

Device simulations of ion-sensitive FETs with arbitrary surface chemical reactions

Leandro Julian Mele*, Pierpaolo Palestri*[†] and Luca Selmi[†]

*DPIA, University of Udine, 33100, Udine, Italy.

[†]DIEF, University of Modena and Reggio Emilia, 44100, Modena, Italy.

[‡]Corresponding author. Email: pierpaolo.palestri@uniud.it

Abstract—In this work, we exploit the general-purpose solver COMSOL, equipped with electrolyte and semiconductor physics modules, to implement a versatile model of potentiometric chemical sensors including arbitrarily complex surface reactions at the oxide/electrolyte interface with examples on 2D device-level simulations of an ISFET. Firstly, Multiphysics simulations of V_{TH} sensitivity to pH sensing are compared with analyses based on semiconductor TCAD. Then, more complex Na^+ sensing experiments are examined and numerical simulations are compared against 1D electrochemical models.

Index Terms—ion-sensitive FETs, TCAD, device simulations, surface chemical reactions, potentiometric sensors

I. INTRODUCTION

Ion-sensitive FETs (ISFETs) have widespread application as on-chip integrated biosensors, offering advantages in terms of miniaturization, low-cost and CMOS compatibility [1]. In ISFETs, the transduction process takes place at the interface between a (functionalized) solid surface and an electrolyte containing ions/analytes. Many ISFET-based sensors have been studied for a variety of analytes [2]; in a few of them the fabrication of the sensing surface occurs in the back-end of line of an unaffected CMOS process flow suited to integrate readout and digitalization functionalities [2], [3].

To predict and engineer the sensor response at the device level, one should combine into a comprehensive model the electrochemical processes taking place in the electrolyte and at the interfaces (i.e. surface chemical reactions), as well as their coupling with the underlying FET device. Such a combination, however, is not always straightforward with commercial TCAD for semiconductor device modeling. Recently, a few solutions to this issue have been proposed based on, e.g. Sentaurus[™] [4], where the electrolyte is modeled as a “generic” semiconductor (with appropriate gap, density of states and mobility to describe cations and anions as electrons and holes) and surface reactions with protons are introduced via physical model interfaces (PMIs) [5], [6]. Clearly, such a workaround is possible only for electrolytes where the ionic concentration is dominated by 1:1 dissolved salts (e.g., Na^+ and Cl^- dissolved in water) [7]. An alternative is offered by general-purpose multiphysics solvers such as COMSOL Multiphysics[®] [8], where semiconductor modeling modules

can be combined with electrolyte modules to simulate multi-ion solutions.

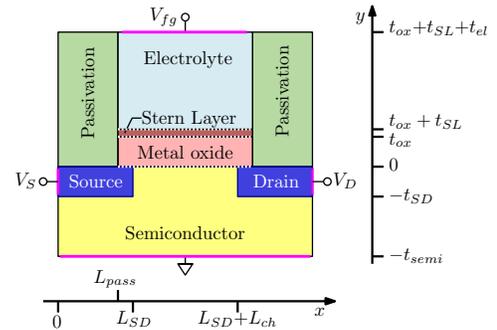


Fig. 1. Template ISFET structure (not to scale) used for the simulations in Sentaurus TCAD and COMSOL. Parameter values are reported in Table I. Electrical contacts are highlighted in magenta whereas dotted lines indicate the boundaries where ad-hoc equations for boundary conditions are used to replace simulation domains and to include surface reactions.

In this paper we investigate the pros’ and cons’ of TCAD and Multiphysics approaches for the simulation of pH ISFETs by simulating the template device in Fig. 1 and validating the COMSOL implementation of a multiphysics model with a Sentaurus model empowered with the workaround presented in [6] to handle pH sensitive surfaces. Moreover, we demonstrate the versatility of multiphysics tools in capturing arbitrary sets of surface reactions, by implementing in COMSOL the recently proposed model [9].

II. DESCRIPTION OF THE TEMPLATE ISFET

We consider the 2D structure shown in Fig. 1 for the TCAD and COMSOL models, with the physical and geometrical parameters reported in Table I. The bulk is p-type semiconductor ($N_A = 10^{15} \text{ cm}^{-3}$) whereas the source and drain have $N_D = 10^{20} \text{ cm}^{-3}$. The device width is $W = 1 \text{ } \mu\text{m}$.

TABLE I
PHYSICAL AND GEOMETRICAL PARAMETERS USED IN THIS WORK

Param.	Value	Units	Param.	Value	Units
t_{SL}	1	[nm]	t_{semi}	0.5	[μm]
t_{el}	0.5	[μm]	L_{SD}	200	[nm]
t_{ox}	3	[nm]	L_{pass}	180	[nm]
t_{SD}	45	[nm]	L_{ch}	200	[nm]
ϵ_{ox}	3.9	-	ϵ_{el}	78.5	-
ϵ_{Si}	11.7	-	ϵ_{Stern}	22.58	-

We acknowledge funding from the European Unions Horizon 2020 research and innovation programme under grant agreement No 862882 (IN-FET project) via the IUNET Consortium.

The ion-sensitivity properties of ISFETs stem from surface chemical reactions taking place at the oxide/electrolyte interface. In order to take into account steric limitations due to finite size of ions, models should include the Stern Layer (i.e. a very thin insulating layer) between the oxide and the electrolyte (see Fig. 1) [6], [10]. In this work, the metal oxide and Stern Layer are explicitly simulated in Sentaurus, whereas in COMSOL these regions are not simulated explicitly but instead described using boundary equations; in particular for the gate oxide, the built-in function ‘Thin Insulating Gate Boundary’ is used to set the gate oxide parameters whereas the equation of an ideal parallel plates capacitor is employed for the Stern Layer. In this way, the otherwise fine mesh grids required in these layers are avoided without loss of accuracy. Clearly, this simplification neglects the presence of traps in the oxide layer.

Surface chemical reactions are implemented at the oxide/Stern Layer interface (dotted line in Fig. 1). In Sentaurus TCAD we used PMIs as explained in [6], whereas in COMSOL surface reactions have been implemented using a boundary equation for the surface charge that depends on the considered surface chemistry. The sensitivity of the ISFET is extracted as the threshold voltage shift, ΔV_{TH} , at $I_{DS} = 0.3 \mu A$, upon changes of the analyte concentration.

III. IMPLEMENTATION IN COMSOL OF THE MODEL FOR ARBITRARY SURFACE REACTIONS

The interactions between ions in the electrolyte and solid surfaces, requires models with different level of complexity depending on the number of participating reactions and ions. The simplest case is represented by the ion-to-ligand surface adsorption, usually studied with the Langmuir isotherm [11]. pH-sensitive ISFETs, instead, are described by two reactions for the double protonation of negatively charged oxygen terminations of metal oxides [12]. A three-reaction model was also proposed to take into account chloride ions adsorption at the doubly protonated sites [13]. In the literature, these models have been presented case-by-case; the complexity of the underlying math increases rapidly with the number of reactions. Recently, we developed a general and systematic methodology [9] to model an arbitrary number of surface chemical reactions involving different types of binding sites. The model uses graphs to represent the changes of the site “states” upon binding/unbinding of ionic species. In fact, any surface reaction can be decomposed in the consecutive binding of ions, each one leading to a different state of the binding site/ligand complex, as shown in Fig. 2.

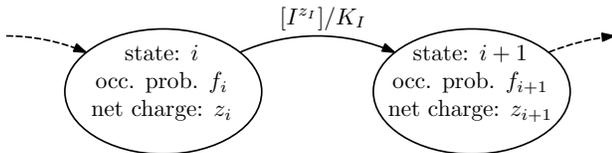


Fig. 2. Graph representing the steady-state relationship between two arbitrary states of a ligand/binding site: from state i to $i+1$ with associated occupation probabilities, f , and net signed numbers of elementary charges, z , upon adsorption of the ion I with valence z_I (i.e. giving $z_{i+1} = z_i + z_I$). K_I denotes the dissociation constant of the reaction.

Therefore, for a set of N possible states there are $N-1$ reactions, i.e., $N-1$ arrows linking the nodes in Fig. 2. Each arrow has a coefficient given by the ratio between the concentration of the ion/analyte $[I^{z_I}]$ and the corresponding dissociation constant K_I . This coefficient sets the relationship between the occupation probabilities of two adjacent states of the ligand/binding site:

$$f_{i+1} = \frac{[I^{z_I}]}{K_I} f_i. \quad (1)$$

Since there are $N-1$ reactions, the system is completed using the normalization condition $\sum_1^N f_i = 1$. The final equation can be written in matrix form as:

$$\mathbf{M} \cdot \mathbf{f} = (0 \dots \dots 0 \quad 1)^T, \quad (2)$$

where $\mathbf{f} = (f_1 \dots \dots f_N)^T$ is a N -elements column vector and the $N \times N$ matrix \mathbf{M} contains the electrochemical reaction parameters [9]:

$$\mathbf{M} = \begin{pmatrix} \vdots & & \vdots & & \vdots & & \vdots & & \vdots \\ 0 & \dots & 0 & \frac{[I^{z_I}]}{K_I} & 0 & \dots & 0 & -1 & 0 & \dots & 0 \\ \vdots & & \vdots & & \vdots & & \vdots & & \vdots \\ 1 & \dots & 1 \end{pmatrix}$$

By solving Eq. 2, one finds $\mathbf{f} = \mathbf{M}^{-1} \cdot (0 \dots \dots 0 \quad 1)^T$.

From the state probabilities f_i , one can finally compute the surface charge density at the sensing surface in equilibrium as the sum of charged states extended to a number of sites per unit of area, N_S , that is

$$Q_S = q N_S \sum_{i=1}^N z_i f_i, \quad (3)$$

where q denotes the absolute value of the elementary charge. Notice that Eq. 3 identifies the surface reactions of a single type of site. When multiple site types coexist on the same sensing surface, the total surface charge density, $Q_{S,tot}$, is given by the sum over each single type of site, j :

$$Q_{S,tot} = q \sum_{j=1}^M N_{S_j} \sum_{i=1}^N z_{j,i} f_{j,i}. \quad (4)$$

In this work, Eq. 2 is solved in symbolic form, where the concentration of ionic species are expressed using Boltzmann statistics and thus dependent only on the electrostatic potential at the oxide/Stern Layer interface. The resulting \mathbf{f} is then inserted into Eq. 3 or 4 and plugged in COMSOL, that uses it as a charge boundary when solving the device electrostatics.

IV. MODEL COMPARISON FOR PH SENSING

pH-sensitive ISFETs are the most studied FET-based potentiometric sensors thanks to the high sensitivity to the pH of the solution featured by most common metal oxides. The surface chemical reactions at each binding site are well explained in the literature by the site-binding (SB) model [10], [12] and

consist of a two-reaction model that describes the interactions of metal hydroxyl groups, MOH, with H^+ ions in the solution.

The SB model is a special case of the model presented in Section III. Its graph representation has three states as reported in Fig. 3.a. The equilibrium dissociation constants

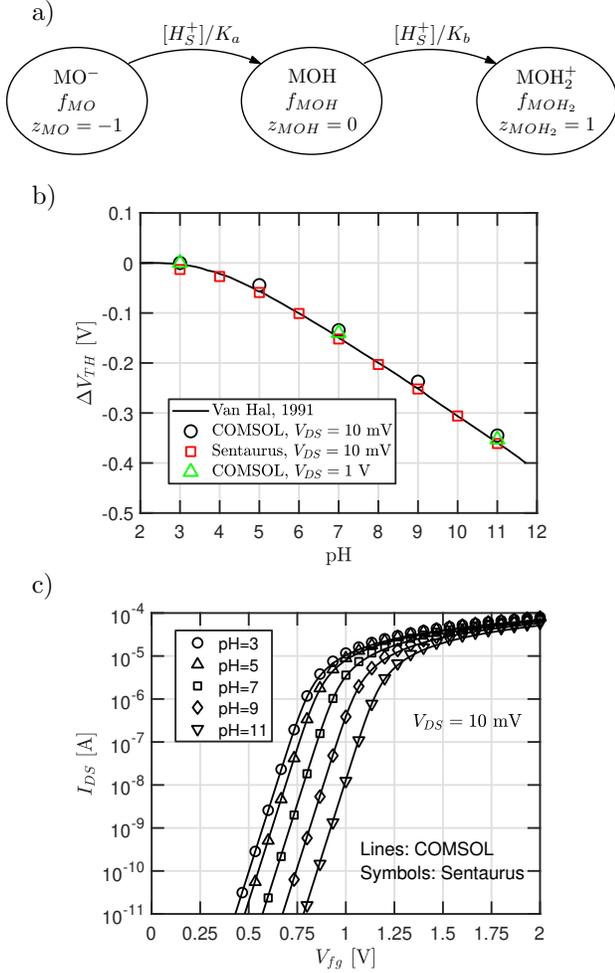


Fig. 3. a) Graph of the SB model following our framework (Fig. 2) for arbitrary surface reactions [9]. b) Simulation of the ISFET threshold voltage shift employing the SB model at the Stern Layer/electrolyte interface of Fig. 1, using Sentaurus (red squares), COMSOL (black circles) and the model from [10]. c) comparison of the full I_{DS} - V_{fg} curves obtained using the two simulation platforms for different pH values. In all cases the electrolyte ionic strength is set to 100 mM and the reaction parameters of the SB model are from SiO_2 , that is, $K_a = 10^{-6}$ M, $K_b = 10^2$ M and $N_S = 5 \cdot 10^{18} \text{ m}^{-2}$ [10].

of the two reactions relate to the dimensionless fractional occupation functions as:

$$K_a = \frac{f_{MO^-} [H_S^+]}{f_{MOH}}, \quad K_b = \frac{f_{MOH} [H_S^+]}{f_{MOH_2^+}}, \quad (5)$$

where $[H_S^+]$ is the proton concentration at the metal oxide/electrolyte surface, that is calculated by the solvers assuming Boltzmann statistics [9]. Since Sentaurus only considers 1:1 ions, an effective electrolyte taking into account the ionic strength must be set to correctly reproduce the electrostatics in the liquid part of the device and $[H_S^+]$ is computed from the

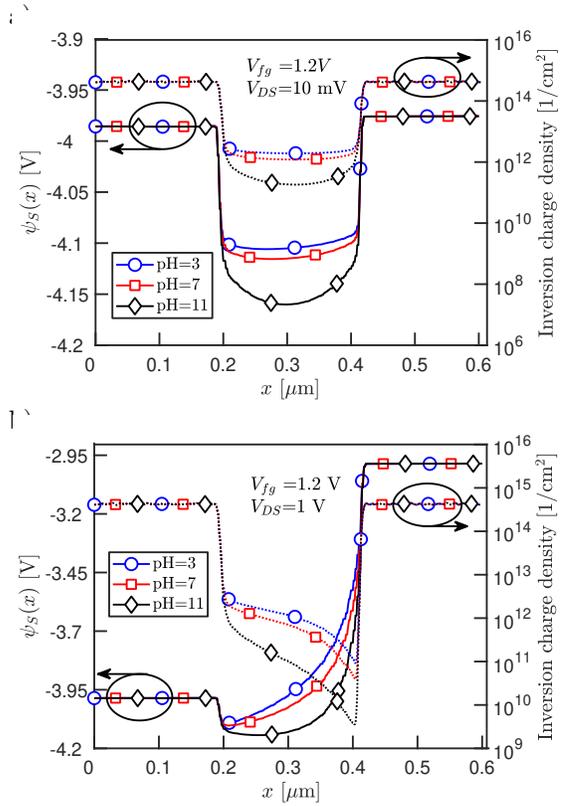


Fig. 4. Surface channel potential ψ_S (left axis) and inversion charge density (right axis) along the x (horizontal) direction for three representative pH values and, $V_{DS} = 10 \text{ mV}$ (a) and $V_{DS} = 1 \text{ V}$ (b). The results are obtained with COMSOL, simulating the structure of Fig. 1 featuring the SB model at the electrolyte/oxide interface.

pH in the bulk looking at the potential difference between bulk and surface [6], [7]. In COMSOL, instead, the ions H^+ , OH^- , Na^+ and Cl^- are explicitly simulated. Figure 3.b, compares the simulated ΔV_{TH} vs pH obtained using COMSOL (circles) and Sentaurus (squares) for the structure depicted in Fig. 1 with device parameters as in Table I and an electrolyte with background ionic concentration of $[Na^+] = [Cl^-] = 100 \text{ mM}$. The two solvers are in very good agreement, and both reproduce well the model results in the literature [10] (black line). We also see that the V_{DS} value has a minor effect on the ΔV_{TH} vs the pH as expected for a well-tempered FET. The comparison of the I_{DS} - V_{fg} trans-characteristics is reported in Fig. 3.c for a few pH values and proves the quantitative agreement between the two solvers. Further analysis is provided in Fig. 4, which reports the results obtained with COMSOL for the electrostatic potential, ψ_S , and the inversion charge density, along the x direction at the channel surface of the ISFET as a function of the electrolyte pH and for $V_{DS} = 10 \text{ mV}$ (a) and $V_{DS} = 1 \text{ V}$ (b). We see that charge and potential are not uniform along the channel, even at low V_{DS} , due to the influence of source and drain. However, 1D models give a fairly accurate estimate of the V_{TH} shift, but 2D ones are needed to model the device as a whole and capture the coupling of 2D short channel electrostatics with the surface charge build-up mechanism.

V. APPLICATION TO COMPLEX SENSING SCENARIOS

As an example of model use and validation against experimental data and independent models, we consider the experiment in [14], where a differential setup consisting of an active and a control ISFET (see Fig. 5.a) was used to sense the concentration of sodium ions, Na^+ . The control ISFET features a gold layer sensitive to pH and Cl^- (i.e. modelled with a modified SB [13]) whereas the active ISFET employed a gold layer functionalized with Na^+ -sensitive ligands. Therefore, $Q_{S,tot}$ in Eq. 4 is the sum of two contributions stemming from a four-states and two-state reaction graphs, respectively (see Fig. 5.a).

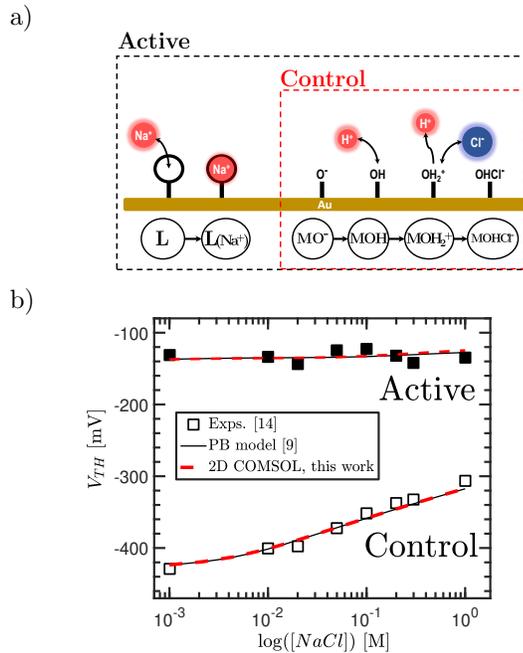


Fig. 5. (a) Sketch of the active and control device surfaces for the differential setup used in [14]. (b) Comparison of the V_{TH} vs the concentration of NaCl in the solution between the experimental data reported in [14] (symbols), the PB model in [9] (black solid line) and the COMSOL implementation of this work (red dashed line). A rigid vertical shift has been applied to the different model results, for the sake of easier comparison.

Figure 5.b shows that experimental data from [14] (symbols) and COMSOL simulations (dashed lines) provide the same ΔV_{TH} , despite in our simulations we use the template ISFET in Fig. 1 that has not the same geometry and only shares with the one in [14] the sensing surface. This underlines that the static response (i.e. the ΔV_{TH}) of these potentiometric electrochemical sensors is marginally affected by the architecture of the underlying FET. This conclusion is corroborated by the good agreement with the steady-state Poisson-Boltzmann (PB) model (solid lines in Fig. 5.b) developed in [9], not including the semiconductor part of the device. Hence, the good agreement between the one-dimensional PB model and 2D simulations of the complete device in COMSOL highlights the capability of the former model to provide accurate predictions with considerably less effort, as far as geometrical factors, FET operation conditions and other effects can be neglected.

VI. CONCLUSIONS

We have reported a Multiphysics framework implementation of the model in [9] that overcomes the limitations of commercial TCAD, allowing for a more complete treatment of the multi-ion nature of the electrolyte and for complex, coupled chemical reactions at the electrolyte/oxide interface. On the other hand, TCAD is more efficient in simulating the semiconductor part of the ISFET especially if using comprehensive sets of S.O.A. microscopic physical models. Our COMSOL simulations suggests that 1D, electrolyte-only models, (e.g., as those in [9]) may be sufficient to interpret experimental data of large ISFETs free of significant short channel effects or at low V_{DS} . Device simulations with TCAD or COMSOL including the semiconductor part, however, can turn useful when studying the impact of technology options on the ISFET response.

REFERENCES

- [1] N. Moser, T. S. Lande *et al.*, “ISFETs in CMOS and Emergent Trends in Instrumentation: A Review,” *IEEE Sensors Journal*, vol. 16, no. 17, pp. 6496–6514, 2016. DOI: 10.1109/JSEN.2016.2585920
- [2] M. Kaisti, “Detection principles of biological and chemical FET sensors,” *Biosensors and Bioelectronics*, vol. 98, pp. 437–448, 2017. DOI: 10.1016/j.bios.2017.07.010
- [3] F. Bellando, L. J. Mele *et al.*, “Sensitivity, Noise and Resolution in a BEOL-Modified Foundry-Made ISFET with Miniaturized Reference Electrode for Wearable Point-of-Care Applications,” *Sensors*, vol. 21, no. 5, 2021. DOI: 10.3390/s21051779
- [4] *Synopsys Sentaurus Device simulator user manual*, Synopsis Inc., Mountain View, CA, USA, 2016.
- [5] I.-Y. Chung, H. Jang *et al.*, “Simulation study on discrete charge effects of SiNW biosensors according to bound target position using a 3D TCAD simulator,” *Nanotechnology*, vol. 23, no. 6, p. 065202, 2012. DOI: 10.1088/0957-4484/23/6/065202
- [6] A. Bandiziol, P. Palestri *et al.*, “A TCAD-Based Methodology to Model the Site-Binding Charge at ISFET/Electrolyte Interfaces,” *IEEE Transactions on Electron Devices*, vol. 62, no. 10, pp. 3379–3386, Oct 2015. DOI: 10.1109/TED.2015.2464251
- [7] F. Pittino, P. Palestri *et al.*, “Models for the use of commercial TCAD in the analysis of silicon-based integrated biosensors,” *Solid-State Electronics*, vol. 98, pp. 63–69, 2014. DOI: 10.1016/j.sse.2014.04.011
- [8] *COMSOL Multiphysics user manual*, COMSOL Inc., Sweden, 2021.
- [9] L. J. Mele, P. Palestri, and L. Selmi, “General Approach to Model the Surface Charge Induced by Multiple Surface Chemical Reactions in Potentiometric FET Sensors,” *IEEE Transactions on Electron Devices*, vol. 67, no. 3, pp. 1149–1156, March 2020. DOI: 10.1109/TED.2020.2964062
- [10] R. Van Hal, J. C. Eijkel, and P. Bergveld, “A general model to describe the electrostatic potential at electrolyte oxide interfaces,” *Advances in Colloid and Interface Science*, vol. 69, no. 1-3, pp. 31–62, 1996. DOI: 10.1016/S0001-8686(96)00307-7
- [11] I. Langmuir, “The adsorption of gases on plane surfaces of glass, mica and platinum,” *Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918. DOI: 10.1021/ja02242a004
- [12] D. E. Yates, S. Levine, and T. W. Healy, “Site-binding model of the electrical double layer at the oxide/water interface,” *J. Chem. Soc., Faraday Trans. 1: Phys. Chem. Condensed Phases*, vol. 70, pp. 1807–1818, 1974. DOI: 10.1039/F19747001807
- [13] A. Tarasov, M. Wipf *et al.*, “Understanding the electrolyte background for biochemical sensing with ion-sensitive field-effect transistors,” *ACS nano*, vol. 6, no. 10, pp. 9291–9298, 2012. DOI: 10.1021/nn303795r
- [14] M. Wipf, R. L. Stoop *et al.*, “Selective Sodium Sensing with Gold-Coated Silicon Nanowire Field-Effect Transistors in a Differential Setup,” *ACS Nano*, vol. 7, no. 7, pp. 5978–5983, 2013. DOI: 10.1021/nn401678u