

ON DEPENDENCE OF CHEMFET SENSOR RESPONSE ON OPERATING POINT

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ABSTRACT: The paper presents some properties of CHEMFET devices which are not commonly known, yet which are important for performing measurements of ionic activity in aqueous solutions.*

INTRODUCTION

CHEMFET is a Field Effect Transistor (FET) based device that is capable of sensing ionic activity in aqueous solutions. The device, as sketched in Fig. 1, embodies a FET, i.e. most of the MOSFET silicon structure – without a gate, though. The gate insulator is covered with a special ion-selective membrane, that separates some internal reference solution from the tested aqueous solution. A contact to the reference electrode, which is immersed in the tested electrolyte, can be seen as a substitute for the gate contact of a MOSFET device¹.

Diffusion of selected ions into the membrane separates charges, and so creates an electric field that is able to influence current conduction in transistor channel. Potential drop between each electrolyte and membrane surfaces depends on types of ions in the solution and their activities (related to molar concentrations), and obviously on selectivity of the membrane. A popular Nikolski-Eisenman model expresses the voltage drop across (each) membrane surface in the following form:

$$U_N = \underbrace{\frac{kT}{q}}_{V_T} \frac{1}{z_m} \ln \left(a_m + \sum_{s \in S} K_{m,s} (a_s)^{\frac{z_m}{z_s}} \right) \quad (1)$$

or in equivalent “exponential” form:

$$\underbrace{\exp \frac{\eta}{z_m \frac{U_N}{V_T}}}_{\eta} = a_m + \sum_{s \in S} K_{m,s} \cdot (a_s)^{\frac{z_m}{z_s}} \quad (2)$$

a_m denotes activity and z_m electrovalency of the main ion (i.e. the one the sensor is most sensitive to), while a_s and z_s – activities and electrovalencies of other (interfering) ions. $K_{m,s}$ stands for selectivity coefficient of the sensor towards the interfering ion (the smaller value the better). Since one surface of the membrane is exposed to (practically) constant ionic activity of the inner electrolyte – voltage drop across that surface is constant.

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¹Electrochemical properties of the reference electrode will not be discussed in this paper.

Fixed content of that electrolyte stabilizes respective surfaces of the membrane and the gate insulator. The other (outer) surface of the membrane contacts the tested solution, and so voltage drop across this surface can be used for sensing ions. The Nikolski-Eisenman equation can then be used to predict changes of voltage drop due to changes of ionic activity in the external solution, i.e. the sensor response curve [2].

Common measurement setup, eg. such as shown in Fig. 2, keeps the operating point of the internal FET of CHEMFET (i.e. its drain current I_D and the drain to source voltage U_{DS}) constant. The main idea behind this setup is to reduce influence of FET properties

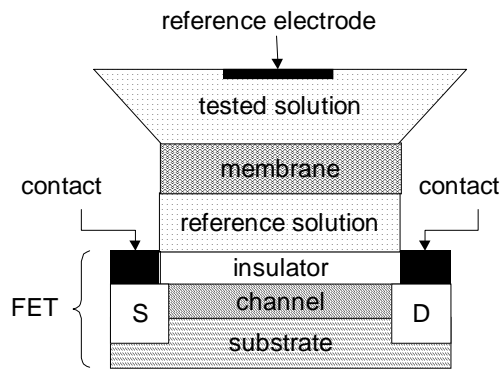


Figure 1: Schematic cross-section of a CHEMFET device

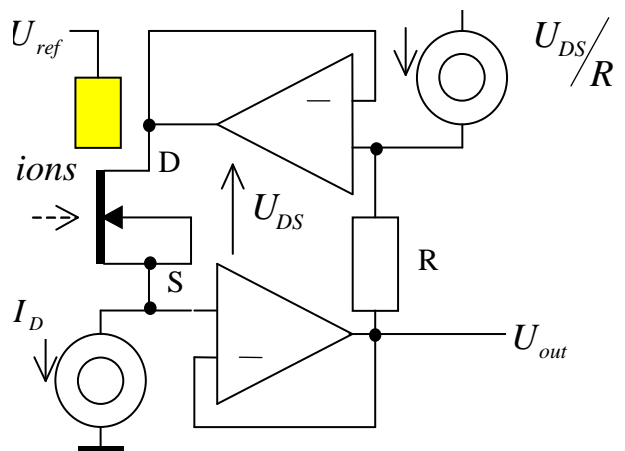


Figure 2: Example measurement setup

upon the measurements, so that changes of across membrane surface voltage (due to changes of ionic activities in the external solution) are directly reflected in changes of the voltage drop between the reference electrode and the source, $U_{RS} = U_{ref} - U_{out}$, and so (for fixed bias U_{ref}) – in changes of the output voltage of this measurement circuit (U_{out}). U_{out} in the circuit from Fig. 2 can be shifted by any amount by changing the biasing voltage U_{ref} . Since this is a feature of this particular circuit in the following analysis we will assign U_{RS} to be the output voltage of the sensor.

Changes of the output sensor voltage due to activity changes of main ion can be typically approximated by the Nikolski-Eisenman equation with surprisingly good accuracy. Fig. 3 illustrates that claim with data for a potassium sensitive CHEMFET². The measurement data was obtained by increasing activity of the primary ion (in range $10^{-6} - 10^{-1} \text{ mol l}^{-1}$) in the 0.1 mol l^{-1} solution of the interfering sodium ion. The upper plot shows dependence $\Delta U(a_k) = U_{RS}(a_k) - U_{RS}(-1)$ for measurements (circles) and for the Nikolski-Eisenman model (solid line). Good predictive capability of the model is confirmed with a plot of absolute discrepancy between the model and data, as shown in the bottom plot.

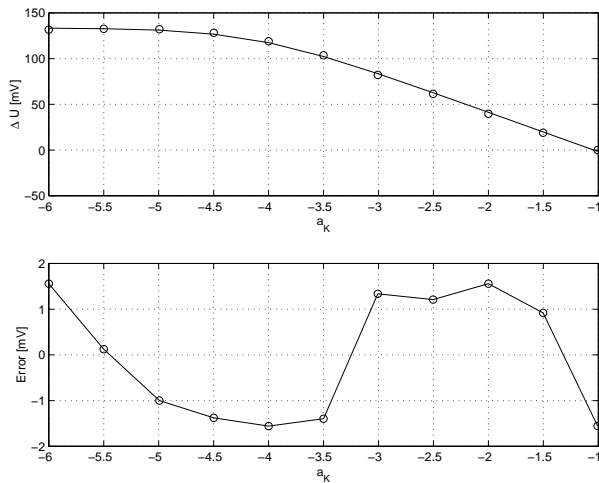


Figure 3: Fitting Nikolski-Eisenmann model (top figure) and absolute error of the mode w.r.t. data points (bottom figure) for a potassium sensitive CHEMFET

The constant I_D, U_{DS} measurement setup is usually very adequate to needs, but it is not obvious what values of I_D, U_{DS} one should select for a given CHEMFET device. A rule of thumb is to take smallest possible values. A long term goal of research the authors are involved in, is creation of a unified electrochemical (and possibly technological) model of CHEMFET devices, a model that would be suitable for simulation and design with contemporary CAD tools. To this end it was necessary to have a closer look at a role of the FET in CHEMFET measurement, and to investigate influence of the operating point

²All CHEMFET devices cited in this paper were made in prof. Z. Brzózka group, Dept. of Anal. Chemistry (DoAC), Warsaw University of Technology (WUT) [1]. The actual measurements used in this paper were performed by Dr W. Wróblewski and Mr Z. Gniewiński. Data processing and modeling were performed by Dr L.J. Opalski.

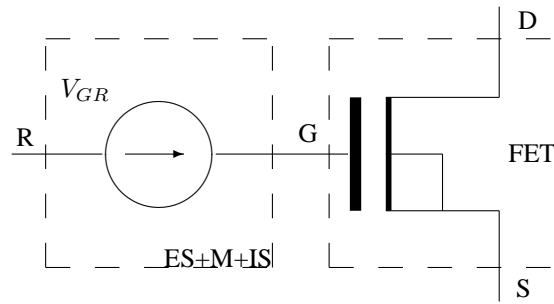


Figure 4: A structure of a simplistic CHEMFET model. $ES+M+IS$ denotes: external solution-membrane-internal solution; FET – a standard MOSFET model

of FET upon the sensor characteristics. This paper reports some interesting findings along the way.

CLOSER LOOK AT FET IN CHEMFET

Let us note, that the above presented “standard approach” to measurement setup (constant I_D, U_{DS}) in fact relies on an assumption of *separability* of CHEMFET model into two independent, although interconnected, parts – as illustrated in Fig 4. The main electrochemical part of the model (transducer) deals with conversion of chemical information on the tested solution (i.e. activity of ions) into electrical information (voltage drop between gate insulator surface and the reference electrode terminal). The silicon structure of a gateless FET device senses potential of the gate-internal solution interface – converting changes of the potential into changes of the drain current. Due to electrical insulation between the two components (gate insulator) – the electrochemical part operates in truly potentiometric mode, and FET transforms that high (input) impedance level to more moderate values which are less prone to external noise.

Taking closer look we can see, that such a separable CHEMFET model could be true under two conditions. First, the FET should have (at least floating) conducting gate, that would provide equipotentiality of the “external” gate insulator surface (looking from the substrate). Second, potential of the gate should not depend on phenomena inside transistor, but be completely, determined by electrical field in electrolytes and the membrane (and so dependent on electrolyte contents). Are these conditions satisfied in CHEMFET devices?

First, CHEMFETs are made of *gateless* FET structures, where the equipotentiality of the gate insulator surface is not provided by conduction of electrons in the gate material, but by movement of mobile ions of the internal solution.

Second, changing gate surface potential involves movement of charge on both surfaces of the gate insulator. Since charge in the semiconductor depends on electric field due to U_{DS} voltage, so the gate surface potential generally also depends on U_{DS} .

To see if (and when) the above presented effects do significantly influence operation of CHEMFET sensor I-V transfer and output characteristics of several potassium

sensitive CHEMFET devices were measured for different sets and concentrations of ions in the external electrolyte. From transfer I-V curves a sensor response function: $U_{RS}(a_m, I_D, U_{DS})$ was determined, that relates the output voltage U_{RS} of the sensor to activity a_m of the main ion for different combination of operating conditions (U_{DS}, I_D). For a given U_{DS} of a n-channel depletion FET and fixed solution contents, increase of I_D demands increase of biasing voltage for the FET in Fig. 4, i.e. U_{GS} . If the separable model is valid then U_{DS} has to increase by the same amount for the same sweep of main ion activity a_m . By the same token the auxiliary function:

$$\Delta U(a_m) \equiv U_{RS}(a_m, I_D, U_{DS}) - U_{RS}(a_m^0, I_D, U_{DS}),$$

where a_m^0 is a reference ion activity, should not depend on I_D (nor U_{DS}), for fixed activities of interfering ions.

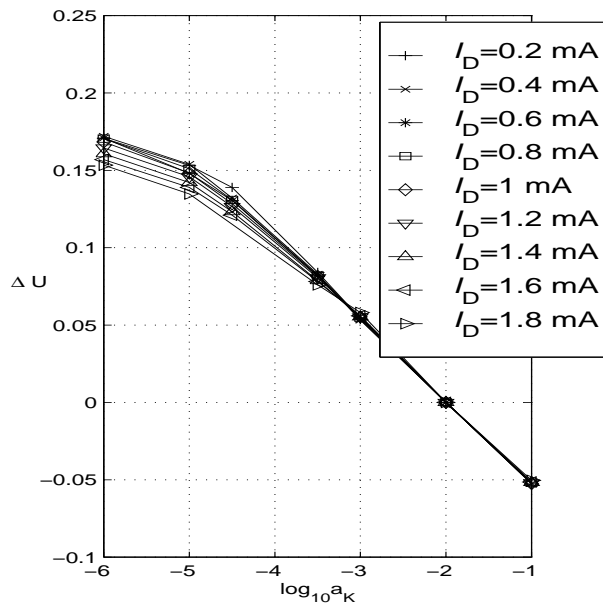


Figure 5: A family of CHEMFET potassium sensor response curves

Figure 5 plots ΔU w.r.t. $a_m \equiv a_K$ (i.e. potassium activity) for fixed $U_{DS} = 0.5$ V, $a_m^0 = 10^{-3}$ and several values of I_D for a potassium CHEMFET sensor. It is seen, that for small values of activity a_m sensor output depends on FET drain current, and so the separable model is not accurate. Variations of ΔU due to change of I_D is about 20 mV for this device. Since maximum slope of the response is approximately 52mV per decade of a_m change the observed ambiguity of sensor output response due to variation of the operating point is significant. It is interesting to note, that the variation decreases to 3mV for $U_{DS} = 1$ V and below 2mV for $U_{DS} = 1.5$ V. Similar values were found for other devices.

To better understand the observed phenomenon the characteristics of the same CHEMFET sensor were modeled with a compact Nikolski-Eisenman equation related 3-parameter model of the form:

$$U_{RS} = U_0 + \phi \ln(a_m + k_s) \quad (3)$$

Fitting was performed using minimax, least squares and least absolute values approaches. Since results were sim-

ilar – only results of the minimax fitting are presented in Fig. 6.

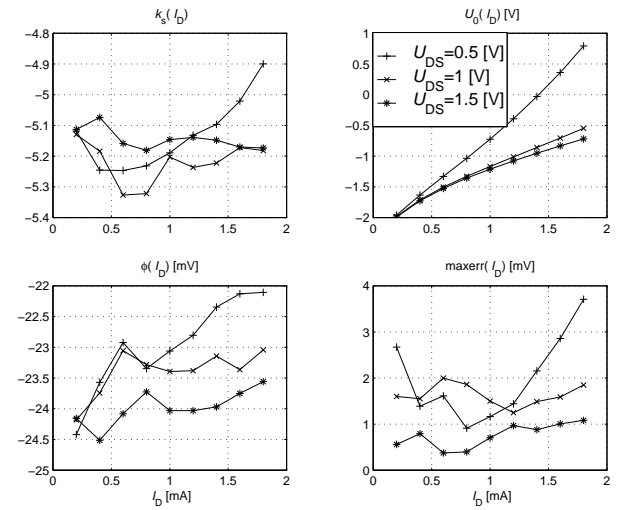


Figure 6: Dependence of CHEMFET sensor model parameters and maximum fit error on I_D , for different U_{DS} .

It is seen that operating point (and, unfortunately, measurement inaccuracies) influence ϕ and k_s parameters significantly. It is evident that small U_{DS} value results in worst fit and strongest influence of I_D upon model parameters. This observation contradicts opinions, which advocate small biasing voltage (U_{DS}).

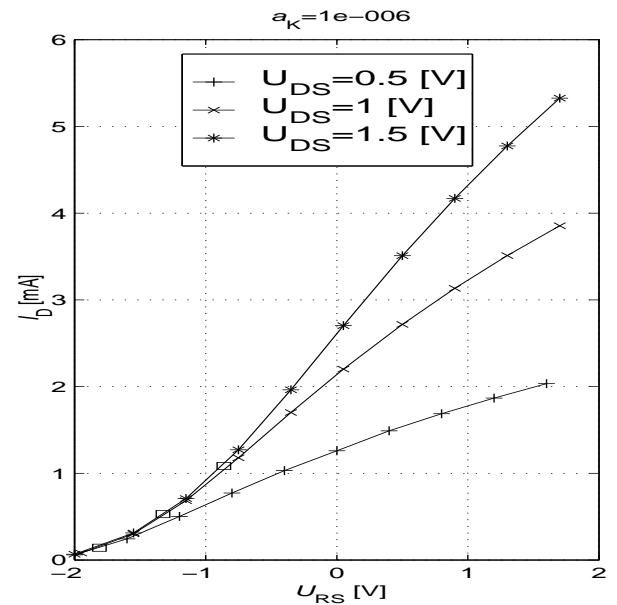


Figure 7: Transfer characteristics of a potassium sensitive CHEMFET device for $a_m \equiv a_K = 10^{-6}$.

To enhance understanding of FET operation peculiarity for low U_{DS} numerical fitting of MOS1 SPICE model [7] was performed, using the transfer characteristics shown in Fig. 7 (of the same CHEMFET which was used to plot Fig. 5 and 6). Fitting resulted in an estimate of the threshold voltage of CHEMFET $V_{T0} \approx -2.2$ V. The voltage separating saturation and linear region of

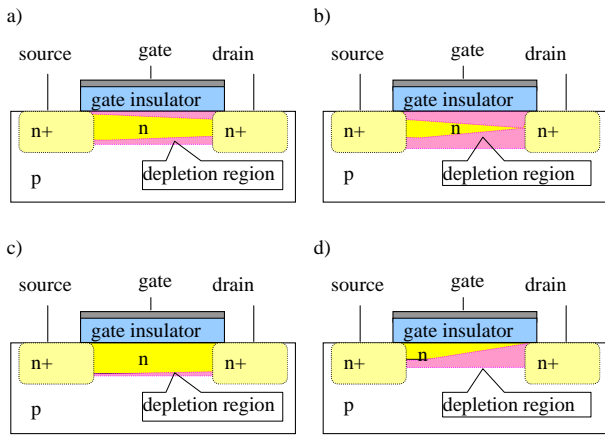


Figure 8: Schematic cross-section of a depletion MOS device under different biasing conditions: a,c – in linear region, b, d – in saturation region, a, b – in depletion mode, c, d – in accumulation mode

operation $U_{RS}^{th} = U_{DS} + V_{T0}$ is marked with squares in Fig. 7. For $U_{DS} = 0.5, 1.0$ and 1.5 V the corresponding $U_{RS}^{th} \approx -1.69, -1.22, -0.79$ V (with related $I_D = I_D^{th} \approx 0.19, 0.62, 1.2$ mA). For $U_{RS} < U_{RS}^{th}$ (and so $I_D < I_D^{th}(U_{DS})$) FET operates in saturation. For $U_{DS} = 0.5$ V indeed all I_D values used in Fig. 5 correspond to linear mode of FET operation ($I_D > I_D^{th} \approx 0.19$ mA), while for $U_{DS} = 1.5$ V only one third. The above presented facts show correlation between significant variations of ΔU in Fig. 5 and linear mode of FET operation.

To see what is happening in the CHEMFET device let us consider operation of a depletion type n-channel MOSFET, used in our measurements. Negative gate biasing of the transistor increases depletion area beneath the gate insulator, and for a cut-off voltage V_{off} reduces the drain current to its minimum (possibly 0, depending on channel doping). For gate biasing that is more positive than V_{off} the depletion area is reduced (cases a and b in Fig. 8), but channel can still be pinched-off on the drain side – if only U_{DS} is sufficiently large (Fig. 8 b). Due to displacement of the conductive channel away from the gate insulator – the charge accumulated by gate (and so gate to channel capacitance) decreases significantly, when FET is going from linear to saturation region of operation. Once in saturation – variability of charge due to gate potential change becomes smaller. If gate biasing is increased further, above so called flat band voltage level – positive gate potential attracts electrons towards the bottom of the gate insulator (accumulation mode of operation), channel conductivity increases, but gate to channel capacitance stays constant.

From this sketchy description of MOSFET operation it is seen, that FET of the CHEMFET device can vary gate capacitance much – only when in depletion mode and when biasing sweeps linear region of operation (i.e. for $I_D > I_D^{th}(U_{DS})$). These arguments explain qualitatively the phenomenon illustrated in Fig. 5.

Quantative analytical justification of the phenomenon is not available at the moment.

CONCLUSIONS

This paper reports dependence of CHEMFET sensor response on operating point. The above presented findings do not contradict opinions (eg. [8]), which consider CHEMFET based sensors a competitive technology for implementation of low cost portable instruments, but the paper rises a warning regarding selection of operating point for a depletion type FET structure.

Quantative modeling of the reported phenomena is currently being developed, based on unified charge-based description of the whole CHEMFET, membrane and electrolytes. The modeling is taking advantage of earlier research and models on CHEMFETs and depletion type MOSFETs, eg. presented in [3, 4, 5, 6].

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