A novel description of ISFET sensitivity with the buffer capacity and double-layer capacitance as key parameters

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Abstract

The pH sensitivity of ISFETs arises from interactions of protons with ISFET gate surface sites. This sensitivity is described by a new simpler model with the intrinsic buffer capacity and the differential capacitance as key parameters. The obtained expression is independent of the models used for the chemical surface equilibria and the charge profile in the solution. The general expression for the sensitivity is elaborated using the site-binding theory and the Gouy–Chapman–Stern theory. The relatively high sensitivity of Ta_2O_5 ISFETs is explained using this elaborated theory. It is shown that the electrolyte concentration has almost no influence on the sensitivity of Ta_2O_5 ISFETs.

Keywords: Buffer capacity; Double-layer capacitance; ISFETs

1. Introduction

Shortly after the introduction of the ISFET, it was noticed that these devices were sensitive to pH [1]. The operational mechanism of the ISFET is described by Bergveld and Sibbald [2] as an expression for the drain current, I_D, in the unsaturated region:

$$I_D = \mu C_{ox} \frac{W}{L} \left\{ \left[V_{GS} - \left(E_{ref} - \psi_0 + \chi^{sol} - \frac{\Phi_{Si}}{q} \right. \right. \right.$$
$$\left. \left. \left. - \frac{Q_{ox} + Q_{ss}}{C_{ox}} - \frac{Q_B}{C_{ox}} + 2\phi_f \right) \right] V_{DS} - 1/2 V_{DS}^2 \right\} \qquad (1)$$

where μ is the average electron mobility in the channel; W and L are respectively the width and the length of the gate; E_{ref} is the contribution of the reference electrode; V_{DS} and V_{GS} are respectively the drain–source voltage and the gate–source voltage; Φ_{Si} is the silicon electron work function; q is the elementary charge; C_{ox} is the capacitance of the gate oxide; Q_{ox}, Q_{ss} and Q_B are the charges located in the oxide, charges located in surface states and interface states and the depletion charge respectively; χ^{sol} is the surface dipole potential of the solution; ϕ_f is the potential difference between the Fermi levels of doped and intrinsic silicon. All parameters are constant except the electrostatic po-

tential at the surface, ψ_0, and the surface dipole potential. The surface dipole potential is supposed to be independent of pH. Therefore changes in the drain current are attributed to changes in the electrostatic potential, ψ_0, only.

From the observed short response times and the sensitivity, which was below 59.2 mV for SiO_2, it was concluded that surface reactions between the gate insulator and the electrolyte should determine the primary response mechanism [3]. In 1974 Yates et al. [4] introduced the site-binding model in colloid chemistry to describe the properties of an oxide–aqueous electrolyte interface. This model was later adapted to describe the insulator–electrolyte interface of an ISFET. Nowadays, the model presented by Bousse [5] is commonly accepted as a good description for the ISFET response. However, the model is not able to give a description of the sensitivity that can easily be interpreted. Moreover, the model is not valid over the entire pH range and the influence of the ionic strength is neglected.

In this paper a simpler theory is presented that is valid over the entire pH range. This theory is derived using the site-binding model, but is valid for all theories that describe the charging of an insulator–electrolyte

interface as a result of interactions that take place at specific sites at the surface.

2. The pH sensitivity of ISFETs

In this section a general expression for the pH sensitivity, which is the change of the insulator–electrolyte potential, ψ_0, on a change of the bulk pH, $\delta\psi_0/\delta pH_B$, is given. This expression is derived from a separate treatment of both sides of the double layer, i.e., the gate insulator and the electrolyte.

The site-binding model describes the charging mechanism of an oxide as the equilibrium between the AOH surface sites and the H^+ ions in the bulk of the solution. The surface reactions are [4]

$$AOH \rightleftharpoons AO^- + H_B^+$$

$$\text{and } AOH_2^+ \rightleftharpoons AOH + H_B^+ \tag{2}$$
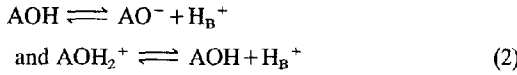
where B refers to the bulk. The equilibrium conditions are

$$\frac{\nu_{AO^-}a_{Hs^+}}{\nu_{AOH}} = K_a \text{ and } \frac{\nu_{AOH}a_{Hs^+}}{\nu_{AOH_2^+}} = K_b \tag{3}$$

where the K values are dimensionless dissociation constants; ν_i is the number of sites per unit area and a_{Hs^+} is the activity of H^+ directly at the insulator surface, related to the bulk activity, $a_{H_B^+}$, by the Nernst equation:

$$a_{Hs^+} = a_{H_B^+} \exp(-q\psi_0/kT) \tag{4}$$

where q is the elementary charge, k is the Boltzmann constant and T is the absolute temperature. The surface charge density, σ_0, is given by

$$\sigma_0 = q(\nu_{AOH_2^+} - \nu_{AO^-}) = qN_s(\Theta^+ - \Theta^-) \tag{5}$$

where N_s is the number of sites per unit area; Θ^+ and Θ^- are the fractions of N_s carrying charge, i.e., AOH_2^+ and AO^-, respectively. The fractions Θ^+ and Θ^- are calculated from the equilibrium reactions and substituted in Eq. (5) to give

$$\sigma_0 = qN_s\left(\frac{a_{Hs^+}^2 - K_aK_b}{K_aK_b + K_ba_{Hs^+} + a_{Hs^+}^2}\right) = -q[B] \tag{6}$$

where [B] is the number of negatively charged groups minus the number of positively charged groups per unit area. pH_{pzc}, pH at the point of zero charge, is defined as the pH were both fractions are equal and [B] is zero. The change in the number of charged groups as a result of an infinitesimal increase in pH_s is the intrinsic buffer capacity, β_{int}:

$$\frac{\delta\sigma_0}{\delta pH_s} = -q\frac{\delta[B]}{\delta pH_s}$$

$$= -qN_s \frac{K_ba_{Hs^+}^2 + 4K_aK_ba_{Hs^+} + K_aK_b^2}{(K_aK_b + K_ba_{Hs^+} + a_{Hs^+}^2)^2} 2.3a_{Hs^+}$$

$$= -q\beta_{int} \tag{7}$$

The charge in the electrolyte is equal but opposite to the charge on the oxide surface. The Gouy–Chapman–Stern model is used to describe the electrolyte side of the double layer. This model involves a diffuse layer of charge in the solution starting at a distance x_2 from the surface. This distance x_2 is the plane of closest approach for the centres of the ions in the solution (Stern layer). The charge in the diffuse layer is [6]

$$\sigma_{DL} = -(8kT\epsilon\epsilon_0 n^0)^{1/2} \sinh\left(\frac{zq\phi_2}{2kT}\right) = -C_i\psi_0 = -\sigma_0 \tag{8}$$

where ϵ_0 is the permittivity of free space and ϵ is the relative permittivity; ϕ_2 is the potential at x_2; n^0 is the number concentration of each ion in the bulk and z is the magnitude of the charge on the ions. The integral capacitance, C_i, is often denoted as K. The ability of the electrolyte to store charge in response to a change in the electrostatic potential is the differential capacitance [6]:

$$\frac{\delta\sigma_{DL}}{\delta\psi_0} = -\frac{\delta\sigma_0}{\delta\psi_0}$$

$$= -\frac{(2\epsilon\epsilon_0 z^2q^2n^0/kT)^{1/2}\cosh(zq\phi_2/2kT)}{1 + (x_2/\epsilon\epsilon_0)(2\epsilon\epsilon_0 z^2q^2n^0/kT)^{1/2}\cosh(zq\phi_2/2kT)}$$

$$= -C_{dif} \tag{9}$$

Combination of both sides of the double layer (Eqs. (7) and (9)) yields

$$\frac{\delta\psi_0}{\delta pH_s} = \frac{\delta\psi_0}{\delta\sigma_0}\frac{\delta\sigma_0}{\delta pH_s} = \frac{-q\beta_{int}}{C_{dif}} \tag{10}$$

The relation between pH_s and pH_B is given by the Nernst equation (Eq. (4)). Substitution of Eq. (4) in Eq. (10) and rearrangement gives the general expression for the sensitivity of the electrostatic potential to changes in the bulk pH:

$$\frac{\delta\psi_0}{\delta pH_B} = -2.3\frac{kT}{q}\alpha$$

$$\text{with } \alpha = \frac{1}{(2.3kTC_{dif}/q^2\beta_{int}) + 1} \tag{11}$$

where α is a dimensionless sensitivity parameter. The value of α varies between 0 and 1 depending on the intrinsic buffer capacity and the differential capacitance. The site-binding theory and the Gouy–Chapman–Stern model were used in the derivation of this model, but other theories can be used as well to determine the intrinsic buffer capacity [7], the differential capacitance and thus the sensitivity parameter α.

3. Calculation of the sensitivity

The previous section showed that the sensitivity of the electrostatic potential to changes in pH_B is related to the intrinsic buffer capacity and the differential capacitance. In this section both parameters will be calculated using the site-binding model to calculate the intrinsic buffer capacity (Eq. (6)) and the Gouy–Chapman–Stern model to calculate the differential capacitance (Eq. (8)). From the corresponding values the sensitivity is calculated (Eq. (10)).

Table 1 shows the literature values for pK_a, pK_b and N_s used to calculate the theoretical sensitivity of several oxides. Figs. 1–3 show respectively the intrinsic buffer capacity, the differential capacitance and the sensitivity as functions of ΔpH in a 0.1 M electrolyte with a Stern capacitance of $0.2 \ F \ m^{-2}$. ΔpH is the difference between pH_B and pH_{pzc}. Fig. 1 shows large variations in the intrinsic buffer capacity between the three oxides. Fig. 2 shows almost no variation in the differential capac-

Table 1
Literature values of several oxide constants

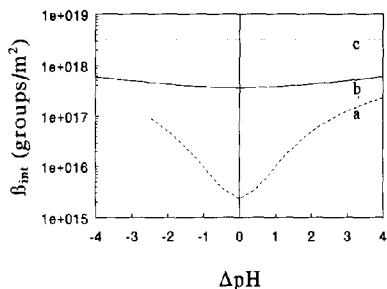|	pK_a	pK_b	N_S	pH_{pzc}	Reference
SiO_2	6	−2	5×10^{18}	2	[5]
Al_2O_3	10	6	8×10^{18}	8	[5]
Ta_2O_5	4	2	10×10^{18}	3	[8]

Fig. 1. Comparison of the theoretical intrinsic buffer capacities of (a) SiO_2, (b) Al_2O_3, (c) Ta_2O_5 (Eq. (7)).
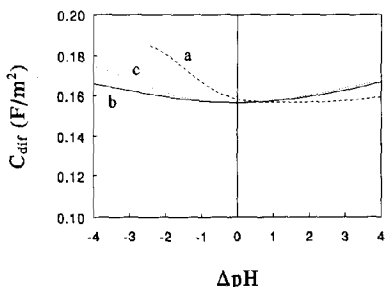

Fig. 2. Comparison of the theoretical differential capacitances for (a) SiO_2, (b) Al_2O_3, (c) Ta_2O_5 (Eq. (9)).
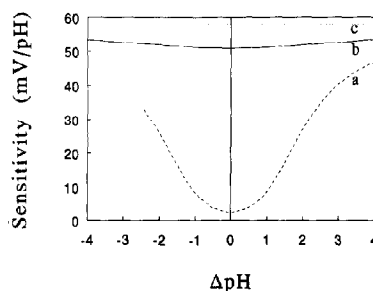

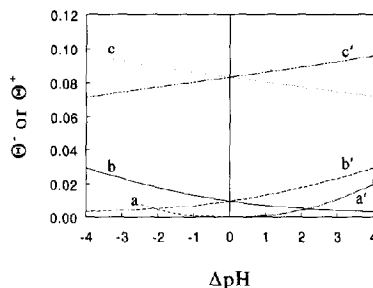Fig. 3. Comparison of the theoretical sensitivities of (a) SiO_2, (b) Al_2O_3, (c) Ta_2O_5 (Eq. (11)).

Fig. 4. Fractions of negatively (without prime) and positively (with prime) charged groups of (a) SiO_2, (b) Al_2O_3, (c) Ta_2O_5 (Eqs. (5) and (9)).

itance, especially near the point of zero charge. In Fig. 3, it is shown that the largest variations in sensitivity are at or near the point of zero charge. Thus, it can be concluded that the intrinsic buffer capacity is the major parameter influencing the sensitivity. The intrinsic buffer capacity should be high to give a sensitivity close to the theoretical maximum of 59.2 mV pH^{-1}.

A high buffer capacity can be achieved when the amount of surface sites is high, as follows directly from Eq. (7), or as ΔpK ($pK_b - pK_a$) is small. A small ΔpK means that there is a relatively large number of charged groups around the point of zero charge. This does not follow immediately from Eq. (7) but is illustrated by Fig. 4, where the fractions of charged groups are given as a function of ΔpH. The calculated sensitivities are in good agreement with measured sensitivities [4].

4. Influence of the ionic strength on the sensitivity of Ta_2O_5 ISFETs

Van Kerkhof et al. showed that Ta_2O_5 ISFETs give a fact response to a stepwise change in the ionic strength [9]. The electrostatic potential returns to its original value, in agreement with the observation that the influence of the ionic strength on the static response of an Ta_2O_5 ISFET is negligible [10]. The response to stepwise changes in the ionic strength is explained [9]

by the change in the integral capacitance (Eq. (8)), which is concentration dependent. From Eq. (9) it follows that the ionic strength also directly influences the differential capacitance. Fig. 5 shows the differential capacitance as a function of pH_B for several ionic strengths using the oxide constants given in Table 1 and a Stern capacitance of 0.2 F m^{-2}.

Fig. 5 shows that the differential capacitance can vary up to 50% around the point of zero charge. A smaller value for the differential capacitance (Fig. 5(c)) causes smaller changes in pH_S around the point of zero charge (Fig. 6(c)). However, due to this relatively small change in pH_S, the intrinsic buffer capacity rises more slowly, as can be seen in Fig. 7(c). These smaller values for the intrinsic buffer capacity partly compensate the
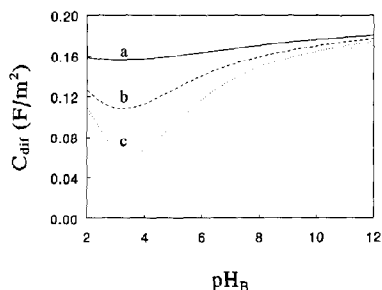

Fig. 5. The differential capacitance of Ta$_2$O$_5$ ISFETs for (a) 0.1 M, (b) 0.01 M and (c) 0.001 M electrolyte solutions (Eq. (9)).
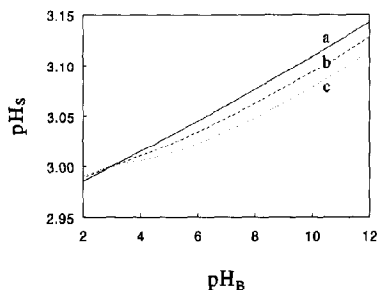

Fig. 6. The pH at the Ta$_2$O$_5$ surface as a function of the bulk pH in (a) 0.1 M, (b) 0.01 M and (c) 0.001 M electrolyte solutions.
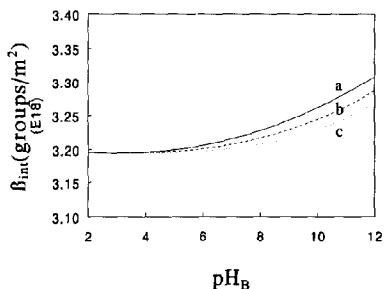

Fig. 7. The intrinsic buffer capacity of a Ta$_2$O$_5$ ISFET in (a) 0.1 M, (b) 0.01 M and (c) 0.001 M electrolyte solutions (Eq. (7)).
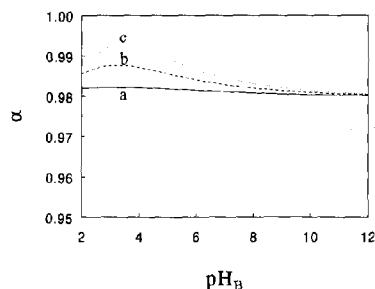

Fig. 8. The theoretical sensitivity parameter for Ta$_2$O$_5$ in (a) 0.1 M, (b) 0.01 M and (c) 0.001 M electrolyte solutions (Eq. (11)).
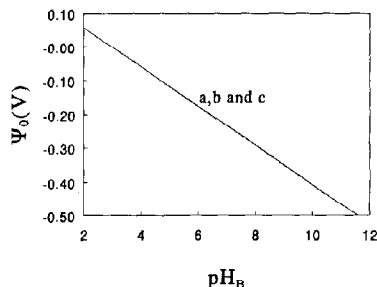

Fig. 9. The theoretical electrostatic potential of Ta$_2$O$_5$ ISFETs as a function of pH in (a) 0.1 M, (b) 0.01 M and (c) 0.001 M electrolyte solutions (Eqs. (6) and (8)).

influence of the ionic strength. The variations in the sensitivity parameter up to 1% (Fig. 8) are therefore smaller than expected from the variations in the differential capacitance (Fig. 5). The theoretical sensitivity at pH 12 is even the same for all calculated concentrations. In Fig. 9 it is clearly shown that the electrostatic potential as measured by the ISFET is negligibly influenced by the ionic strength.

The same compensating mechanism can be expected for other oxides. However, due to the relatively low intrinsic buffer capacity of Al$_2$O$_3$ compared with Ta$_2$O$_5$ (Fig. 1), a larger influence on the sensitivity of the electrostatic potential for pH_B can be expected. This smaller sensitivity was indeed found by Bergveld et al. [10].

5. Conclusions

A new general expression for the pH sensitivity of ISFETs is derived. This expression can be used for all theories that describe the charging of an oxide–electrolyte interface as a result of specific interactions that take place at specific sites. The sensitivity is described in terms of the intrinsic buffer capacity and the differential capacitance. It is shown that a high buffer capacity is necessary for a high sensitivity, which can be achieved by using an oxide with a large amount

of surface sites as well as by using oxides with a small ΔpK. Furthermore, it is shown that a high intrinsic buffer capacity minimizes the influence of the electrolyte concentration on the electrostatic potential as measured by the ISFET.

Acknowledgements

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