

ION SENSITIVE FIELD EFFECT TRANSISTOR (ISFET) MODEL IMPLEMENTED IN SPICE

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Abstract

An ISFET model is developed and implemented in the electronic circuit simulation program SPICE. The proposed model leads to a set of new parameters that the user of SPICE can specify in the .MODEL card. The model is used to simulate the ISFET behavior under various physico-chemical conditions, including temperature variations.

1. INTRODUCTION

Much work has been recently done to characterize ISFETs based on MOS technology. Among these devices, proton-sensitive ISFETs are the more deeply analyzed and we will refer to them in the following. The response of these devices to pH is commonly explained by using the so-called site-binding model [1], which states that H^+ specific binding sites at the surface of the insulator exposed to the electrolyte are responsible for the pH-dependence of the charge distribution of the ISFET insulating layer. In the following, this theory (generalized to two kinds of binding sites), together with the Gouy-Chapman-Stern description of the potential profile in the electrolyte, is coupled to the MOS physics, in order to give a complete description of the ISFET behavior. As a result, a set of equations is derived and introduced into a modified version of the electronic circuit simulation program SPICE [2]. This program is then utilized to predict the dependence of the pH-sensitivity upon parameters such as binding site density and temperature.

2. ISFET MODEL

a) Static model

The static behavior of the ISFET is derived by taking into account the potential differences among the interfaces of Fig. 1. In this way the following expression for the threshold voltage is obtained:

$$V_{th} (ISFET) = (E_{ref} + \phi_{lj}) - (\phi_{eo} - \chi_{eo}) - \left[\frac{Q_{ss} + Q_{sc}}{C_{ox}} - 2\phi_f + \frac{\phi_s}{q} \right] \quad (1)$$

which contains terms derived from the standard MOST theory as well as terms that are electrochemical in nature. More specifically, ϕ_f is the Fermi potential of the semiconductor (p-type for the n-channel ISFET here considered), Q_{ss} is the fixed surface-state charge density at the insulator-semiconductor interface, Q_{sc} is the semiconductor surface depletion region charge density, C_{ox} is the insulator capacitance per unit area, E_{ref} is the potential of the

reference electrode (*Ag/AgCl* here considered), ϕ_{ij} is the potential difference between reference solution and electrolyte, ϕ_{eo} is the potential of the electrolyte-insulator interface, χ_{eo} is the electrolyte-insulator surface dipole potential, and ϕ_s/q is the semiconductor work function. It is worth analyzing in some detail the insulator-electrolyte potential ϕ_{eo} , which determines the ISFET sensitivity to specific chemical species. As anticipated, a generalized site-binding theory, considering two possible kinds of binding sites (i.e. silanol and amine groups) is utilized. More details about the physical-chemistry of the Si_3N_4 binding sites can be found in [3].

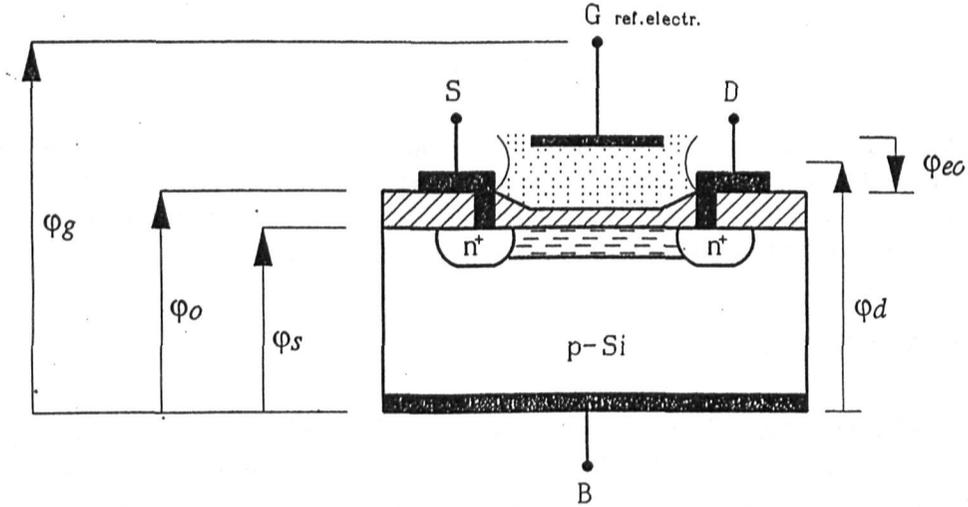


Fig. 1 - ISFET structure.

By utilizing the Gouy-Chapman-Stern theory [4], it can be shown that :

$$\phi_g = \phi_d + \frac{2kT}{q} \sinh^{-1} \left[\frac{C_h (\phi_d - \phi_o)}{\sqrt{8\epsilon_w k T C_o}} \right] \quad (2)$$

where $C_h (\phi_d - \phi_o) = \sigma_d$ is the charge density in the diffuse layer, C_h and C_o are the Helmholtz layer capacitance per unit area and the solution concentration, respectively, and ϵ_w is the water permittivity.

The condition of charge neutrality for the structure of Fig. 1 gives :

$$\sigma_d + \sigma_o + \sigma_{mos} = 0 \quad (3)$$

where σ_o is the charge density of the surface sites, σ_{mos} is the charge density in the semiconductor given by:

$$\sigma_{mos} = \pm \sqrt{2\epsilon_s k T p_o} \left[\left(\frac{q \phi_s}{k T} - 1 + \exp\left(-\frac{q \phi_s}{k T}\right) \right) + \frac{n_o}{p_o} \left(-\frac{q \phi_s}{k T} - 1 + \exp\left(\frac{q \phi_s}{k T}\right) \right) \right]^{1/2} \quad (4)$$

and n_o and p_o are the equilibrium concentrations of electrons and holes, respectively.

The charge density σ_{mos} is taken positive for $\phi_s < 0$ and negative for $\phi_s > 0$. Otherwise σ_{mos} can be written as :

$$\sigma_{mos} = C_{ox} (\phi_s - \phi_o) \quad (5)$$

By considering two kinds of binding sites, the charge density σ_o is given by:

$$\frac{\sigma_o}{qN_s} = \left(\frac{[H^+]_s^2 - K_+K_-}{[H^+]_s^2 + K_+ [H^+]_s + K_+K_-} \right) \frac{N_{sil}}{N_s} + \left(\frac{[H^+]_s}{[H^+]_s + K_{N+}} \right) \frac{N_{nit}}{N_s} \quad (6)$$

where N_s is the total number of available surface binding sites, N_{sil} and N_{nit} are the numbers of silanol sites and primary amine sites per unit area, respectively; K 's are the dissociation constants for the chemical reactions at the insulator interface, and $[H^+]_s$ is the concentration of the protons at the insulator surface.

To obtain the relationship between pH and ϕ_{eo} we are looking for, the above equations must be completed with a Boltzmann-type equation relating $[H^+]_s$ at the surface with $[H^+]_b$ in the bulk of the electrolyte:

$$[H^+]_s = [H^+]_b \exp\left(-\frac{q}{kT} \phi_{eo}\right) \quad (7)$$

Equations (2) to (7) form a set of equations that describe the ISFET static model with two kinds of binding sites and gives the electrolyte-insulator potential ϕ_{eo} to be used in Eq. (1).

b) Large-signal model

The ISFET large-signal model is obtained by taking into account that the oxide capacitance consists of two elements connected in series: the MOST insulator capacitance and the Helmholtz capacitance. Thus, to model the large-signal behavior of the ISFET, it is necessary to consider a capacitance:

$$C_{ox}^* = \frac{C_{ox} C_h}{(C_{ox} + C_h)} \quad (8)$$

c) Thermal model

Semiconductor terms

The mobility μ of carriers in the channel is related to the absolute temperature T according to :

$$\mu(T) = \mu(300) (300/T)^a \quad (9)$$

where the exponent a ranges between 1.0 and 1.5.

The temperature dependence of the Fermi potential ϕ_f can be expressed as :

$$\varphi_f(T) = \frac{kT}{q} \ln\left(\frac{N}{n_i}\right) \quad (10)$$

where N is the ionized impurity density. The intrinsic electron density n_i is assumed to be given by :

$$n_i = BT^{1.5} \exp\left(\frac{-qE_g(T)}{2kT}\right) \quad (11)$$

where B is a constant and the energy gap E_g depends on temperature by the relationship :

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\gamma + T} \quad (12)$$

For silicon, $\alpha = 7.02 \times 10^{-4}$, $\gamma = 1108$ and $E_g(0) = 1.16$ eV.

Electrochemical terms

The φ_{eo} potential is directly related to the temperature through the thermal voltage kT/q . In regard to the dissociation constants K 's, in accordance to [5], we assume that the standard chemical potentials of the insulator surface species are temperature independent. Following [5], we suppose :

$$K(T) = K(300)^{300/T} \quad (13)$$

Reference electrode terms

Assuming an $Ag/AgCl$ electrode with filling solution of 3.5 M KCl, saturated with $AgCl$, the temperature dependence of the potential E_{ref} can be written as [5] :

$$\begin{aligned} E_{ref}(T) &= E_{abs}(H^+|H_2) + E_{rel}(Ag|AgCl) + \left(\frac{dE_{ref}}{dT}\right)(T-298.16) = \\ &= 4.7 + 0.205 + 1.4 \cdot 10^{-4} (T - 298.16) \end{aligned} \quad (14)$$

The liquid-junction potential φ_{lj} is typically quite small (a few millivolts), thus its dependence on temperature is insignificant in comparison to that of any other temperature-dependent term and then it is not considered.

3. IMPLEMENTATION IN SPICE

The equations describing the MOST static model [6] in the MOSFET subroutine of SPICE are modified by introducing Eqs. (2) to (7). The result is the introduction of ten new parameters to be specified in the .MODEL card, i.e., E_{rel} (ZEREL), X_{eo} (ZCHIEO), C_o (ZSCON), K_{N+} (ZNKAP), K_+ (ZAKAP), K_- (ZBKAP), C_h (ZCHL), N_{sil} (ZNOX), N_{nit} (ZNNIT), pH (ZPH).

Finally, in order to simulate ISFETs with more than one insulator layer (in fact SPICE has built-in parameters for SiO₂ only), we have introduced two new parameters for the .MODEL card : the thickness t_{oxl} (ZTOXN) of the added insulator (e.g., Si₃N₄ or Al₂O₃) and its dielectric constant ϵ_{oxl} (ZEPSOX).

The .MODEL keywords for the new parameters of the ISFET static model are indicated in the round brackets.

The equations describing the MOST large-signal model in the CMEYER subroutine of SPICE are then modified by introducing Eq. (8). Thus, to simulate the large-signal behavior of the ISFET, the user of SPICE has to introduce the C_h (ZCHL) parameter in the .MODEL card.

As far as the temperature dependence is concerned, the parameters common to the MOST and the ISFET retain their definition in the TMPUPD subroutine of SPICE. Therefore only Eq. (13) and Eq. (14) have been implemented in SPICE to characterize the ISFET thermal model.

4. SIMULATION RESULTS

The proposed ISFET model implemented in SPICE has been investigated for various proton-sensitive insulators. The simulated input characteristics of a Si₃N₄-gate ISFET is shown in Fig.2 for a fixed temperature. The influence of the density of the binding sites on the pH sensitivity is simulated in Fig.3, where V_{out} is the output voltage of a measurement circuit [7] for an ISFET device.

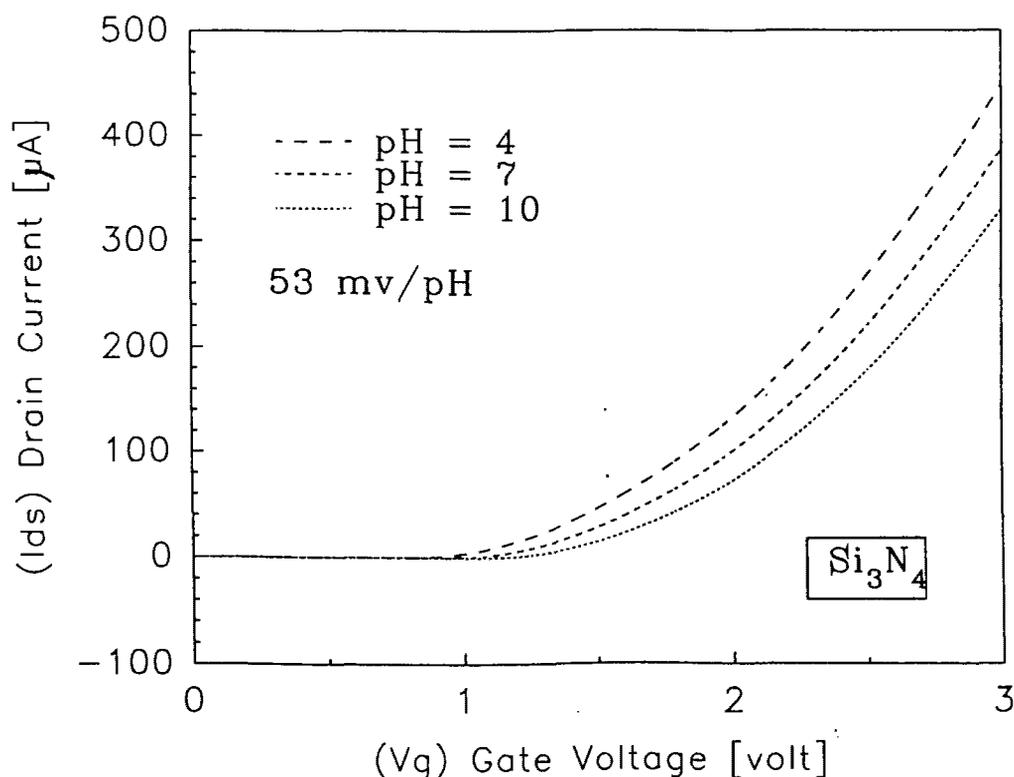


Fig. 2 - Input characteristics of a Si₃N₄-gate ISFET.

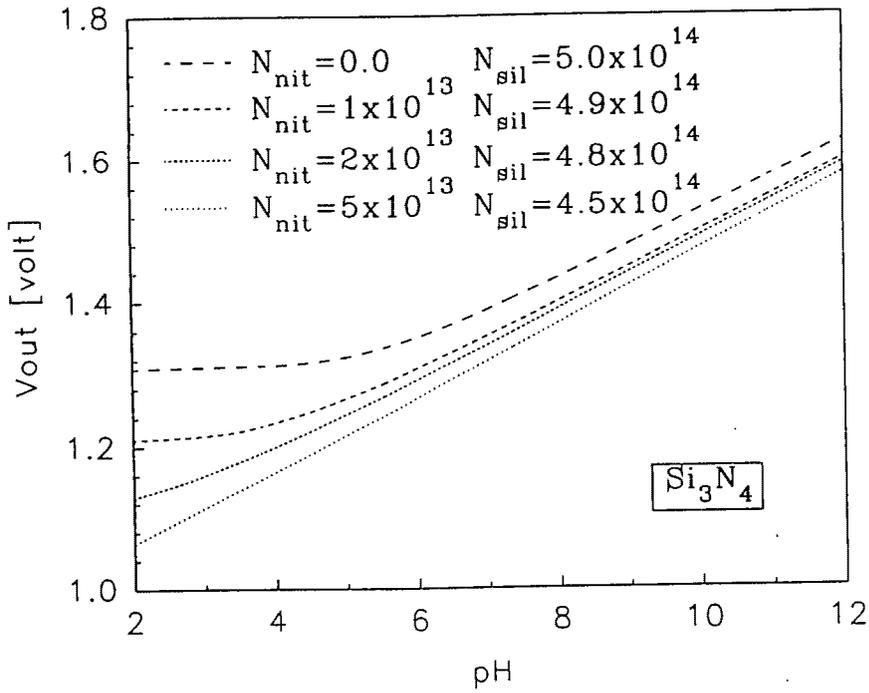


Fig 3 - Influence of the number of binding sites on the pH sensitivity.

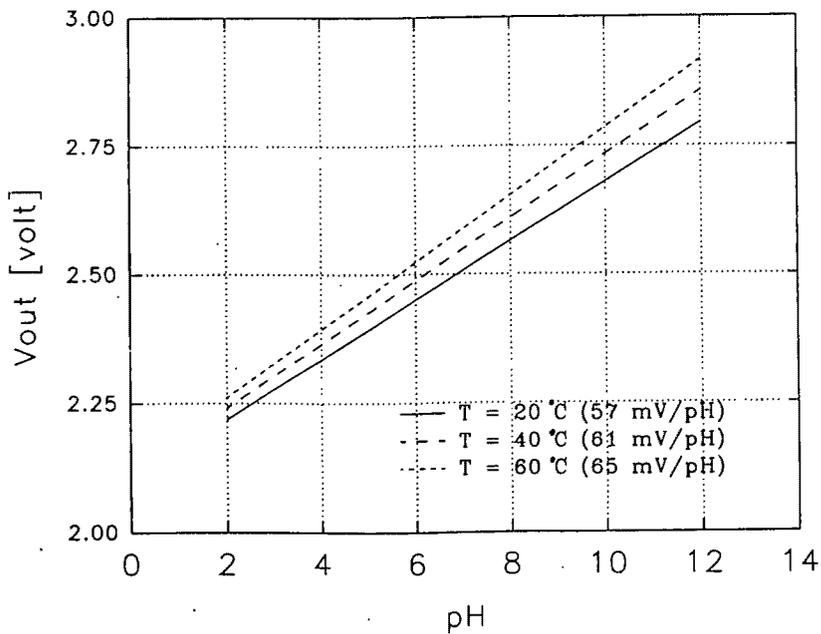


Fig. 4 - Output voltage (V_{out}) as a function of pH for a measurement circuit at different values of temperature.

Fig. 4 shows the effects of temperature changes on the pH sensitivity for the Al_2O_3 insulator. Similar results (not shown) were obtained for SiO_2 and Si_3N_4 - gate ISFETs.

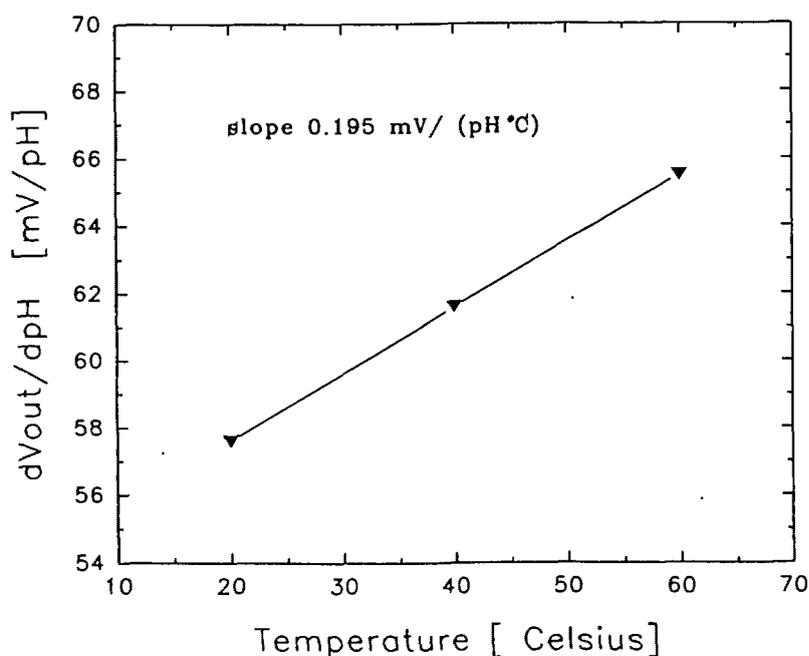


Fig. 5 - pH sensitivity as a function of temperature.

Fig. 5 shows the pH sensitivity as a function of temperature for the above mentioned measurement circuit.

The obtained slope is in good agreement with data reported in the literature [8].

5. DISCUSSION

In this paper the introduction into the simulation program SPICE of a physico-chemical model describing H^+ sensitive ISFETs has been presented. The model proved to be appropriate for analyzing the ISFET behavior as a function of basic physical parameters such as binding site density and temperature. For the latter case, a deeper characterization of the electrochemical components is still needed before comparing the simulations with experimental data. Nevertheless, the obtained results point out the usefulness of considering physical models instead of circuitual macromodels. Moreover, the structure of the fundamental set of equations could be easily modified in order to describe, at the physical level, more complex phenomena.

We hope that this approach, followed by other researchers, will result in a greater standardization of ISFETs and other semiconductor-based chemical sensors.

Acknowledgments

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