

Numerical study of surface chemical reactions in 2D-FET based pH sensors

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Abstract—This work numerically evaluates the impact of surface chemical reactions on the performance of 2D-FET based pH sensors. More precisely, we focus on the adsorption of chlorine ions and the expulsion of protons at the sensing interface of FET sensors. This analysis is performed through numerical simulations encompassing the modelling of both the semiconductor device and the liquid solution to be analysed. In the semiconductor region the 2D Poisson - 1D Continuity equations are self-consistently solved, while in the electrolyte region we deal with the modified Poisson - Boltzmann system [1]. The simulator also includes the interactions taking place at the electrolyte-sensing layer interface through: i) the non-constant profile of water permittivity, and ii) the steric effects in the surface ions concentration by means of the Potentials of Mean Force (PMFs) [2], [3]. This comprehensive description of the electrolyte-device interface provides a suitable framework to unveil the relevance of multiple chemical reactions, such as the adsorption of chlorine ions, on the behaviour of 2D-FET based pH sensors.

Index Terms—pH, ISFET, Site-Binding, modified Site-Binding, Potential of Mean Force

1. INTRODUCTION

The Ion-Sensitive FET (ISFET) was introduced back in the 70s by P.Bergveld et al. [4] as a device to detect neural activity. Since then, it has also been widely used as a chemical sensor. Very recently, 2D-materials have shown up as promising candidates to implement this kind of sensors, due to their atomic thickness [5], deeply impacting on their design and performance. Compared with the plethora of experimental results provided by numerous research groups [6]–[9], the activities carried out to develop analytical and numerical approaches able to describe these devices have been quite limited [10]–[12]. In the case of pH sensing, previous studies only consider the chemical reactions between the sensing interface and protons, neglecting the impact of additional reactions in the adsorption of hydrogen ions. In order to assess them, we have integrated the generalised approach presented in [13], [14] in our numerical simulator allowing us to evaluate the impact of the adsorption of chlorine ions on the pH sensor performance.

2. SIMULATION OF 2D-ISFETS

The semiconductor device and electrolyte models are combined to achieve a comprehensive description of the whole device [12]. To do so, we first employ different models to estimate the charge in each region and then the 2D Poisson equation is solved to estimate the electrostatic potential.

A. Semiconductor device modelling

In the semiconductor region we consider a diffusive transport [15]. Under equilibrium conditions, the electron (hole) density profile, n_L (p_L), is calculated using the 2D density of states. This information is then used to solve the non-equilibrium situation. In that case, n_L (p_L) is calculated using the 1D Drift-Diffusion transport equation.

B. Electrolyte and sensing interface modelling

Regarding the electrolyte region, the local concentration of the i -th ion is related to the potential by the equation [1]:

$$c_i = \frac{c_{i,0} \exp\left(-V_{PMF,i} - qz_i \frac{V - V_{Ref}}{k_B T}\right)}{1 - 2 \frac{c_{i,0}}{c_{max}} \left(1 - \cosh\left(|z_i| \frac{V - V_{Ref}}{k_B T}\right)\right)} \quad (1)$$

where $c_{i,0}$ is the bulk concentration, z_i the valence, $c_{max,i}$ the maximum allowed concentration and $V_{PMF,i}$ is the PMF profile. This potential is combined with a non-constant water permittivity profile at the device - electrolyte interface. The parameters required for these models are extracted from [2], [3]. As for the reactions taking place at the sensing interface, we integrate the approach reported in [13], [14]. There, each reaction is defined by a simple relation between the active element concentration f_i and the product concentration, f_j :

$$A + B \rightleftharpoons AB, \quad [AB] = \frac{[B]}{K} [A] \Rightarrow f_j = \frac{[B_j]}{K_{ij}} f_i \quad (2)$$

Once the concentrations of the different components are obtained, the net charge in the surface

with an active site density N_s can be calculated as:

$$Q_{net} = qN_s \sum_i z_i f_i \quad (3)$$

The reactions considered in the Site-Binding (SB) model and its modified version (mSB) are depicted in Figure 1. In both models the behaviour of the sensing interface is captured by the reaction constants K_a and K_b . In the case of the mSB model, there is a third reaction constant K_c concerning the adsorption of chlorine ions.

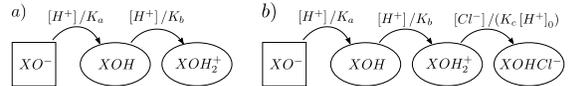


Fig. 1: Reactions considered in the SB model (a) and its modified version, the mSB model (b). The material of the sensing layer is indicated as X and K_a , K_b and K_c are the reaction constants. $[H^+]$ is the hydrogen ion concentration near the interface, $[H^+]_0 = 10^{-pH}$ is the bulk hydrogen concentration and $[Cl^-]$ is the chlorine concentration near the interface.

3. RESULTS

In all the simulations, the structure considered, depicted in Figure 2, is a MOSFET whose channel is formed by a 100nm long monolayer of MoS_2 sandwiched between a 20nm-thick SiO_2 layer, which acts as a substrate, and a 5nm-thick Al_2O_3 layer acting as the sensing layer. The electrolyte considered is based on KCl along with NaOH and HCl, whose concentration change according to the pH. We assume pH values ranging from 4 up to 10, along with four different KCl concentrations, [KCl]: 10mM, 50mM, 100mM, 500mM. Concerning the reactions constants used for the SB models, they are summarised in Table I.

TABLE I: Al_2O_3 parameters. The reaction constants pK_i are $pK_i = -\log_{10}(K_i)$

Material	ϵ	pK_a	pK_b	pK_c	N_s (cm^{-2})
Al_2O_3	$14\epsilon_0$	6	10	2.48	$8 \cdot 10^{14}$

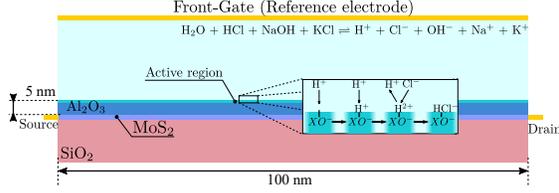


Fig. 2: Structure of the device considered in the simulations. The channel is defined by a mono-layer MoS₂ semiconductor sandwiched between a SiO₂ layer, acting as substrate, and an Al₂O₃ layer interface with the electrolyte.

Those parameters give rise to the $N_{it} - V_{it}$ profiles depicted in Figure 3 when using the SB model (a) or the mSB model (b).

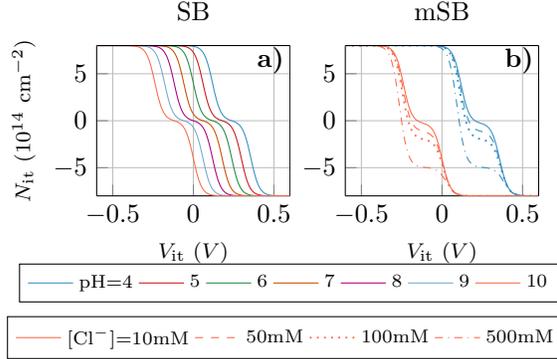


Fig. 3: $N_{it} - V_{it}$ when using the SB (a) or the mSB (b) models. In (b) the data for pH values between 5 and 9, both included, were omitted as they show the same shift than in (a) when the pH is reduced.

The results for both SB models show a shift towards positive interface potentials as the pH is reduced. These results could be expected as reduction of pH give rise to an increase in $[H^+]$, and higher potential is required to obtain a null net charge at the interface. In (b) the mSB considers the presence of $[Cl^-]$ and its effect becomes evident. As the bulk Cl^- concentration increases, the light plateau of the profiles moves down towards negative charge values, and it might even disappear for higher values of $[Cl^-]$.

This preliminary analysis shows clear differences in the $N_{it} - V_{it}$ profile achieved with each model. So that, it would be interesting to shed light on the impact of these differences on the device response.

A. Site-Binding

Figure 4 depicts the sensor transfer characteristic making use of the basic SB model, showing a decrement of the threshold voltage V_{th} as the pH is reduced: the lower the pH, the higher the concentration of positive H^+ ions, and thus the lower the potential required to switch on the device. To evaluate the influence of KCl, we calculate the change in the current ΔI with respect to the minimum concentration $[KCl]=10mM$, Figure 4 (bottom). The maximum values of ΔI are quite low compared with I . The results show an interesting feature with pH as ΔI changes from negative to positive at $pH=8$. This can be associated to the characteristics of the active layer, Figure 3, as it shows a neutral charge for $V_{FG} = 0V$ at that pH value.

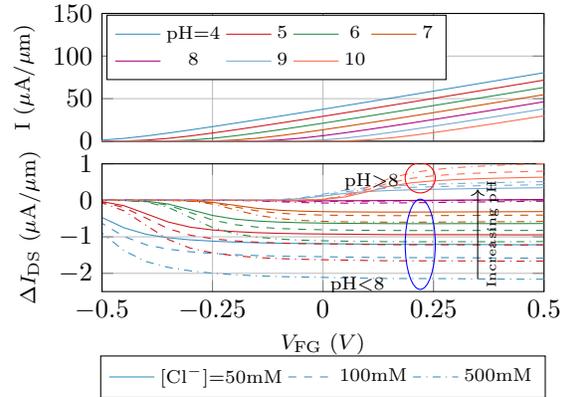


Fig. 4: Sensor $I - V_{FG}$ curves for $[KCl]=10mM$ using the SB model (top) and increment of current when $[KCl]$ is increased (bottom).

B. Modified Site-Binding

The results obtained for that scenario are depicted in Figure 5. The magnitude of ΔI is almost seven times larger than the SB model,

and the trend with V_{FG} is monotonic, i.e. there is not a change in the ΔI sign showing that the current always decreases as $[KCl]$ increases, independently of the pH considered. This is consistent with the additional reaction considered in the model: the chlorine ions generate a negative charge in the active layer that reduces the amount of the electrons in the channel. Moreover, the higher the concentration of these ions, the more acute is this effect.

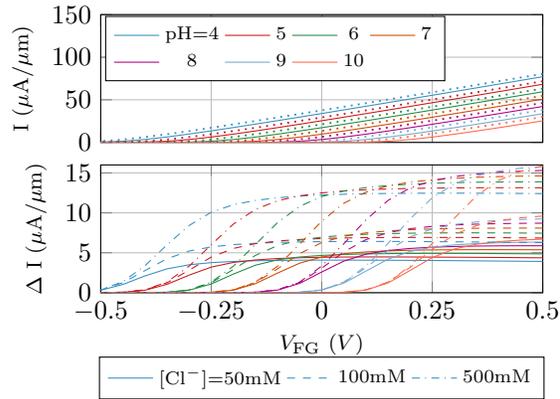


Fig. 5: Sensor I - V_{FG} curves for $[KCl]=10mM$ using the mSB model (top) and ΔI when $[KCl]$ is increased (bottom). Dotted lines show the previous results with the SB model.

4. CONCLUSIONS

In this work we have evaluated the transfer response of a MoS_2 FET based pH sensor making use of two models for the active layer. The first model only considers the adsorption of hydrogen ions, while the second one includes an additional reaction concerning the adsorption of chlorine ions.

Relevant differences have been revealed comparing both models, highlighting the importance of side reactions on the modelling of chemical sensors. Once the side reactions are included through the mSB model, the impact of the changes of $[KCl]$ is assessed: as the concentration of chlorine ions increases, the output current diminishes notably. These changes make possible

to obtain the same response by either increasing the pH or the KCl concentration. Therefore, it becomes critical to take this effect into account when analysing pH sensors, due to the “crosstalk” between hydrogen and chlorine ions adsorption.

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