

# Ion selective transistor modelling for behavioural simulations

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## Abstract

Computer aided design and simulation of complex silicon microsystems oriented for environment monitoring requires efficient and accurate models of ion selective sensors, compatible with the existing behavioural simulators. This paper concerns sensors based on the back-side contact Ion Sensitive Field Effect Transistors (ISFETs). The ISFETs with silicon nitride gate are sensitive to hydrogen ion concentration. When the transistor gate is additionally covered with a special ion selective membrane, selectivity to other than hydrogen ions can be achieved. Such sensors are especially suitable for flow analysis of solutions containing various ions. The problem of ion selective sensor modelling is illustrated here on a practical example of an ammonium sensitive membrane. The membrane is investigated in the presence of some interfering ions and appropriate selectivity coefficients are determined. Then, the model of the whole sensor is created and used in subsequent electrical simulations. Providing that appropriate selectivity coefficients are known, the proposed model is applicable for any membrane, and can be straightforwardly implemented for behavioural simulation of water monitoring microsystems. The model has been already applied in a real on-line water pollution monitoring system for detection of various contaminants.

## Keywords

CAD, CHEMFET, Design, Measurement, Modelling, Simulation

## INTRODUCTION

Pollution of the natural environment has become one of the major problems in many industrialised countries, which has raised consciousness and understanding of the necessity of environmental care. Consequently, the idea of the so-called sustainable development, allowing economical growth and technological progress while protecting the environment, was born. This idea constitutes currently a fundamental building block of governmental policies in many countries, including the European Union. One of the ways of implementing the sustainable growth policy is the creation of specialised networks dedicated for continuous monitoring of the air, water and soil pollution, which employ different kinds of chemical sensors. The research presented here is a part of a larger international project supported by the 5<sup>th</sup> Framework Programme of the European Union. The project is aimed at the creation of a water pollution monitoring system. During the project realisation, several different structures of sensing elements have been already proposed and manufactured. The base for all the ion concentration sensors will be the Ion Sensitive Field Effect Transistors (ISFETs) sensitive to the hydrogen ion concentration. These transistors furnished with various ion-selective membranes will be integrated with a special data acquisition unit. Next, the pre-processed data will be transmitted to a water quality monitoring station gathering information from the so-called field posts. Then, if necessary, appropriate actions will be undertaken according to sensor indications. This approach appears to be particularly attractive because it allows low cost continuous real time monitoring of water pollution and saving on time consuming and expensive periodic analysis.

The presented approach is particularly well suited for simulation of real time monitoring systems employing multi-ion flow sensor heads analysed by Jimenez et al. (1996) or Chudy et al. (2001). The next section of the paper gives brief description of the operation principles of the ion selective transistors as well as the existing device models. Then, the measurement results of the manufactured structures are presented in detail and compared with the behavioural simulations. Finally, some important conclusions and indications for future work are provided.

## SENSOR DESCRIPTION

### Operation principle

The ion selective transistors are solid-state miniature sensors based on silicon technology. From the chemical point of view, these sensors can be an attractive alternative on the market to the classical potentiometric sensors because of their relatively good analytical performance, low price, and small size. These sensors, often referred as Chemically Modified Field Effect Transistors (CHEMFETs), are devoted to the detection of particular species in surrounding electrolyte. The base for all CHEMFETs constitutes the Ion Sensitive Field Effect Transistor (ISFET). As shown in Figure 1, in ISFETs the classic gate of an ordinary FET is replaced by a more complex structure consisting of a reference electrode, an analysed solution and a gate dielectric. The hydrogen ion concentration in the solution 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. Such structure is capable of sensing the concentration of the hydrogen ions and is used as a pH sensor. Moreover, if the gate dielectric is covered with some ion-selective membrane and a PolyHEMA hydrogel, which contains an inner electrolyte of known composition and stabilizes the sensor operation, the sensor can be used for the detection of other ions than the hydrogen ones. These additional layers introduced into the FET gate structure influence the transistor threshold voltage creating potential drops in the gate circuit. The sensors are usually operated under the constant drain current mode, which means that the change of the drain current due to the variation of the ion activity is compensated for by the adjustment of the gate voltage. Therefore, the device sensitivity is usually expressed in terms of the gate voltage change per decade of the ion concentration.

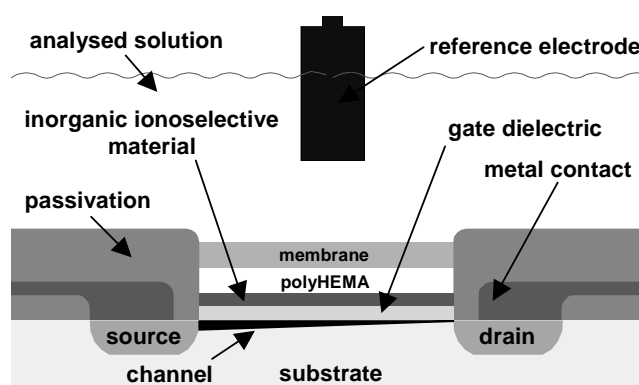


Figure 1. Cross section of CHEMFET structure.

The particular sensors considered in this publication are based on ISFETs manufactured at the Institute of Electron Technology in Warsaw, Poland. The transistors possess a built-in n-type channel 640  $\mu\text{m}$  wide and 14  $\mu\text{m}$  long and the drain/source contacts placed on the back side of the silicon wafer. For technological compatibility reasons, the gate dielectric was manufactured as a composite of silicon oxide and nitride. The fact that the transistors have the back-side contacts renders them suitable for real time flow analysis, because these sensors mounted in special flow-through cells can be submerged directly in the analysed solution.

The most important part of the CHEMFET is the ion selective membrane, because it determines its selectivity and consequently the measurement range. The crucial component of the membrane is the so-called ionophore (ion carrier) responsible for the complexation and transport of the main ion through the membrane. Another component is the lipophilic salt, which prevents the ions of the opposite sign from penetration to the membrane. Both the ionophore and the salt constitute only a few weight percent of the entire membrane and they are suspended in a polymer matrix (e.g. plasticized PVC, polysiloxane, polyurethane).

The measured polysiloxane ammonium selective membranes deposited on the ISFET gate dielectric were prepared at the Department of Analytical Chemistry of the Warsaw University of Technology. Before the membrane deposition, the polyHEMA layer was conditioned in 0.1 M  $\text{NH}_4\text{NO}_3$  solution over 3 hours. Then, the membrane solution was deposited on polyHEMA layer. After subsequent solvent evaporation in nitrogen and UV polymerization, the sensors were stored again for a few hours in nitrogen atmosphere.

### Membrane Modelling

The analysis of the CHEMFET membrane processes has been already undertaken by many authors. Generally, there can be distinguished two approaches to the membrane potential description: the physical one and the behavioural one. The physical approach, whose foundations were given by van den Berg (1988) and developed by Morf *et al.* (1999), is based on the thermodynamic theory explaining the partition of ions between the membrane and the solution in the presence of electric field. The sensor simulations employing the physical model produce accurate results, but they are time consuming and often hard convergent. The other approach is derived from the well-known Nernst equation and it leads to the formulation of the so-called Nikolski–Eisenman (NE) equation (Eisenman *et al.*, 1957). The main advantage of this approach is that it is time efficient, reasonably accurate and it can be easily implemented in any behavioural simulation environment. Moreover, the model parameters, such as the selectivity coefficients, can be determined analytically without any difficulties. On the other hand, these parameters are not directly linked to the physicochemical processes in the membrane, though they have physical interpretation, hence they do not allow the optimisation of membrane composition. However, numerous investigations proved that these two approaches are to some extent equivalent, or even under some specific conditions yield exactly the same formulae (Ogrodzki, 2002). Moreover, it was shown that the differences do not exceed several percent, especially for high activities of the main ion (Daniel *et al.*, 2002). Thus, considering the trade off between simulation accuracy and time, in this research we will focus on the behavioural NE model, because of its simplicity and ease of physical interpretation.

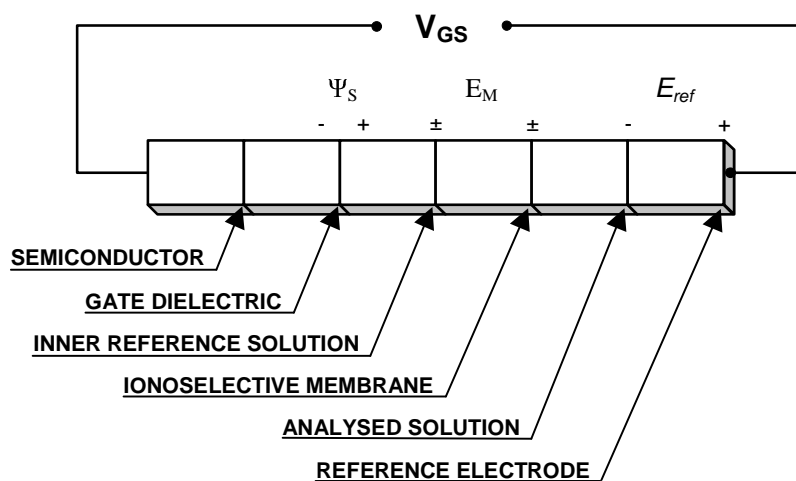


Figure 2. Electric potential in the gate circuit.

For both types of membrane models, the overall electric potential drops in the gate electric circuit can be represented as it is visualised in Figure 2. Starting the analysis from the transistor channel side, the first potential drop induced in the gate circuit is the dielectric surface potential  $\Psi_s$ . Unlike in the case of ISFET where the value of this potential serves as the measure of the hydrogen ion concentration (Szermer *et al.*, 2003), CHEMFET operation does not depend significantly on the properties of the gate dielectric because the dielectric contacts directly only with the polyHEMA hydrogel containing the electrolyte of known and constant composition. Thus, the dielectric surface potential, at least theoretically is constant, if good enough adhesion of the hydrogel is ensured.

The analysis of the membrane potential  $E_M$  is more complex because it has three components. The membrane separates two electrolytes containing the ion to be detected, however the activities of this ion in each electrolyte are different. The first electrolyte is the unknown solution, the other is the solution contained in the polyHEMA hydrogel, serving as a reference electrolyte of known main ion activity. The total membrane potential drop  $E_M$  results from the potential drops  $E_{B1}$  and  $E_{B2}$  created by the activity difference between the solutions at the two phase boundaries and the membrane diffusion potential  $E_D$ . From the CHEMFET operation point of view, the membrane potential  $E_M$ , expressed by the beneath equation, is the most important component, since it is the only one which is directly dependent on the composition of the analysed solution (Ogrodzki, 2002).

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

The reference electrode potential  $E_{ref}$  is dependent on the type of the electrode, i.e. its electrode material and inner solution composition. Summarising, compared to the ordinary MOS transistor, the threshold voltage of the CHEMFET can be computed using Equation 2. Then, this threshold voltage value can be substituted to some electrical simulator, so as to obtain the sensor electrical characteristics.

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

Furthermore, from the NE model, the change of the membrane potential, and consequently the threshold voltage, due to the presence of ions in the measured electrolyte can be computed using Equation 3. As can be seen, the membrane potential varies not only with the activity of the main ion to be detected  $a_i$ , but also it depends on the concentration of some other ions  $a_j$ , called interfering ions. The interfering ion activity is multiplied in the formula by the relative selectivity coefficient  $k$ .

$$\Delta V_T = 2.303 \frac{RT}{z_i F} \log \left[ a_i + \sum_{j \neq i} k_{ij} a_j \frac{z_i}{z_j} \right] \quad (3)$$

where:

$F$  – Faraday constant = 96 500 C;  $R$  – gas constant = 8.314 J/K M;  $T$  – absolute temperature [K]  
 $a$  – ion activity [mol/dm<sup>3</sup>];  $i, j$  – main and interfering ion indices;  $z$  – ion electrovalence

The problem of membrane selectivity, illustrated in Figure 3, is currently one of the most important issues related to CHEMFETs. The curves in the figure were obtained using the above equation for two different selectivity values and five different interfering ion concentrations. As can be seen from the figure, due to the limited selectivity, the ideal curve flattens out for certain activities of the main ion  $K_m$  and as the result the sensor becomes insensitive to the main ion at its low activities. The location of the bending point and the measurement range are determined both by the selectivity and the activity of the interfering ion  $pK_d$ .

The presented model was coupled together with the MOS transistor model, as shown by Janicki *et al.* (2003) and implemented both in the SPICE electrical simulator and the hAMStEr behavioural simulator using the VHDL-AMS language. The obtained simulation results are compared with the measurements in the next section.

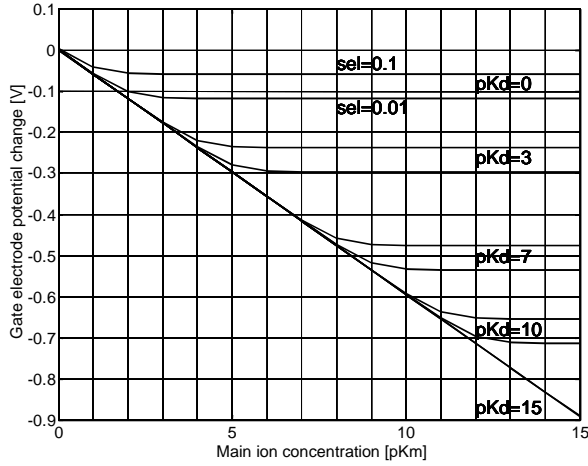


Figure 3. Gate potential dependence on ion concentration for different selectivity coefficient values.

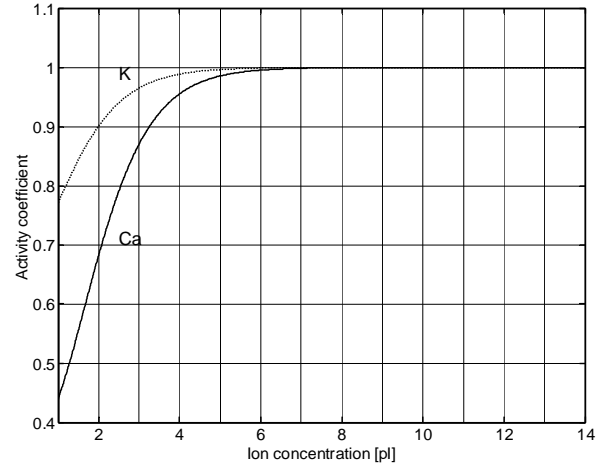


Figure 4. Activity coefficient dependence on ion concentration for small and large ions.

Another issue, which must be commented on, is the relation between the two terms sometimes used interchangeably: the ion concentration  $c$  and the ion activity  $a$ . The ion activity is the product of the ion concentration and its activity coefficient  $f$ . Furthermore the activity coefficient is not a constant, because it depends on the ionic strength  $J$  of all ions  $i$  present in a solution, which can be computed using the following equation:

$$J = 0.5 * \sum_i z_i^2 c_i \quad (4)$$

For known ion radius  $\delta$  (expressed in nm), the value of the activity coefficient can be determined using the Debye-Hückel formula presented in Equation 5. The activity coefficient values computed for a small univalent ion (potassium) and a larger bivalent ion (calcium) are presented in Figure 4. As can be seen, these two quantities are almost equal for low ion concentrations. For significant ion concentrations or larger ions, the difference between the ion concentration and the ion activity should be taken into consideration.

$$\log_{10}(f) = -0.51 * z^2 \sqrt{J} / (1 + 3.29 * \delta \sqrt{J}) + 0.1 * z^2 J \quad (5)$$

## MEASUREMENT AND SIMULATION

The model of the CHEMFET sensor presented in the previous section will be employed here for behavioural simulation of a microsystem containing the analysed electrolyte, the sensor itself and the sigma-delta ( $\Sigma-\Delta$ ) analogue-to-digital converter (A/D C). First, based on the measurements, unknown parameters of the sensor electrochemical model will be determined. Next, the CHEMFET electrical simulations are compared with the measurements. Finally, the simulations of the whole microsystem are presented.

### Selectivity determination

The process of the membrane selectivity determination will be illustrated in detail on the example of the ammonium selective membrane. The measurements were performed for different main ion concentrations with three kinds of interfering ions, namely potassium, sodium and calcium. The interfering ion concentration was constant and equal to  $10^{-2}$  mol/dm<sup>3</sup>. The membrane selectivity with respect to each interfering ion was determined at the operating point  $V_{DS}$  equal to 2V and  $V_{GS}$  equal to 1V. The measured values of the gate voltage maintaining constant drain current with the variable main ion concentration are marked in Figure 5. Additionally, the curves fitted using the NE model are plotted with solid lines.

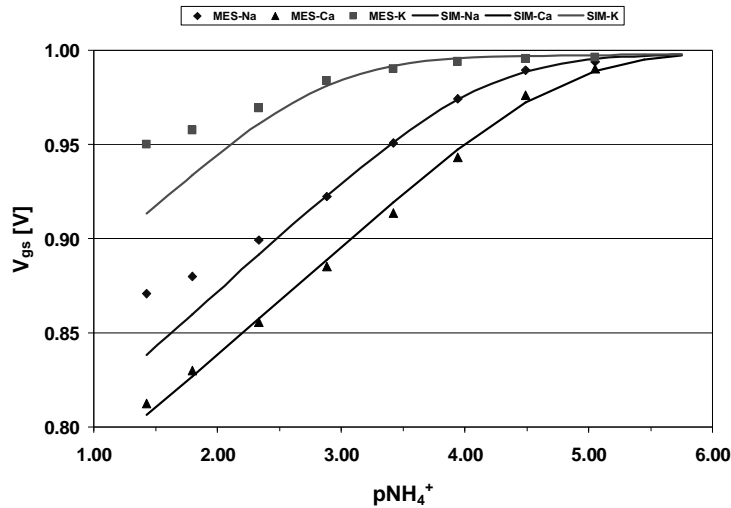


Figure 5. CHEMFET gate voltage dependence on main ion activity (constant drain current).

The presented in the above figure measurement results were a bit surprising, because the obtained shape of the curve resembles rather a sigmoid and cannot be exactly approximated by the simple NE model, in which the curve bends only from one side. However, large discrepancies between the simulations and the measurements occur only for extremely high activities of the main ion rarely encountered in the natural environments. Nevertheless, if this sensor is to be used for analysis of highly polluted waters, then the physical model, taking into account also the influence of the ion of the opposite sign, has to be employed.

The estimated based on the measurements selectivity coefficient values are compared in Table 1 with the ones provided in the scientific literature. As shown, the measured selectivity coefficient values are acceptable and lie within the range reported in other sources. The main conclusion from this part of the experiment is that the presence of potassium ions has to be avoided, if the concentration of the ammonium ions is to be measured. Otherwise, only the aggregate concentration of the ions can be assessed, without determining the precise composition of the analysed solution.

Table 1. Ammonium membrane selectivity coefficients ( $\log_{10} k$ ).

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

### Electrochemical sensor simulations

The selectivity coefficients measured in the previous subsection are used here to compute the change of the CHEMFET threshold voltage according to the formula given in Equation 3. The remaining parameters of the sensor model were determined earlier, as demonstrated by Janicki *et al.* (2003), during the measurements of the ISFETs before the membrane deposition. The simulated CHEMFET output characteristics (solid lines) obtained in the cases of calcium and potassium interfering ions are compared with measurements (crosses) in Figures 6-7. As can be seen, in the case of calcium interfering ions, the sensor work as expected with sensitivity reaching almost 60 mV per decade in the range of high ammonium ion activities below pNH<sub>4</sub> equal to 5. However, when potassium ions are present in the solution the sensor is virtually insensitive to the main cation.

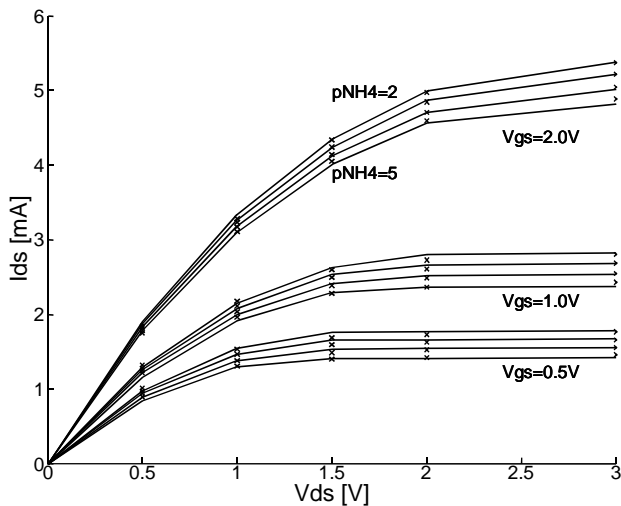


Figure 6. CHEMFET output characteristics with calcium interfering ions.

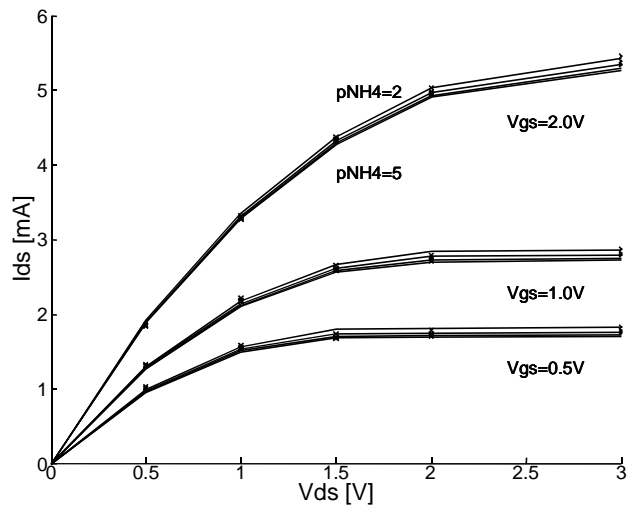


Figure 7. CHEMFET output characteristics with potassium interfering ions.

### Behavioural system simulations

Finally, the previously presented and validated CHEMFET sensor model was implemented using the VHDL-AMS language in the hAMster environment for multidomain simulations of a system consisting of the sensor and a data processing unit containing a 3<sup>rd</sup> order 8 bit sigma-delta analogue-to-digital converter ( $\Sigma-\Delta$  A/D C). The system simulated in this section could in turn constitute some part of a larger microsystem.

The entire microsystem was fully simulated using the VHDL-AMS models of the components presented in Figure 8. The analogue input signals of the system are the ion concentration and temperature. The output signal is the digital value stored in the output ADC register corresponding to the measured ion activity. The final simulation results are presented in Figure 8. The simulated resolution of the converter, obtained dividing the maximum range of input signal ( $1 V_{p-p}$ ) by the maximal number of logic levels (256 for 8 bit), amounts to 3.9 mV. This value corresponds to the resolution of about 0.08 pI in terms of the main ion concentration if there are no other ion present in the solution. However, it should be stressed that the converter resolution can be improved when the converter bit number is increased. For example, for a 12 bit converter the resolution is 0.24 mV (0.005 pH). More detailed considerations on the  $\Sigma-\Delta$  A/D C operation principles together with the analysis of different realisations can be found in the book by Candy and Temes (1991).

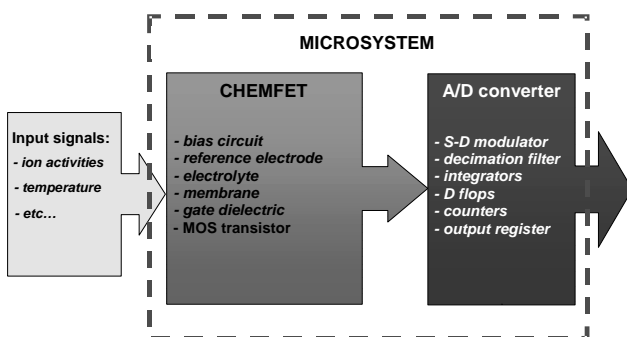


Figure 8. Signal flowchart of simulated microsystem

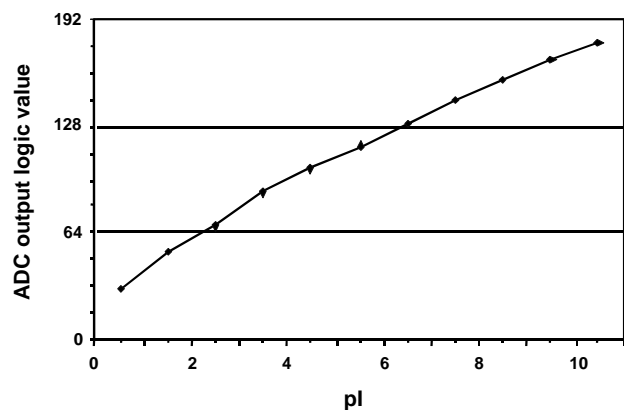


Figure 9. Digital output signal dependence on ion concentration

## CONCLUSIONS

This paper presented relatively simple, but accurate model of the CHEMFET sensor. The proposed model is based on a modified MOS transistor model in which the threshold voltage is influenced by the membrane potential induced by different ions present in the electrolyte flowing over the gate structure. The model combines in a single set of mathematical equations different chemical, thermal and electrical phenomena occurring in the device. In spite of its apparent complexity, the number of model parameters is fairly low. The model takes into account the influence of interfering ions and is suitable for simulations of the device operating in a relatively wide range of temperatures and ion activities. Furthermore, the model was successfully employed for the simulation of real devices. The model parameters were determined based on the measurements and the behavioural simulations performed for the extracted parameter values showed good agreement with the measurements. Moreover, the model was implemented in the VHDL-AMS language. Owing to this solution it was possible to perform in a single environment multidomain mixed mode simulations of the more complex system containing the CHEMFET sensor and the data processing unit. The main advantage of the VHDL-AMS simulations at the system level is the possibility of reducing significantly the design cost and the simulation time comparing to the traditional transistor level simulations. The presented approach has been already successfully implemented in the SEWING project for on-line monitoring of water pollution.

## ACKNOWLEDGEMENTS

This work was supported by the 5<sup>th</sup> European Framework Program SEWING, IST-2000-28084.

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