

pHFETs-CONSTRUCTION AND INSTRUMENTATION**Braun B, Drugă C, Ionescu E¹**

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Abstract: *The measurement of pH is arguably the most widely performed test in the chemical laboratory, reflecting the importance of water as a ubiquitous solvent and reactant. In the 90 years since the first use of an electrode to determine hydrogen ion concentration, the glass electrode and its variants have matured into routine tools of analytical and process chemists. Yet, there continue to be developments that promise to broaden the scope and reach of these measurements. Among recent developments are miniature pH sensitive field-effect transistors (pHFETS) being incorporated into pocket-sized pH “pens,” metal/metal oxide pH sensors for measurements at high temperatures and pressures, and flexible fiber-optic pH sensors for measuring pH within the body.*

Key words: ISFET, pH, concentration, reference electrode .

1. Introduction

The monolithic implementation of biomedical sensors on-chip together with signal processing electronics for improved diagnostics and therapy is an important research issue. Several fabrication processes of ISFET devices in standard CMOS technology were recently presented, offering a basis for future development of miniature implantable device for “in vivo” monitoring of pH changes in biological fluids. Miniaturization allows compatibility for clinical catheter applications and bio-telemetry. Integration of various interfaces and sensors on-chip makes the design suitable for implantable sensor systems.

The continuous measurements of different physico-chemical parameters of the blood, such as the temperature, the pressure, the pH value, the volume of the flow have a big importance for surgeons or neurosurgeons. In these areas the invasive measurements are very risky for patients through the danger of infections appearance.

2. Definition of pH

In its most common interpretation, pH is used to specify the degree of acidity or basicity of an aqueous solution. Historically, pH was first defined as the negative logarithm of the hydrogen ion concentration, to simplify the handling of the very small concentrations (on the order of 10^{-7} moles liter⁻¹) encountered most commonly in nature.

This definition of pH is expressed as Equation 1.1, where $[H^+]$ is the molar concentration of solvated protons in units of moles per liter.

$$pH = -\log[H^+] \quad (1.1)$$

As a greater understanding of the behavior of ionic solutes in solution developed, chemists recognized that the measurement techniques used to determine hydrogen ion concentration were in fact measuring the hydrogen ion activity, often referred to as the “effective concentration.” This led to the adoption of the more rigorous definition of pH as the negative logarithm of the hydrogen ion activity in solution, where a_{H^+} is the hydrogen ion activity and γ is the activity coefficient.

$$pH = -\log a_{H^+} = -\log \gamma[H^+] \quad (1.2)$$

3. ISFET – the principle

The Ion Sensitive Field Effect Transistor (ISFET) is a chemical sensitive device based

on structure of Metal-Oxide-Semiconductor (MOSFET). The ISFET was first developed by Bergveld in 1970. The sensitivity to ions is derived by eliminating the metal gate contact of the MOSFET and exposing the gate insulator to an electrolyte solution. The contact to the electrolyte gate is provided by a reference electrode.

The ISFET sensing principle is based on the charge adsorption at the ion-solid interface between the sensing layer which contains hydroxyl groups and the electrolyte, from

which hydroxyls may accept or donate protons (fig.1.1). In this process a double-layer capacitance is created with a potential drop, which influences the threshold voltage of the transistor depending on the value of H^+ protons concentration (pH).

The pH sensitivity that is observed during the exposure to the electrolyte makes ISFET a highly useful tool for obtaining measurements in various fields of applications:

agricultural, environmental, food, etc. Most important applications are in biomedical engineering, for which the ISFETs was initially developed.

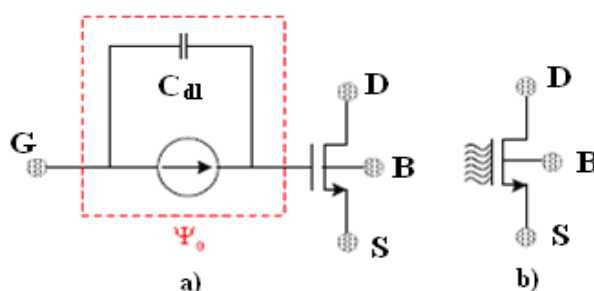


Fig. 1.1. ISFET representation: (a) equivalent circuit, (b) symbolic

ISFETs are based on a standard FET structure but with an insulating layer on top of the gate oxide. In order to explain the behavior of ISFET, the concept of the standard MOSFET structure is presented. The characteristics of MOSFET are based on the Shockley model, where the drain current I_{dS} in saturation region is expressed as follows:

$$I_{dS} = \frac{\beta}{2} \cdot (V_g - V_T)^2 \cdot (1 + \lambda \cdot V_{ds}) \quad (1.3)$$

where λ is channel length modulation parameter and β is a parameter determined by physical properties of device:

$$\beta = \mu \cdot C_{ox} \cdot \frac{W}{L} \quad (1.4)$$

where μ is the mobility, C_{ox} is the gate region capacitance, W and L are width and length of the channel. The threshold voltage is given by:

$$V_T = V_{FB} - \frac{Q_B}{C_{OX}} + 2 \cdot \Phi_F \quad (1.5)$$

where V_{FB} is the flat-band voltage, Q_B is the depletion charge in the silicon and Φ_F the Fermi potential. The flat-band voltage is given by:

$$V_{FB} = \frac{\Phi_M - \Phi_{SI}}{q} - \frac{Q_{SS} + Q_{OX}}{C_{OX}} \quad (1.6)$$

with Q_{SI} the silicon work-function, Q_M the work-function of the gate metal, Q_{SS} the surface state density at the silicon surface, and Q_{OX} the fixed oxide charge.

In case of ISFET the gate voltage is the voltage at the reference electrode, while an insulating layer is applied on top of the gate structure. The threshold voltage of ISFET contains terms dependent on interfaces between the reference electrode and the liquid, and between the solution and the oxide on the gate. This results in a change in the expression of flat-band voltage:

$$V_{FB} = E_{ref} - \Psi_O + \chi_{sol} - \frac{\Phi_{SI}}{q} - \frac{Q_{SS} + Q_{OX}}{C_{OX}} \quad (1.7)$$

where the term E_{ref} is a constant related to the reference electrode potential, χ_{sol} is the constant surface dipole potential of the liquid.

The surface potential ψ_0 is created because of the chemical reactions of the hydroxyl groups on the surface of the oxide and the aqueous solution. During this reaction, the hydroxyl sites bind or release hydrogen ions. This reaction creates a charge on the oxide surface that is opposite to the ion charge in the solution. In this way a double layer structure is created with capacitance C_{dl} and a variable potential drop ψ_0 , which is operating as a serial voltage source with the gate electrode, and is linearly dependent on hydrogen concentration in the solution (pH). Figure 1.1 shows the ISFET equivalent electrical circuit containing the FET, the double layer capacitance C_{dl} and the current source representing the charge resulting in the potential drop ψ_0 on the double layer capacitor. The sensitivity of ISFETs is defined by linear dependence ψ_0 / pH and for high-performance sensors is up to 58mV/pH.

4. pHFETs

A schematic cross-section of a pH-sensitive ISFET is presented in figure 1.2. The pHFET differs from a MOSFET in that the metal gate of the MOSFET is replaced by a pH-responsive membrane material such as silicon nitride, aluminum oxide, or tantalum oxide, which contacts the sample solution directly. As with the glass electrode, electrical contact is made to the sample through a reversible reference electrode. A suitable voltage applied to the reference electrode (relative to the silicon substrate) will charge the capacitor formed by the solution, insulating layers, and silicon substrate, and create mobile charge in the channel region.

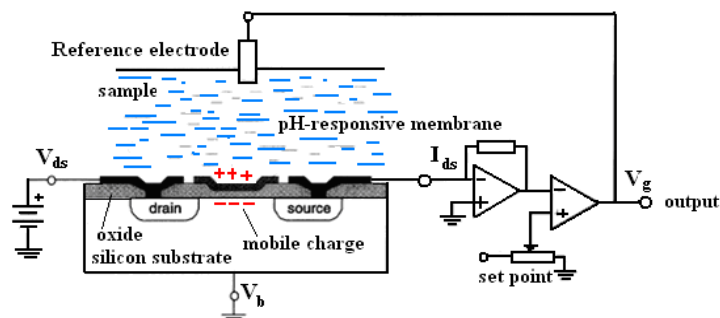


Fig.1.2. pH measurement using an ISFET, including an amplifier circuit for constant drain current operation.

The drain current, I_{ds} can be described by:

$$I_{ds} = A \cdot V_{ds} \cdot Q_c = A \cdot V_{ds} \cdot C_{OX} \left(V_g - V_T - \frac{V_{ds}}{2} \right) \quad (1.8)$$

where the constant A includes geometrical factors, V_{ds} is the voltage applied to the drain, and Q_c is the mobile channel charge. The mobile charge is a function of V_g , the voltage applied to the reference electrode; V_T , the “threshold voltage” needed to produce mobile charge, and C_{OX} , the capacitance of the gate region. The threshold voltage includes a number of terms, one of which is the phase-boundary potential at the interface between the sample and the pH-responsive insulating layer. Adsorption of protons at the surface of this layer leads to a Nernstian dependence of this potential on hydrogen ion activity with the result being that changes in pH modulate the drain current of the device.

$$I_{ds} = A \cdot V_{ds} \cdot C_{OX} \left(V_g - V_T + 2.3 \frac{RT}{F} pH - \frac{V_{ds}}{2} \right) \quad (1.9)$$

Equation 1.9 illustrates the dependence of ISFET current on pH. The preferred method of operation of the pHFET is to operate at a constant drain current. A circuit for doing this is illustrated schematically in Figure 1.2. A trans-conductance amplifier converts the drain current to a voltage, which is referenced against a set-point. The output of the comparator drives the reference electrode, V_g . Since the mobile channel charge Q_c is constant, as are V_{ds} and V_T , changes in the comparator output directly reflect changes in the hydrogen ion activity. That is, a 59-mV change in output corresponds to a change in pH of one unit. Interface circuitry similar to that of Figure 1.2 allows the device to be connected directly to a glass electrode pH meter.

5. Conclusion

Some important developments, such as pHFETs and metal/metal oxide pH sensors, have already occurred and are now achieving noteworthy commercialization. Investigators continue to seek new materials for constructing transducers. Examples include electroconductive (electroactive and inherently conductive) polymers such as polyaniline and polyelectrolyte hydrogels, which form pH-responsive membranes suitable for the construction of microsensors.

A noteworthy innovation is the application of pH measurement devices as transducers that are integrated into more complex analytical systems directed at other analytes. A pH indicator dye forms the basis of the pCO₂ measurement in an indwelling fiber-optic catheter. Because protons are generated and/or consumed in many biological reactions involving enzymes, pH sensors have found use as transducers in biosensor devices.

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