Modeling and Practical Verification of the Ionophore Based Chemically Modified Field Effect Transistor

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ABSTRACT

Proper CAD design of electronic microsystems oriented for environment monitoring requires accurate models of various sensors, which would be compatible with the existing behavioral simulators. In this paper the analysis of the ion sensitive transistor was performed and two models of the CHEmically Modified Field Effect Transistors (CHEMFETs) were applied to the sensor model. Two models of the membrane potential were also compared. The models were implemented in Hardware Description Language (VHDL-AMS) in order to provide the future possibility for the mixed domain, mixed signal simulation of the microsystem incorporating the sensors, operating circuit and analog to digital conversion circuits. Both models were validated by the measurements of the real structures. The most important parameters were identified as a result of parameter extraction procedure.

Keywords: CHEMICAL SENSORS, VHDL–AMS, MICROSYSTEMS, MIXED SIGNAL SIMULATION

1 INTRODUCTION

Pollution of the natural environment is one of the most serious problems of industrialized countries. Consciousness of importance of environment protection gave rise to the program of sustainable development, which sets up the standards of economical growth and technological progress with consideration given to environmental care. This idea is being realized by the 5th Framework Programme of the European Union, which supports the SEWING project. The main aim of the project is to provide a cheap and efficient system dedicated to water pollution monitoring. This project is based on a sensing element - the ion sensitive transistor. The base structure is Ion Sensitive Field Effect Transistor (ISFET) dedicated to detection of the hydrogen ion. In order to obtain a sensor dedicated to ion other than hydrogen, the sensor has to be covered with special ion selective membrane. The membrane sensors are called CHEMFETs. The set of such sensors will be incorporated with data processing and acquisition unit, as well as a data transmission system. Data from the sets of sensors will be further transmitted to the acquisition center. Then, according to the sensor indication appropriate alarms will be generated. This approach to the subject of distributed system is especially efficient due to low cost and fast analysis of the measured samples. It allows constant supervision and fast counteraction in case of alarms. In the next section the operation of the sensor as well as existing models are described. After that the measurements of the manufactured structures are presented. On the basis on presented models the parameter estimation is performed.

2 CHEMFET MODELING

OPERATION PRINCIPLE
CHEMFET- Chemically Modified Field Effect Transistor is the miniature sensor that bridges the silicon technology with analytical chemistry. The base of the sensor is represented by the gateless Field Effect Transistor. This kind of sensor can be efficiently applied as the ISFET sensor [2,7,10] dedicated to hydrogen ion monitoring. The CHEMFET sensor is created by covering the ion sensitive inorganic material of ISFET with polymer ion selective membrane and the reference electrolyte (polyHEMA) layer preventing the membrane from mechanical replacement and ensuring thermodynamical stability of the electrolyte-membrane-semiconductor system.
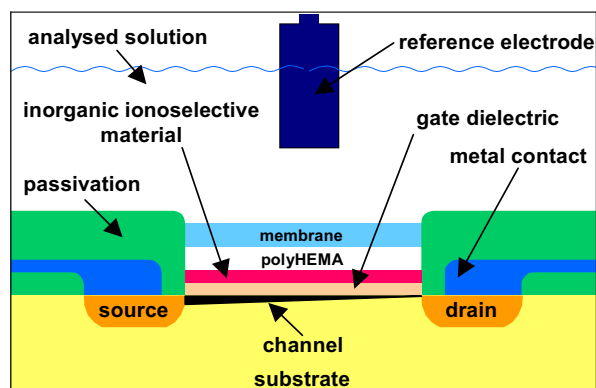

Figure 1. Cross section of the CHEMFET sensor

The crucial part of the sensor is the ion selective membrane. Among various kinds of ion selective membranes the most promising are the polymeric ones with ionophore. The ionophore is responsible for reversible compellation of the main ion and its transport through the membrane. The chemical constants characterizing the ionophore determine the measurement range and selectivity of the whole sensor. The other component of significant importance is lipophylic salt, which prevents the anti-ions from into the membrane phase. All the mentioned components are suspended in a

polymer matrix. The modeling of the CHEMFET sensor requires a common approach to the modeling of the semiconductor part of the sensor as well as the ion selective membrane. In this paper an analysis of available models of the membrane is performed and a simple but accurate model of semiconductor part is proposed.

The sensor system can be described as a multi phase system consisting of the phase of reference electrode, measured solution, and sensor system. The schematic representation of such system with potential distribution on the phase boundaries is presented in Figure 2.
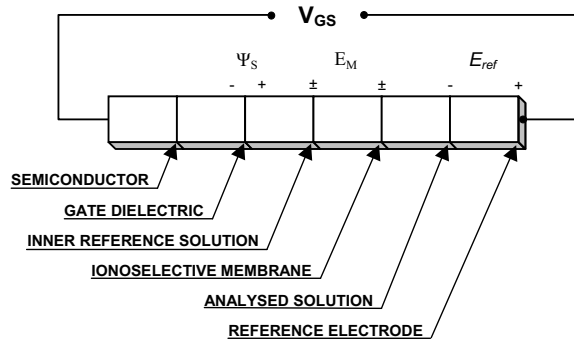

Figure 2.

The operation of the CHEMFET sensor can be explained by considering the system of potential drops on the phase boundaries. The only potential, which depends on the activity of the certain ion in the measured solution, is the membrane potential. It can be formulated regarding the two potential drops on the boundaries membrane-reference electrolyte, membrane-measured electrolyte and diffusion potential. From the CHEMFET point of view, the membrane potential is the most important component, since it is the only one, which is directly dependent on the composition of the analyzed solution.

$$E_M = E_{B1} - E_{B2} + E_D \quad (1)$$

where:

E_M – membrane potential

$E_{B1,2}$ – boundary (Donnan) potential drops

E_D – diffusion potential

Bearing in mind that the membrane potential is a part of the gate circuit of the transistor, this modifies the threshold voltage formula as follows:

$$V_T^{CHEMFET} = E_{OFFSET} - E_M + V_T^{MOSFET} \quad (2)$$

Where $V_T^{CHEMFET}$, V_T^{ISFET}, E_{OFFSET} – threshold voltage of CHEMFET sensor, MOSFET transistor and offset voltage respectively.

Usually, the FET based chemical sensor operates in a compensation circuit in the constant current mode. It means that changes of the drain current of the CHEMFET sensor

are compensated by additional potential applied to the reference electrode. The output signal of the chemical sensor is represented by the changes of the reference electrode potential keeping the drain current constant. However, in order to provide a complete model of the sensor as a part of the bigger system it is necessary to characterize not only the sensorical properties of the sensor but the electrical ones as well.

ION SELECTIVE MEMBRANE MODELING

The authors have considered two description of the membrane potential. The first one is based on the well-known Nikolski-Eisenman formula [3] and can be applied to describe all kinds of membrane (even inorganic ones). Despite its simplicity the Nikolski-Eiseman model offers good accuracy in a wide range of operation as well as numerical efficiency.

$$E_{Ms} = 2.303 \frac{RT}{z_i F} \log[a_i + \sum_{j \neq i} k_{ij} a_j^{\frac{z^i}{z^j}}] \quad (3)$$

As presented above, the change of the membrane potential (directly influencing the threshold voltage) can be calculated using Equation 3. It depends on the activity of the ion to be detected a_i (called the main ion), but it also depends on the concentration of some other ions a_j, called interfering ions. The influence of an interfering ion is multiplied in the formula by the relative selectivity coefficient k, which models the membrane preference to disturbing ion in reference to the main one.

The other model describing the membrane potential is based on a physical representation of the electrochemical processes, which take place both at the boundaries of the membrane phase and inside the membrane. It was first developed by van der Bergh and continued by other authors [2,4,5]. The detailed description of the model can be found elsewhere and will not be discussed in this paper.

The most important problem refers to the selectivity of the membrane. In Figure 3 the simulation results of the membrane potential were shown for two different models of the membrane for certain activity of the interfering ion concentration. The NH$_4^+$ sensor with presence of exemplary interfering ion in concentration of 0.01M/dm^3 was simulated with application of Nikolski-Eisenman formula (NI) and van der Berg model (VDB). As can be seen in Figure 4, for the range of small to medium concentration, both models offer comparable accuracy. For the very high concentration range, which is rarely encountered in real conditions, the difference can be easily noticeable due to the phenomenon of anionic error, which can be adequately modeled only by the van der Bergh model. It can be also seen that, due to the limited selectivity, the linear part of the curve (called the Nerstian range) flattens out. As a result the sensor becomes insensitive to the main ion at low activities. The location of the bending point and the measurement range are determined by the selectivity of the membrane to the main ion. In case of physical model the Nerstian range

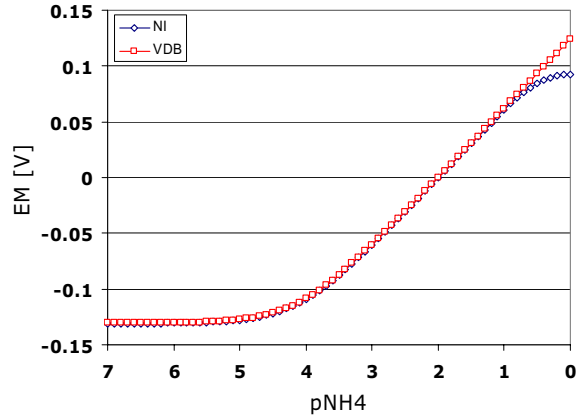of the membrane potential is limited also from the high concentration side.

Figure 3. Simulation results of two membrane potential models: physical (VDB) and empirical (NI). Simulated sensor for main NH_4^+ ion, interfering ion concentration $0.01M/dm^3$
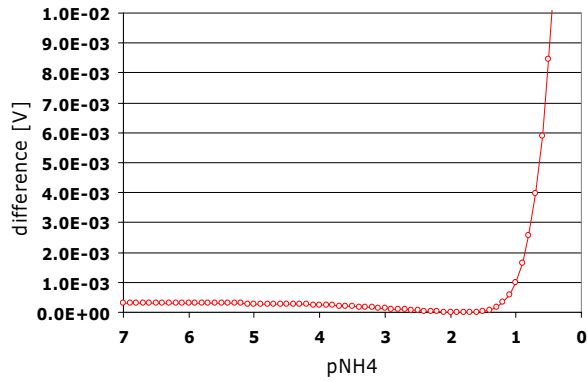

Figure 4. Difference between two presented models

SEMICONDUCTOR PART MODELING

Providing accurate description of the semiconductor part of the sensor is an equally important issue from the CAD point of view. For the electrical simulations, the authors adapted the existing SPICE Level 3 compatible MOSFET model, in which the threshold voltage is chemically modified through the surface potential. The fact that the transistor under consideration was wide and long allowed the simplification of the model by neglecting most of the terms describing short channel effect. This approach is not entirely new and was proposed already in [7].

The transistor output curves can be well described by the following equation:

$$I_D = \frac{C_{ox}\, \mu_{eff}}{2} \frac{W_{eff}}{L_{eff}} \left(2\left(V_{GS} - V_T\right) - V_{DS}\right) V_{DS} \qquad (4)$$

where:

I_D – transistor drain current, C_{ox} – gate dielectric capacitance per unit area, μ_{eff} – effective carrier mobility, W_{eff}, L_{eff} –

effective channel width and length, V_{DS}, V_{GS} – drain-source and gate-source voltages, V_T – transistor threshold voltage

The carrier mobility depends on the electric fields generated both by the gate and the drain potentials. Then, the effective carrier mobility μ_{eff} can be expressed by the following equation:

$$\mu_{eff} = \frac{\mu_s}{1 + \mu_s \dfrac{V_{DS}}{v_{max}\, L}} \qquad (5)$$

where μ_s is equal to:

$$\mu_s = \frac{\mu_0}{1 + \theta\left(U_{GS} - V_T\right)} \qquad (6)$$

Θ is the mobility modulation coefficient, which has to be determined in the simulations. v_{max} is the maximal carrier velocity in the channel. μ_0 is the initial carrier mobility. When the transistor is operating in the saturation region, the drain-source voltage V_{DS} must be substituted by the voltage V_{DSsat}. The saturation voltage of an ISFET can be expressed as:

$$V_{DSsat} = V_{GS} - V_T + v_{max}\frac{L_{eff}}{\mu_{eff}} + \sqrt{\left(V_{GS} - V_T\right)^2 + \left(v_{max}\frac{L_{eff}}{\mu_{eff}}\right)^2} \qquad (7)$$

The threshold voltage of an ISFET modified by the membrane potential as it shows Equation 2. More detailed implementation of this model as well as its experimental verification can be found in [10].

3 SENSOR MEASUREMENTS

The object of the measurements was the CHEMFETs developed by the Institute of Electron Technology from Warsaw (Poland). The NH_4^+ selective membranes were deposited by the Department of Analytical Chemistry of WUT (Warsaw University of Technology). The detailed technological description of the semiconductor part as well as the chemical membrane can be found in [1,2,10]. The measurements were performed using the specially designed measurement stand described in [8]. The stand allows fully automated measurements of several transistor characteristics with various ion concentrations at different temperatures. The presented measurements were taken simultaneously for 10 CHEMFETs with various main ion concentration and single disturbing ion concentration. Two interfering ion were taken into account: Na^+ and Ca^{2+}.

The aim of the CHEMFET measurements was to capture the output electrical characteristics of the transistor so as to verify the model of the electrical part of the sensor. On the basis of these curves the chemo-sensorical curves were possible to obtain. Obtained results are shown in the next section.

4 ELECTROCHEMICAL MODEL SIMULATION AND MODEL PARAMETER EXTRACTION

The presented measurements provided a base for the CHEMFET model verification as well as model parameter extraction. The parameters were extracted using the Newton-Gauss method based automatic procedure already implemented in the MATLAB environment. The procedure uses the least mean squares criterion so as to find the best possible set of model parameters. The detailed description of the model parameter procedure can be found in [10]. The extracted parameters identifying the CHEMFET transistor are presented in Table 1. The value of threshold voltage was extracted separately from the measurements of the CHEMFET structure before the ion selective membrane was deposited. The measurements of such structure were performed for the buffer solution of pH=7. For this value the potential drop on the border the solid-liquid interface is close to 0 (point of zero charge for the silicon nitride) thus V_T can be efficiently determined.

Parameter	Value	Unit
Channel width W	638	μm
Channel length L	14	μm
Gate capacitance	4.42e-4	F/m^2
Threshold voltage V_T	-0.368	[V]
Low field carrier mobility μ_0	0.0970	$[m^2/Vs]$
Maximal carrier velocity ν_{max}	$1.00*10^5$	[m/s]
Mobility modulation coefficient Θ	0.176	$[V^{-1}]$

Table 1. The most important parameters of the semiconductor part of the sensor

In Figures 5 and 6 the simulation results are compared to the measured values. As can be seen, the simulation results match the measurement results well. It is worth noticing that such accuracy is obtained with the application of relatively simple transistor model (SPICE Level 3).

In Figures 7 and 8 the changes of the reference electrode voltage were showed. The changes of this voltage compensate the influence of the measured solution on the drain current. Initially the measured reference electrode changes were fitted with application of the Nikolski-Eisenman model and afterwards the van der Bergh model was implemented so as to fit the measured curves. As it was mentioned before two interfering ions were taken into account: calcium and sodium. Their activity maintained the same level of $0.01M/dm^3$ during the measurements.
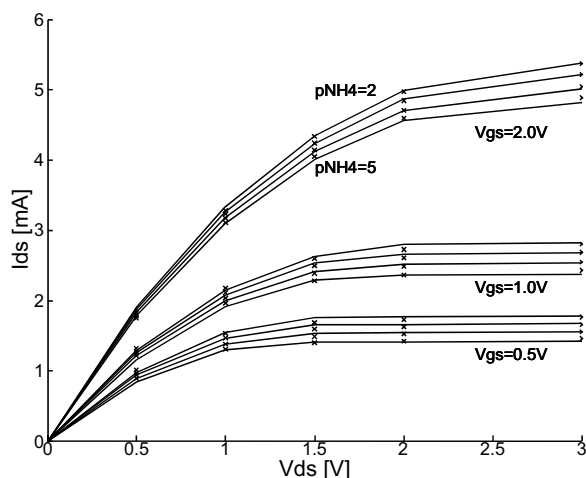
Figure 5. CHEMFET output characteristics with calcium interfering ions (dots) fitted with model (solid)
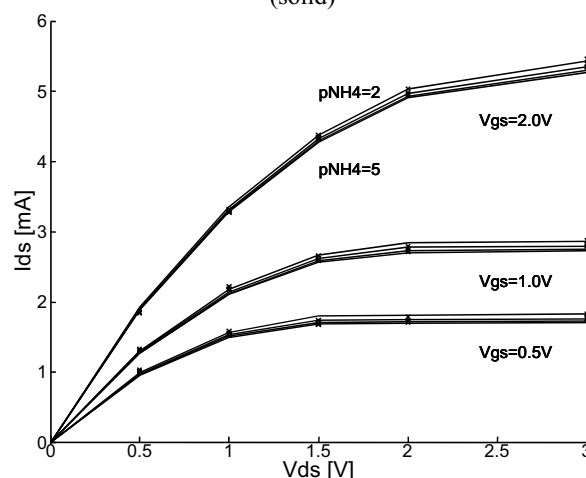
Figure 6. CHEMFET output characteristics with sodium interfering ions (dots) fitted with model (solid)
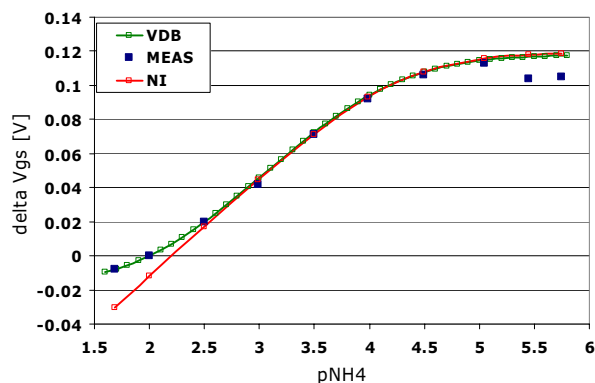
Figure 7. Measurements of NH_4^+ selective CHEMFET interfered by Na^+ ions, and simulation results for both Nikolski (NI) and van der Bergh model (VDB)
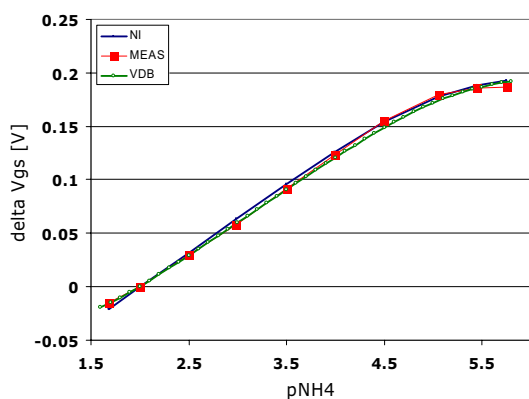
Figure 8. Measurements of NH_4^+ selective CHEMFET interfered by Ca^{2+} ions and simulation results for both Nikolski (NI) and van der Bergh model (VDB)

5 CONCLUSSIONS

In this paper a simple but efficient model of the CHEMFET sensor was presented. The model combines the standard SPICE MOSFET model and two electrochemical models of the membrane potential, which influences the threshold voltage of the semiconductor model. In the model at least two different domains are considered - electrical and chemical ones. Apart from these, the thermal one can be easily introduced to the model. For the purpose of efficient simulation a multidomain simulation with application of the VHDL-AMS standard can be easily applied.

The presented measurement results indicated that the membrane potential for higher activity of the main ion cannot be accurately modeled by the semi empirical Nikolski Eiseman model. In order to obtain satisfying accuracy for the wide range of activities, it is advisable to use rather the more complex, physical van der Bergh model. On the other hand, such high values of the activities normally do not occur in the natural environment so they can probably be neglected in the case of river or lake water monitoring. What seems much more problematic is the poor selectivity of the NH_4^+ membrane (for example to K^+ ions). Nevertheless, if this sensor is to be used for analysis of highly polluted waters, then it is necessary to apply the physical model.

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