THE INFLUENCE OF THE pH ON THE ELECTROLYTE–SiO₂–Si SYSTEM STUDIED BY ION-SENSITIVE FET MEASUREMENTS AND QUASI-STATIC C–V MEASUREMENTS

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The responses of ion-sensitive FETs (ISFETs) with thermally grown SiO₂ gate regions and of electrolyte–SiO₂–Si (EOS) structures to stepwise changes in the pH were studied.

In addition to a change in the boundary potential at the electrolyte–SiO₂ interface which accounts for the observed initial response of ISFETs, a mechanism is also proposed in which one or other hydrogen-bearing species interacts with the surface states at the SiO₂–Si interface.

This proposed mechanism is based on the observed time drift in the response of ISFETs and on the changes in the shape of the quasi-static C–V curves of the EOS structures.

1. INTRODUCTION

Since the ion-sensitive FET (ISFET) was announced in 1970 as a new tool in electrophysiology¹, there have been a number of both theoretical and experimental studies which deal with the influence of variations in the electrolyte composition on the drain current of an ISFET^{2–4}.

In addition to an electric-potential-generating (polarization) mechanism at the electrolyte–insulator (SiO₂) interface, a further polarization at the SiO₂–Si interface has also been discussed⁴. This latter polarization is caused by a change in the density of surface trapping states at the SiO₂–Si interface.

In this paper results are presented of ISFET measurements in comparison with capacitance–voltage (C–V) measurements on electrolyte–SiO₂–Si systems, in view of the discussion mentioned.

2. EXPERIMENTAL

2.1. ISFET measurements

The devices used were fabricated according to standard MOS technology as described previously².

The gate insulator consists of a layer of oxide 500 Å thick grown by thermal oxidation of p-type (111)silicon in dry O₂ at a temperature of 1200 °C. Aluminium was evaporated onto the oxide prior to heat treatment at 450 °C in wet N₂ for 10 min. This aluminium was etched away before the ISFETs were tested.

The measurement of the drain current was performed with a bridge circuit. The electrolyte was brought into contact with a saturated calomel electrode (SCE) whose potential was adjustable in order to balance the bridge after a change in the pH of the electrolyte. The negative value at the adjusted potential, in fact the liquid gate potential V_g , is shown as a function of the pH of the electrolyte in Fig. 1. Here, the pH of the solution was changed by the dropwise addition of an acid or a base. The acid-base combination used was acetic acid-triethanolamine. In Fig. 1 the solid line corresponds to the response of the ISFET immediately after changing the pH and the dotted line to the response after a certain period of time (in this case 4 min) in which the device drifts to a stable value. As can be seen, the change with time is positive for a pH below about 6 and is negative above this value. Typical curves for the change $V_g(t)$ in V_g as a function of time in the two pH regions mentioned are shown in Fig. 2.

Fig. 1. The liquid gate potential V_g immediately after changing the pH (full line, $t = 0$) and after a period of time $t = 4$ min (broken line); $V_d = 100$ mV.

Fig. 2. Transient behaviour of $V_g(t)$ after a stepwise change in pH in two pH ranges: (a) $\text{pH} < 6$; (b) $\text{pH} > 6$.

If the initial fast response value of V_g is denoted by $V_g(0)$, the final equilibrium value is denoted by $V_g(\infty)$ and τ is the time constant, then the drift effect can be described by

$$\frac{V_g(t) - V_g(0)}{V_g(\infty) - V_g(0)} = \frac{\Delta V_g(t)}{\Delta V_g(\infty)} = 1 - e^{-t/\tau}$$

as can be seen from Fig. 3, where

$$\ln \left\{ 1 - \frac{\Delta V_g(t)}{\Delta V_g(\infty)} \right\}$$

is plotted as a function of time at a pH lower than 6. For relatively short times this equation is not applicable, owing to the process with the initial fast response. The conclusion is that probably two processes take place, one with a small (of the order of milliseconds) and the other with a large (of the order of 5 min) time constant.

Fig. 3. Plot of $\ln\{1 - (\Delta V_g(t)/\Delta V_g(\infty))\}$ vs. time for the pH range below pH = 6; $\tau = 5.7$ min.

The process with the small time constant is regarded as the ion exchange process at the electrolyte-SiO₂ interface which gives the ISFET the initial fast response. The process with the large time constant may be a process of diffusion through the 500 Å thick SiO₂ layer⁵. It is striking that the measured time constant of 5 min is of the same order as that found for the diffusion of molecular hydrogen in SiO₂⁵. The diffusion of charged species will directly influence the drain current, while the diffusion of neutral species may influence the drain current by means of an interaction with the silicon surface.

Experiments with various voltages applied between the reference electrode and the ISFET did not result in changes in the observed time constants. As is known from the literature, hydrogen-bearing species in particular may interact with surface states at the SiO₂-Si interface^{6,7}. However, the concentration of hydrogen-bearing species depends on the pH of the electrolyte. Therefore a model is suggested in which the observed time drift of an ISFET is a result of the formation of hydrogen-bearing species at the electrolyte-SiO₂ interface which diffuse through the oxide layer to the SiO₂-Si interface, where they react in a reversible way with the interface states.

In order to investigate whether and how variations in the pH of the electrolyte may influence the surface state density at the SiO₂-Si interface, quasi-static $C-V$ measurements were carried out on electrolyte-SiO₂-Si structures, as is described in the following section.

2.2. C-V measurements

In order to obtain quasi-static C-V curves, the displacement current of the electrolyte-SiO₂-Si structure was measured in response to a linear voltage ramp (the voltage sweep rate was about 35 mV s⁻¹). The electrolyte was brought into contact with an SCE. The SiO₂ layer used was a thermally grown oxide 500 Å thick pretreated with aluminium, just as in the case of ISFETs described in the previous section. The aluminium was etched away before the start of the experiment. This method has the advantage that any series resistances in the cell, such as those of the reference electrode and the solution, do not influence the displacement current.

We have shown in a previous publication that the measured C-V curves for an electrolyte-SiO₂-Si (p-type) capacitor shift along the voltage axis in a pronounced fashion depending on the pH. The shift, a first order effect, can be explained as being due to a change in the electric potential difference across the electrolyte-SiO₂ interface. The shift observed previously between the curves for pH 13 and pH 1 was about 330 mV⁸. If the change in the electrolyte-SiO₂ potential difference is linear across the whole pH range this change would correspond to about 30 mV per pH unit, which is in agreement with the results in Fig. 1. Furthermore it was found that the minimum in the capacitance ratio $(C/C_{ox})_{min}$ for the C-V data depends on the pH. The change in $(C/C_{ox})_{min}$ is the result of a change in the surface state density at the SiO₂-Si interface. This conclusion supports the model suggested earlier with respect to the pH-dependent drift observed in ISFETs.

3. SUMMARIZING REMARKS AND CONCLUSIONS

The pH responses of both an ISFET and an EOS structure, each with a thermally grown SiO₂ layer in contact with the solution, were studied as a function of the pH.

The initial response of the ISFET to a change in pH is ascribed to a change in the boundary potential between the SiO₂ and the solution, whereas the observed time drift is correlated with a process of diffusion of one or other hydrogen-bearing species through the SiO₂ and the chemical interaction of these species with surface states at the SiO₂-Si interface.

This view is supported by the results of quasi-static C-V measurements on EOS structures. In addition to a shift along the voltage axis of the curves as a result of a change in the boundary potential across the electrolyte-SiO₂ interface, a change in the shape of the curves as a function of pH was also observed. This effect most probably corresponds to a change in the surface state density at the SiO₂-Si interface.

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