

TEMPERATURE DEPENDENT MODEL OF ION SELECTIVE TRANSISTOR FOR MULTIDOMAIN SIMULATIONS

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ABSTRACT

The proper CAD of modern electronic microsystems oriented for environment pollution monitoring requires compact and accurate models of various sensors, which would be compatible with the existing behavioural simulators. This paper presents the analysis of the ion selective transistor employed as a chemical sensor. Since the sensor has to operate in a wide temperature range, the analyses were carried out with the special consideration of the temperature phenomena on the device operation. Two different models of the ion selective sensor membrane were compared and combined with the model of the ion sensitive transistor previously developed by the authors. The models were validated with measurements of real structures.

Keywords: VHDL-AMS MULTIDOMAIN SIMULATION SILICON MICROSYSTEM MODELLING, CHEMICAL SENSORS.

1. INTRODUCTION

Pollution of the natural environment is a serious problem of industrialized countries. Thus, the concept of the so-called sustainable development, which ensures both the economical growth and the technological progress with the special consideration of the environmental care, was developed. This idea is also being implemented in the 5th Framework Programme of the EU supporting the SEWING project, the results of which are presented in this paper.

The main aim of the project is to provide a low cost and efficient system dedicated to real time water pollution monitoring. The sensors developed in the frames of the project are based on a common sensing element - the Ion Sensitive Field Effect Transistor (ISFET), dedicated to the measurement of the hydrogen ion concentration. In order to obtain devices sensitive to other ions than the hydrogen ones, the sensor has to be covered with special ion selective membrane. Such sensors are known as the CHEmically Modified Field Effect Transistors (CHEMFETs).

In the project, sets of ISFET sensors equipped with membranes for detection of various ions will be integrated with data acquisition and processing units, as well as data transmission systems. The processed data collected in the field units will be transmitted to the water quality monitoring station, where adequate actions will be taken if necessary.

This paper presents a model of the CHEMFET sensor suitable for multidomain behavioural simulations of entire microsystems. The model takes into account all the complex physical phenomena occurring in the device. Particular attention has been paid to the thermal analysis of the device, which requires examination of many various temperature dependent phenomena known not only from the ordinary FETs but also related to the chemical reactions occurring in the transistor gate structure. The next section of the paper provides some theoretical background on the CHEMFET operation principle. Then, the electro-thermo-chemical model used by the authors in the later described simulations is presented in detail. Finally, the model is validated with the measurements of real CHEMFET devices.

2. CHEMFET OPERATION PRINCIPLE

The semiconductor ion sensitive sensors based on Metal Oxide Semiconductor FETs (MOSFETs) were suggested already in 1970 by Bergveld [1]. The sensors were realized by removing the metallic gate of an ordinary MOSFET and submerging the device in an analysed solution. Then, the potential drop proportional to the logarithm of ion activity appears at the boundary with gate oxide.

Further modifications were made in 1975 when Moss made the first potassium selective CHEMFET by attaching a polymer membrane to the gate dielectric [2]. The sensors were significantly improved in the nineties by Bergveld and van der Berg through the introduction of the polyHEMA hydrogel stabilizing the sensor operation [3].

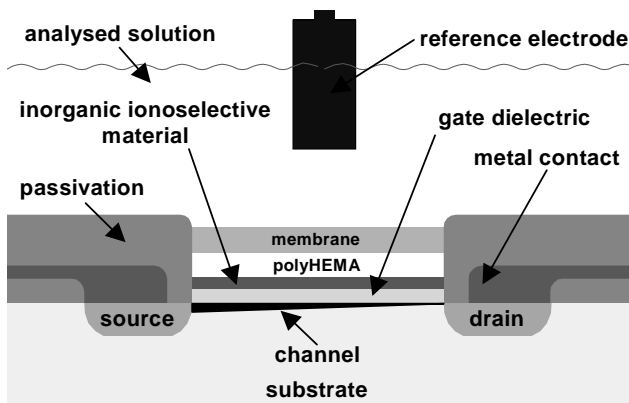


Figure 1: CHEMFET cross-section.

The final structure of the state-of-the-art CHEMFET is shown in Figure 1. Compared to the standard MOSFET, on the gate dielectric organic layers such as a polyHEMA hydrogel and an ion selective membrane are deposited. The polyHEMA layer contains a solution of the main ion having constant and known concentration, serving as a reference solution. However, the key component of the sensor is the ion selective membrane, which separates two electrolytes containing the main ion: the analysed electrolyte and the inner reference electrolyte.

The most important component of the ion selective membrane is called ionophore, which is responsible for the reversible complexation and the transport of the main ion through the membrane. The ionophore determines overall measurement range and selectivity of the sensor. Another important component of the membrane is a lipophilic salt, which prevents the ions of the opposite sign than the main ion from the penetration into the membrane. Both above mentioned components constitute only 5 weight percent of the membrane. Around two third of the membrane constitutes a solvent and the remaining part is a polymer matrix in which all the components are suspended.

From the electrical point of view, the electrolyte flowing over the gate closes the gate circuit. The ion concentration in the electrolyte influences the gate potential, which in turn modifies the transistor threshold voltage. In this way, the ion concentration exercises electrostatic control on the drain-source current. Usually, the FET based chemical sensors operate in the constant current mode, as shown in Figure 2. Then, the drain current variations caused by the threshold voltage shift due to the change of the ion concentration are compensated through the operational amplifier OP2 in the feedback loop by adjusting the reference electrode potential.

Thus, the CHEMFET sensitivity is typically expressed as the gate voltage change per decade of ion concentration pI , where pI denotes $-\log [I^{z\pm}]$. For example, if the value of pI is equal to 2, the concentration of the ions amounts to 10^{-2} mole per litre.

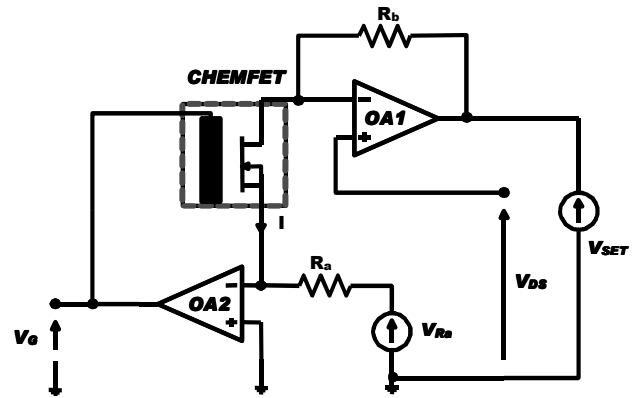


Figure 2: CHEMFET operating circuit.

3. TEMPERATURE DEPENDENT CHEMFET MODEL

The modelling of CHEMFET sensor is a complex task since it requires taking into consideration many coupled chemical, electrical and thermal phenomena. The model proposed by the authors can be regarded as an extended MOS device model taking into account not only the semiconductor part of the device but also all the remaining components such as the reference electrode, the analysed electrolyte, the ion selective membrane, the inner reference electrolyte and the gate dielectric. All these factors influencing the CHEMFET operation, summarised in Figure 3, will be analysed in this section in detail.

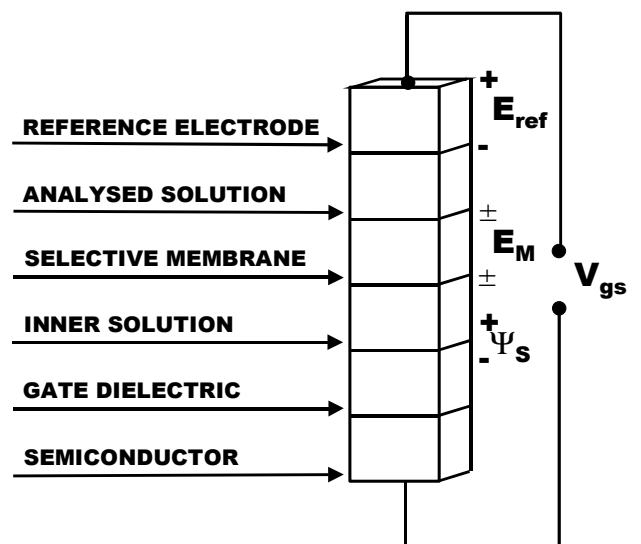


Figure 3: Structure of the gate circuit.

Starting from the top of the above-presented figure, the first component is the reference electrode potential E_{ref} . This potential results from the Fermi level difference between the solid metal electrode (silver) and liquid solution containing a salt of the electrode metal (silver chloride). The reference electrode potential does not depend on the electrical current or the chemical composition of the solution and is assumed to change with temperature as follows:

$$E_{ref} = E_0 + E(T) (T - 300) \quad (1)$$

where:

E_0 – material dependent reference electrode potential [V]

From the CHEMFET operation point of view the most important is the membrane potential E_M because it is the only one component directly dependent on the composition of the analysed electrolyte. The membrane potential can be expressed as the sum of the membrane diffusion potential E_D and the difference of the potential drops at the phase boundaries E_B (see Equation 2). The difference results from the inequality of the ion concentrations in the analysed and the inner solution as shown in Figure 4.

$$E_M = E_{B1} - E_{B2} + E_D \quad (2)$$

The most commonly employed model of the phenomena occurring in the sensor membrane is based on the semi-empirical Nikolski-Eisenman equation, derived from the well-known Nernst equation. Although the model has theoretical bases it belongs to semi-empirical models and its coefficient can be easily determined directly from the sensor calibration curves. The final equation to compute the membrane potential is formulated analysing the diffusion of various ions through the phase boundaries between the membrane and the surrounding electrolytes and within the membrane itself. In the thermodynamic equilibrium the membrane potential is equal to:

$$E_M = E_0 \pm \frac{RT}{z_m F} \ln \left[c_m + \sum_{m \neq d} K_{md} c_d^{z_m / z_d} \right] \quad (3)$$

where:

F – Faraday constant

K – selectivity coefficient

R – gas constant

T – absolute temperature

c – ion concentration

z – ion valence

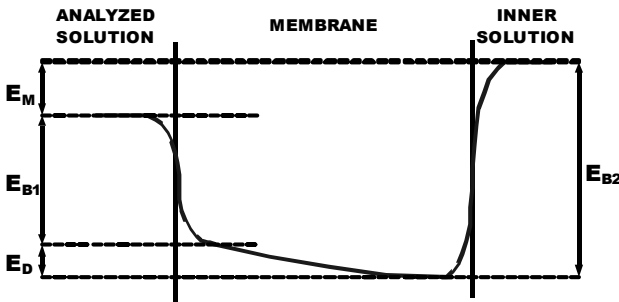


Figure 4: Distribution of membrane potentials.

The index m corresponds to the main ion and the index d to the interfering ion (disturbing) respectively. Both the relative selectivity coefficient K_{md} and the independent from the ion concentration membrane potential drop E_0 depend on temperature as shown in Equations 4-5, where α and β are empirical coefficients.

$$K_{md}(T) = K_{md} \left(\frac{T}{T_0} \right)^\beta \quad (4)$$

$$E_0(T) = E_0(T_0) (1 + \alpha(T - T_0)) \quad (5)$$

There exists also physical membrane model based on the analyses of the thermodynamics of the phase boundaries and the stoichiometry of the membrane. This model, developed by van der Berg, will not be presented here due to the scarcity of place. For the full description of the model, refer to [4]. This does not limit the scope of the considerations since both approaches are to some extent equivalent and the empirically determined parameters can be related to the physical ones [5]-[6].

The above considerations are illustrated on a practical example of the ammonium sensor in the presence of some interfering ion having concentration of 0.01 M/l. The results obtained using the Nikolski-Eisenman model (NE) and the van der Berg model (VDB) are shown in Figure 5. As can be seen in the range of moderate concentrations of the main ion both models produce similar results. However, for the very high concentration range, rarely encountered in the real conditions, the difference is visible due to the phenomenon of the so-called anionic error, which is adequately modelled only by the van der Berg model.

Another observation is that the linear part of the curve flattens out due to the limited membrane selectivity. Then, the sensor becomes virtually insensitive to the main ion at its low activities. The exact location of the bending point and consequently the measurement range are determined by the membrane selectivity. Obviously, in the case of the physical model the linear response range is limited also for the high concentrations of the main ion.

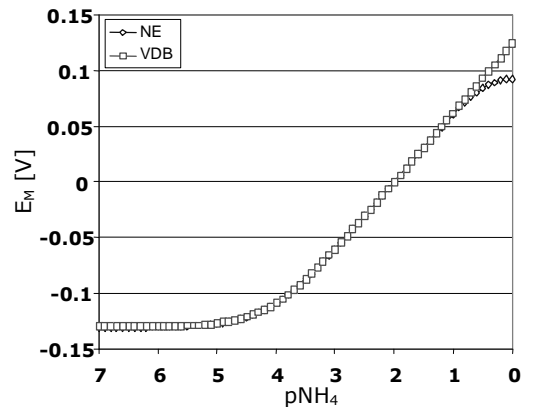


Figure 5: Comparison of membrane models.

The last unknown potential drop in Figure 3 is the dielectric surface potential Ψ_s . Without the presence of the membrane, in ISFET sensors this potential is the measure of the hydrogen ion concentration. However, due to the invariant composition of the reference solution contained in the polyHEMA, this potential is constant in CHEMFETs.

The detailed analysis concerning the semiconductor part of the device will not be presented in this paper since the authors described this problem earlier in [7]-[8]. Because the thermal phenomena occurring in the semiconductor part of the sensor are already modelled in the SPICE simulator, the authors decided to adapt the existing MOSFET model for the overall chemo-thermo-electrical device simulations. This approach is not entirely new and was proposed already in the early nineties, e.g. in [9]. Then, all the potentials generated in the gate circuit, i.e. the reference electrode potential, the membrane potential and the surface potential, modify the threshold voltage of the transistor.

Finally, the ion selective transistor threshold voltage can be computed using Equation 6, where the value of the MOS transistor threshold voltage V_T^{MOS} can be estimated based on the measurements whereas the value of the potentials E_{ref} , E_M and Ψ_s are found using the earlier presented equations. The constant c represents all the potential drops independent from the ion concentration compensating for the difference in transistor gate structures.

$$V_T^{CHEMFET} = V_T^{MOS} + E_{ref} + E_M - \Psi_s + c \quad (6)$$

4. MEASUREMENT AND SIMULATION

The measured CHEMFET structures were manufactured at the Institute of Electron Technology in Warsaw, Poland. The transistors have a built-in n-type channel 640 μm wide and 14 μm long. The most important feature of this semiconductor structure is that it has drain and source contacts at the backside of the wafer, which allows direct electrolyte flow at the top surface over the gate as shown in the below figure.

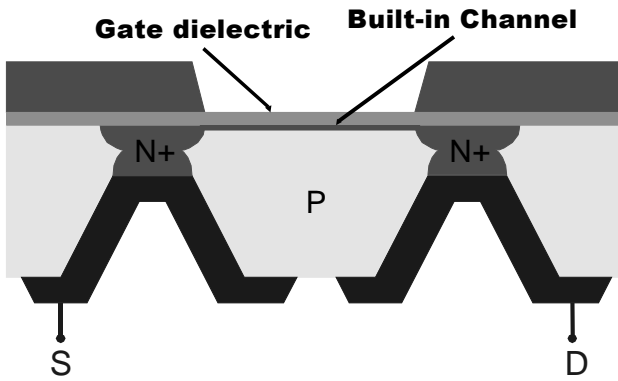


Figure 6. IET transistor cross-section.

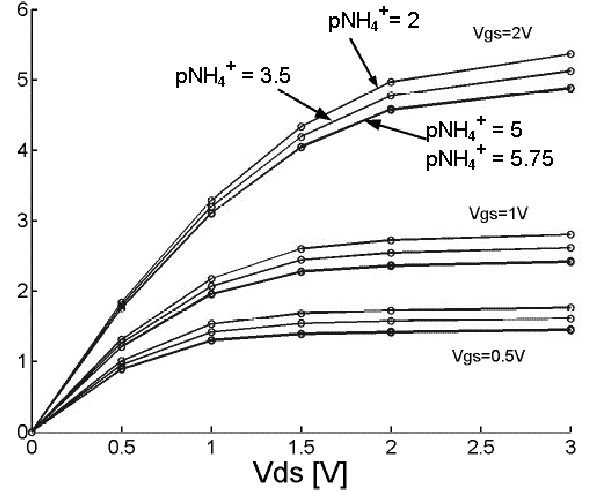


Figure 7. Ammonium sensor output characteristics - calcium interfering ion $pCa=2$ ($T = 25^\circ\text{C}$).

The ammonium selective membranes were deposited in the Department of Analytical Chemistry of the Warsaw University of Technology. The presented measurements were performed at the Institute of Electronic Systems of the same university on the especially designed measurement stand described in [10]. This stand allows fully automated measurements of transistor characteristics for various ion mixtures and in different temperatures.

The measurements were taken simultaneously for several ammonium sensitive CHEMFETs with the variable main ion concentration in the presence of constant calcium, sodium and potassium interfering ion concentrations. All the measurements were repeated in temperature of 10, 25 and 40 $^\circ\text{C}$. The main goal of the measurements was to capture the electrical characteristics of the devices so that to provide data necessary for the sensor model parameter extraction and the determination of membrane selectivity coefficients.

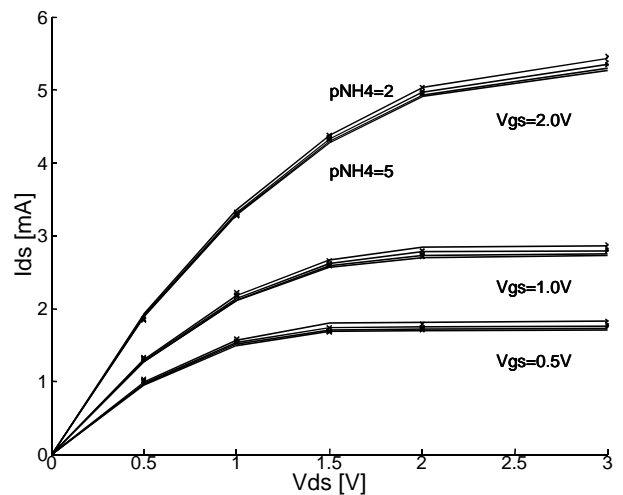


Figure 8. Ammonium sensor output characteristics - sodium interfering ion $pNa=2$ ($T = 25^\circ\text{C}$).

Table 1. Selectivity coefficients of ammonium membrane.

Interfering ion:	Na ⁺	K ⁺	Ca ²⁺
Literature:	-2.7 ÷ -1.8	-0.9 ÷ -0.5	-3.8 ÷ -3.9
Measurement:	-2.1	-0.8	-3.7

The measured output CHEMFET characteristics with calcium and sodium interfering ions are presented together with simulation results in Figures 8 and 9 respectively. The measured values are represented in the figures by crosses or circles whereas the simulated curves with solid lines. As can be seen from the figures, the fitted curves match accurately the measured values. It is worth noticing that such good accuracy is obtained with the application of relatively simple transistor model (SPICE Level 3).

Another interesting conclusion from the figures concerns the membrane selectivity. Namely, the presence of calcium interfering ions allows the measurements of the ammonium ion concentration in the range of pNH_4 less than 5, whereas for potassium or sodium interfering ions the measurements are perturbed even for very high activities of the main ion. However, it should be underlined that the concentration of the interfering ions during the measurements were high and normally not encountered in the natural environment.

The values of the selectivity coefficients were extracted from the calibration curve constructed based on the output transistor characteristic. One of such curves for sodium interfering ions is shown in Figure 9. Additionally, the measured values (MES) are compared in the figure with the van der Berg (VDB) and the Nikolski-Eisenman (NE) models. The extracted values of the selectivity coefficients are given in Table 1 together with the values provided in the scientific literature. The obtained results demonstrated clearly that the Nikolski-Eisenman equation cannot model accurately the calibration curve also for high concentrations of the main ion because the shape of the curve resembles rather a sigmoid and the bending is visible from both sides of the curve.

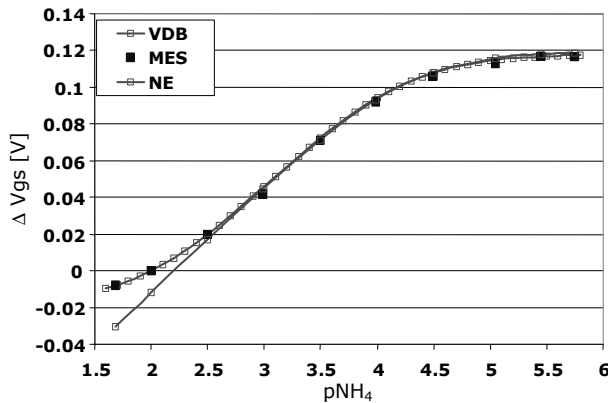


Figure 9. Model comparison for ammonium membrane with sodium interfering ions.

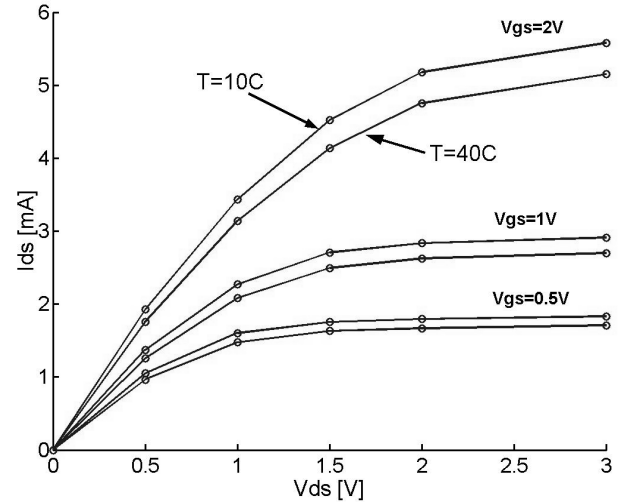


Figure 10. Ammonium sensor output characteristics - $pNH_4 = 3.5$, $pCa=2$.

Additionally, the authors have investigated the influence of temperature on the CHEMFET sensor operation. Both the measured and modelled temperature dependence of the output characteristic and the calibration curve are shown in Figures 10-11. As can be seen the temperature influences significantly the sensor operation and the temperature effects cannot be neglected in the sensor models.

5. CONCLUSIONS

This paper presented a relatively simple but fairly accurate temperature dependent model of the CHEMFET sensor. As demonstrated, the proposed model is suitable for the simulations of the device operating in a wide range of temperatures and ion concentrations because it reflects equally well the change of the transistor characteristics both due to the variation of the ion concentration and due to the temperature change.

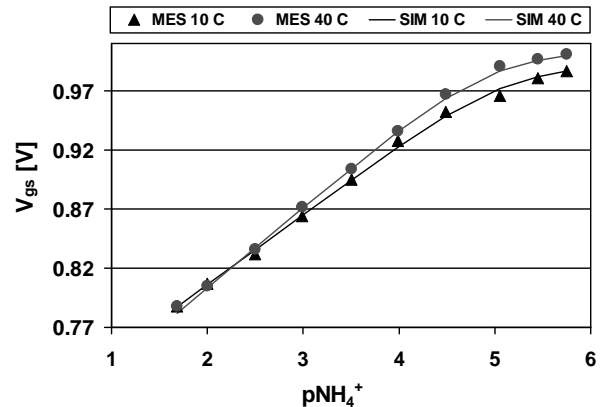


Figure 11. Dependence of ammonium sensor response on temperature - $pCa = 2$.

The model combines the standard SPICE MOSFET model and the electrochemical model of the ion selective membrane potential, which in turn influences the device threshold voltage as a function of the ion concentration in the electrolyte flowing over the gate.

The presented measurement results indicated that the membrane potential for higher activity of the main ion cannot be accurately modelled by the semi-empirical Nikolski-Eiseman model. In order to obtain satisfying accuracy for the wide range of activities, it is advisable to use the more complex, physical van der Berg model. On the other hand, such high values of the activities normally do not occur in the natural environment so they can be neglected in the case of river or lake water monitoring. Much more serious problem is the poor selectivity of the ion selective membranes which limits significantly the usable measurement range.

Additionally, the membrane models coupled with the SPICE transistor models were successfully implemented by the authors in VHDL-AMS for behavioral simulations. The main advantage of this approach is the possibility of performing multidomain simulation of microsystems at different abstraction levels in the same simulator. For example, the SPICE simulations of the Σ - Δ A/D converter alone lasted 5 hours, whereas the multidomain simulations of the entire microsystem containing the sensor and the converter were carried out in 20 minutes maintaining the same accuracy.

ACKNOWLEDGEMENTS

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