phys. stat. sol. (a) **203**, No. 14, 3412–3416 (2006) / **DOI** 10.1002/pssa.200622447

Transistor based study of the electrolyte/SiO_2 interface

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Received 15 May 2006, revised 7 September 2006, accepted 13 September 2006

PACS 73.30.+J, 82.45.Mp, 82.47.Rs, 85.30.Tv

An experimental and theoretical study of the silica surface in aqueous environment is presented. The current/voltage characteristics of silicon field effect transistors are measured as a function of the salt concentration of a KCl solution in contact with the SiO_2 gate oxide. We find that a model assuming constant interface charge can describe the global trend of the measured salt dependence. A refined model, allowing for a varying interface charge, provides a quantitative description of the measurements.

1 Introduction

Detecting surface-binding of biomolecules in aqueous enviroment is of paramount importance to many applications in biotechnology. Among other label-free approaches [1–3], field effect detection [4–7] has recently attracted a lot of interest. The principle of field effect detection is to sense a variation of the potential drop across a solid/liquid interface by a measurement of the interface capacity or the conductivity in a transistor channel. In aqueous solution, DNA is a strong negatively charged polyelectrolyte and impedance and field effect transistor (FET) detection of DNA have been achieved over the last years [8–13].

Descriptions of the silica surface in aqueous environment [14] and of its modifications induced by biomolecule binding [15] are complex, combining surface chemistry, statistical mechanics and electrostatics. In these systems the ionic strength is an important parameter, controlling the biomolecule interaction with the surface as well as the sensitivity of the electronic detection. Therefore, as a first step towards understanding FET based DNA detection, we here present a combined experimental and theoretical study of the salt dependence of the interface potentials of a bare SiO_2 surface in contact with a KCl electrolyte. This subject is related to the modelisation of pH detection by field effect devices [16, 17].

2 Experimental techniques

The measurements presented in this paper use silicon p-channel FET arrays, with 29 FETs linearly arranged with a period of 40 µm. The sensing area of the individual transistors are 24 or 40 μm^2 in size and are covered by a 10 nm thick SiO_2 layer. These semiconductor devices have been fabricated in the Membrane and Neurophysics department of the Max-Planck-Institute for Biochemistry, Germany, as described elsewhere [18, 19].

The sample surface is covered by a KCl electrolyte solution during the electronic measurements. Two voltages U_{SE} and U_{SD} are generated by a multifunction data acquisition board and applied to the FET

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array through a custom build analog circuit. U_{SE} is applied between the common source contact of the sample and an Ag/AgCl electrode introduced in the electrolyte. U_{SD} is applied between source and drain. We measure the drain currents I_{D} of all transistors as a function of U_{SE} and U_{SD}, by multiplexing with a computer controlled switch unit. Finally, a numerical interpolation of the $I_{\mathrm{D}}(U_{\mathrm{SE}}, U_{\mathrm{SD}})$ characteristics allows us to derive the voltage U_{SE} that corresponds to a given $(I_{\mathrm{D}}, U_{\mathrm{SD}})$ working point. A more detailed description of the experimental configurations is given elsewhere [11].

3 Theoretical description

3.1 Constant charge model

The measured characteristics is $I_{\mathrm{D}} = f(U_{\mathrm{SD}}, U_{\mathrm{SE}})$. We consider a simple one-dimensional description, which takes into account the electric field $E_{\mathrm{SiO_2}}$ in the oxide layer, but neglects its lateral variation between source and drain. If we experimentally impose the values of I_{D} and U_{SD}, the electric field $E_{\mathrm{SiO_2}}$ is fixed and, therefore, the potential drop between the inversion layer and the $\mathrm{SiO_2}$ surface remains constant, whatever changes occur in the aqueous part of the configuration.

The $\mathrm{SiO_2}$/electrolyte interface is described by an interface charge σ_{int} followed by a diffuse layer charge. A common description of the interface considers two charge planes, a negative surface charge σ_1 (mainly ionized silanol groups $\mathrm{SiO^-}$) and a positive Helmholtz plane charge σ_2 (adsorbed cations); the total interface charge $\sigma_{\mathrm{int}} = \sigma_1 + \sigma_2$ remains negative [20]. Here, we neglect the spatial separation between the σ_1 and σ_2 planes and replace them by a unique plane of charge σ_{int}. A detailed account of a constant charge model with separate σ_1 and σ_2 planes is provided in Ref. [11].

The diffuse layer, which forms in the KCl electrolyte, is described in a Gouy–Chapman model [21]. The potential difference between the interface and the bulk of the electrolyte is given by

$$\phi_1 = \phi(0) - \phi(\infty) = \frac{2kT}{e}\,\mathrm{arsinh}\left(\frac{\sigma_{\mathrm{eff}}}{\sqrt{[\mathrm{KCl}]\,8kT\varepsilon_0\varepsilon_{\mathrm{r}}^{\mathrm{H_2O}}}}\right), \tag{1}$$

where we introduced the effective charge $\sigma_{\mathrm{eff}} = \sigma_{\mathrm{int}} + \sigma_{\mathrm{S}}$. The term $\sigma_{\mathrm{S}} = \varepsilon_0\varepsilon_{\mathrm{r}}^{\mathrm{SiO_2}} E_{\mathrm{SiO_2}}$ arises from the electric field boundary condition. [KCl] denotes the volume concentration of the monovalent salt.

The salt dependence of the potential drop at the Nernstian Ag/AgCl electrode is given by [22]

$$\phi_2 = \phi(\infty) - \phi_{\mathrm{E}} = \frac{kT}{e}\ln a(\mathrm{Cl^-}) + \mathrm{const.}, \tag{2}$$

where $a(\mathrm{Cl^-})$ denotes the activity of the $\mathrm{Cl^-}$ ions.

The constant charge model assumes that σ_{int} (hence σ_{eff}) does not depend on the salt concentration [KCl]. Since, as mentioned above, the potential drop between the inversion layer and the $\mathrm{SiO_2}$ surface remains constant, the shifts in U_{SE} observed in changing [KCl] at fixed I_{D} and U_{SD} are described by

$$\Delta U_{\mathrm{S}} = \Delta\phi_1 + \Delta\phi_2\,. \tag{3}$$

3.2 Salt-dependent charge model

This model accounts for the dependence of σ_{int} on the salt concentration of the electrolyte. Different experimental techniques, in particular Raman spectroscopy and NMR [23–25], have been used to identify the molecular species present on silica surfaces in aqueous environment. For pH above about 4, silanol (SiOH) groups ionize to siloxane $\mathrm{SiO^-}$. An investigation based on crystallography [23] revealed an order of magnitude of the surface density of ionisable groups, $N_{\mathrm{S}} = 5\times10^{18}\ \mathrm{m^{-2}}$. According to

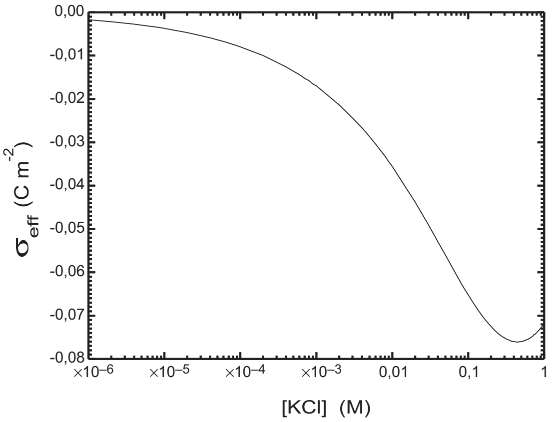

Fig. 1 Effective interface charge σ_{eff} as a function of the salt concentration, obtained by a numerical solution of Eq. (8). We take $K_1 = 10^{-6.8}$ M, $K_2 = 10^{-0.5}$ M, $N_S = 5 \times 10^{18}$ m^{-2} from the Ref. [23]); and use $\sigma_S = 0$, pH = 7.

Ref. [26], the evolution of the surface charge can be described by the following reactions:

$$\mathrm{SiOH} \rightarrow \mathrm{SiO^-} + \mathrm{H^+} \qquad K_1 = 10^{-6.8}\ \mathrm{M} \tag{4}$$

$$\mathrm{SiOK} \rightarrow \mathrm{SiO^-} + \mathrm{K^+} \qquad K_2 = 10^{-0.5}\ \mathrm{M}\,. \tag{5}$$

The concentrations $[\mathrm{H^+}]$ and $[\mathrm{K^+}]$ of the mobile ions in the vicinity of the silica surface determine the equilibrium of these reactions and are related to their volume concentrations $[\mathrm{H^+_\infty}]$ and $[\mathrm{K^+_\infty}]$ by a Boltzmann factor

$$[\mathrm{H^+}]/[\mathrm{H^+_\infty}] = [\mathrm{K^+}]/[\mathrm{K^+_\infty}] = \exp\left(-e\phi_1/kT\right), \tag{6}$$

with the potential difference ϕ_1 given by Eq. (1). The total surface density of ionisable sites is given by

$$N_S = [\mathrm{SiO^-}] + [\mathrm{SiOH}] + [\mathrm{SiOK}]\,. \tag{7}$$

Identifying $\sigma_{\mathrm{int}} = -e[\mathrm{SiO^-}]$ and combining Eqs. (1), (4)–(7) we finally obtain

$$\ln\left(\frac{eN_S}{\sigma_S - \sigma_{\mathrm{eff}}} - 1\right) = -2\,\mathrm{arsinh}\left(\frac{\sigma_{\mathrm{eff}}}{\sqrt{[\mathrm{K^+_\infty}]\,8kT\varepsilon_0\varepsilon_r^{\mathrm{H_2O}}}}\right) + \ln\left(\frac{10^{-\mathrm{pH}}}{K_1} + \frac{[K^+_\infty]}{K_2}\right). \tag{8}$$

Numerical solution of Eq. (8) provides the charge σ_{eff} as a function of the salt concentration $[\mathrm{KCl}] = [\mathrm{K^+_\infty}]$, as presented in Fig. 1. Regarding the equilibrium Eq. (5), an increase in [KCl] reduces the number of SiO$^-$ groups, which should reduce the absolute value of σ_{eff}. In the case of Fig. 1, this effect becomes effective only at concentrations exceeding a few hundred mM and is observable at the right of the minimum of σ_{eff}. For smaller concentrations, an increase in [KCl] screens the potential ϕ_1, which according to the Boltzmann factor in Eq. (6) reduces the H$^+$ concentration at the interface, making σ_{eff} more negative.

4 Comparison between measurements and theory

In Fig. 2, a measurement of the salt dependence of ΔU_{SE} is compared to calculations based on the two previously described models. Starting at 5×10^{-6} M, a series of increasing concentration has been obtained by successively adding concentrated KCl to the electrolyte. At a step in salt concentration the

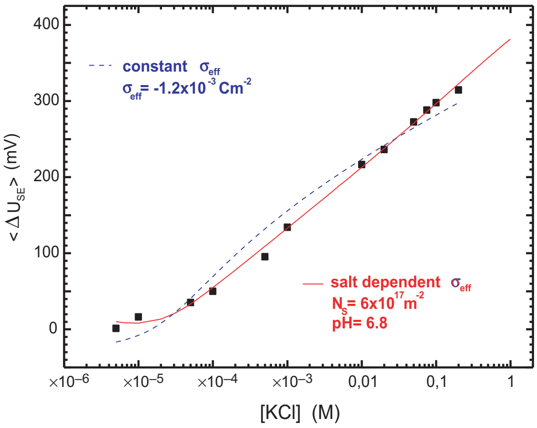

Fig. 2 (online colour at: www.pss-a.com) Average shifts ΔU_{SE} of an array of 29 transistors as a function of the salt concentration of the buffer solution. Zero voltage shift corresponds to the reference measurement performed with a concentration [KCl] of 5×10^{-6} M. The experimental data (squares) are compared to two fitting curves. The first is based on the model assuming constant interface charge, the second one on the salt dependent charge model. The salt dependent charge model (solid line) provides a quantitative description of the measured results and represents a significant improvement with respect to the model of constant interface charge (dashed line).

current–voltage characteristics of the transistors start to vary and stabilize to new settling values after a typical timescale of a few minutes. Each data point of Fig. 2 corresponds to the average shift between the settling values of the 29 transistors of the array.

A fit of the presented experimental data set to the constant charge model gives an effective charge of $\sigma_{\mathrm{eff}} = -1.2\times10^{-3}$ C/m^2. This global fit describes the amplitude of the continuous increase of ΔU_{SE} with salt, but the shape of the measured salt dependence is not well reproduced at low and at high salt.

The model including salt dependent surface charge provides a better description of the experimental data. In this case N_{S} and pH have been adjusted, while literature values have been used for K_1 and K_2. For eight measurement series convincing fits have always been obtained, with an average N_{S} of $(1.95\pm0.72)\times10^{17}$ m^{-2} and pH values in the range 6.5–6.8. The surface density of ionisable sites N_{S} is an order of magnitude smaller than the value reported in [23]. It is expected that this quantity depends on the details of the oxidation protocol and the surface preparation preceeding the measurements; our SiO_2 oxides have been grown by a rapid thermal process at 1100 °C and we prepared the surfaces as described in Ref. [11]. Finally, the fact that the experimental data can be theoretically described assuming $\sigma_{\mathrm{S}} = 0$, indicates that the influence of the electric field $E_{\mathrm{SiO_2}}$ in the oxide is weak compared to the influence of the interface charge, i.e. $\sigma_{\mathrm{S}} \ll |\sigma_{\mathrm{int}}|$.

5 Conclusions

We have investigated the salt dependence of the SiO_2/electrolyte interface potentials, using a FET based electronic measurement. The salt concentration of the KCl electrolyte has been varied from 5×10^{-6} M to 2×10^{-1} M. A theoretical description allowing for a rearrangement of the charges between the interface and the bulk solution is shown to describe the measured salt dependence.

Acknowledgements We thank A. Kaul, G. Zeck, and P. Fromherz for providing the FET arrays and F. Pouthas for helpful discussions. LPA is associated with the CNRS (UMR 8551) and the universities Paris VI and VII.

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