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Ion-Sensitive Field Effect Transistor as a PH Sensor

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In this work, both the static and dynamic behaviors as well as the signal read-out circuits of ISFETs were studied. The standard NMOS structure in conjunction with the insulator-electrolyte capacitor was used to model the ISFET under study. The site-binding theory was incorporated to describe the chemistry occurring at the insulator/electrolyte interface. The mechanism of the threshold voltage drift was further explored. We propose that to better understand the drift, both slow responding sites and hydration effects need to be considered. It was found that, to better simulate the voltage drift, two exponential terms had to be employed with one governing the initial drift and the other the long term drift. In addition, a low noise differential signal read-out circuit was designed and simulation was carried out using LTspice. The output voltage of the system changes from -2.1 V to 0.5 V when the pH of the electrolyte changes from 12 to 0.

Keywords: ISFET, Threshold Voltage Drift, Hydration, Slow Responding Sites, Read-Out Circuits.

1. INTRODUCTION

Ion-Sensitive Field Effect Transistor (ISFET) is a device where the gate oxide is in direct contact with an analytic solution. This type of device is advantageous over the conventional electrodes due to its high sensitivity, fast response time, micro-size and on-chip circuit integration. It is useful in continuous monitoring of various ion species in biological and chemical sensing applications.^{1,2}

Even though the technology of ISFET sensing system has progressed since the first ISFET was reported in 1970,³ this type of device exhibit some non-ideal behaviors, including the threshold voltage drift with time. It has been reported that an ISFET sensor with a pH gate could have a drift of 0.02–0.06 pH/hour and the initial drift could be even higher.² The mechanism of the device instability, especially the threshold voltage drift with time, was still unclear. Several hypotheses have been proposed. Among these, the popular one is based on the hydration effect of the insulating layer.^{4, 5} Although it can describe part of the drift behavior of the *n*-channel pH FET's, it is difficult to explain the initial large drift with only hydration effect considered.

In this paper, a site-binding model was used to first describe the static behavior of H⁺-sensitive FET to better understand the operation of ISFET.⁶ Based on this model, the ion-specific binding sites on the surface of the insulator is responsible for the potential changes at the

electrolyte/insulator interface. Following the study of the static behavior of the ISFETs, the dynamic behavior, especially the threshold voltage drift, was investigated. We propose that the mechanism that governs the drift is both the slow responding sites in the insulating layer and the hydration effect. The output signal from the ISFET was processed with a low noise differential read-out circuit.

2. STATIC MODELING

The pH sensor system under study includes a SiO_2 gate ISFET biased by the AgCl reference electrode, an *n*-channel MOSFET whose gate is controlled by a controllable external voltage and operates in a feedback mode, and a differential read-out circuitry. Both ISFET and MOSFET were fabricated on the same *p*-type silicon substrate using the same MOS fabrication technology. The two transistors are identical except that the ISFET does not have a metal gate immediate to the insulating layer.

When the ISFET is placed in a solution (electrolyte), the surface of the insulator interacts with hydrogen ions in the electrolyte, creating a charge layer on the insulator surface and generating a potential, ψ_{eo} , at the insulator/solution interface. This charge layer is opposed to an ionic charge in the solution, which form a double layer capacitance (C_{dl}) across which the potential drop occurs.² A reference electrode, also in the solution, acts as a gate terminal allowing the ISFET to be biased in the same way as the standard MOSFET. The threshold voltage of the ISFET consists of two parts, the threshold voltage of

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the MOSFET, $V_{th|mos}$, and that determined by the reference electrode, the electrolyte, and the insulator/electrolyte interface, V_{th_chem} . Any changes in V_{th_chem} will result in an equal shift in the threshold voltage, V_{th} , of the ISFET.

$$V_{\rm th(ISFET)} = V_{\rm th_chem} + V_{\rm th_mos}$$
(1)

$$V_{\rm th_chem} = E_{\rm Ref} + \varphi^{ij} + \chi_{\rm sol} - \psi_{eo} \tag{2}$$

Where $V_{\text{th_chem}}$ denotes the chemical threshold voltage of the ISFET; E_{Ref} is the potential of Ag/AgCl reference electrode (typ. 0.205 V); φ^{ij} denotes the potential drop between the reference electrode and the solution with a typical value of 3 mV; ψ_{eo} is a chemical input parameter which is a function of the solution pH; χ_{sol} is the surface dipole potential of the solvent independent of the pH, with a typical value of 50 mV.⁷

The ISFET can be represented by a model depicted in Figure 1. It combines a chemical part and a MOS transistor part. In the chemical part, the capacitor consists of two serially connected capacitors, the Gouy–Chapman and Helmholtz capacitors.² This model indicates that the ISFET (Silicon-Insulator-Electrolyte System) consists of a pH sensitive oxide surface (SiO₂) and a standard NMOS transistor.

The ISFET device is commonly biased to operate in the linear mode. Based on the MOSFET theory, the drain current is given by:

$$I_{\rm DS} = k[(V_{\rm GS} - V_{\rm th}) - (V_{\rm DS}/2)]V_D$$
(3)

where $V_{\rm DS} << V_{\rm GS} - V_{\rm th}$.

Since $V_{\rm DS} << (V_{\rm GS} - V_{\rm th})$, Eq. (3) can be approximated as

$$V_{\rm DS} \approx k[(V_{\rm GS} - V_{\rm th})]V_{\rm DS}$$
 (4)

Rearranging Eq. (4), we obtain

$$V_{\rm GS} = (I_{\rm DS}/kV_{\rm DS}) + V_{\rm th} \tag{5}$$

It can be seen from Eq. (5) that, with constant drain current and voltage, any changes in $V_{\rm th}$ directly transfer to the gate voltage, $V_{\rm GS}$.

As indicated earlier, the threshold voltage is affected by the surface potential at the electrolyte/insulator interface. The mechanism responsible for the surface potential and



Fig. 1. The model of the ISFET used in the analysis.

the insulator surface charge can be described by the sitebinding model,⁶ which accounts for the binding of H⁺ and OH⁻ ions to the surface sites. They undergo the reactions with the associated equilibrium constants. The Boltzmann distribution can be used to relate the hydrogen ion concentration at the surface, Hs⁺, to that in the bulk solution, H⁺, as shown in Eq. (6). This can be related to ψ_{eo} by the Gouy–Chapman–Stern theory of interface capacitance as depicted in Eq. (7).⁸

$$[H^+] = \frac{[H_s^+]}{\exp[(-q * \psi_{eo} * [H^+]/k * T)]}$$
(6)

$$=\frac{q*N_{s}*(([H_{s}^{+}]^{2}-K_{a}^{OH}*K_{b}^{OH})/([H_{s}^{+}]^{2}+K_{a}^{OH}*[H_{s}^{+}]+K_{a}^{OH}*K_{b}^{OH}))}{Cdl}$$

$$+\frac{2*k*T}{q}*\sinh^{-1}\times[(q*N_{s}*S*(([H_{s}^{+}]^{2}-K_{a}^{OH}K_{b}^{OH})/([H_{s}^{+}]^{2}+K_{a}^{OH}*[H_{s}^{+}]+K_{a}^{OH}*K_{b}^{OH})))$$

$$\cdot(\sqrt{8*k*T*c_{0}*e_{w}})]^{-1}$$
(7)

Equations (6) and (7) show that the change in the pH of the electrolyte leads to the change in the surface potential, ψ_{eo} , which in turn leads to the change in the threshold voltage.

3. DYNAMIC MODELING

h(H)

ISFETs are known to have a drift which is characterized by a change in threshold voltage without pH variation. Explanations include electrochemical non-equilibrium conditions at the insulator/solution interface which could be true especially if the bulk ion concentration is high. It can also be from electric field enhanced ion migration within the gate insulator as well as hydration effect of the insulator under certain conditions.⁹ In this paper, we propose that both the slow silanol binding sites and hydration effect should be included when describing the threshold voltage drift.

According to the buried sites model,⁸ the sites $SiOH_2^+$ and SiO^- , buried beneath the insulator surface, have a finite time constant when responding to a pH change. The time dependence of the number of these buried sites follows an exponential decay:

$$N_{s1}(t) = N_s(\infty) * \varepsilon * \exp(-t/\tau)$$
(8a)

where $N_{s1}(t)$ represents the amount of slow responding sites and $N_s(\infty)$ is the number of total sites; ε is the fraction of the slow responding sites to the total sites; and τ is the time constant of the response. Substituting N_s in Eq. (7) with Eq. (8a) results in a time dependent surface potential, $\psi_{ep}(t)$.

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The insulating layer not only has slow responding sites but also undergoes hydration effect which alters the chemical composition of the insulator. Therefore, the dielectric constant of the hydration layer differs from that of the original insulator. The thickness of the hydration layer in the insulator can be determined with a hopping and/or traplimited transport mechanism.⁴

$$x_{\rm HL}(t) = x_{\rm HL}(\infty) * (1 - \exp(-t/\tau)^{\beta})$$
 (8b)

where β is the dispersion parameter satisfying $0 < \beta < 1$.

The change in the gate voltage of the ISFET can be written as:

$$\Delta V_G(t) = (V_{\rm FB}(t) - V_{\rm FB}(0)) + (V_{\rm ins}(t) - V_{\rm ins}(0))$$
(9a)

where $V_{\rm FB}$ and $V_{\rm ins}$ represent the flat band voltage and the voltage drop across the insulator, respectively. The change in $V_{\rm FB}$ results from the change in the surface potential, ψ_{eo} (*t*); the change in $V_{\rm ins}$ results from the change in the thickness of the hydration layer. Eq. (9a) can be rewritten as:

$$\Delta V_G(t) = (\varphi_{e0}(0) - \varphi_{e0}(t)) - (Q_D + Q_I + Q_{inv}) \\ \times \left(\frac{\varepsilon_{ins} - \varepsilon_{HL}}{\varepsilon_{ins} \varepsilon_{HL}}\right) x_{HL}(t)$$
(9b)

where Q_D and Q_{inv} represent the charges stored in the semiconductor depletion layer and inversion layer, respectively; Q_I is the effective charge induced in the semiconductor. Eq. (9b) indicates that the voltage drift results from both the surface potential change due to the slow responding sites and the insulator thickness change due to hydration effect.

4. READ-OUT CIRCUIT DESIGN

The proposed read-out circuit is depicted in Figure 2. The ISFET can operate in either constant current mode or constant gate voltage mode. Due to the simplicity in biasing the ISFET, the constant gate voltage mode is preferred. The circuit uses two NMOS transistors AO6408 to mimic the MOSFET and the ISFET. Both transistors have identical characteristics as they are fabricated on the same substrate. To achieve the body reduction effect that causes random drift, both the pH FET and NMOSFET were biased in the same way. Two buffers were used to isolate the input circuit from the processing circuit and match input impedances. The differential amplifier obtains the difference between the supplied voltages resulting in



Fig. 2. The schematic of the low noise differential read-out circuit of ISFET.

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Fig. 3. The drain current of ISFET as a function of pH at $V_D = 0.8$ V.



Fig. 4. The gate voltage drift with time considering both slow response sites and hydration effects.

the output signal that is only the function of pH value. This configuration also allows some temperature compensation since the two FETs have the same dimensions. The signal was further filtered by the low-pass Butterworth filter to eliminate any noise above 20 Hz range (working range).

5. RESULTS AND DISCUSSION

Equations (3)–(7) were implemented in Matlab to simulate the static behavior of ISFETs. Figure 3 shows the drain current of SiO₂-gate ISFET when the gate was exposed to different pH electrolytes. The gate (reference) voltage and the drain voltage were kept at 2 V and 0.8 V, respectively. The width and length of the ISFET are 160 μ m and 2 μ m, respectively. It can be seen from Figure 3 that the drain current is less sensitive to the pH region of 2 to 4, which is corresponding to the point of zero charge pH (pzc) at which there is no net charge on the surface of the insulator.

To simulate the threshold voltage drift, both slow responding sites and hydration effect were considered. The time varying terms in Eqs. (8) and (9) were incorporated in the static modeling to obtain the gate voltage (in turn threshold voltage) drift. The simulation results for SiO₂gate ISFET, kept in a pH=9 electrolyte, is shown in Figure 4. It can be seen that even though there is no change in pH of the electrolyte and the drain current and voltage, there is a increase in gate voltage (drift). The shape of the curve is in agreement with the reported data. Such a shape can only be explained by two exponential terms with distinct time constants. It was found that the slow responding sites are responsible for the initial voltage drift and the hydration effect is responsible for the long-term drift.

In order to simulate the read-out circuit, the chemical potential of -0.42 V (pH=12) was set to change within two hundred milliseconds to 0.1 V (pH=0). Reference electrode voltage, V_G , was set to be 2 V. In addition, 0.1 V 1 Kherz noise was added to the input. The output signal of the circuit can be seen in Figure 5. The results show that with the change from 12 to 2 in pH of the electrolyte there is a change from -2.1 V to 0.5 V in the output signal. In addition, the body effect was eliminated and 0.1 V 1 Kherz noise was filtered out by the Butterworth filter.



Fig. 5. Output signal of the low noise differential read-out circuit for pH changing of 12 to 2.

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6. CONCLUSIONS

The site-binding model was used to describe the static behavior of the ISFETs. The derived sets of equations were implemented in Matlab. It was found from the sensitivity study that the drain current is less sensitive to pH of the electrolyte near the point of zero charge, 2 < pH < 4, in the case of SiO₂-gate ISFETs. The dynamic modeling showed that both slow responding sites and hydration effects are responsible for the threshold voltage drift. While hydration effect governs the long-term drift, slow responding sites are responsible for the initial drift. A read-out circuit was designed and proved to be sensitive to pH of the electrolyte. It eliminated the influence of the body effect as well as any background noise signal.

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