Drift and light characteristics of EGFET based on SnO_2/ITO sensing gate

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Abstract: In this research, the drift and temperture characteristics of extended gate field effect transistor (EGFET) based on tin oxide/indium tin oxide (SnO_2/ITO) sensing gate were investigated. This separate structure EGFET is formed by dividing an ion sensitive membrane from the field effect transistor. This separative ion sensitive membrane has the advantages of simple structure, fabrication and encapsulation. Accordingly, the field effect transistor does not need to put into solution, so we can realize the pure characteristics of optical and temperature of SnO_2 sensing film. The device exhibited a drift amount in pH2,4,6,8 and 10 are 0.884, 1.58, 1.71, 1.8 and 2.51 mV/hr, respectively. The temperature coefficient of sensitivity of SnO_2/ITO glass EGFET is 0.31 (mV/pH)/℃The pH value with a zero temperature coefficient, which can be defined as pH_{ZTC}, is found as pH2.5.

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1. Introduction:

The ion-selective field effect transistor (ISFET), introduced in 1970 [1], is a solid state device which combines the chemical-sensitive properties of a membrane with the field-sensing characteristics of a transistor. Many theoretical and experimental studies have been published for describing the behavior of this chemical-sensing electronic device. Silicon dioxide (SiO2) was first used as a pH-sensitive dielectric for the ISFET [1]. Subsequently, Al_2O_3, Si_3N_4, Ta_2O_5, and SnO_2 have been used as the pH-sensitive dielectric because of their higher pH responses[2-7].

As reported before, we have widely presented five structure EGFETs based on glass substrates which are ITO glass, SnO2/Al/micro slide glass, SnO2/Al/corning 7059 glass, SnO2/ITO glass and SnO2/glass[8]. By a results above, SnO2/ITO glass shows a best basal stability characteristics in those five structures. This paper will detail discuss the overall characteristics, which include sensitivity, linearity, hysteresis, drift, temperature effect, light induced effect and contact window effect of SnO2/ITO glass sensing gate EGFET. In additional, the relative performances of SnO2/ITO EGFET will be compared with commercial and other structures ISFET devices.

2. Methodology

2.1. Materials

Tin oxide thin films were formed by the R.F. sputtering system (tin oxide target : 99.9%) at a substrate temperature of 150^oC. The ITO glasses (50 - 100 Ω/sq, ITO coating thickness: 230 Å) were supplied by the Wintek corporation.

2.2. Fabrication of sensing layer structure

The SnO2/ITO EGFET was fabricated as the methods of ref.[8]. In this chapter, the readout circuit, instrumentation amplifier, is LT1167 which own a good temperature characteristic of 0.3 μV/℃. The output signal, Vo, was measured with a HP3478 multimeter. A computer was used for the data acquisition and for the system control through GBIP card. A PID temperature controller case used to keep a constant measured temperature. The pH value of the buffer solution was calibrated by a combined pH glass electrode.

3. Results and discussions

3.1. Sensitivity and drift of SnO2/ITO glass EGFET

The pH sensitivity was performed in the pH range loop between pH2 and pH12. The pH loop measurement is start from pH6 and in variation of one pH unit and extreme values of pH12 and pH2. One unit pH was measured for 2min. The full range of pH loop is pH6 → pH12 → pH2 → pH8. The mean values of the output voltage of every pH value step was used to plot the figure of pH versus output voltage, which is shown in Fig. 1.

The sensitivity of the SnO2/ITO EGFETs is the slope of the linear fit line and the hysteresis is represented as the residual of linear fit line for the output voltage of every pH values. In additional, the linearity of the device is defined as the correlation coefficient of the linear fit. The SnO2/ITO glass

EGFET shows a high sensitivity and linearity of 59.9 mV/pH and 0.99936 respectively.

The drift behavior of SnO2/ITO glass EGFETs were measured in different pH values of the buffer solutions. To consider the stabilization of device, the drift data were acquired after measured 5 hrs. Therefore, the drift of EGFET is the slope of linear fit of time response from 5 to 15 hr.

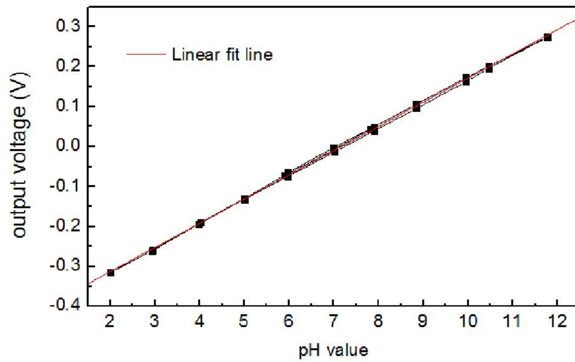

Fig. 1 Calibration curves of pH-sensitive EGFET

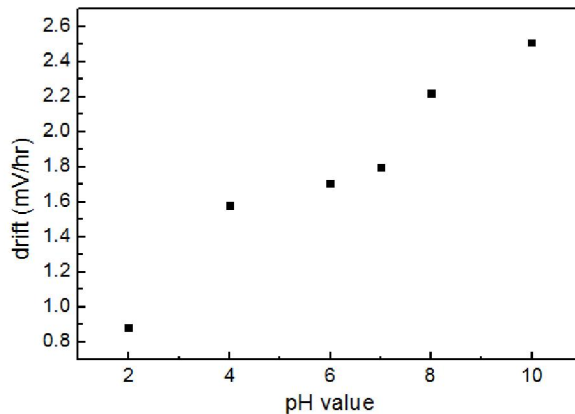

Fig. 2 Relation between pH value and drift

The drift amount in pH2,4,6,8 and 10 are 0.884, 1.58, 1.71, 1.8 and 2.51 mV/hr, respectively, which shown as Fig.2. The results agree with other articles which the drift shows a trend that the drift is larger in higher pH value[9,12,13,14]. Moreover, the drift research of Torbicz et al.[9] shows a negative value in low pH value. General explanations proposed for drift include[14]:

1. Electrochemical non-equilibrium conditions at the insulator-solution interface causes the electric field enhanced ion migration within the gate insulator[15,16].
2. Negative space charge inside the insulator films were created by the injection of electrons from the electrolyte[17].

1998, Jamasb et al.[14, 18, 19] proposed a physical model for drift in pH ISFETs, which depend on the "dispersive transport". The hypothesis that chemical modification of the gate insulator is governed by a dispersive transport mechanism is supported by the presence of buried surface sited and/or the presence of traps (e.g. electrically active silicon dangling bond in CVD nitride films) in the insulator. As shown in Fig.3 for an ISFET with a dual dielectric composed of a low layer of SiO_2 of thickness, x_o, and an upper layer of pH-sensitive insulator of thickness, x_{ins}, the initial effective insulator capacitance, $C_{ox}(0)$, is given by the series combination of oxide capacitance, ε_o/x_o, and the initial pH-sensitive insulator capacitance, $\varepsilon_{ins}/x_{ins}$, where ε_o and ε_{ins} are the dielectric constants of the oxide and pH-sensitive insulator, respectively. By a hydration effect, the chemically-modified effective insulator capacitance, $C_{ox}(t)$, is obtained by the series combination of three capacitances: the oxide capacitance, ε_o/x_o, the capacitance of the chemically-modified surface layer, $\varepsilon_{SL}/x_{SL}(t)$, and the capacitance of the remaining insulator, $\varepsilon_{ins}/(x_{ins}(t)-x_{SL}(t))$, where ε_{SL} is the dielectric constant of the chemically-modified surface layer.

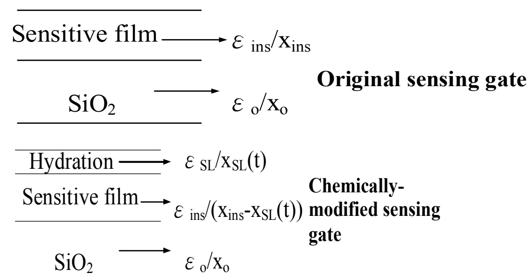

Fig. 3 Capacitance variation of the sensing gate by a hydration effect

The operational mechanism of the ISFET is described by Bergveld and Sibbald using an expression for the drain current, I_D, in the unsaturated region [20]:

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

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 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_R are the charges located in the oxide, charges located in surface state and interface state and the depletion charge respectively; χ^{sol} is the surface dipole potential of the solution, and ϕ_f is the potential difference between the Fermi levels of doped and intrinsic silicon[10]. The electrostatic potential, Ψ_0, is the actual driving force of the ISFET which were build up by surface reactions at oxide surface interface layer between solid and liquid.

By the Eq.(1), if we keep the I_D and V_{DS} constant and neglect the variation in E_{ref}, Ψ_0, χ^{sol}, Φ_{si} and ϕ_f in a fixed pH value, the change in the gate voltage can be written as[14]:

$$\Delta V_{GS} = V_{GS}(t) - V_{GS}(0) = \left[-\frac{Q_{ox}+Q_{ss}}{C_{ox}(t)} - \frac{Q_B}{C_I(t)}\right] - \left[-\frac{Q_{ox}+Q_{ss}}{C_{ox}(0)} - \frac{Q_B}{C_{ox}(0)}\right] = -(Q_{ox}+Q_{ss}+Q_B)\left(\frac{\varepsilon_{ins}-\varepsilon_{SL}}{\varepsilon_{ins}\varepsilon_{SL}}\right) \quad (2)$$

Kühnhold et al. proposed that the buried site are assumed to be in a hydrated surface layer a few nanometers thick. The slow response of these sites is determined by diffusion of H^+ and OH^- ions from the electrolyte to into the hydrated layer. Buried sites were found to increase the sensitivity of the silicon nitride to values higher than the Nernstian response. Due to high hydrogen ion concentration, the effect of buried sites is increased with decreasing pH value[19].

To conclude the drift theories above, we can assume the model of drift effect by sensing gate dielectric variation and the diffusion of H^+ and OH^+ ions, which depend on the pH value. The chemically modified of the sensing gate will cause two effects, which are the capacitance variation by chemically modified within sensitive membrane, and Q_{ox} variation by OH^+ or H^+ ions impurity, which depend on the pH value.

By the first effect, the dielectric constants will be lower in modified-hydrated surface layer, which will form a increase of drift voltage (ΔV_{GS}), regardless of the impurity of positive or negative charge (as shown in Fig.4(a)). The second effect is depend on the pH value. To refer a surface potential, ψ_0, that is derived by site binding model:

$$\psi_0 = 2.303\frac{kT}{q}\frac{\beta}{\beta+1}(pH_{pzc} - pH) \quad (3)$$

where q is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, pH_{pzc} is the pH value with zero surface potential and β is the sensitive parameter[21]. In the situation of $pH>pH_{pzc}$, the surface potential, ψ_0 is negative. It's meaning more OH^- ions close to the surface of sensing film. The OH^- ions own more chance to diffusion into the sensing film, which will cause a increase of ΔV_{GS} (as shown in Fig.4(b). In acid environment that $pH<pH_{pzc}$, the oppositive result will be occurred which is shown as Fig.4(c). In this situation the two effect of drift will be compensated. So the drift in acid shows a lower value than in basic, even it shows a negative drift value in acid.

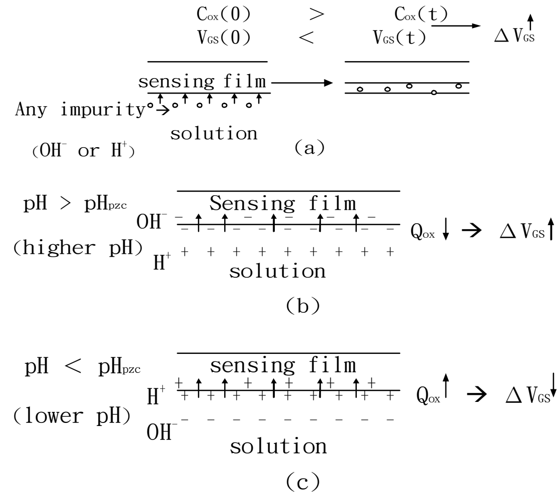

Fig. 4 Drift model depend on (a)capacitance variation and pH value, (b) $pH>pH_{pzc}$, (c) $pH<pH_{pzc}$

3.2 Temperature effect of SnO_2/ITO glass EGFET

For the structure of EGFET in this study, the part of MOSFET was displaced by instrumentation amplifier LT1167. The temperature coefficient of LT1167 is 0.3μV/℃, and it wasn't dipped into solution, so the temperature coefficient of field effect transistor can be neglected. In this study, the measurement of the voltage characteristic curves for a fixed temperature was performed in pH 2 to pH10, one step with 2 pH. The temperature was controlled by repeating the step of 25,35,45 and 55 ℃, respectively. These pH sensitivities for different temperature are shown in Fig.5.

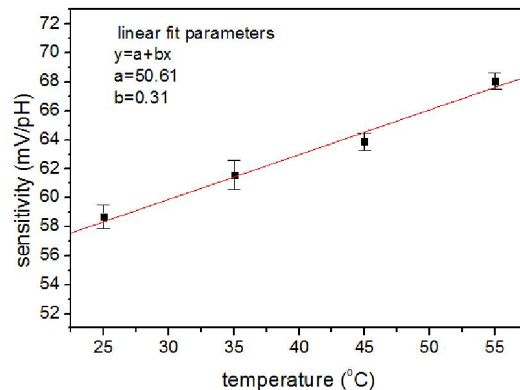

Fig. 5 Temperature coefficient of sensitivity

By the Eq.(3), if β>>1 , the temperature coefficient of sensitivity, T.C.$_s$, can be derived as follow:

$$T.C._s = -\frac{\partial^2 \psi_0}{\partial pH \partial T} = 2.303\frac{k}{q}\frac{\beta}{\beta+1} \approx 0.198 (mV/pH)/℃ \quad (4)$$

Fig. 6 shows the T.C.s of SnO2/ITO glass EGFET is 0.31 (mV/pH)/℃, and the theoretical value of T.C.s is 0.198 (mV/pH)/℃. Fig.5 and Fig.6 show the temperature coefficient in pH10 and temperature coefficient of output voltage between pH2 and 10, respectively. It also shows a linear increase as the temperature and pH value. If we define the sensitivity in T℃ as S_T, then the sensitivity in 0℃, which can be defined as S_0, is 50.61mV/pH (obtained by Fig.5). The sensitivity in T℃, S_T, can be written as:

$$S_T = S_0 + T \times T.C._s \quad (5)$$

In Fig.7, the pH value with a zero temperature coefficient, which can be defined as pH_{ZTC}, is found as pH2.5. By a definition of pH sensitivity, the sensitivity in T℃, S_T, can be written again as:

$$S_T = (V_o - V_{ZTC}) / (pH - pH_{ZTC}) \quad (6)$$

which the V_o is the output voltage that be measured, V_{ZTC} is the output voltage in pH_{PTC}. At the last, a calibration equation can be derived as:

$$pH = [(V_o - V_{ZTC}) / (S_0 + T \times T.C._s)] + pH_{ZTC} \quad (7)$$

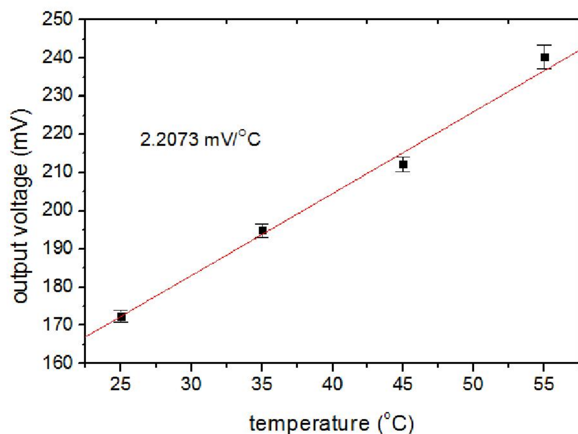

Fig. 6 Temperature coefficient in pH10

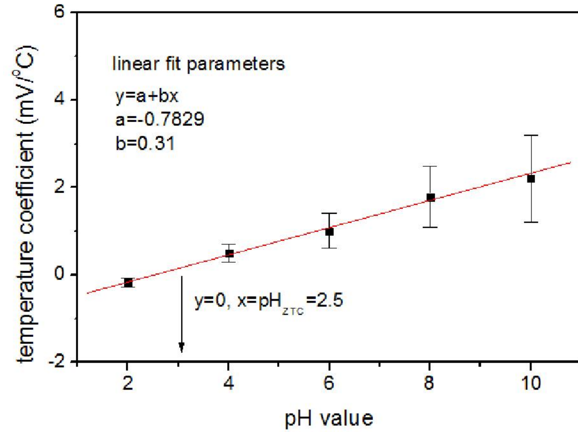

Fig. 7 Temperature coefficient of output voltage between pH2 and 10

4. Conclusions

The experimental data show that the separative EGFETs based on SnO_2/ITO glass have a linear pH response of 59.9 ± 1.037 mV/pH with the linearity being 0.99936 ± 3.5056×10^{-4}. A drift model and a temperature calibration equation were proposed in this paper. The device exhibited a drift amount in pH2,4,6,8 and 10 are 0.884, 1.58, 1.71, 1.8 and 2.51 mV/hr, respectively. The drift model was proposed by combining capacitance and diffusion charge variation in the surface of the sensing film. This model makes a description of which the drift in acid shows a lower value than in basic. For temperture effect for separative EGFETs, the T.C.$_s$ of SnO_2/ITO glass EGFET is 0.31 (mV/pH)/℃ and the pH value with a zero temperature coefficient, which can be defined as pH_{ZTC}, is found as pH2.5. By the result, the temperture effect can be calibrated by a lineaer euquation.

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