e^{\alpha}$ and the surface dipole term $\eta^{\alpha}$

$$\Phi_e^{\alpha} = \mu_e^{\alpha} + e\eta^{\alpha} \quad (4)$$

There is a subtle difference in the meaning of these two terms when they are discussed in the context of physics or electrochemistry [4].

In this paper the term $\mu_e$ is the chemical potential of the electron and the electron work function $\Phi_e$ is the energy required to remove the electron from the bulk of a phase (Fermi level) and to place it in vacuum outside the electrostatic forces (Fig.2). If the gate phase $\alpha$ and the semiconductor are connected externally the system comes to electrostatic equilibrium (i.e. Fermi levels are equal) and the difference
in the electron work function $\Phi_{ms}$ establishes the equilibrium distribution of electrons between the two phases. Thus, more electrons in the semiconductor mean higher drain-to-source current (more negative $V_T$) and *vice versa*. This model applies equally to palladium hydrogen sensitive FETs [1] and to the suspended gate FET (Fig. 1) [2,3]. From the structural point of view the air gap in the SGFET can be regarded as an additional insulator.

Let us assume that a new species is added to phase $\alpha$. According to the Gibbs - Duhem equation the chemical potential of other species must change (including $\mu_e^\alpha$) so that the equilibrium is maintained

$$\Sigma_i m_i d\mu_i = 0 \quad \text{(5)}$$

Because

$$\mu_i^\alpha = \mu_i^{\alpha,0} + RT \ln a_i^\alpha \quad \text{(6)}$$

there is a logarithmic dependence of the electron work function on the...
activity of species $i$ in the bulk of the phase $\alpha$ (if the interaction follows the Boltzmann statistics).

The dipolar term in Eq. 4 changes with adsorption of species at the surface of phase $\alpha$. If the adsorbing species has a permanent dipole and/or if it forms a dipole on adsorption the term $\epsilon \eta_e \alpha$ is affected. The concentration dependence of this term is determined by the type of adsorption isotherm for that particular species. Because the relative contribution of these two effects to the overall change of work function cannot be predicted \textit{a priori} the response of a SGFET can be a complex function of the concentration of interacting species.

The placement of the chemically interactive layer within the transistor structure is important. Let us assume that species $i$ reversibly changes the electron work function of phase $\alpha$ by the mechanism discussed above. If this phase is interposed between two electronic conductors $n_1$ and $n_2$ (Fig.3a) with which it forms ohmic contacts A and B, respectively, the Fermi level in these three adjacent phases must be equal. Contact potentials are established at the two interfaces and the field at the semiconductor surface is determined by
the potential difference, $V_{\text{INS}}$. If the interface between phases $n_1$ and $\alpha$ is resistive (Fig. 3a) the voltage across the insulator is

$$V_{\text{INS}} = \phi_{\text{SC}} - \phi_1 = \phi_\alpha - \phi_1 + \phi_2 - \phi_\alpha + \phi_{\text{SC}} - \phi_2 \quad (7)$$

where $\phi$'s are the inner electrostatic potentials in the respective phases. In that case $\phi_\alpha$ cancels out and the contribution of the work function to its change cannot be detected. If, however the interface A is capacitive (Fig. 3b) then the Fermi levels in phases $\alpha$ and $n_1$ are not equal and the change of the contact potential $\phi_\alpha - \phi_1 = \Delta \phi$ is distributed between the two capacitors $C_A$ and $C_i$.

$$V_{\text{INS}} = \frac{C_A}{C_i} \Delta \phi \quad (8)$$

A similar argument can be made for capacitive interface B. Thus, for a CHEMFET based on work function change of a chemically sensitive layer at least one interface of that layer must be capacitive or must maintain a constant potential. This condition is satisfied in the Pd
hydrogen FET [1]. If the Pd layer were interposed between two electronic
conductors the sensitivity to hydrogen would be lost regardless of the
fact that the electron work function of palladium would change; The
change of the contact potentials at either side of the Pd layer would be
equal and opposite and would cancel out. In the hydrogen sensitive
transistor the Pd layer is in contact with an insulator. Therefore, the
conditions for operation as outlined above are satisfied. There is an
important corollary of this analysis: A reference SGFET (non-responsive)
can be made by covering the chemically reactive layer with a
non-reactive electronic conductor [5]. It must be remembered, however,
that adsorption of dipolar molecules on the surface of otherwise
non-reactive layer can still change its work function and give rise to
electrical signal.

Selectivity

Unlike palladium transistor, SGFET is not limited only to species
which can diffuse through the gate but instead is accessible to all
species. Its selectivity is determined by the affinity of the analyte for the bulk and/or the surface of the outermost layer inside the transistor gate gap. Probably the easiest method of modification of the chemical sensitivity of the basic device is by electrodeposition of inorganic or organic layers. Well established procedures exist for electroplating of metals and for electrochemical modification of electrodes [6]. In this work we have deposited various polypyrroles under different electrochemical conditions and investigated the changes of work function of these layers upon interaction with several alcohols.

EXPERIMENTAL

Fabrication of SGFET has been described previously [2]. For this study the silicon chips were eutectically attached to gold plated Kovar TO4 headers and roughly encapsulated with Epon 826 epoxy to protect the leads during electroplating. The electroplating was done by connecting the suspended platinum gate mesh as a working electrode (one by one) and electropolymerizing polypyrrole (Aldrich Chemicals Co.) from acetonitrile (Aldrich), 0.1 M tetrabutyl ammonium tetrafluoroborate solution [7]. A platinum wire was used as the auxiliary electrode and Ag/AgCl, 0.1M KCl
(H₂O)// TBA-TFB (acetonitrile) as the reference electrode unless stated otherwise. The deposition was done either in DC mode or in a normal pulse mode (IBM EC 225 Potentiostat), with pulse repetition rate 5 sec, the initial potential 800 mV and the scan rate 10 mV sec⁻¹. The deposition potential is meant to be the final potential at which the electrode was held until the desired amount of charge has passed through the cell (usually 15 mC). Prior deposition the platinum gate was cleaned with concentrated nitric acid and water. The surface was the conditioned by pulse (0 to +1.25 V) pre-electrolysis in the background electrolyte. Immediately after the deposition the sensors were rinsed repeatedly with pure acetonitrile, inspected under a metallurgical microscope, dried at 60°C and their electrical characteristic were tested.

GOW-MAC gas chromatograph (Model 69-560) was used for handling the gas mixtures (Fig. 4). The outlet from the column has been divided using a Y-splitter. One branch was directed into a conventional thermal conductivity detector and the other branch into a chamber housing the SGFET. This chamber was mounted outside the gas chromatograph and operated at close to ambient temperature as monitored with a thermocouple. The dead-volume in this chamber was approximately 0.5 ml.
The carrier gas was nitrogen flowing at 20 - 45 ml min\(^{-1}\). The transitors were operated in a constant-current mode [5].

RESULTS AND DISCUSSION

As expected the electrical characteristics of the SGFET change after the deposition of polypyrrole. Shift of the threshold voltage (measured in air), after deposition of polypyrroles, with respect to the uncoated platinum gate depends on the deposition conditions (Table I).

The reduced thickness of the gate gap results in increased slope of the \(I_D - V_G\) curve but only for heavily coated transistors (\(Q > 10\) mC). However, because the deposition takes place also on the outside surface of the platinum mesh it is not possible to correlate the deposition charge with any electrical parameter or with the thickness of the organic layer.

In order to study the response dependence of our SGFETs, 5 \(\mu l\) samples of solutions of alcohols in toluene or ligroin (60-90) were injected into the gas chromatograph. It has been established previously [2] for Pt-SGFET, and verified also for polypyrrole coated SGFET, that
neither of these two hydrocarbons gives any signal. Typical response for 5 \mu l injections of toluene solutions of ethanol of various concentrations are shown in Fig.5 and response to different alcohols is shown in Fig. 6. There has been no significant difference between response to pure alcohols or to toluene solutions containing the equivalent amount of alcohol. The dependence of the threshold voltage shift on the injected amount of various alcohols (in moles) is shown in Fig. 7. The effect of deposition potential of polypyrrole on threshold voltage and on sensitivity to methanol is shown in Fig. 8. In this experiment the Ag/0.1M AgNO\textsubscript{3} acetoniitrile, TBA/TFB reference electrode was used (this electrode is + 0.37 V with respect to the aqueous reference electrode).

In this paper we have described a preparation and performance of new class of generic sensor which is based on chemically induced change of electron work function. It has been shown that chemical selectivity can be achieved by electrochemical modification of the surface of the suspended gate inside the transistor gap. Because of the restricted mass transport within the transistor gap it is preferable to use a potentiostatic pulse method for electrodeposition of the modifying layer. Charge of 15 mC yields a smooth continuous polypyrrole coating which
leaves the holes in the gate mesh open. There are other, perhaps more convenient, techniques possible for chemical modification of the gate such as solvent casting or sublimation. However, the electrochemical modification offers a fine control of the deposition conditions and ensures a good electrical contact between this layer and the gate metal. Preliminary results show that the sensitivity to various species depends not only on the chemical nature of the monomer but also on the deposition conditions. This is very important because it opens a possibility for design of large arrays of chemical sensors with different selectivity.

At present it is difficult to assign the origin of the change of the electron work function on the basis of the results presented in this study or to explain the minimum in the shift of the threshold voltage and the concurrent maximum in the response to methanol for polypyrrole deposited at +0.8 V (Fig.8). However, the fact that the threshold voltage shifts in the positive direction when the transistor is exposed to alcohol vapor means that electrons in polypyrrole are become bound more tightly or that alcohols adsorb on polypyrrole through the -OH group or both. The slope of approximately 60 mV/decade indicates that the bulk term is involved although such slope would be obtained also if the adsorption
isotherm was logarithmic. It should be also noted that all the results presented in this paper have been obtained under nonequilibrium conditions (injections into the gas chromatograph), therefore no definitive statement about the origin of the signal can be made at this time and this question will be subject of further study. In principle, these devices can be used as new chemical sensors as well as tools of study of gas/solid interactions over wide range of experimental conditions.

**Definition of terms**

- \( a^\alpha_i \): activity of species \( i \) in phase \( \alpha \)
- \( m_i \): number of moles of species \( i \)
- \( C_i \): gate capacitance
- \( I_D \): drain-to-source current
- \( L \): length of the transistor channel
- \( Q_B \): charge density in the space-charge region
- \( Q_{ss} \): surface state charge density
- \( R \): gas constant
- \( T \): absolute temperature
- \( V_D \): drain voltage
- \( V_G \): gate voltage
- \( V_T \): threshold voltage
- \( W \): channel width
- \( \alpha \): chemically sensitive phase
- \( \chi \): semiconductor electron affinity
- \( \eta_{\alpha} \): surface dipole on phase \( \alpha \)
$\phi$ inner potential of a phase
$\mu_e$ chemical potential of electron
$\mu_n$ mobility of electron in the channel
$\phi_e$ work function of electron
$\phi_F$ Fermi level
$\phi_{ms}$ metal-semiconductor work function difference
ACKNOWLEDGEMENT

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REFERENCES

CAPTIONS

1. Schematic diagram of suspended metal gate field effect transistor. 1-susbsstrate, 2-insulator, 3-platinum gate, 4-gap, 5-polypyrrole coating.

2. Definition of the work function difference

3. Chemically sensitive gate with (a) resistively, (b) capacitively coupled phase ∝


5. Response of polypyrrole coated SGFET to 5μl injections of toluene solutions of methanol. V_D = 1.0V; I_DS = 375 μA; carrier gas: N_2 (45 ml min⁻¹). Deposition was done by DC current at 1.1 V (against the aqueous reference electrode)

6. Response of polypyrrole coated SGFET to various alcohols. Same testing conditions were used as specified in Fig. 5
7. Dependence of threshold voltage shift on injected amount (in moles)
   for various alcohols. Same conditions as specified in Fig.5.

8. Dependence of (a) shift of threshold voltage $\Delta V_T$ and (b) sensitivity
to methanol on deposition potential $E$. Nitrogen flow was 20 ml

$\min^{-1}$, $V_D = 2 \ V$, $I_D = 300 \ \mu A$
ABSTRACT

A generic type of new type of solid state gas sensor is described which uses change of electron work function of a chemically sensitive layer in response to interaction with a gas or vapor. It is shown that if this layer is electrochemically deposited polypyrrole the device responds to lower aliphatic alcohols. The new sensor operates at room temperature and has time response in seconds.
BRIEF

A new type of generic solid state gas sensor is described. It uses electrodeposited polypyrrole layer to impart sensitivity to alcohols.
CREDIT

This work has been supported in part by the contract from the Office of Naval Research.
### TABLE 1

<table>
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<tr>
<th>POLY-</th>
<th>DEPOSITION POTENTIAL VOLTS</th>
<th>$\Delta V_T$ mV</th>
<th>RESPONSE</th>
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<tr>
<td>PYRROLE</td>
<td>0 - 1.2</td>
<td>-230</td>
<td>alcohols, acetone, water</td>
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<td>N-METHYL PYRROLE</td>
<td>0 - 1.15</td>
<td>-246</td>
<td>small, broad response to alcohols acetone and water</td>
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<td>N-PHENYL PYRROLE</td>
<td>0 - 2.0</td>
<td>-380</td>
<td>no response</td>
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<td>PYRROLE-2-CARBOX ALDEHYDE</td>
<td>1.0 - 2.1</td>
<td>-71</td>
<td>no response</td>
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Fig. 2
RESISTIVE

CAPACITIVE

Fig 3
Fig. 8
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