

國立交通大學

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碩士論文

以二氧化鋯為感測層之離子場效電晶體其離子偵測與
干擾之特性研究

**The study of ion detection and interference on ZrO_2
gate pH-ISFETs**



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中華民國九十八年八月

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這篇論文我們將利用一個建構基礎在傳統的參考電極(RE)以及金屬場效電晶體(MOSFET)的電子感測元件，離子感測場效電晶體(ISFET)來處理一個多種離子混合之反面議題；這個議題正是 ISFET 的離子干擾與離子偵測現象的研究。其中由於感測層 ZrO_2 對某些離子有較高的感測性與選擇性，以及氫離子(H^+)、鉀離子(K^+)與鈉離子(Na^+)對人體機能的影響有相當的重要性，所以這篇文章將著重探討於由薄膜二氧化鋯(ZrO_2)做成的離子感測場效電晶體(ISFET)之技術製程與其對於氫離子(H^+)、鉀離子(K^+)以及鈉離子(Na^+)偵測的電性分析。而該電子感測元件對於多種的，甚至是不同的離子之感測度的獲得，是利用參考電極、電解液及特定的感測層來取代傳統場效電晶體的金屬閘極結構，其中參考電極的部份將會直接接觸並浸泡在溶液之中去決定待測溶液的酸鹼值(pH 值)的大小，甚至是其他離子的濃度。

正如我們所知，這個由薄膜二氧化鋯(ZrO_2)做成的離子感測場效電晶體

(ISFET)化學電子元件的感測度表現出大約為 58 mV/pH，這個偵測能力與理論中能士特方程式的吻合度高達百分之九十八左右。不過 pH 的響應並不是我們的主要研究目標，並且 ZrO_2 這個薄膜(也就是感測層)對離子的選擇性在含有較多且複雜的離子溶液之中，其主要離子的感測度將會被次要離子們所影響。因此，在這篇論文中，我們將會先研究在酸鹼溶液中的鉀離子與鈉離子的電性量測與感測度分析，也就是 pK 以及 pNa 的量測實驗。而經由實驗結果的討論與驗證，鈉離子與鉀離子的感測度兩者大致上都低於 20 mV/pH 左右，並且氫離子的感測度在較高的鈉離子與鉀離子濃度(pK 以及 pNa 的值低於 3)之中會比較不明顯。這個結果也就表示，氫離子(H^+)、鉀離子(K^+)以及鈉離子(Na^+)的感測度會彼此相互影響的原因就是高濃度離子所造成的飽和現象。



The study of ion detection and interference on ZrO_2 gate pH-ISFETs

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ABSTRACT

This article deals with an inverse problem of ion mixture composition estimation using electronic sensors based on conventional reference electrode (RE) and MOS transistors; this topic exactly is ion detection and interference of ISFET. As a result of higher sensitivity as well as selectivity of the sensing layer ZrO_2 for some ion and the importance of H^+ , K^+ and Na^+ ions to human body mechanism, it reports the technological fabrication and the electrical characterization of ZrO_2 ion sensitive field effect transistors (ISFET) for the detection of H^+ , K^+ and Na^+ ions. The device sensitivity to various ions is obtained by replacing the traditional transistor metal gate electrode with the series combination of the reference electrode, electrolyte and specific sensing layers, the first one is immersed the aqueous solution to detect the pH value and sensitive to the other ions in an electrolyte flowing over the gate.

So far as we know, ZrO_2 ISFET chemical sensors show quasi-nernstian pH response with sensitivities around 58 mV/pH. Its detection yield is 98% compared to

the Nernst equation. However, it is not our main goal for pH response as well as selectivity of the membrane (i.e. sensing layer) ZrO_2 is limited and ions other than the main one also influence the measurement in complex solutions. Therefore, in this study, we will first investigate K^+ and Na^+ ions measurement in acid or base solution, that is, pK and pNa measurement. By way of evidencing, sensitivities of K^+ and Na^+ ions is lower than 20 mV/pH and non-nernstian pH-dependent phenomena for highest K^+ or Na^+ ions concentrations (pK and pNa lower than about 3). It is shown that the detection properties of H^+ , K^+ and Na^+ ions are dependent on each other, being responsible for saturation effects for the highest concentrations.



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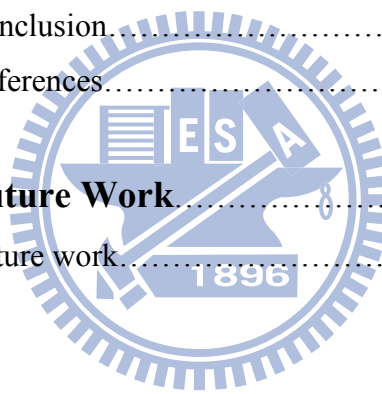


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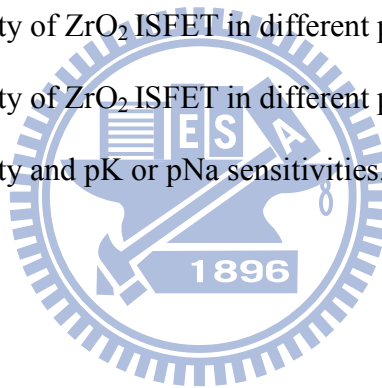
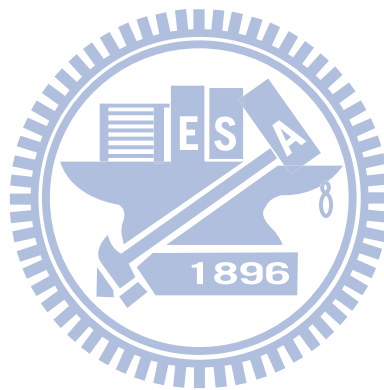


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Chapter 1

Introduction

1.1 The cognition of ISFET

Ion-sensitive-field-effect-transistor (ISFET), the most importance of lots of biomedical sensors, was first pretended by P.Bergveld in the early 1970s [1]. Its numerous properties are very like to metal-oxide-semiconductor-field-effect-transistor (MOSFET) and its basic wafer is in Table 1-1 because it just uses silica as gate and integrate MOSFET with the peculiarity of traditional ion-sensitive-electrode (ISE). Thus the obvious distinction of ISFET and MOSFET is that the MOSFET metal/poly gate is replaced by sensing (silica) layer exposed to the solution directly. It will make that ISFET can sense diverse pH solutions and detect a number of various ions by means of H^+ or other ions accumulating on the top of sensing material. Furthermore, it also can be calculated by the current transformation caused by H^+ ions difference on sensing layer..

1.2 The characteristics of pH-ISFETs

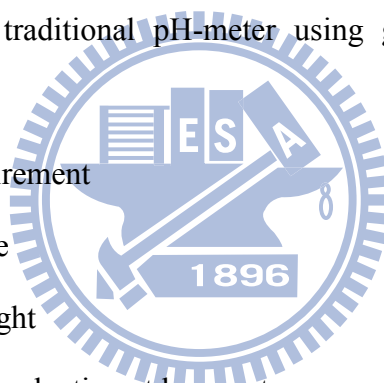
The development of ISFET has been on going for more than 35 years from the 1970s as an alternative to the fragile glass electrode for the measurement of pH or concentrations of ions (Na^+ , K^+ , Cl^- , NH_4^+ , Ca_2^+ , etc.), and the first ISFET sensing layer exploited was silicon dioxide (SiO_2), which showed an unstable sensitivity and a large drift. Recently, there are many materials have been investigated and applied for the ion sensing layer. Table 1-2 shows the sensitivity and test ranges of different

sensing layers. It is found that pH sensitivity is one of the important characteristic parameters of the ISFET device and the response of the ISFET is mainly determined with the type of the sensing layer, thus its material plays a significant role in ISFET field. So in this study, we will use zirconium oxide (ZrO_2) as the ion sensing layer.

The structure of ISFET is similar to the MOSFET except for metal gate electrode removed and deposited a sensing film on the gate oxide, as shown in Fig. 1-1. The utmost sensing layer will have chemical reactions with the test or buffer solutions and build up charges at the surface so that the surface charges will induce surface potential as well as change the threshold voltage of the ISFET, hence the operation current I_D will also change.

Comparing with the traditional pH-meter using glass electrode, ISFET has following features:

- (1) Small sample requirement
- (2) Short response time
- (3) Small size and weight
- (4) Potential of mass production at low cost
- (5) Compatible with the standard CMOS process



Nevertheless, it is possible to generate a variety of chemical sensors with small size down to micrometer scale so that only a small amount of the test solution should be necessary, but this is useless owing to the lack of a miniaturized reference electrode [2].

1.3 The introduction of reference electrode

An ideal reference electrode for use as the ISFET gate terminal should provide [3]:

- (1) An electrical contact to the solution from which to define the solution potential;
- (2) An electrode/solution potential difference that does not vary with solution composition.

The conventional silver chloride or calomel electrode provides both of these functions by maintaining an electrochemical equilibrium with the solution. Novel techniques are to fabricate electrodes in miniaturized dimensions [4] [5]. The on-chip fabrication of a reference of a reference electrode with IC-compatible techniques would make ISFET suitable for biomedical sensing because of the low cost, small size and rigidity.

1.4 Motivation of this work

Although we previously come at that ion-sensitive-field-effect-transistors (ISFETs) could be developed as an alternative to the fragile glass electrode for the measurement of pH and concentrations of ions such as Na^+ , K^+ , Cl^- , NH_4^+ , Ca_2^+ , etc from many famous studies, however, we rarely focus on the ion interference for above-mentioned ions. Certainly, we also find some sensing layers for ISFETs with good hydrogen ion sensitivity, but we also did not concentrate on the sensing layers with good selectivity or not. It will be very essential for the simultaneous measurement or detection.

On the bases of upward description, in this article, we will show that ZrO_2 can provide a solution for the pH, pK or pNa simultaneous measurements since it is sensitive to H^+ , K^+ and Na^+ ions. And it also reports the technological fabrication and the electrical characterization of ZrO_2 ISFET chemical sensors, investigating more precisely the detection properties of the H^+ , K^+ and Na^+ ions and their mutual

influences for simultaneous pH, pK and pNa measurement.

1.5 References

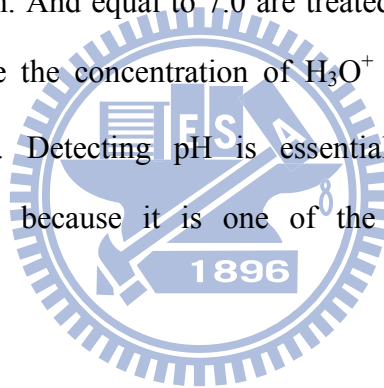
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Chapter 2

Theory Description

2.1 Introduction to pH

The word, pH, was formed by two letters p and H, and the first means 'Power' as well as the second means 'Hydrogen' [1]. As implied in the name, pH is a basic measurement of how many H^+ ions in a unknown solution is. In general, aqueous solutions with a pH value less than 7.0 are treated as acid solutions, greater than 7.0 are treated as basic solution. And equal to 7.0 are treated as neutral solution at room temperature 25 °C because the concentration of H_3O^+ equals the concentration of OH^- in pure water [2]. Detecting pH is essential in finding the chemical characteristics of material because it is one of the most common biomedical measurements.



2.1.1 Basic definition of pH

Generally speaking, there are acid (H^+) and alkali (OH^-) ions in any complex solution, and they are in equilibrium all the time.



The basic definition of pH is expressed as

$$pH = -\log a_{H^+} = -\log \gamma[H^+] \quad (2-2)$$

where a_{H^+} is the hydrogen ion activity, γ is the activity coefficient which equals to 1 when diluted solution, and $[H^+]$ is the molar concentration of solvated protons in

units of moles per liter. Actually, pH depends on a lot of factors, such as the concentration of the added acid and its dissociation constant [3].

2.1.2 How to detect pH

Previously, there are many methods measuring the pH value, including:

- (1) Indicator reagent
- (2) pH test strips
- (3) Metal electrode
- (4) Glass electrode

There are critical drawbacks on above methods, except for glass electrode. For example, the first and second methods are differentiated from colors and both are impossible to reach high accurate pH value, and the third method is difficult for daily use due to the inconvenience of reproducing hydrogen gas [4]. The fourth method glass electrode modernly becomes the most extensively used method for the pH measurement on account of some limitations in practical applications of the first three methods. Therefore, we need to illustrate this topic glass electrode conscientiously.

The first pH glass electrode was improved by M. Cremer with Fritz Haber. It composed of an electrode membrane that determines the pH value, and a stationary concentration of HCl or a buffered chloride solution inside in contact with an internal reference electrode, which use of Ag/AgCl, as shown in Fig. 2-1.

When the glass electrode is immersed in pH buffer solution, the outer bulb surface will be hydrated and exchange sodium ions for hydrogen ions to build up a surface layer of hydrogen ions [2], the build up of charges on the inside of the membrane is proportional to the amount of hydrogen ions in the outside solution. The potential difference between inside and outside can be derived by nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln a_{H^+} \quad (2-3)$$

where E = electrode potential, E_0 = standard potential of the electrode, R = gas constant ($8.31441 \text{ JK}^{-1}\text{mol}^{-1}$), T = temperature (in Kelvin), n = valance ($n = 1$ for hydrogen ions), F = Faraday constant and a_{H^+} = activity of hydrogen ions.

According to the equation, providing that side of the interface the activity of the ion of interest is kept constant, the electrode potential is direct logarithmic function of the ion activity on the other side [5]. As a result of ideal Nernstian response independent of redox interferences, short balancing time of electrical potential, high reproducibility, high selectivity, reliability, wide pH range, and long lifetime. It is most universal used for pH measurement. Nevertheless, glass electrode has some drawbacks for many industrial applications:

- (1) Unstable in alkaline or HF solutions or at high temperature
- (2) Exhibiting a sluggish response and Difficult to miniaturize
- (3) Cannot be used in food due to their brittle nature
- (4) Must be used at the vertical position for chemical reproducibility

Consequently, there is an increasing need for alternative pH sensor, the ISFET-based pH sensor is a new and appropriate technique for pH detection.

2.2 The realization of ISFET

Since the first ion-sensitive-field-effect transistors (ISFETS) study by P. Bergveld [6], ISFET had gone into a new potential type of chemical sensing device. This device is very similar to metal-oxide-semiconductor-field-effect transistor (MOSFET) except for the metal gate electrode replaced with a reference electrode inserted in a buffer solution which is in touched with the sensing layer above gate

oxide. Deserving to be mentioned, The ISFET used to measure or sense ion concentration in unknown solution. The brief construction of MOSFET and ISFET are shown in Fig. 1-1 once again.

2.2.1 Comparison between MOSFET and ISFET

Because there are numerous similarities between with ISFET and MOSFET and the main difference between ISFET and MOSFET is that MOSFET metal/poly gate electrode is replaced with sensing layers, the series combination of the reference electrode, electrolyte, and chemically sensitive insulator or membrane. The best method to interpret this ISFET device is to review the operation of the MOSFET device firstly.

While MOSFET is operated in the so-called non-saturated region, the general expression for the drain current I_D is given by:

$$I_D = \frac{C_{OX}\mu W}{L} \left\{ (V_{GS} - V_T) - \frac{1}{2} V_{DS} \right\} V_{DS} \quad (2-4)$$

where C_{OX} is the gate insulator capacitance per unit area, W and L are the channel width and the channel length respectively such that W/L is the width-to-length ratio of the channel, μ is the electron mobility in the channel, V_{GS} is gate to source voltage, V_{DS} is drain to source voltage and V_T is the threshold voltage. By the way, if the fabrication process is controlled and biased well in designed applied electronic circuit, we will hold the geometric sensitivity parameter $\beta = \mu C_{ox} \frac{W}{L}$, V_{DS} , and V_T , the drain I_D will be a unique function of the only variable V_{GS} .

The so-called threshold voltage V_T of the MOSFET is:

$$V_T = V_{FB} - \frac{Q_B}{C_{OX}} + 2\phi_F \quad (2-5)$$

where V_{FB} is the flat-band voltage, Q_B is the depletion charge in the silicon substrate,

ϕ_F is the potential difference between the Fermi level and intrinsic Fermi level and it is dependent on the doped concentration. V_{FB} also can be illustrated by the following expression:

$$V_{FB} = \frac{\Phi_M - \Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS}}{C_{OX}} \quad (2-6)$$

where the first term describes the difference between the gate metal work function Φ_M and the silicon work function Φ_{Si} , the second term is caused by the charge accumulated in the oxide Q_{OX} and at the oxide-silicon interface surface Q_{SS} .

Then we Substitute Eq. (2-5) in Eq (2-6), the common form of the threshold voltage of the MOSFET can be described by the following expression:

$$V_T = \frac{\Phi_M - \Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS} + Q_B}{C_{OX}} + 2\phi_F \quad (2-7)$$

The threshold voltage of ISFET contains terms that the interface between the liquid and oxide, the others between liquid and reference electrode when ISFET is immersed in a liquid. So that, The surface potential must take in into account. In a word, the threshold voltage becomes the following expression:

$$V_T = E_{ref} + \chi^{sol} - \Psi_0 - \frac{\Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS} + Q_B}{C_{OX}} + 2\phi_F \quad (2-8)$$

where E_{ref} is the constant potential of the reference electrode, χ^{sol} is the surface dipole potential of the solution which also has a constant value. The surface dipole potential is different from aqueous solution, even though a little variation of surface dipole potential at disparity aqueous solution. The value compare to other term is too small to take as a constant. All terms are constant except Ψ_0 , it is the kernel of ISFET sensitivity to the electrolyte pH which is controlling the dissociation of the oxide surface [7]. In order to obtain an accuracy pH value, to investigate a high pH sensitivity ISFET on the electrode-electrolyte interface is necessary.

In brief, the ISFET is very similar to the MOSFET structurally and electronically, but with one more property: the possibility to chemically modify the threshold voltage

via the interfacial potential at the oxide-electrolyte interface. And we will focus on the key point of the ISFET, the oxide-electrolyte interface.

2.2.2 The Oxide-Electrolyte Interface pH response

Based on the site-binding model introduced by Yate et al [8], the oxide/electrolyte interface will build up charges and generate an extra electrostatic potential while we are immersing the ISFET in the pH buffer solution. That is, the properties of the ISFET are exactly controlled by the performance of the oxide-electrolyte interface, protonation/deprotonation of the gate material is influenced by the pH solution which dominate the surface potential.

The charging mechanism at the surface is the most well-known Site-Binding model introduced by Yate et al [8]. It describes the charging mechanism at the oxide/electrolyte interface in Fig. 2-2 and Fig. 2-3. The surface of any metal oxide always contains hydroxyl groups, for example, in the case of silicon dioxide is SiOH groups [9]. These groups consist of donate and accept a proton from the solution. Therefore, as ISFET sensing layer like SiO₂ contact an aqueous solution, the change of pH will change the SiO₂ surface potential. These reactions can be expressed by:



where H_S^+ represents the protons at the surface of the oxide, κ_1 and κ_2 are chemical equilibrium constants. the equilibrium constants κ_1 and κ_2 are given by:

$$K_1 = \frac{[SiOH_2^+]}{[SiOH][H^+]_s} \text{ or } \frac{v_{SiOH} \cdot a_{H_s^+}}{v_{SiOH_2^+}} \quad (2-11)$$

$$K_2 = \frac{[SiO^-][H^+]_s}{[SiOH]} \text{ or } \frac{v_{SiO^-} \cdot a_{H_s^+}}{v_{SiOH}} \quad (2-12)$$

where S denotes the surface.

The potential between the gate insulator surface and the electrolyte solution causes a proton concentration difference between bulk and surface that is according to Boltzmann [10].

$$a_{H_s^+} = a_{H_B^+} \exp \frac{-q\Psi_0}{kT} \quad (2-13)$$

or

$$pH_S = pH_B + \frac{q\Psi_0}{2.3kT} \quad (2-14)$$

where $a_{H_s^+}$ is the activity of the oxide surface and $a_{H_B^+}$ is the activity of the solution bulk individually, q is the elementary charge, k is the Boltzmann constant, T is the absolute temperature, pH_S is the pH value at the oxide surface and pH_B is the pH value in the solution bulk, Ψ_0 is surface potential. By the way, the subscripts B and S refer to the bulk and the surface, respectively.

Now we can start with the fixed number of surface site per unit area N_s :

$$N_s = v_{SiOH} + v_{SiO^-} + v_{SiOH_2^+} \quad (2-15)$$

Based on some electrochemical knowledge and math derivation, the surface charge density $\sigma_0 [C/m^2]$ can be available:

$$\sigma_0 = q(v_{SiOH_2^+} + v_{SiO^-}) = -qB \quad (2-16)$$

where B is the number of negatively charged groups minus the number of positively charged groups in mole per unit area. It can show that when the number of positively and negatively charged groups on the surface is equal and consequently, there will be no net charge on the surface. In this situation, we can say the pH value at the point of zero charge is pH_{pzc} . One more thing we have to know is that different operations of ISFETs (flat band condition and linear region) will yield different value of pH_{pzc} [11]. Then:

$$\sigma_0 = qN_s \left(\frac{a_{H_s^+}^2 - K_a K_b}{K_a K_b + K_b a_{H_s^+} + a_{H_s^+}^2} \right) \quad (2-17)$$

where K_a and K_b are dissociation constant. And a detailed derivation can see the Ref. [2] [7]. After getting the surface charge density, then we can look for the intrinsic buffer capacity β_{int} , the capability of the surface to store charge as result of a small change in the H^+ concentration, defined as

$$\frac{\partial \sigma_0}{\partial \text{pH}_s} = -q \frac{\partial B}{\partial \text{pH}_s} = -q \beta_{\text{int}} \quad (2-18)$$

Now we can obtain the equation for intrinsic buffer capacity from above equation (2-17) and (2-18):

$$\beta_{\text{int}} = N_s \frac{K_b a_{H_s^+}^2 + 4K_a K_b a_{H_s^+} + K_a K_b^2}{\left(K_a K_b + K_b a_{H_s^+} + a_{H_s^+}^2 \right)^2} 2.3 a_{H_s^+} \quad (2-19)$$

Possibly owing to buffering small changes in surface pH (pH_s) and not in the bulk pH (pH_B), so that it is called “intrinsic” buffer capacity. We also can see that the value of N_s , K_a , and K_b are oxide dependent. More surface sites will have greater β_{int} . In accordance with [7], Hydrolysis of the surface will create more surface sites and thus a rise in the intrinsic buffer capacity and the sensitivity.

The surface charge density will affected by the surface reaction and the background electrolyte that result from variations in the double layer capacitance.

Because of charge neutrality, an equal but opposite charge is built up in the electrolyte solution side of the double layer σ_{DL} , shown in Figure 2-2. This charge can be described as a function of the integral double layer capacitance, C_i and the electrostatic potential:

$$\sigma_{DL} = -C_i \Psi_0 = -\sigma_0 \quad (2-20)$$

The integral capacitance will be used later to calculate the total response of the ISFET on changes in pH. The ability of the electrolyte solution to adjust the amount of stored charge as result of a small change in the electrostatic potential is the differential capacitance, C_s :

$$\frac{\Delta \sigma_{DL}}{\Delta \Psi_0} = -\frac{\Delta \sigma_0}{\Delta \Psi_0} = -C_s \quad (2-21)$$

As a result, combination of (2-18), (2-20), and (2-21) lead to an expression for the sensitivity of the the electrostatic potential change in a_{H^+} :

$$\frac{\Delta \Psi_0}{\Delta pH_s} = \frac{\Delta \Psi_0}{\Delta \sigma_0} \frac{\Delta \sigma_0}{\Delta pH_s} = \frac{-q\beta_s}{C_s} = \frac{\Delta \Psi_0}{\Delta(pH_B + \frac{q\Psi_0}{2.3kT})} \quad (2-22)$$

Rearrange Eq. 2-15 gives a general expression for the sensitivity of the electrostatic potential to changes in the bulk pH [9]:

$$\Delta \Psi_0 = -2.3\alpha \frac{kT}{q} \Delta pH_B \quad (2-23)$$

with

$$\alpha = \frac{1}{\frac{2.3kTC_s}{q^2\beta_s} + 1} \quad (2-24)$$

The parameter α is a dimensionless sensitivity parameter that varies between 0 and 1, depending on the intrinsic buffer capacity, β_s , of the oxide surface and the differential capacitance C_s . We can get the maximum value α so that the

sensitivity become -59.2 mV/pH at 298K which is called Nernstian sensitivity. Therefore, the intrinsic buffer capacity β_s need to be the more higher or the double layer capacity C_s to be the more lower. In ideal, the intrinsic buffer capacity $\beta_s = \infty$ or the double layer capacity

$C_s = 0$ would be the best. It appears that the usual SiO_2 from MOSFET does not fulfil the requirements of a high value of β_s . The pH sensitivity is low depending also on the electrolyte concentration through C_s . Therefore other films such as ZrO_2 were introduced to increase the values of β_s . The higher the intrinsic buffer capacity so that the less important of the value of C_s which means that independent of the electrolyte concentration a Nernstian sensitivity can be achieved over a pH range from 1 to 13.

In sum, to use SiO_2 from the MOSFET process does not obtain the requirements of a high value of β_{int} . The pH sensitivity is only about 30mV/pH , so the research nowadays is to find high sensitivity sensing film. The material found by high sensitivity is Si_3N_4 , Al_2O_3 , and SnO_2 [13-17].

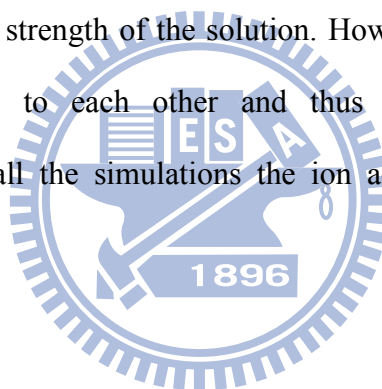
2.3 The phenomenon of membrane selectivity

The most important problem encountered during measurements of the ion concentration with CHEMFETs is related to the limited membrane selectivity. As a result, the membrane potential varies not only with the concentration of the main ion to be detected, but also it is dependent on the concentration of some other ions, called interfering ions. The most commonly employed model of the phenomena occurring in the sensor membrane is based on the semi-empirical Nikolski-Eisenman equation, derived from the Nernst equation [18]. The main advantage of this approach is that it is time efficient, quite accurate and it can be easily implemented in any simulation

environment. Moreover, the model parameters, such as the selectivity coefficients k_{ij} , can be found analytically without any difficulties. According to this model, the membrane potential changes ΔV_T in presence of various ions in the analyzed solution can be expressed by the following equation [19]:

$$\Delta V_T = \frac{RT}{z_i F} \ln \left[a_i + \sum_{j \neq i} k_{ij}(T) \cdot a_j^{\frac{z_i}{z_j}} \right] \quad (2-25)$$

where F is the Faraday constant, R is the gas constant, T is the absolute temperature, a is the ion activity, i, j are the main and interfering ion indices respectively and z is the ion electrovalence. The issue, which has to be commented on, is the difference between the ion concentration and its activity. These two quantities are related through the so-called ionic strength of the solution. However, except for very strong solutions, they are equal to each other and thus these terms will be used interchangeably although all the simulations the ion activity is always taken into account.



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Chapter 3

Experiment and Measurement

3.1 The fabrication process of ISFET

All procedures of experiment are done in NDL (National Nano Device Laboratory) and NFC (Nano Facility center), similar to the manufacturing process of MOSFET [1]. The process flow of ISFET is illustrated in Figure 3-1. The sensing layers ZrO_2 is deposited onto the SiO_2 gate ISFET which prepared by Sputter in Nano Facility center. Before every step, besides after sensing membrane deposited onto SiO_2 gate, the initial clean immersed in $H_2SO_4+H_2O_2$ about 5 minutes and dipped in HF solution were done. The fabrication and its parameters are listed in Fig. 3-1 and the fabrication procedures are listed as follows:

- 1) RCA clean
- 2) Wet-oxidation of silicon dioxide(6000Å, 1050°C, 65 mins)
- 3) Defining of Source/Drain (Mask 1)
- 4) BOE wet-etching of SiO_2
- 5) Dry-oxidation of SiO_2 as screen oxide (300Å, 1000°C, 12 mins)
- 6) S/D ion implantation
(Dose= $5e15$ [$1/cm^2$], energy=25Kev [Phosphorus] for p-type ISFET)
- 7) S/D annealing (950°C, 60min)
- 8) PECVD SiO_2 for passivation (1 μ m)
- 9) Defining contact hole and gate region (Mask 2)
- 10) BOE wet-etching of SiO_2

- 11) Dry growth of gate oxide (100Å, 850°C, 60mins)
- 12) Defining the sensing layer region (mask3)
- 13) Sputtering ZrO₂ as sensing layer, 300Å (mask 3)
- 14) ZrO₂ sintering (600°C, 60min)
- 15) Define the contact hole region (mask4)
- 16) Contact hole and reference electrode Al deposition
- 17) Backside Al evaporation, 5000 Å
- 18) Al sintering (400°C, 30min)

3.2 The key steps of the experiment

3.2.1 Na⁺ and K⁺ ion solutions allocation

For a start, we need to artificially allocate Na⁺ and K⁺ ions solution with different pH buffer solutions because of no precise machine for titration, so that we can proceed ion detection.

- 1) Preparing 3M NaCl and KCl solution and pH=3,5,7,9,11 buffer solutions
- 2) Diluting NaCl and KCl with pH buffer solutions as following:
 - a) Taking 3M NaCl or KCl 1ml into pH=3,5,7,9,11 buffer solutions 30ml such that the concentration of the new solution is 0.1M Na⁺ or K⁺ ion solutions.
 - b) Taking just allocating solution 0.1M Na⁺ or K⁺ ion solutions 1ml into pH=3,5,7,9,11 buffer solution 100ml such that the concentration of the new solution is 0.001M Na⁺ or K⁺ ion solutions.
 - c) Repeating step2) until pNa and pK are equal to 10.

3) Beginning to measuring and detecting ion interference.

3.2.2 Gate region formation

RCA clean is usually performed at wafer starting to reduce the possible pollution such as particles, organics, diffusion ions and native oxide. Careful RCA clean will ensure the integrity of device electricity. The next step 600nm thickness wet oxide is deposited as barrier layer for S/D implant. The density and the energy of S/D implant is $5E15$ ($1/cm^2$) and 25Kev with phosphorous dopant for n-type ISFET. After S/D implanting, in order to activate the dopants, a $950^\circ C$ 30 min N^+ anneal for n-type ISFET.

The extra $1\ \mu m$ thickness PECVD oxide deposition is essential, which protect the other pH-ISFET from aqueous solution overflowing pH-ISFET [2]. During a long period of electrolyte immersing, ions may diffuse and affect the ISFET's electrical characterization [3]. It is a significant difference compare with standard MOSFET processes. A thick PECVD oxide deposition can eliminate the effect. Following the PECVD oxide deposition, 100\AA thickness dry oxide was grown in a dry oven as gate oxide formed.

3.2.3 Sensing layer deposition

This procedure is the kernel of the pH-ISFET in our important part in our experiment. The ZrO_2 sensing film 300\AA is growth by the sputter which appear a good sensitivity nearly Nernstian sensitivity [4]. The detailed parameters of sputter are listed in Table 3.1.

3.3 Measurement system

3.3.1 Preparation of measurement

To investigate the characteristics of the ZrO_2 as sensing layers, we measured the I-V curves for the pH-ISFETs by using HP4156 as measurement tool and the system is shown in Fig. 3-2. For getting correct result of measurement, the entire measurement procedures were executed in a dark box to prevent light influence and the electromagnetic wave.

In order to make the sensing film immersed in the aqueous solution, some extra works on wafers must be done before measurement with HP4156. At first, we glued a container on the wafer. This step is very important for following complex and frequently solution change activities which also can protect the other ISFET from immersed aqueous solution. The container, to load the test electrolyte, was open at its bottom and covered the whole sensing region on wafer to keep electrolyte contact with sensing layers exactly.

The pH-standard solution is purchased by Riedel-deHaen corp. and the pH-values are 1, 3, 5, 7, 9, 11, 13. The electric potential of the pH-solution will be floating [5] during open-loop circuit. The disturbance from the environment would induce the electric potential variance of the solution. By eliminating this variance, a reference electrode is needed to immersion in the pH-solution to close the circuit loop.

3.3.2 Current-Voltage measurement set-up

A HP-4156 semiconductor parameter analyzer system were set up to measure the current-voltage (I-V) characteristics curves, in which included I_{ds} - V_{gs} and I_{ds} - V_{ds}

curves at controlled temperature. All measurements were arranged in a dark box to minimize the effects of photoelectric and temperature.

In the I-V measurements, due to the sensing areas were so small, prevention of air bubbles from being generated between the sensing membrane and the buffer solution during the testing is needed to take care.

In the setup of HP-4156, substrate voltage is ground to avoid the body effect and the reference electrode is sweeping to different voltage. In the measurement of sensitivity, the response of the pH-ISFET is the function of time. According to P. Woias, the first equilibrium will achieves in a minute.

In order to obtain the sensitivity, at first we measure the I_{ds} - V_{ds} to observed the linear area. Secondly, we make the V_{ds} as constant to measure I_{ds} - V_{ds} from pH 13 to pH 1 in turn. As changing the pH buffer solution, we diluted next butter solution which under test twice, and stay 1min to avoid the effect of the buffet solution that measured before. This step can make our the measurement of pH-ISFET more easily. The variation of the gate voltage exhibits the pH sensitivity of the sensing oxide. Fig. 3-3 illustrates the detection principle of pH

3.4 References

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Chapter 4

Results and Discussions

4.1 Introduction

We exactly know that ion sensitive field effect transistors (ISFETs) have shown good properties for the detection of numerous ions in solution from the above article, and it is an inevitable phenomenon of pH-ISFETs from other studies for the second time [1]. In spite of ISFET with many ions detecting, however, their use in the case of complex chemical solutions and simultaneous detection of different ions is characterized by different drawbacks:

- (1) Few ionosensitive layers are able to detect several ions with a good and distinct sensitivity for each of them
- (2) The measurement technique based on charge detection is unable to separate the influences of similar ions and is therefore responsible for poor selectivity.

All in all, multi-ion detection in complex solutions of ISFET requires generally adapted characterization, multi-ISFET sensors and information processing [1].

In the following article, we will find out that the original sensitivity of pH-ISFETs compared with the later sensitivity after adding Na^+ or K^+ ions into solutions should be smaller because of the ion interference. And we will soon discuss and show this peculiar phenomenon with some powerful experience data.

4.2 The glass reference electrode for pH measurements

In chapter 1, we have mentioned the potential of glass electrode is very stable

and accurate. Thus we will first discuss the sensitivity of ZrO₂-pH-ISFET by glass reference electrode. The good functioning of the ZrO₂ ISFET chemical sensor has been demonstrated by studying the H⁺ ion detection (see Fig. 4-1). And its sensitivity is in Fig. 4-2 [2]. A quasi-nernstian pH response has been obtained on a 1-13 pH range and pH sensitivity has been finally estimated to 58.73 mV/pH (detection yield of 99.2% compared to the Nernst law).

4.3 pK and pNa measurements

The pK and pNa responses of the ZrO₂ ISFET chemical sensor have been studied for buffered solutions of KCl or NaCl salts (pH 9), respectively (see Fig. 4-3 and Fig. 4-4). We can conclude that similar results have been obtained for both ions (i.e. K⁺ and Na⁺). For the lowest concentrations (pK > 5 or pNa > 3), no detection properties have almost been obtained. And for the highest concentrations (pK < 5 or pNa < 3), linear responses are evidenced and sensitivities to K⁺ and Na⁺ ions have been estimated to 12 mV/pX (X = Na or K ion and detection yield of 20.3% compared to the Nernst law).

4.4 Simultaneous pH, pK and pNa measurements

The simultaneous detection of the H⁺ ion with the K⁺ or the Na⁺ ion has been accomplished. This purpose has been performed by researching the ZrO₂ ISFET responses to pK or pNa for different solution pH (see Fig. 4-5 to 4-12). These may be not clear, so we show normalized pK and pNa response of ZrO₂ ISFET in Fig. 13 and 14. As already shown in Section 4.3, K⁺ and Na⁺ ions are only detected for the highest concentrations. Nevertheless, as the solution pH decreases gradually, detection limits

also decrease by degrees and no detection properties are ultimately obtained for the lowest pH.

In order to clarify these phenomena, let us study the different sensitivities of the ZrO₂ ISFET chemical sensor and more precisely the pK and pNa sensitivities as a function of pH (see Fig. 4-29) and the pH sensitivity as a function of pK and pNa (see Fig. 4-15 to 4-28).

As a result, it shows that the sensitivity to the K⁺ or Na⁺ ion increases almost linearly with the solution pH. Maximal values around 12 mV/pX can be estimated for the more basic solutions (pH 11) while no detection properties ($s < 3.5$ mV/pX) are obtained for the more acidic solution (pH 3). By turns, when K⁺ or Na⁺ ions are present in solution, the sensitivity to the H⁺ ion is lowered around 45 mV/pH as well as 40 mV/pH and decreases further for the lowest pK or pNa values, reaching 40 mV/pH as well as 35 mV/pH when pK or pNa is equal to 1.

At least, the simultaneous detection of the K⁺ and Na⁺ ions have been studied for buffered solutions of mixed KCl and NaCl salts (pH 9). Thus, for the lowest pK and pNa values, electrical characterisation has effectively evidenced the detection of ions. However, it has been impossible to indicate any comprehensive results, to separate clearly the influences of the K⁺ and Na⁺ ions and to define precisely the different ionic selectivity and sensitivity.

All these results demonstrate that the use of ZrO₂ as an ionosensitive layer for the simultaneous detection of H⁺, K⁺ and Na⁺ ions is characterized by complex phenomena, saturation effects and mutual influences. In order to clarify the simultaneous detection mechanisms, the modeling of the EIS structure must be further improved. (EIS = electrolyte/insulator/semiconductor)

4.5 Simultaneous detection explanation of the H⁺, K⁺ and Na⁺ ions

Until now, the theory of this phenomenon has considered two types of surface sites (silanol SiOH and silylamine SiNH₂) and has neglected the sensitivity to others ions like K⁺ or Na⁺ [6] [7]. This last assumption cannot be in agreement with the complex phenomena, saturation effects and mutual influences of the pH, pK and pNa simultaneous measurements described previously. For high pK or pNa values, even if the K⁺ or Na⁺ ions do not react directly with the ZrO₂ ionosensitive layer, their presence in the solution, and more precisely in the inner and outer Helmotz planes [8], should be responsible for electrostatic or/and chemical influences. These phenomena should lead to shifts of the equivalent capacitor or/and of the reactivity of the insulator interface. The presence of chloride ions Cl⁻ in solution (from the KCl or/and NaCl salts) should also be taken into account in a similar way.

For low pK or pNa values, the K⁺ or Na⁺ ion binding with the silanol SiOH or silylamine SiNH₂ sites of the ZrO₂ ionosensitive layer occurs. These reactions should be responsible for a decrease of the effective surface density of sites as well as for electrostatic repulsion of other cations such as H⁺ ions. In return, the same effect holds good for the detection of K⁺ or Na⁺ ions in the case of low pH values.

Therefore, by theoretically developing them and by improving the site-binding model, the pH, pK or pNa simultaneous measurement of the ZrO₂ ISFET sensor will be precisely described.


4.6 Conclusion

According to above results, we can find that ZrO₂ ISFET chemical sensors have been studied for the detection of H⁺, K⁺ and Na⁺ ions in aqueous solution, evidencing maximal sensitivities of 57.2 mV/pH, 12.22 mV/pK and 11.55 mV/pNa, respectively

(ranges available: $1 \leq \text{pH} \leq 13$, $1 \leq \text{pK} \leq 4$, $1 \leq \text{pNa} \leq 3$). The study of the simultaneous detection evidence complex phenomena, saturation effects and mutual influences of the H^+ , K^+ or Na^+ ion detection properties for the highest ionic concentrations in solution.

Results finally demonstrate that ZrO_2 ISFETs are well adapted to the H^+ ion detection, are usable for the K^+ or Na^+ ion detection separately in the case of buffered basic solutions, and are not suitable for the H^+ , K^+ and Na^+ ion simultaneous detection in the case of complex solutions or medical analysis [3] [4].

4.7 References

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Chapter 5

Future Work

5.1 Future Work

In our experiment of this study, we find the truth that ZrO_2 will be sensitive to H^+ , Na^+ and K^+ ions. Based on this peculiar phenomenon, we can know that characteristics of some ion detection are researched. For these last applications of this study, multi-ions detection will only be possible by developing new characterization techniques or by realizing multi-ISFETs chemical sensors with specific ionosensitive layers for the different ions.



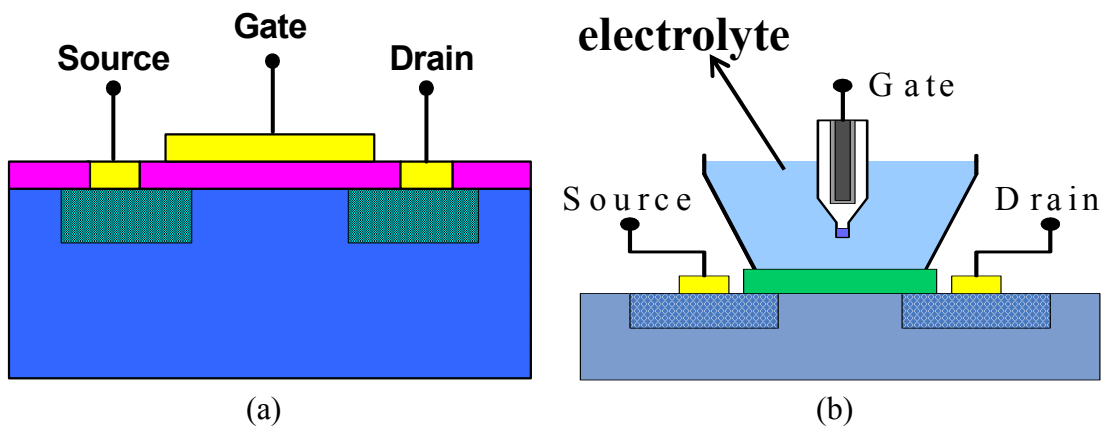


Fig. 1-1 Schematic representation of (a) MOSFET (b) ISFET

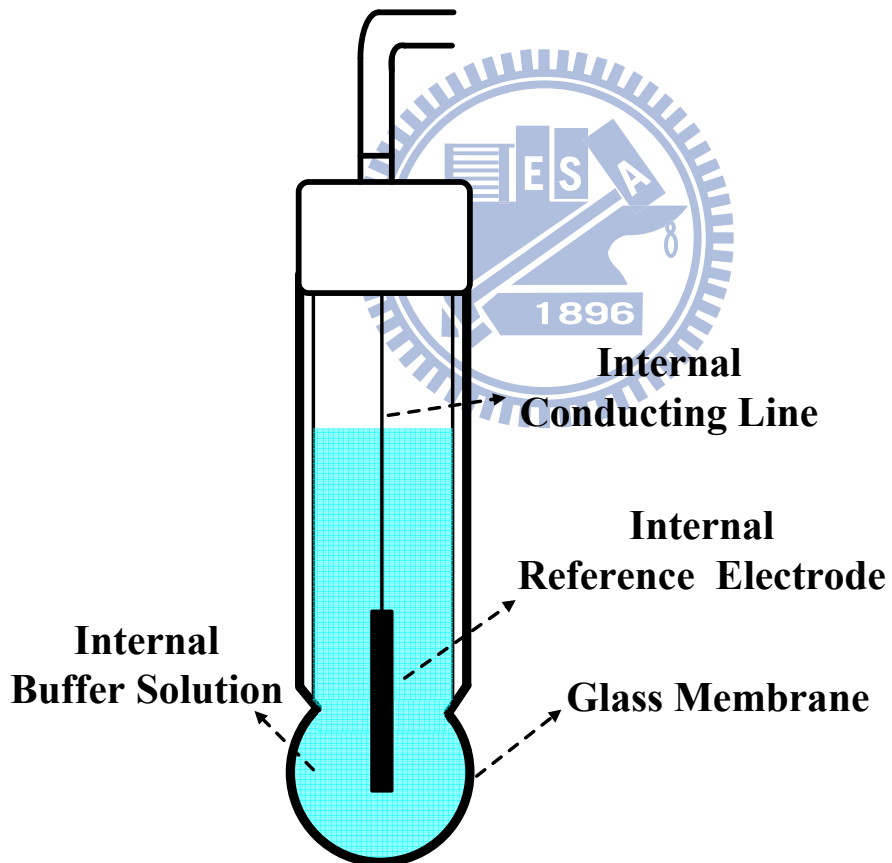


Fig. 2-1 Conventional pH glass electrode

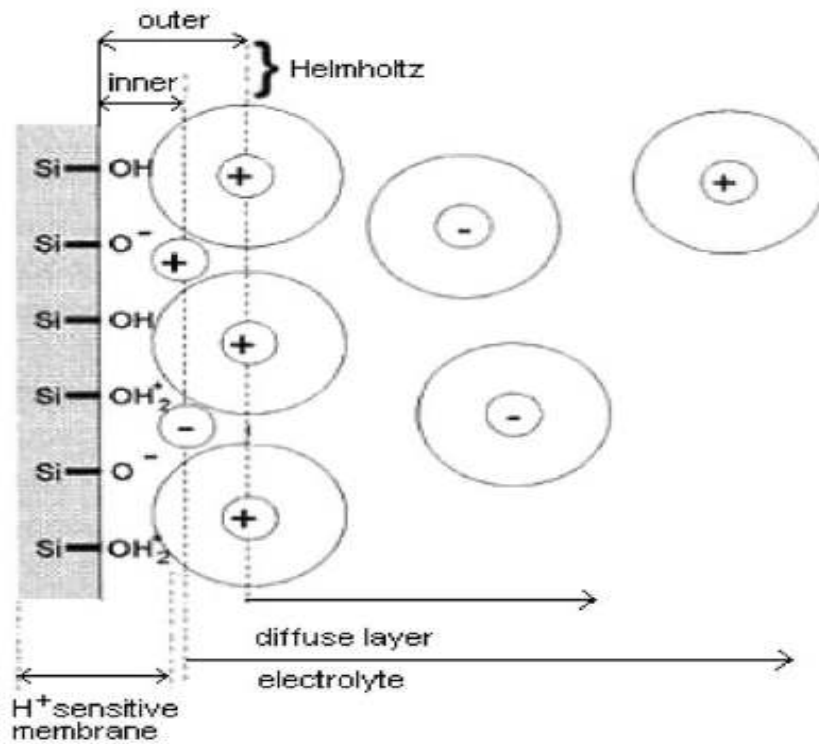


Fig. 2-2 Electrode and electrolyte interface

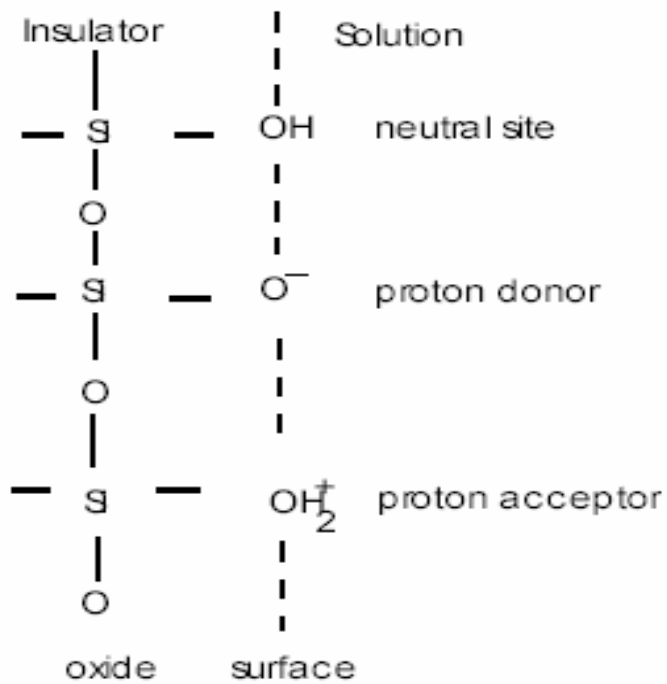
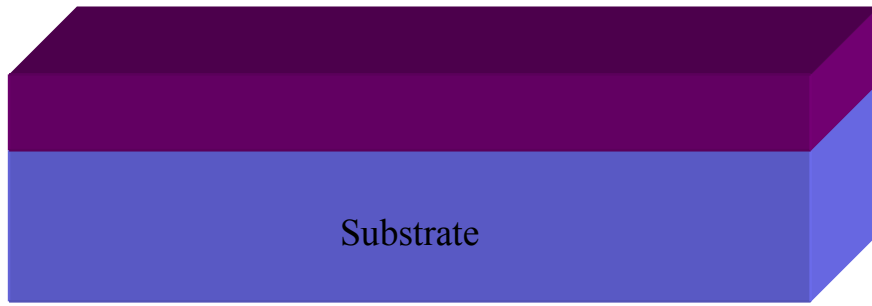
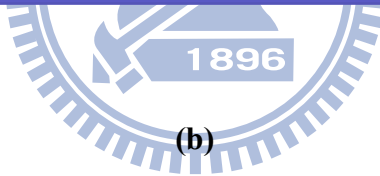
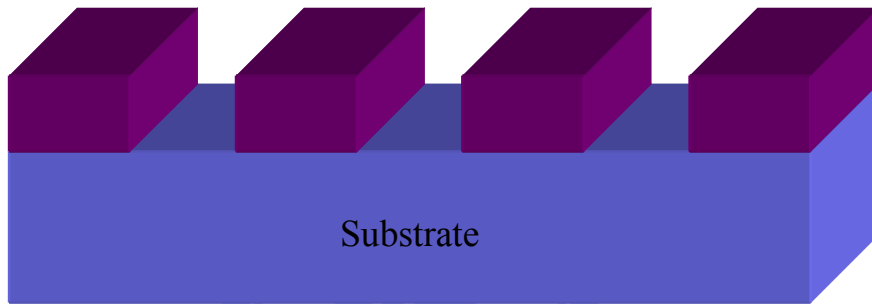


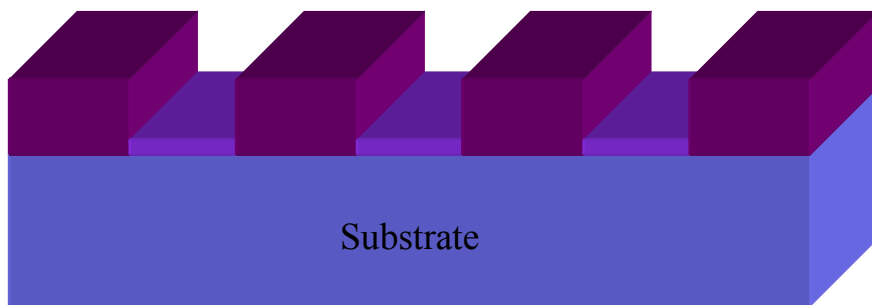
Fig. 2-3 Schematic representation of the side-binding model



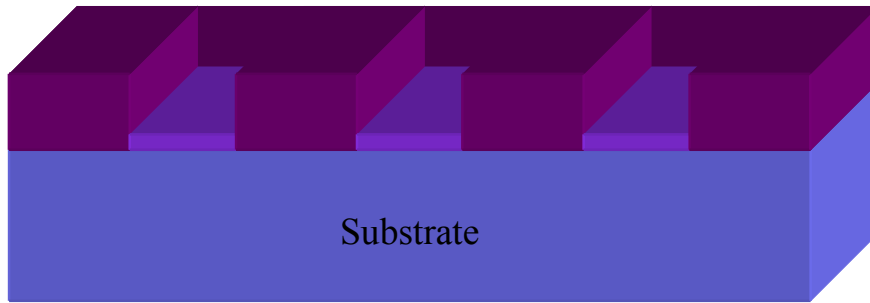
(a)



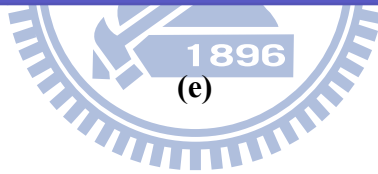
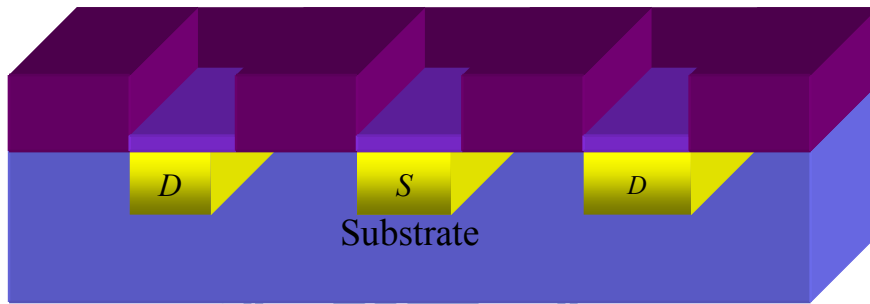
(b)



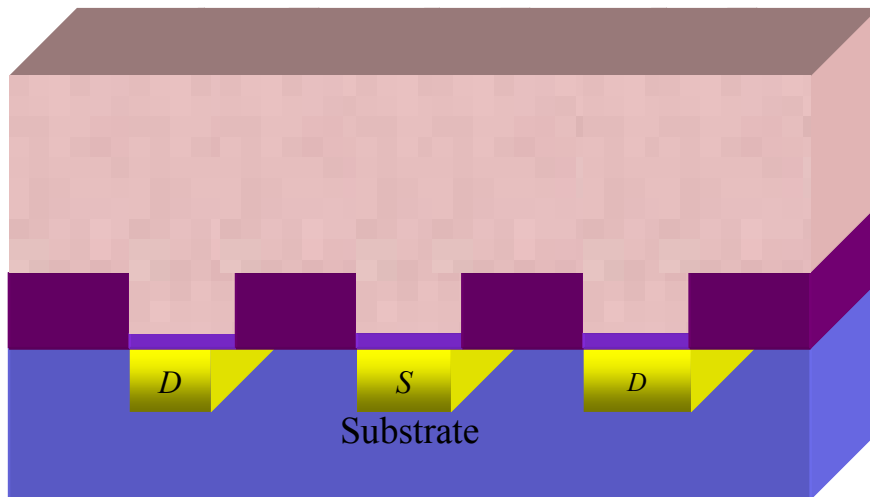
(c)



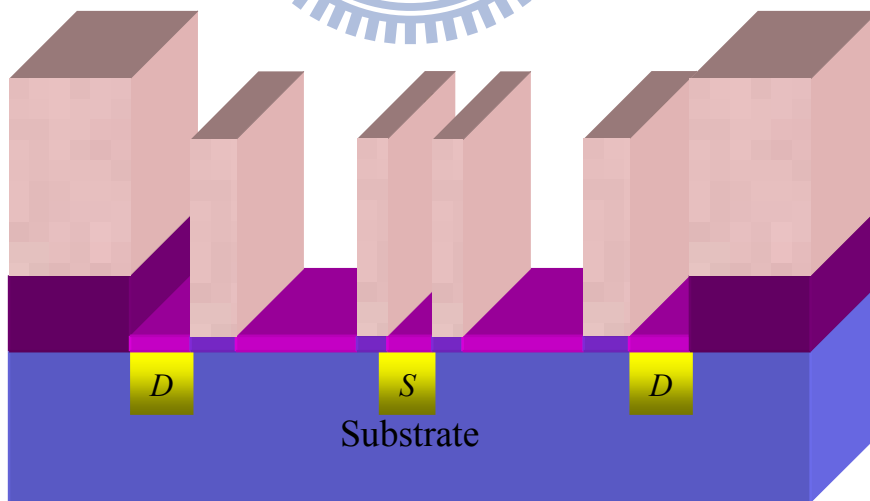
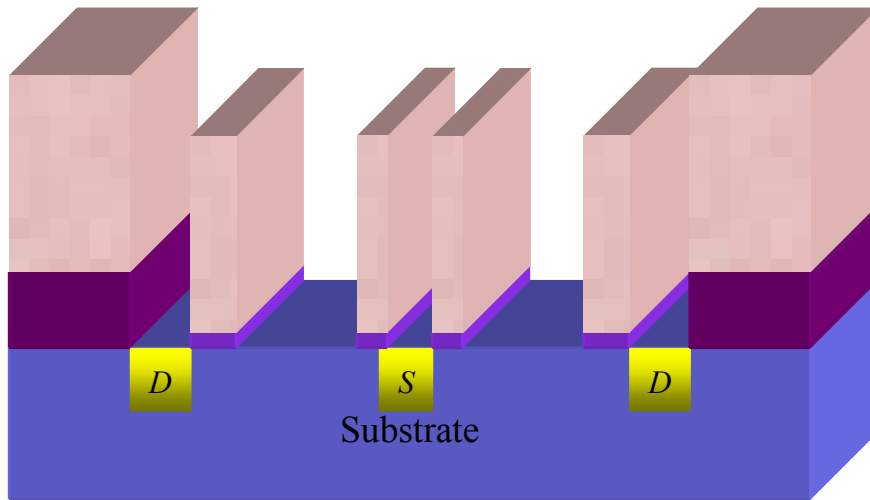
(d)



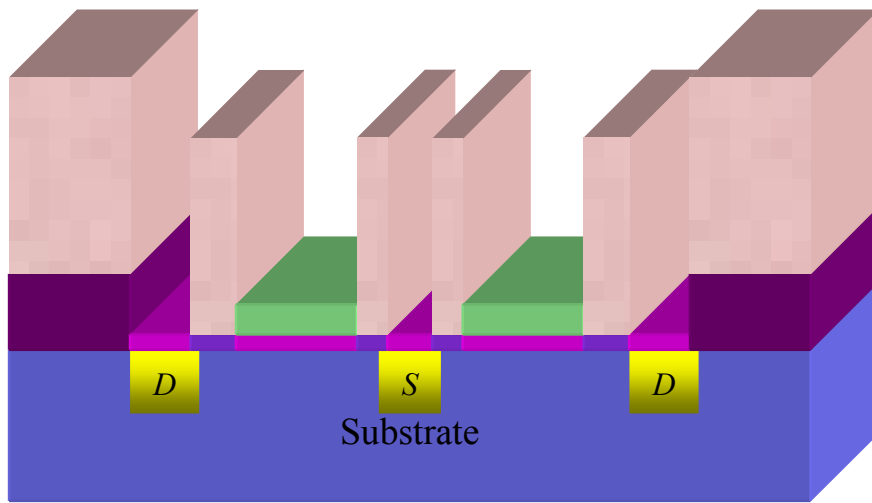
(e)



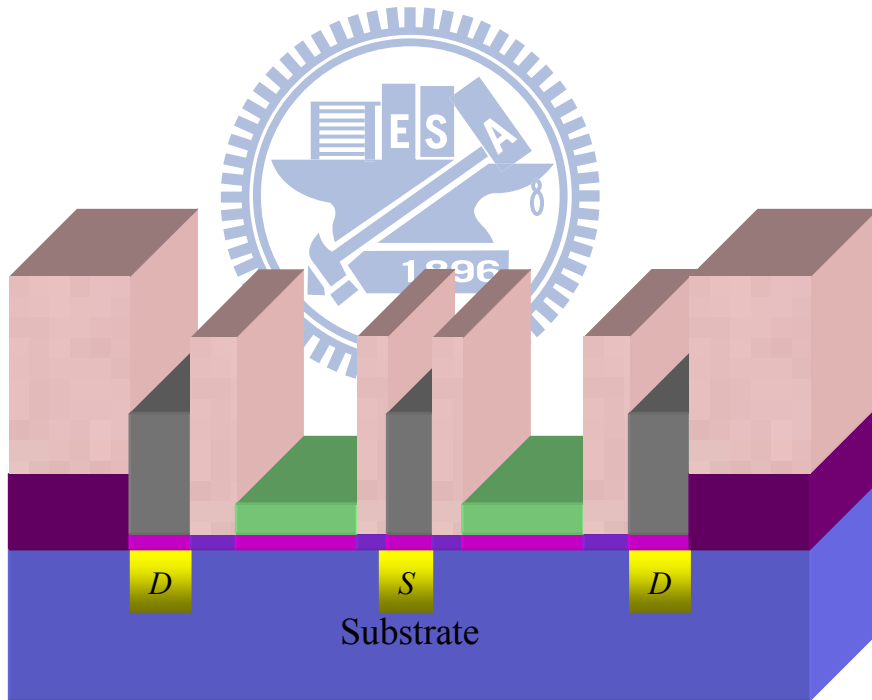
(f)



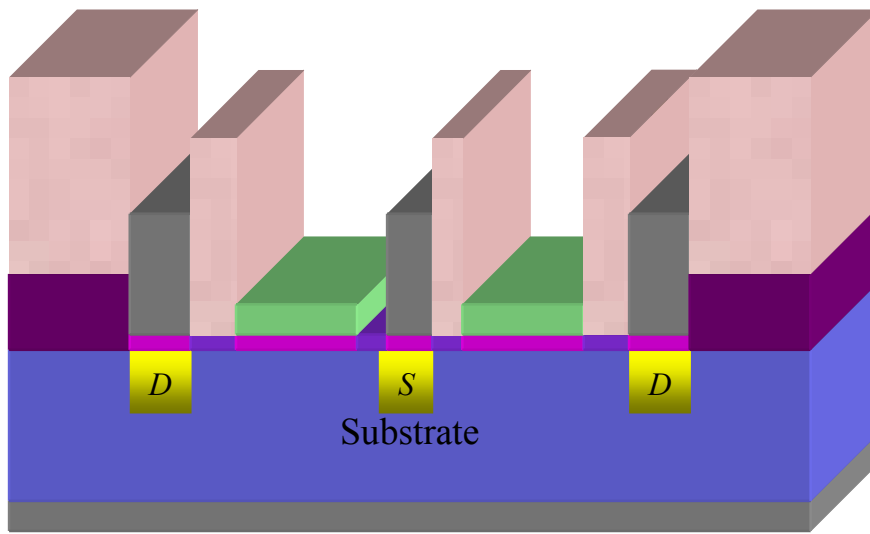
(h)



(i)



(j)



(k)
Fig. 3-1 Fabrication process flow

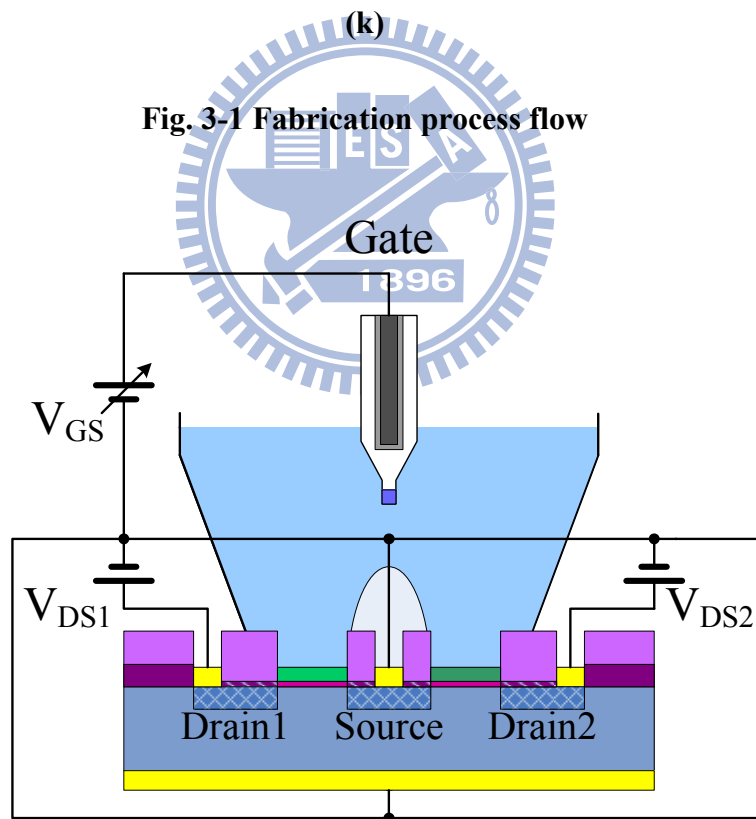


Fig. 3-2 Measurement setup

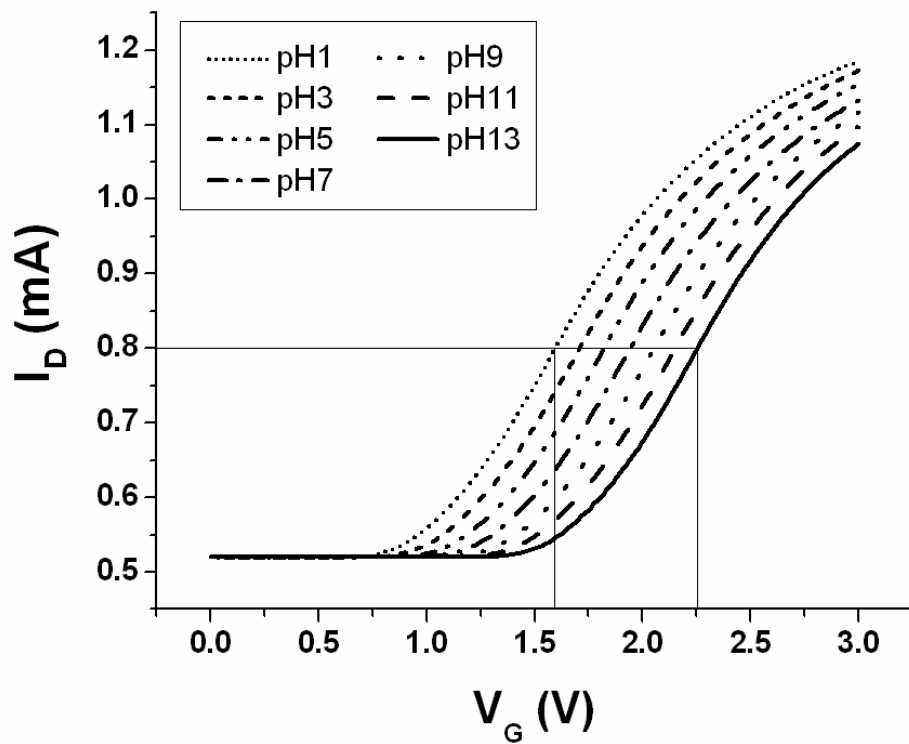
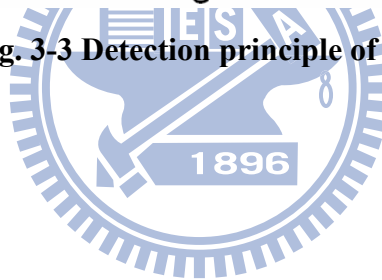


Fig. 3-3 Detection principle of pH



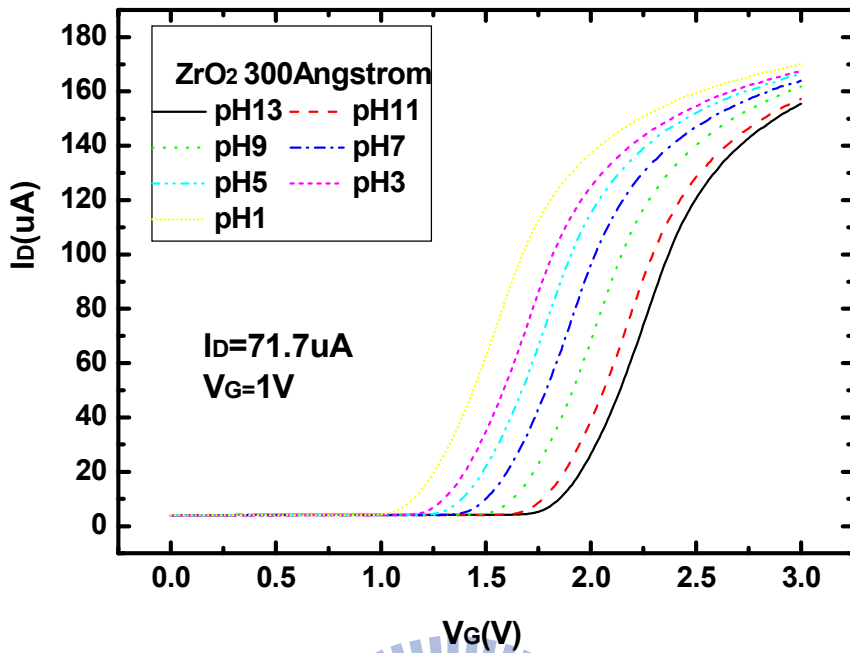


Fig. 4-1 I_D - V_G curve of ZrO_2 to n-type ISFET before drift

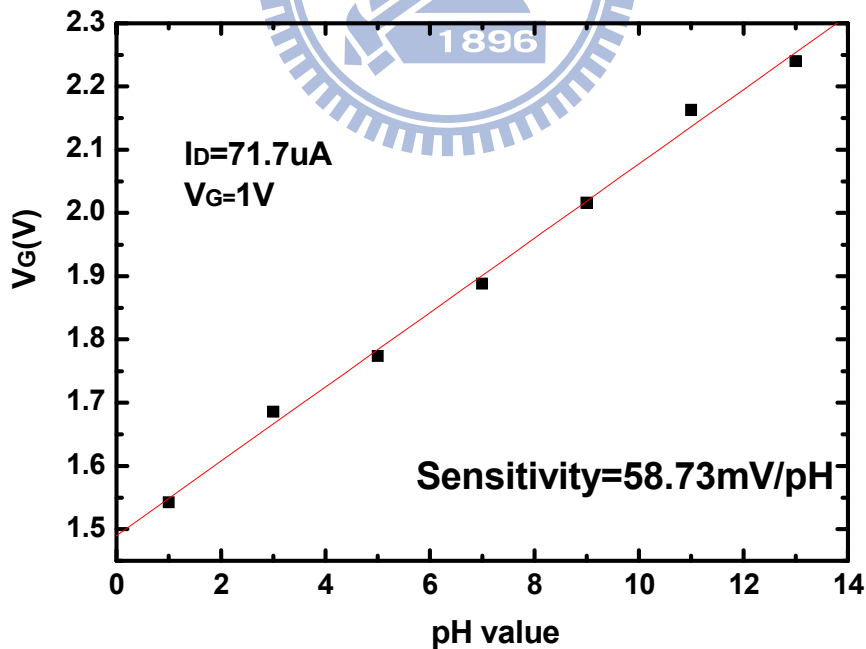


Fig. 4-2 Sensitivity characteristic of ZrO_2 to n-type ISFET

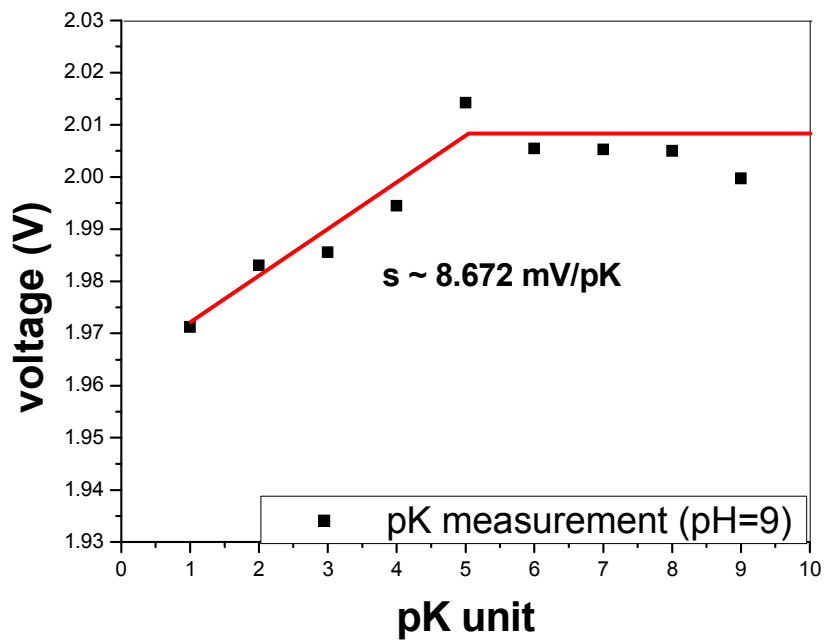


Fig. 4-3 pK response of ZrO₂ ISFET for pH=9 buffer solution

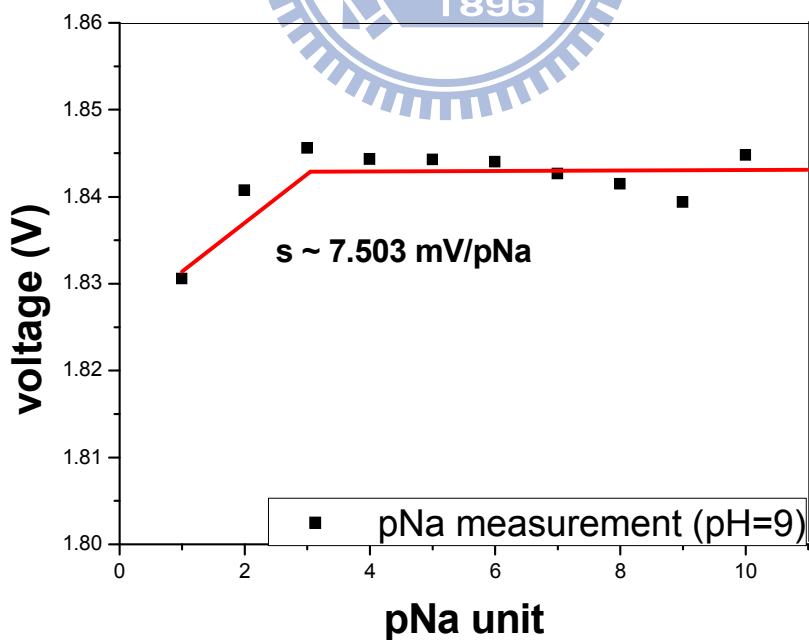


Fig. 4-4 pNa response of ZrO₂ ISFET for pH=9 buffer solution

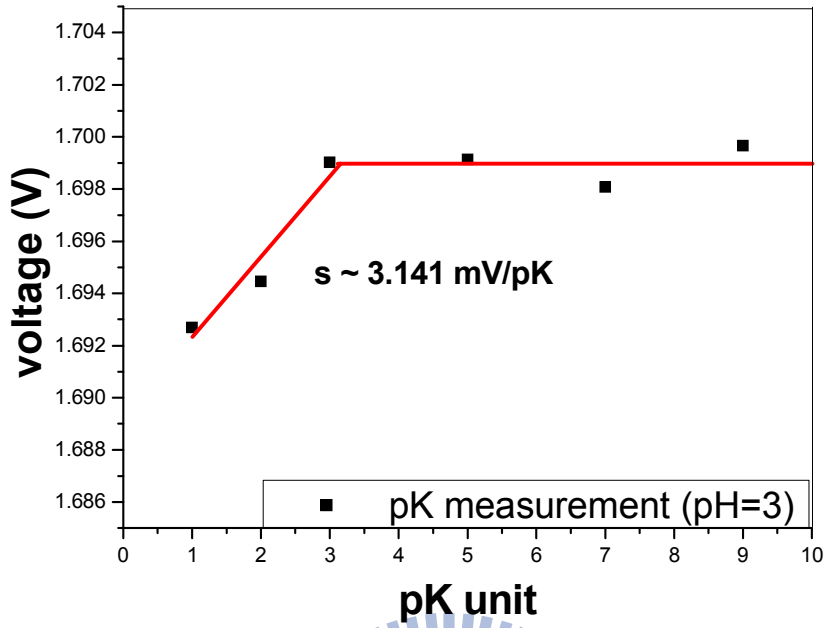


Fig. 4-5 pK response of ZrO₂ ISFET for pH=3 buffer solution

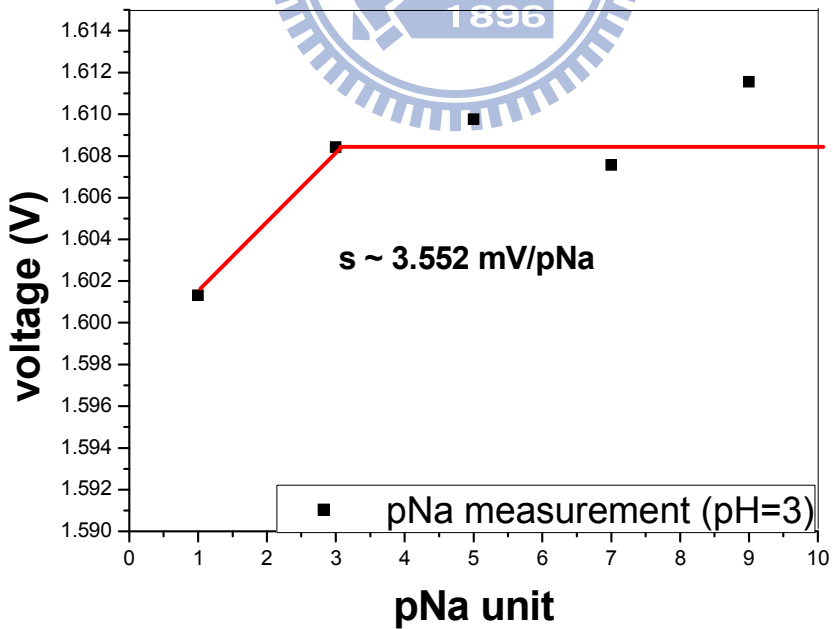


Fig. 4-6 pNa response of ZrO₂ ISFET for pH=3 buffer solution

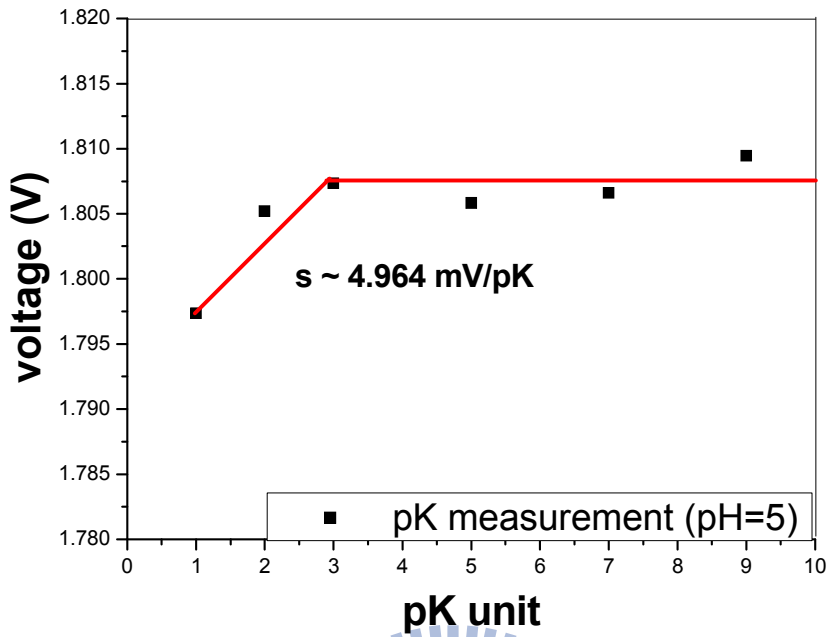


Fig. 4-7 pK response of ZrO₂ ISFET for pH=5 buffer solution

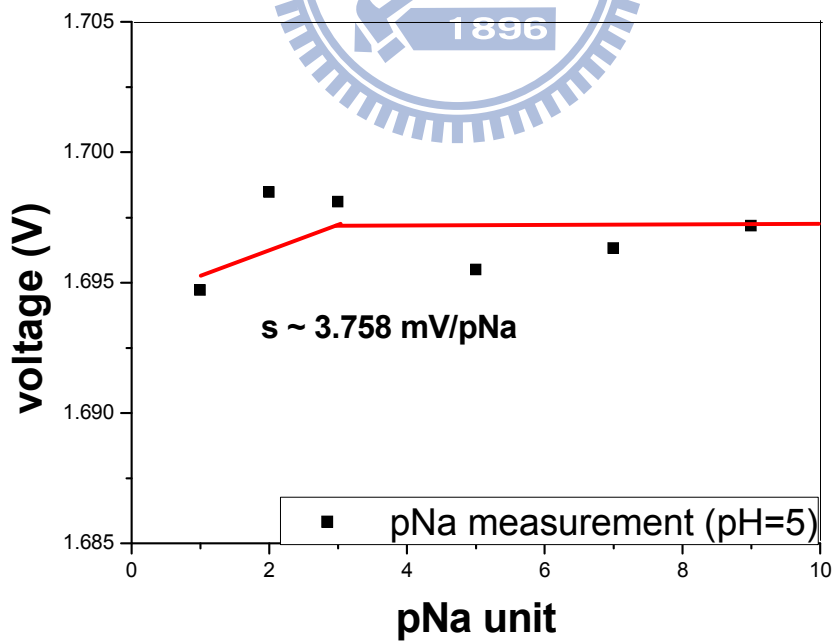


Fig. 4-8 pNa response of ZrO₂ ISFET for pH=5 buffer solution

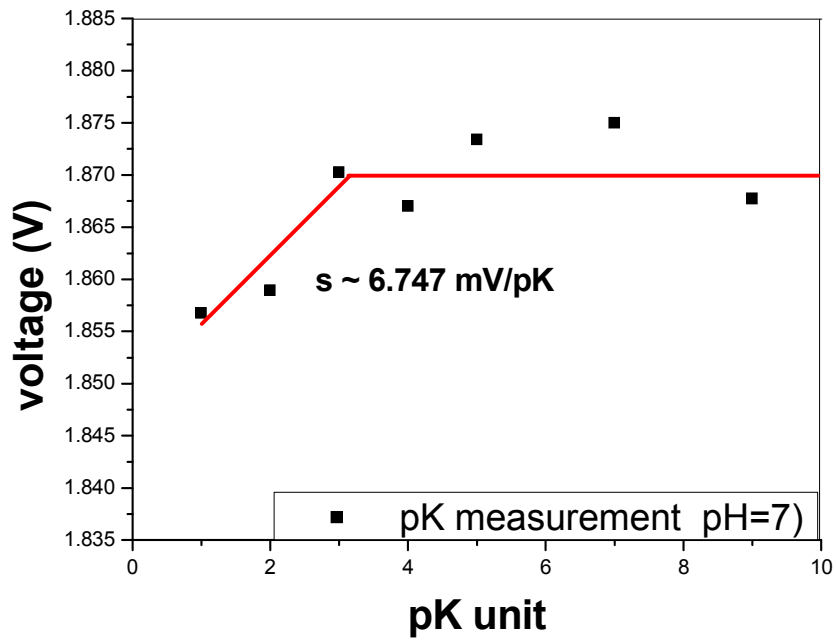


Fig. 4-9 pNa response of ZrO₂ ISFET for pH=7 buffer solution

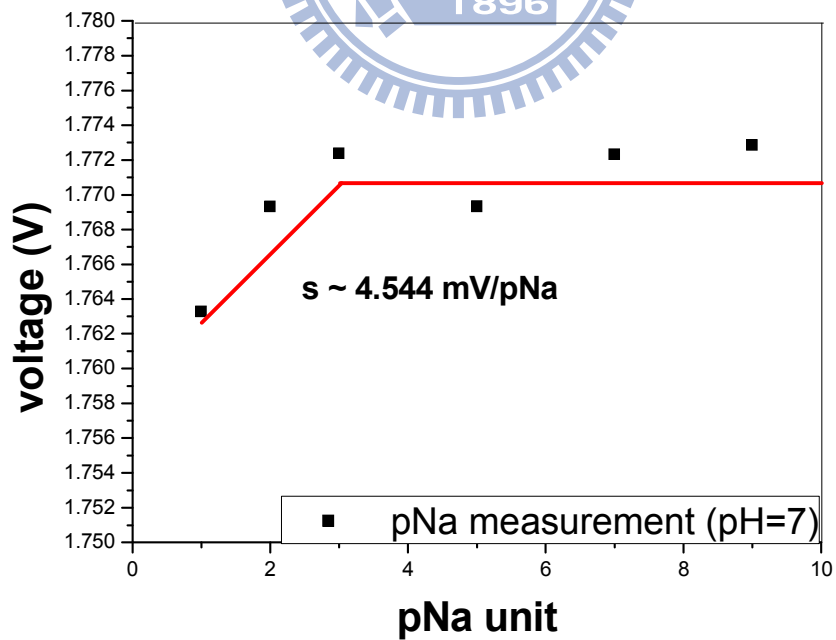


Fig. 4-10 pNa response of ZrO₂ ISFET for pH=7 buffer solution

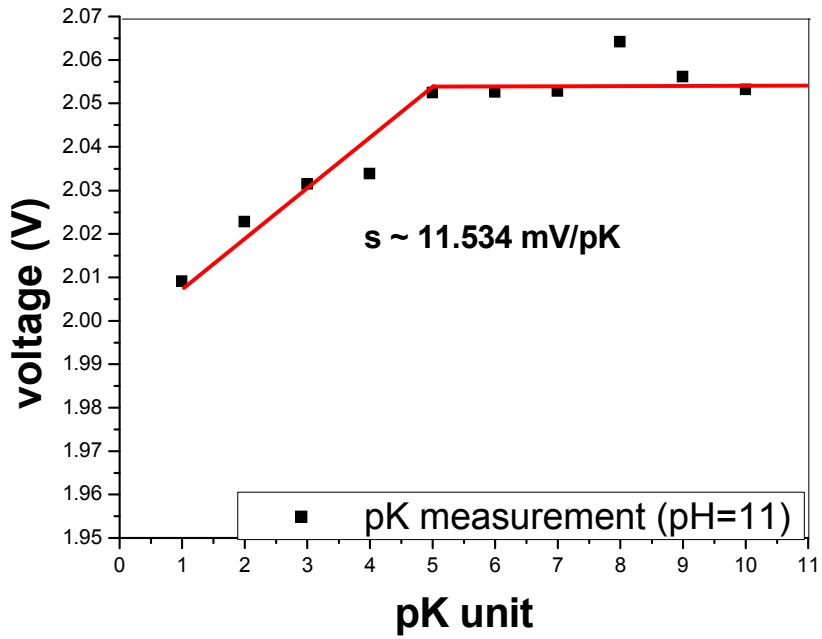


Fig. 4-11 pNa response of ZrO₂ ISFET for pH=11 buffer solution

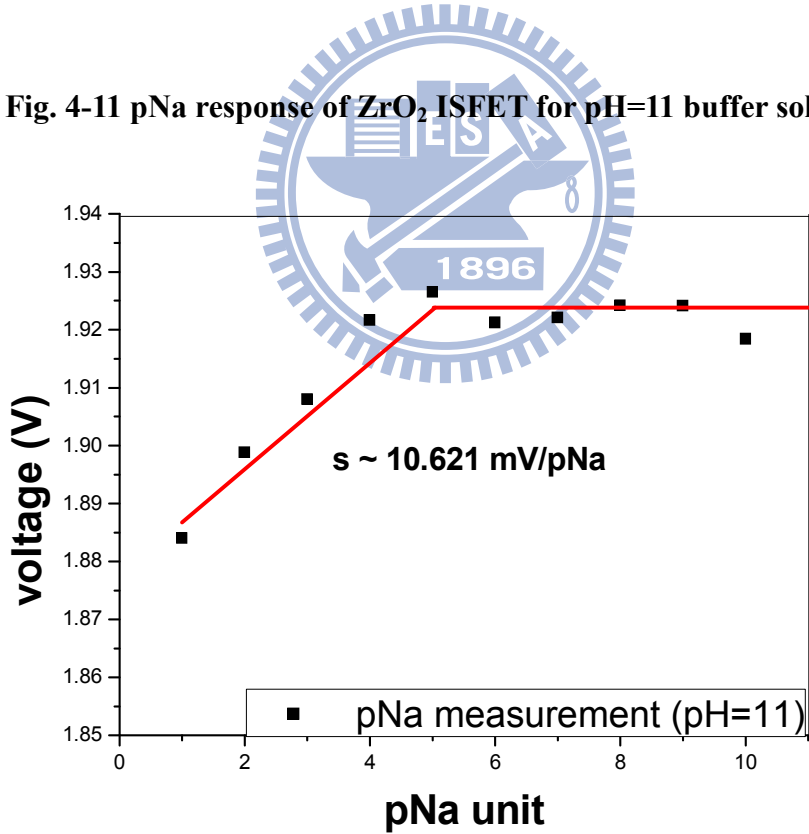


Fig. 4-12 pNa response of ZrO₂ ISFET for pH=11 buffer solution

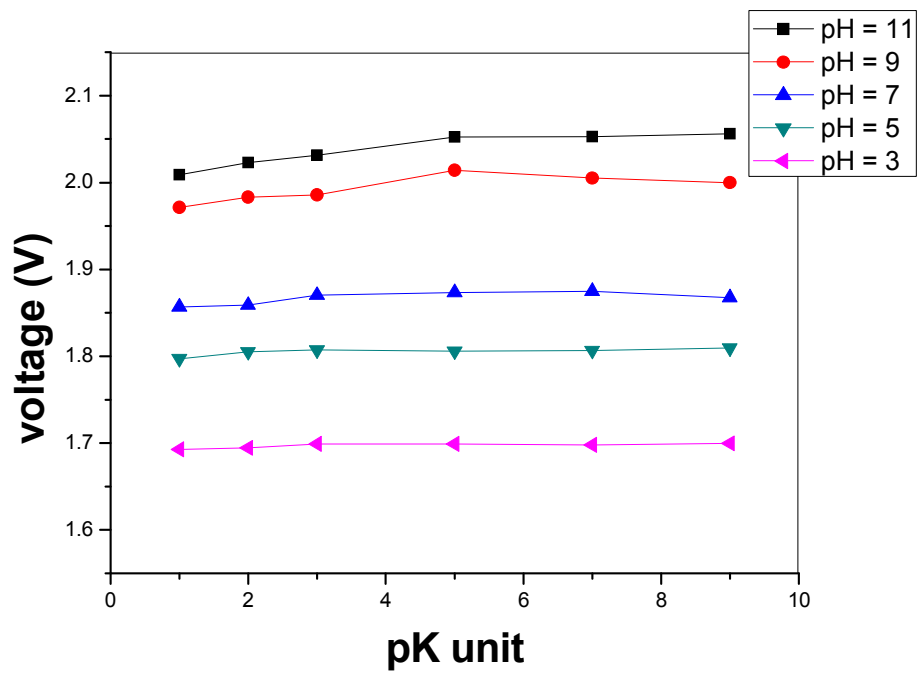


Fig. 4-13 pK response of ZrO₂ ISFET

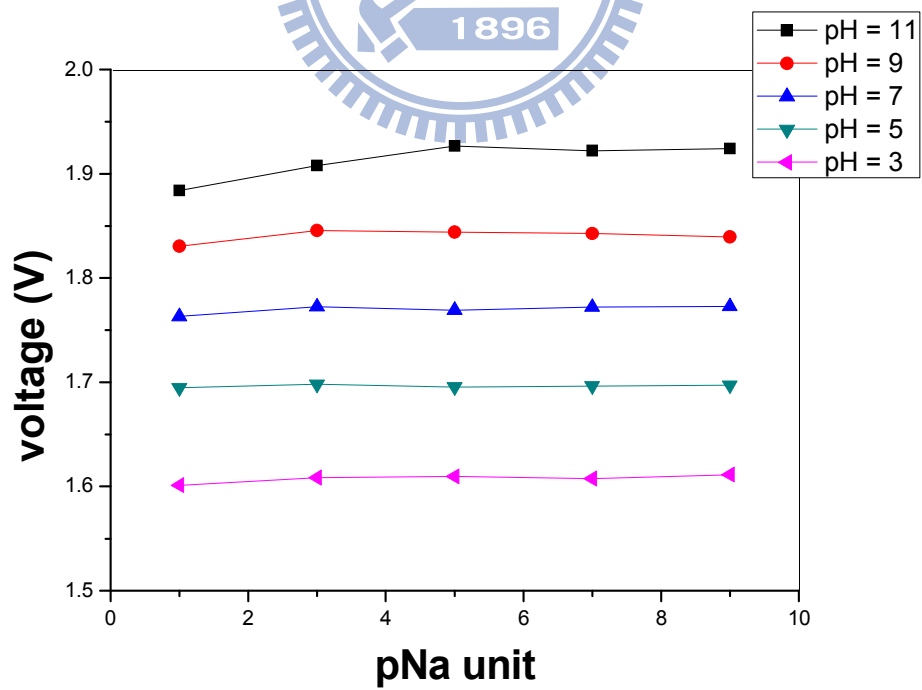


Fig. 4-14 pNa response of ZrO₂ ISFET

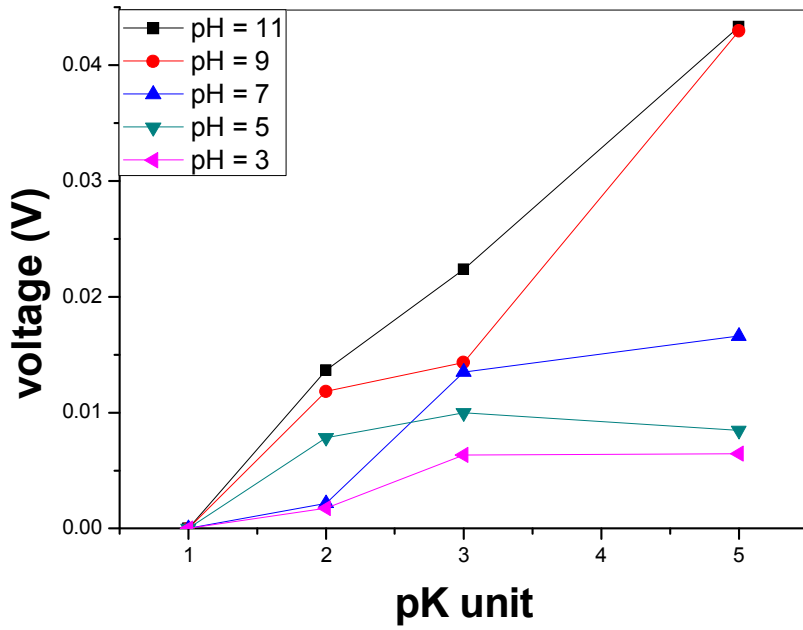


Fig. 4-15 normalized pK response of ZrO₂ ISFET

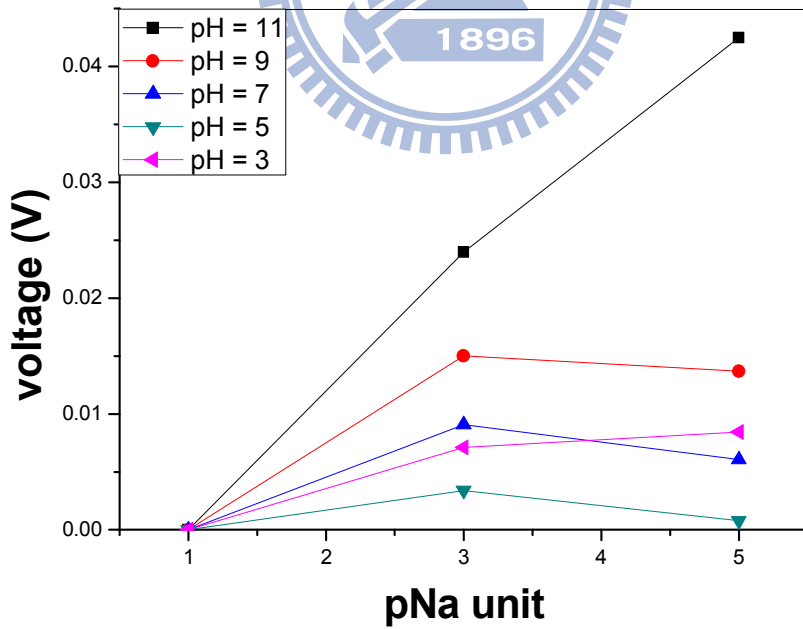


Fig. 4-16 normalized pNa response of ZrO₂ ISFET

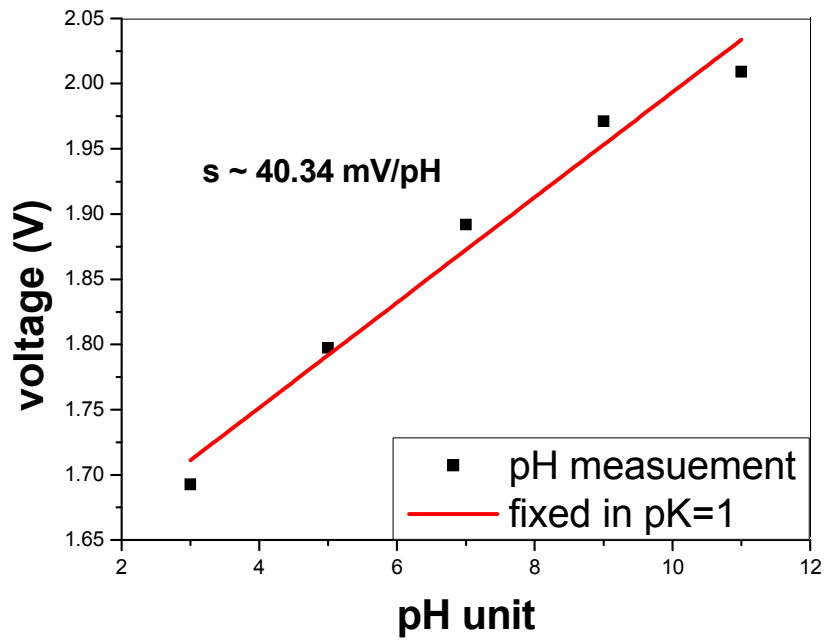


Fig. 4-17 pH response of ZrO₂ ISFET in pK=1 solution

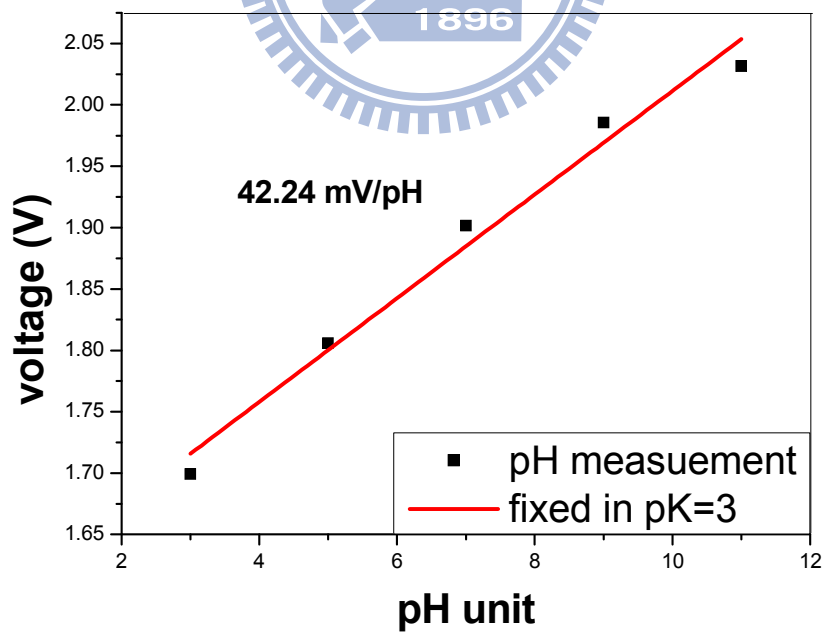


Fig. 4-18 pH response of ZrO₂ ISFET in pK=3 solution

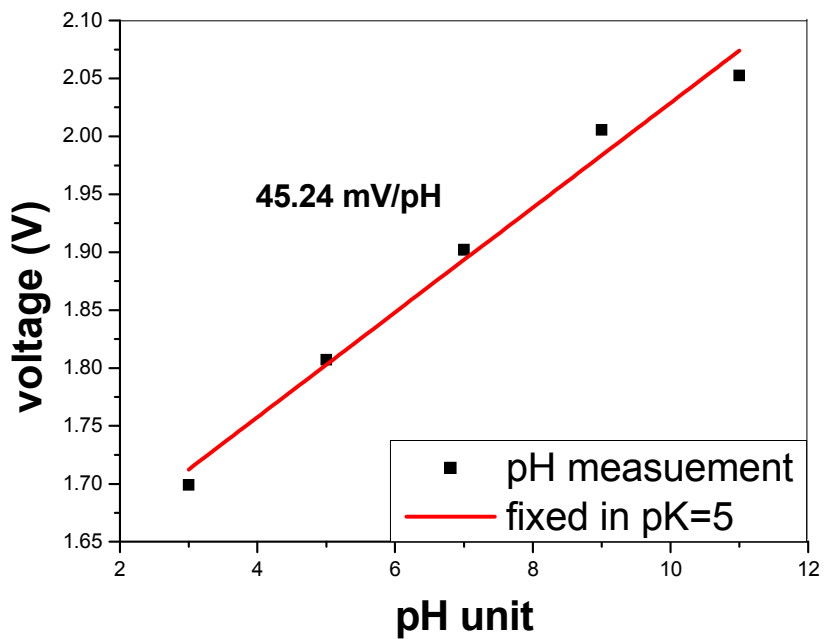


Fig. 4-19 pH response of ZrO_2 ISFET in pK=5 solution

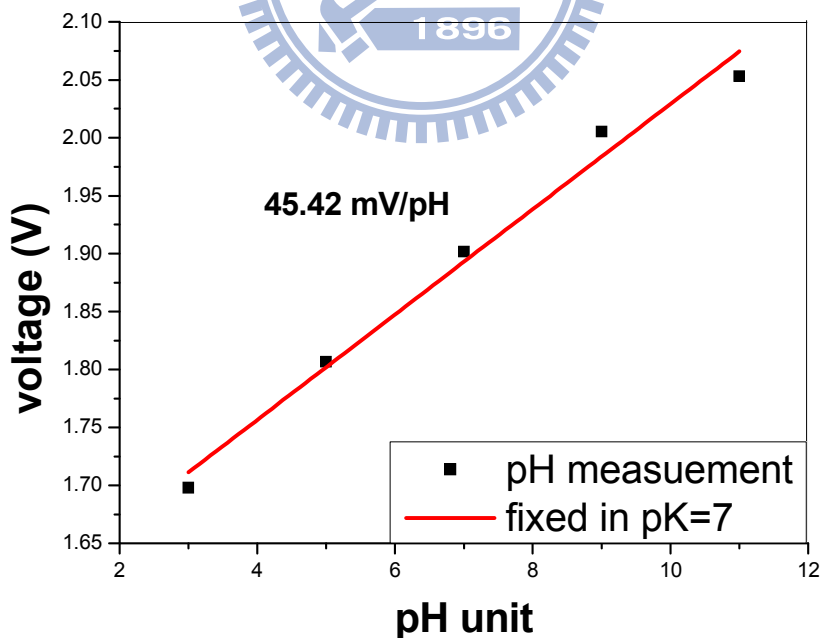


Fig. 4-20 pH response of ZrO_2 ISFET in pK=7 solution

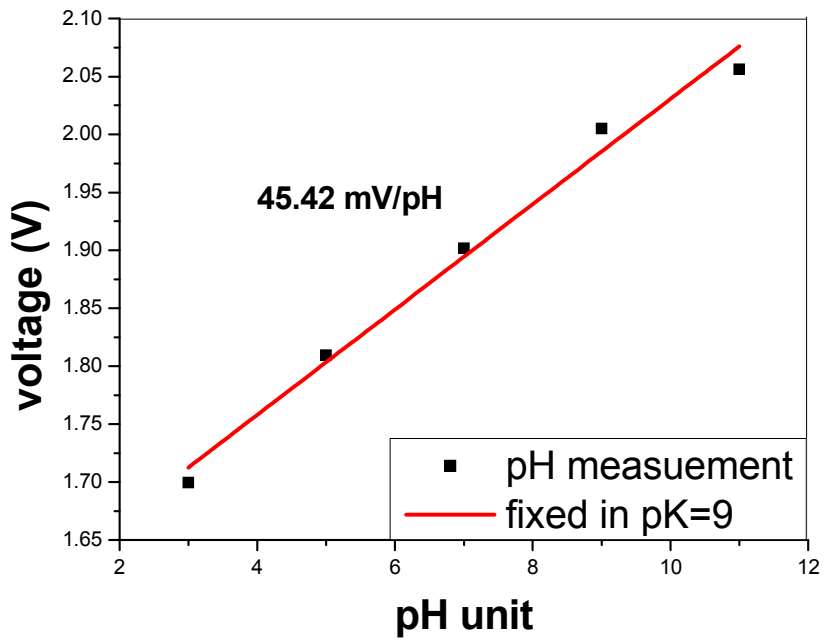


Fig. 4-21 pH response of ZrO_2 ISFET in pK=9 solution

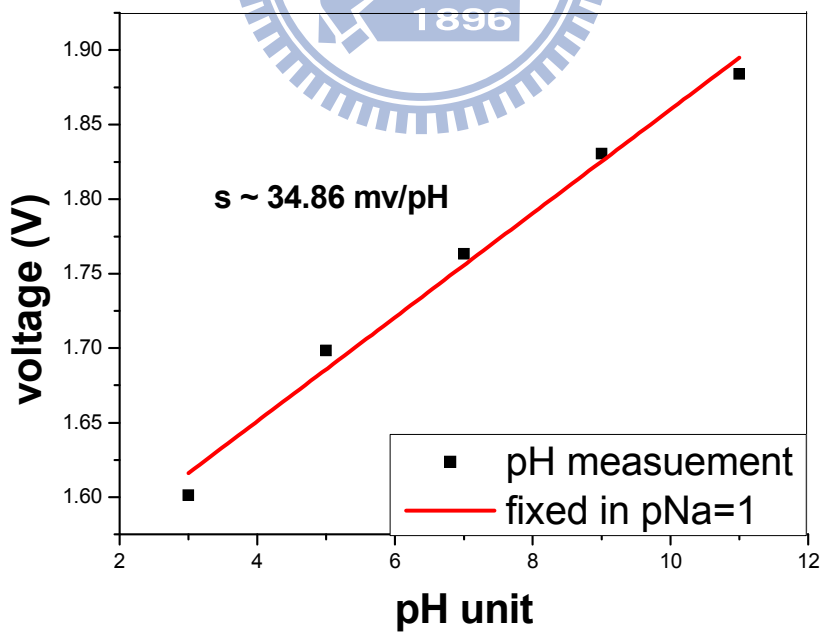


Fig. 4-22 pH response of ZrO_2 ISFET in pNa=1 solution

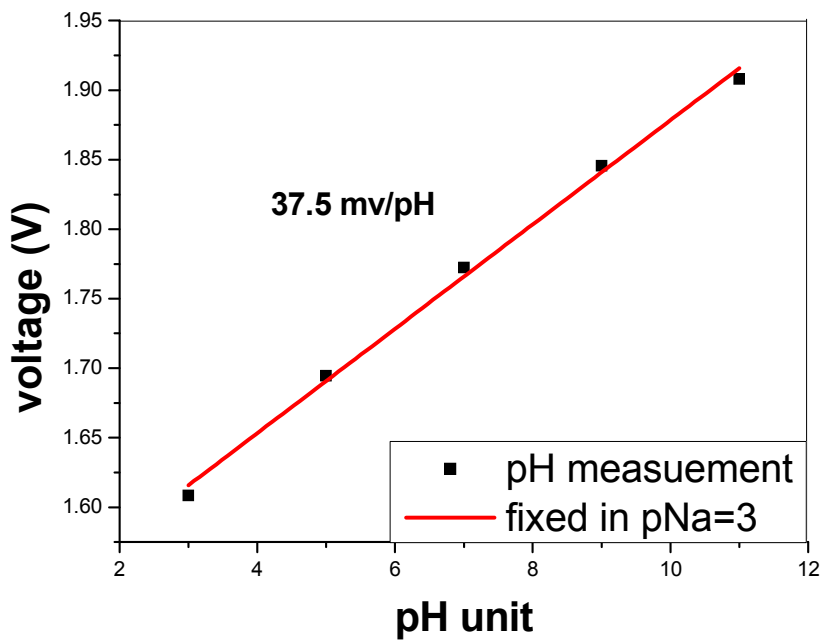


Fig. 4-23 pH response of ZrO_2 ISFET in pNa=3 solution

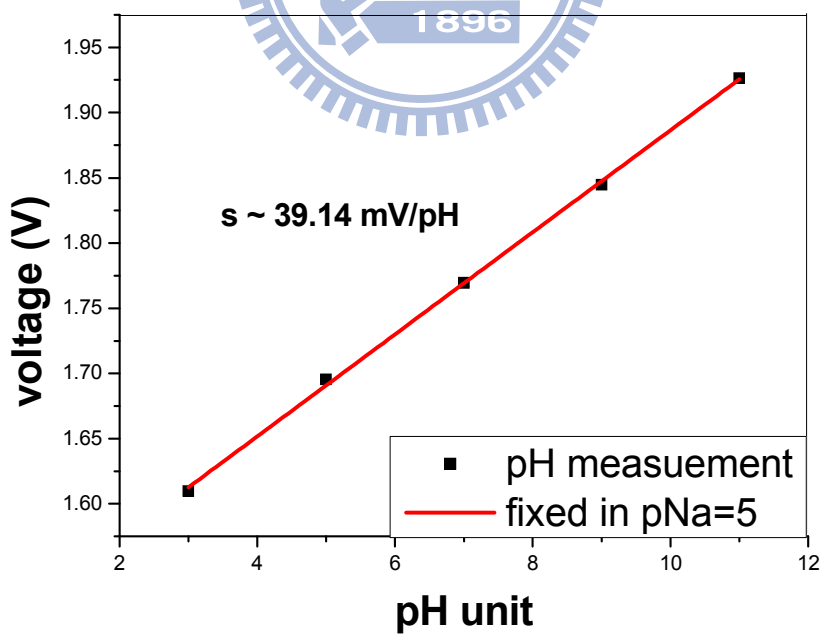


Fig. 4-24 pH response of ZrO_2 ISFET in pNa=5 solution

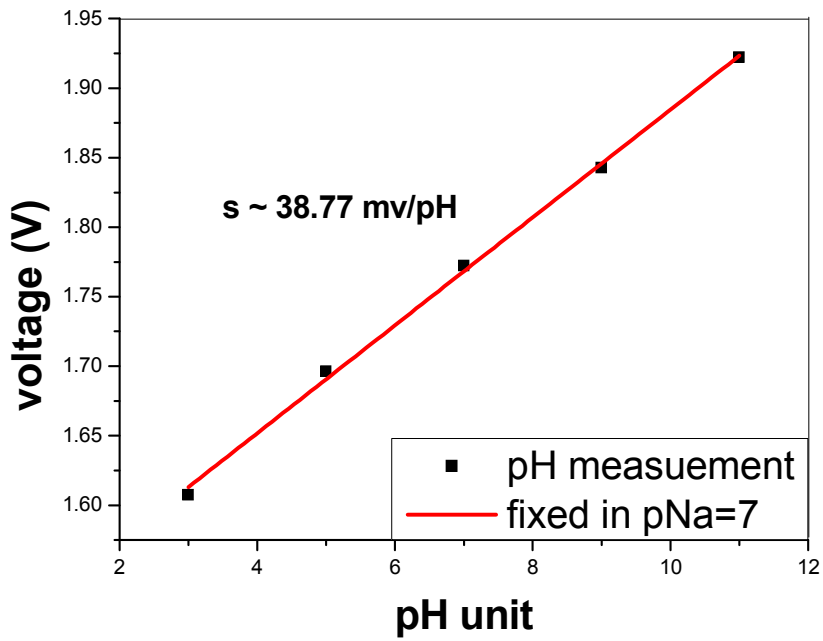


Fig. 4-25 pH response of ZrO₂ ISFET in pNa=7 solution

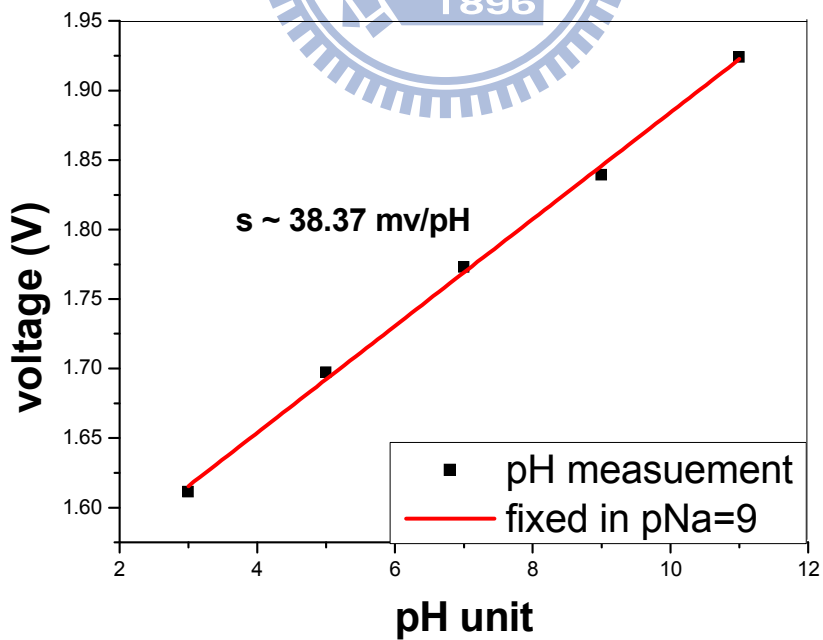


Fig. 4-26 pH response of ZrO₂ ISFET in pNa=9 solution

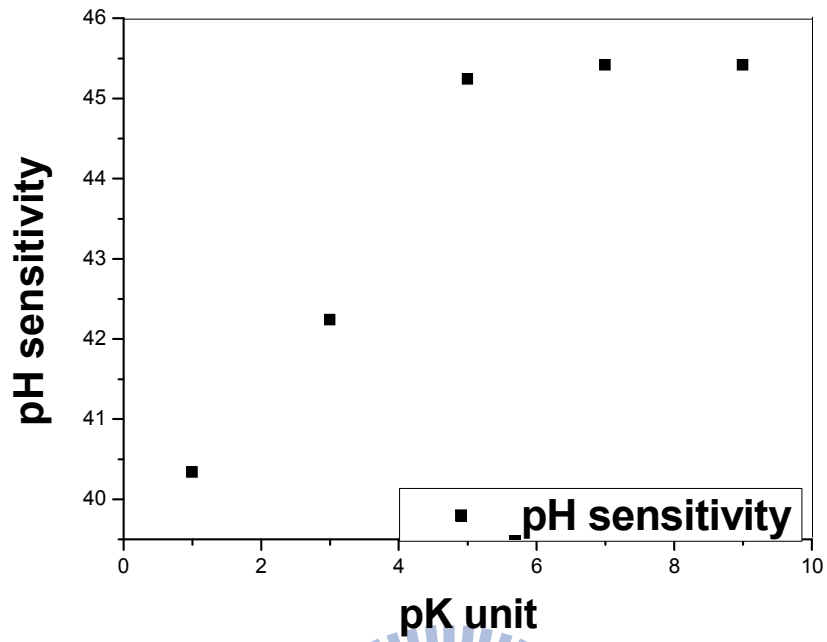


Fig. 4-27 pH sensitivity of ZrO_2 ISFET in different pK solutions

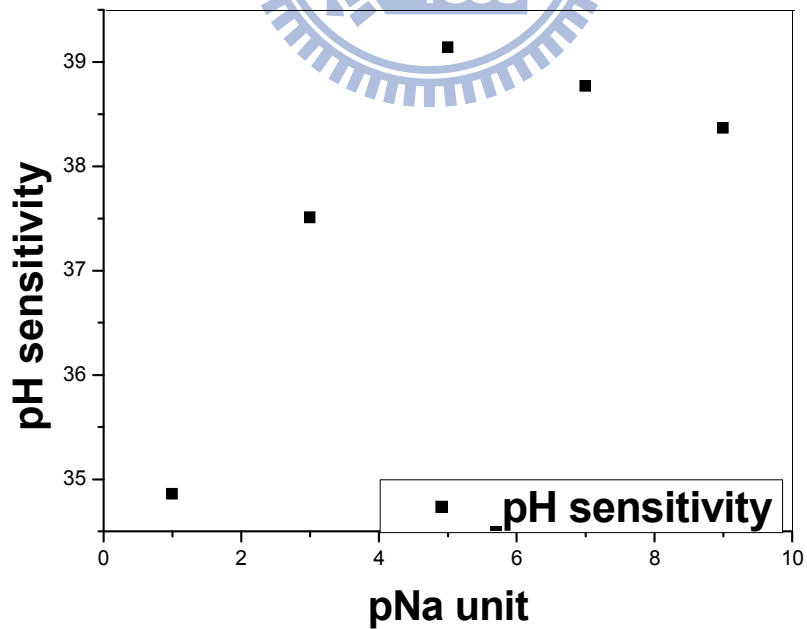


Fig. 4-28 pH sensitivity of ZrO_2 ISFET in different pNa solutions

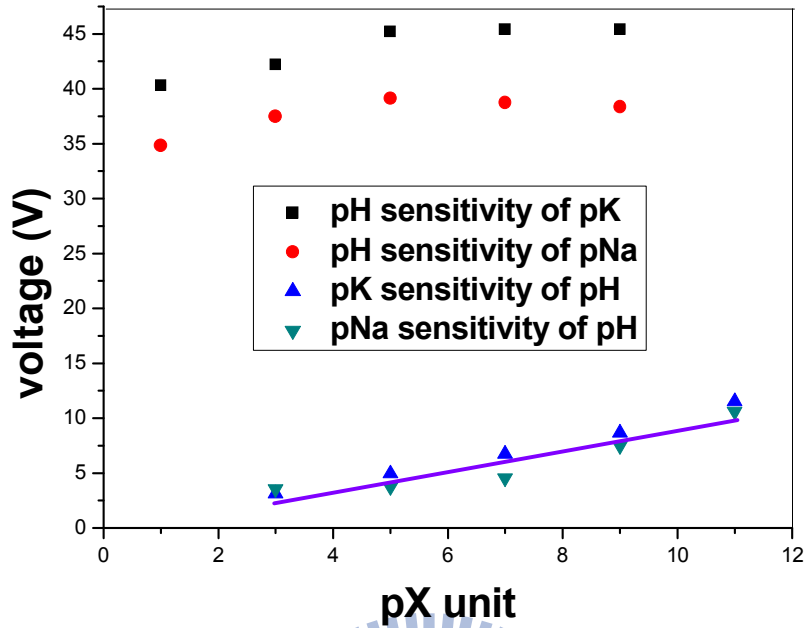


Fig. 4-29 pH sensitivity and pK or pNa sensitivities



Table 1-1 Specifications of wafers

Diameter (mm): 100+/-0.5
Type / Dopant : P / Boron
Orientation : <100>
Resistivity (ohm-cm):1-10
Thickness (μ m) : 505-545
Grade : Prime

Table 1-2 Sensitivity for different sensing layers

Sensing layer	Test range (PH)	Sensitivity (mV/pH)	Reference
ZrO ₂	1-13	57.5	5
SiO ₂	4-10	25-48	6
Si ₃ N ₄	1-13	46-56	6
Al ₂ O ₃	1-13	53-57	6
Ta ₂ O ₅	1-13	56-57	6
SnO ₂	2-10	58	7

**Table 3-1 Specifications of wafers
Parameters of sensing layers deposition with Sputter**

parameters of ZrO₂ sputter
power : 200 W
Ar / O₂ : 24 / 8 (sccm)
Density : 6.51
Acoustic impedance : 14.72
Tooling factor : 0.533
Rate : 0.01 Å / s
pre sputter 60W for 10 min
Pressure : 7.6×10⁻³