

國立交通大學

電機學院微電子奈米科技產業研發碩士班

碩士論文

以Nafion™/PR包埋結構作為參考場效電晶體之感測層研究

The study of Nafion™/PR entrapment structure as REFET sensing film



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中華民國九十七年二月

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摘 要

離子場效電晶體(Ion-sensitive Field Effect Transistor, ISFET)是由 Bergveld 在 1970 年提出，因其元件的特性尺寸小，反應速度快、可承受外部應力，且相容於現今的 CMOS 製程相容性，所以在現今的感測元件開發中具有極大的潛力。在微小化的技術上，必須要整合一個固態參考電極在 ISFET 上，然而先天上固態電極的金屬/溶液界面電位不易穩定，使得研究方向朝向開發參考電極場效電晶體(Reference Electrode Field Effect Transistor, REFET)。REFET 本身是一個低靈敏度的 ISFET，利用一差動放大測量電路來抑制未經處理之金屬固態電極造成的不穩定參考電位。

為得到一個低靈敏度的 ISFET，本篇論文中以利用一質子交換膜 Nafion^T 包覆 PR(FH6400) 的結構來完成一個 REFET，成功的降低了感測層對離子的感測能力，從未包覆前的 57.5mv/pH 降至 8mv/pH。此外，本實驗還利用二氧化鋯(ZrO₂)和二氧化矽(SiO₂)兩種不同的感測層當基底，探討 Nafion 包埋 PR 結構降低了對氫離子感測靈敏度的機制與基底材料之間的關係。最後，再利用不同 Nafion 包埋 PR 條件來做 pH1~pH13 的靈敏度(sensitivity)和漂移(Drift)量測，並研究其元件特性的重現性及可靠度。

我們成功地以 NafionTM 包埋 PR 結構完成對氫離子感測靈敏度的降低，從實驗結果得到其感測靈敏度從未包覆前的 57.5mv/pH 降至 8mv/pH。目前推論其靈敏度的降低主要來自 Nafion 所包埋的 PR 所致，與下層所疊的材料無直接的影響性，且在 Nafion 混合 PR 的結構所製作出 REFET 的感測層可維持在一個穩定且固定的電位且不受外部的離子所影響，由實驗值得到在四小時內的漂移(Drift)量相當穩定。

The study of Nafion™/PR entrapment structure as REFET sensing film

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The logo of National Chiao Tung University is a circular emblem. It features a gear-like outer border. Inside the circle, there is a stylized building or industrial structure. The year '1896' is inscribed at the bottom of the inner circle. The word 'ABSTRACT' is printed in a bold, sans-serif font across the center of the logo.

ABSTRACT

Ion-sensitive Field Effect Transistor, ISFET is proposed by Bergveld in 1970 since its feature of the component is small size, rapid response, strong robustness and be acceptable to the process of CMOS nowadays, it has the great potential on the development of nowadays sensitive component. It has to integrate a solid state reference electrode on the miniaturized technology. However, the metal of solid state reference/electrolyte is not to defined, so the direction of the research moves toward developing Reference Electrode Field Effect Transistor, REFET, which is a low sensitivity ISFET itself using a differential amplifier measuring the circuit to set off the unstable voltage caused by the metal solid state without handling.

For attaining a low sensitivity ISFET, this academic essay utilizes the structure of proton exchange membrane. Nafion entrap with PR (FH6400) to finish a REFET which successfully reduce the sensitivity to 8.3mV/pH. Moreover, this experiment use ZrO₂ and SiO₂ the two different sensing film as the base to discuss the relationship between the mechanism that the structure of Nafion entrap PR reduce the sensitivity to H⁺ ion and the base material. At the end, it also measures the sensitivity of pH1 to pH13 and Drift on the condition of different Nafion entraps PR and research the repeatability and reliance of the component's feature.

We finish successfully the reduction of the sensitivity to H⁺ ion with the structure. Nafion entrap PR, and it get its sensitivity reduces from the 57.5mV/pH unentrapped to 8.3mV/pH in the

experiment result. Now it refer the reduction of sensitivity mainly to Nafion entrap PR and sensing layer beneath Nafion/PR membrane will affect the overall performance in sensitivity and drift. The sensing layer of REFET manufacture on the structure of Nafion mix PR could maintain a stable potential without the effect of the outer ion, the Drift quantity is very stable in four hours according to the experiment data.



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明聰

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Chapter 1

Introduction

1.1 What is ISFET?

The fervor of researching ISFET device started from P.Bergveld present Ion-sensitive-field-effect-transistor (ISFET) [1] which use SiO_2 as gate in 1970, since device combine Metal-oxide-semiconductor-field-effect-transistor (MOSFET) with the concept of traditional Ion-sensitive-electrode. The main difference of structure is replacing the traditional MOSFET metal gate with SiO_2 layer of insulation as sensing layer. The sensitivity and the pH value in buffer solution can be calculated by the current transformation caused by H^+ ions difference on sensing layer when component dropped into different pH buffer solution.

Incipient research drawback is there is unstable reference voltage waiting for the solution of measure, so the researcher adds a stable reference electrode in succession to waiting for the solution of measure in the later research. Different application of material is found out because the property is not ideal when the device with SiO_2 sensing layer. For instance, the property of (Table 2-1) ZrO_2 [2], Si_3N_4 [3], Al_2O_3 [4], Ta_2O_5 [5] and SnO_2 [6] sensing layer are all better than SiO_2 sensing layer. With the study of sensing layer, some material is found can detect different ions that are the structure based in ISFET, for example, K, Na, Ca ions in the human body, hence, ISFET open the way to BioElectronics further. The structure can apply on medicine, agriculture and chemistry widely.

For the mature of IC process techniques, ISFET has developed to another peak. There are some features:

- (1) Small size
- (2) Rapid response
- (3) Strong robustness
- (4) Compatible the CMOS process nowadays and lower the cost

But the stability and minimization of the component is another developing worry, if it replace the traditional glass electrodes with solid-state electrode made by noble metals, it would produce an unstable voltage though benefit the minimization. The significant challenge is finding a structure with stable voltage after the minimization, and it also open up a new page on ISFET field to Nano Technology.

1.2 Application of various kinds of electrodes in ISFET

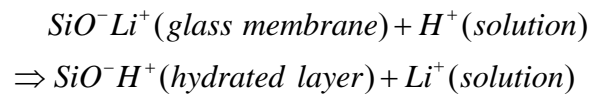
In the research of ISFET, it can produce the electrodes which stabilize the electric potential to utilize one successively, to analyze pH value in the solution. The electrodes applied most are glass electrode and solid-state electrode. (Shown in Fig.1-3)

1.2.1 The glass electrode

The first glass electrode is developed by Cremer in 1906 and after that many efforts have been to take up with improves its application. The glass electrode is composed of a bulb of glass membrane, which only allows hydrogen ions to pass through a small channel, and a buffered chloride solution inside in contact or a fixed concentration of HCl with an internal reference electrode, which use of Ag/AgCl, as shown in Fig. 1-4.

When the glass electrode immersed in pH buffer solution, it can produce ion

transfer in interface of bulb surface and pH buffer solution. This reaction can for hydrogen ion in the solution exchanged stable and build up hydrogen ions on surface of ISFET [6]. For the purpose of good and stable sensing glass, the sensing glass often contained other component like Na₂O-CaO-SiO₂, Li₂O-BaO-SiO₂, Li₂O-Cs₂O-La₂O₃-SiO₂, et al. [7]. For example, the introducing of alkali (ex. Li) oxide will break the stable Si-O bond and result the change between Li⁺ and H⁺:



At reaction, the charges produced and regard as the carrier by Li, with the defect principle of the glass; jump from valance band to another, becoming electric potential competently, the relation between it activity of hydrogen ions is according to Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln \alpha_{H^+}$$

where E=electrode potential, E₀=standard potential of the electrode, R=gas constant (8.31441JK⁻¹mol⁻¹), T=temperature (in Kelvin scale), n=valance (n=1 for hydrogen ions), F=Faraday constant and α_{H^+} =activity of hydrogen ions.

According to equation, providing that at one side of the interface the activity of the ion of interest is kept constant, the electrode potential is a direct logarithmic function of the ion activity on the other side [7]. Then can easily define a stable potential, provided that no interference reaction will occur. The volume of glass electrode is too large. To apply ISFET more generally, it is necessary to miniaturize the glass electrode. The ISFET-based pH sensor is a new technique for pH detection and it has a big potential for widely application because of the advanced IC fabrication techniques nowadays.

1.2.2 The solid-state reference electrode

The solid-state reference electrode materials usually use noble metal as Ag, Pt, et al, but it relatively expensive. However the characteristic of the noble metal material is steady, it is difficult reaction in the solution. But it is unable to produce ion-exchange reactions like glass electrode. When turn on a potential in solid-state reference electrode, it causes the main factor of the unstable voltage because the metal surface forms the ion absorbs unstably. The characteristic is just like electric capacity. Some scholars utilize this characteristic; make another model of detection pH sensor [8]. (Shown in Fig1-5) The axiom is utilizing two ISFET; one of the ISFET is high sensitivity, the other is low sensitivity. In the same condition, ISFET use solid-state reference electrode to give a voltage. Solid-state reference electrode will produce an unstable voltage, but the value of pH buffer solution can be measured by circuit principle of op amplifier.

The unstable problem may come from the redox reaction or other reactions at noble metal reference electrode and the liquid interface, i.e. the liquid/solid interface. In ISFET, to integrate a stable potential at the interface is a way to the solid-state reference electrode.

1.3 Motivation of this work

There are two ways for ISFET to attain diminution, one is replacing ISFET' s glass electrode with solid state electrode, and another is REFET. Because solid state electrode in electrolyte interface is thermodynamically undefined, it will produce an unstable electrolyte. If modifying the solid-liquid interface is difficult, it use two devices, ISFET and REFET both output on a DIFFETENTIAL AMPLIFER and REFET make low

sensitivity to an ISFET. There are two popular manufacturing way of REFET now, one is in the original sensing layer with plasma treatment, another is deposition on top of sensing film with polymer membrane. This study use polymer as sensitivity to compare with DRIFT, and it make a better REFET.

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Chapter 2

Theory Description

2.1 The concept of pH

pH is a measure of the acidity or alkalinity of a solution. The letters "pH" stands for Potential of Hydrogen. Aqueous solutions at 25 °C with a pH less than seven are considered acidic, while those with a pH greater than seven are considered alkaline. The pH of 7.0 is defined as 'neutral' at 25 °C because at this pH the concentration of H_3O^+ equals the concentration of OH^- in pure water[1]. The name, pH, can be derived from a combination of "p" the word power with "H" for the symbol of the element hydrogen [2]. The formula for calculating pH value is defined as:

$$pH = -\log_{10} \alpha[H^+] \quad (2-1)$$

where α is the activity coefficient and $[H^+]$ is the molar concentration of solvated protons in units of moles per liter. From equation (2-1) pH is used to specify the degree of acidity or basic of an aqueous solution at a given temperature. The term activity is used because pH reflects the amount of available hydrogen ions, not the concentration of hydrogen ions.

2.2 Theory of ISFET

P. Bergveld developed Ion-selective field effect transistors (ISFETs) first in 1970s. The ISFET was developed by MOSFET (Metal Oxide Semiconductor Field Effect Transistor). The ISFET used to measure ion concentration in solution. Besides the gate electrode is replaced by reference electrode and inserted in buffer solution which contact with the sensing layer. The reference electrode provide for stable ion transfer, because the electrolyte potential will be unstable and is influenced by noise easily without it. The structure of MOSFET and ISFET are shown in Fig 2-1. [3]

2.2.1. Operation of ISFET

The ISFET structure is similar to MOSFET. The general expression for the drain current of MOSFET and thus also of the ISFET in non-saturated region is:

$$I_D = \beta(V_{gs} - V_T - \frac{1}{2}V_{ds}) \cdot V_{ds} \quad (2-2)$$

in which β is a parameter determined by the mobility μ of the majority carrier in the inversion layer, C_{ox} is the oxide capacity per unit area and W and L is the width and length of the channel, according to:

$$\beta = \mu C_{ox} W / L \quad (2-3)$$

The threshold voltage V_T is given by:

$$V_T = \frac{\Phi_M - \Phi_{si} - \frac{Q_{ox} + Q_{ss} + Q_B}{C_{ox}} + 2\phi_F}{q} \quad (2-4)$$

With Φ_M the workfunction of the gate metal, Φ_{si} the silicon workfunction, Q_{ox} the fixed oxide charge and Q_{ss} the surface state density at the silicon surface, Q_B is the depletion charge in the silicon and ϕ_F the Fermi-potential.

From equation (2-4) it can be seen that the threshold voltage of a MOSFET is determined by material properties such as the workfunction Φ and charge accumulation. For a stable operation of a MOSFET it is of importance that the threshold voltage is constant which can be achieved by applying an appropriate MOS process such as ion implantation. Equation (2-2) shows that the drain current is now only a function of the gate voltage, using a constant drain-source voltage [1].

In the case of ISFET has different item. The threshold voltage contains also terms which the interface between the liquid and oxide, the others between liquid and reference electrode. The term is the reference electrode potential relative to vacuum E_{ref} , which includes Φ_M . The interface potential at the gate oxide-electrolyte interface is determined by the surface dipole potential of the solution χ_{sol} , which is a

constant, and the surface potential Ψ_0 , which results from a chemical reaction, usually governed by the dissociation of oxide surface groups. The resulting equation for an ISFET is thus given by:

$$V_t = E_{ref} - \Psi_0 + \chi_{sol} - \frac{\Phi_{Si}}{q} - \frac{Q_{ss} + Q_{ox}}{C_{ox}} + 2\phi_f \quad (2-5)$$

The Ψ_0 of this term which makes the ISFET sensitive to the electrolyte pH, which is controlling the dissociation of the oxide surface groups. To design a pH sensitive ISFET with a maximum sensitivity and selectivity need applies on a detailed investigation of the oxide-electrolyte interface in order to be able to choose the best oxide, which is not a priori silicon dioxide as used for MOSFETs.[4]

2.2.2 Oxide/electrolyte interface

The site-binding model introduced by Yates et al [5]. The oxide/electrolyte interface will build up charge when the ISFET in pH solution, so site-binding model explains oxide-electrolyte interface basic theory of ISFET. In fig 2-2, fig 2-3, and fig2-4 are indicated that reaction can between protons in the solution and hydroxyl groups formed at the SiO₂-solution interface. [1][4][6] The mechanism can describe interface for the combination and generation of hydroxyl. To describe the equilibrium the so-called amphoteric SiOH surface sites and H⁺-ions in the solution. The surface reaction:



where the H_s^+ represents the protons at the surface of oxide, K_a and K_b are the chemical equilibrium constants.

the equilibrium constants K_a and K_b are given by:

$$K_a = \frac{[SiO^-][H^+]_s}{[SiOH]} \text{ or } \frac{v_{SiO^-} \cdot a_{H^+_s}}{v_{SiOH}} \quad (2-8)$$

$$K_b = \frac{[SiOH_2^+]}{[SiOH][H^+]_s} \text{ or } \frac{v_{SiOH} \cdot a_{H^+_s}}{v_{SiOH_2^+}} \quad (2-9)$$

where S means the surface.

The potential between insulator oxide and electrolyte solution causes a proton concentration difference between the bulk and surface (Fig. 2-4) that based on Boltzmann. [7]

with Boltzmann equation :

$$a_{H^+_s} = a_{H^+_b} \exp \frac{-q\psi_0}{kT} \text{ or } (pH_s - pH_b) = \frac{q\psi_0}{kT} \quad (2-10)$$

where the $a_{H^+_s}$ and $a_{H^+_b}$ are activities of H^+ at oxide surface and solution bulk, k is the Boltzmann constant, T is the absolute temperature, pH_s is the pH value at the oxide surface, pH_b is the pH value in the solution bulk, ψ_0 is surface potential.. then we can get the fixed number of surface sites per unit area, N_s

$$N_s = v_{SiOH} + v_{SiO^-} + v_{SiOH_2^+} \quad (2-11)$$

where v is

to depend on some electrochemical knowledge and math derivation, a surface charge density $\sigma_0 [C/m^2]$ exist:

$$\sigma_0 = q(v_{SiOH_2^+} + v_{SiO^-}) = -qB \quad (2-12)$$

where B is the number of negatively charged groups minus the number of positively charged groups in mole per unit area. There will be no net charge on the surface when the number of positively and negatively charged groups on the surface is equal and consequently. We say the pH value at the point of zero charge is pH_{pzc} in

this case. 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} [8].

σ_o is given by:

$$\sigma_o = qN_s \left(\frac{a_{H_s^+}^2 - K_a K_b}{K_a K_b + K_b a_{H_s^+} + a_{H_s^+}^2} \right) \quad (2-13)$$

A detailed derivation can see the Ref [1] [4]. When we obtain the surface charge density, we can find the intrinsic buffer capacity; to take the pH variation on surface can be defined:

$$\frac{\partial \sigma_o}{\partial pH_s} = -q \frac{\partial B}{\partial pH_s} = -q \beta_{int} \quad (2-14)$$

β_{int} is known as intrinsic buffer capacity, to depend on the activity of surface H^+ -ions. Finally we can obtain the equation for the intrinsic buffer capacity:

$$\beta_{int} = N_s \frac{K_b a_{H_s^+}^2 + 4K_a K_b a_{H_s^+} + K_a K_b^2}{(K_a K_b + K_b a_{H_s^+} + a_{H_s^+}^2)} 2.3 a_{H_s^+} \quad (2-15)$$

It is only capable of buffering small changes in surface pH (pH_s), and not in bulk pH(pH_b), so it is called intrinsic in this case. The values of N_s , K_a and K_b are oxide dependent. It can be seen that the number of surface sites influences the intrinsic buffer capacity. Hydrolysis of the surface will create more surface sites and thus a rise in the intrinsic buffer capacity and sensitivity. [4]

Both surface reaction and electrolyte will influence the surface charge density. In order to charge neutrality, the surface charge σ_o was balanced off an equal but opposite charge in electrolyte. The two opposite charges, σ_o and σ_{dl} , parallel to each other from the electrical double layer structure. The position of this charge density σ_{dl} defines the double-layer and the two opposite charge, σ_o and σ_{dl} , parallel to each other from the integral double-layer capacitance $C_{dl,i}$.

the relation between then is

$$\sigma_{dl} = -\sigma_0 = -C_{dl,i} \times \psi_0 \quad (2-16)$$

where the potential of the oxide surface and the bulk solution, $\psi_0 = \psi_S - \psi_B$. [4]

Gouy-Chapman-Stern model can calculate the integral double-layer capacitance $C_{dl,i}$.

(Fig.2-5) [9] The double-layer capacitance consists of a series network of a Helmholtz-layer capacitance (the Stern capacitance) and a diffuse-layer capacitance.

The Gouy-Chapman-Stern model involves a diffuse layer of charge in the solution starting at a distance x_E from the surface. The charge in the diffuse layer σ_{dl} is given by:

$$\sigma_{dl} = -\sqrt{8kT \varepsilon_r \varepsilon_0 n^0} \sinh\left(\frac{zq\phi_E}{2kT}\right) \quad (2-17)$$

where ϕ_E is the potential at x_E , n^0 is the concentration of each ion in the bulk solution in number, and z is the valence of the ions. The parameters ε_r , ε_0 , k , q and T have their usual meaning.

The difference between the potential ψ_1 at Y_T and the surface potential ψ_0 is the potential difference across the Stern capacitance. Therefore the potential ψ_1 can be described by:

$$\psi_1 = \psi_0 - \frac{\sigma_0}{C_{Stern}} = \psi_0 - \frac{\sigma_0 x_E}{\varepsilon_r \varepsilon_0} \quad (2-18)$$

now it is possible to calculate the integral double-layer capacitance as a function of ψ_0 and the electrolyte concentration with eqns.2-15 and eqns.2-16. The ability of the double layer to store charge in response to a small change in the potential $\frac{\partial \sigma_0}{\partial \psi_0}$

is defined as the differential double-layer capacitance, C_{dif} , and can be calculated:

$$\frac{\partial \sigma_0}{\partial \psi_0} = -\frac{\partial \sigma_{dl}}{\partial \psi_0} = C_{dif} \quad (2-19)$$

For reasons of simplicity, not the expression for C_{dif} is started here, but of its inverse, which also clearly shows that this capacitance is made up of two components in series:

$$\frac{1}{C_{dif}} = \frac{\partial \psi_0}{\partial \sigma_0} = \frac{1}{C_{Stren}} + \frac{1}{\sqrt{\frac{2\varepsilon_r \varepsilon_0 z^2 q^2 n^0}{kT} \cosh\left(\frac{zq\psi_1}{2kT}\right)}} \quad (2-20)$$

To combine eqns.2-12 and eqns.2-17 shows the effect of a small change in the surface pH(pH_s) on the change in the surface potential ψ_0 :

$$\frac{\partial \psi_0}{\partial pH_s} = \frac{\partial \psi_0}{\partial \sigma_0} \cdot \frac{\partial \sigma_0}{\partial pH_s} = \frac{-q\beta_{int}}{C_{dif}} \quad (2-21)$$

cause the general expression for pH sensitivity of an ISFET:

$$\frac{\partial \psi_0}{\partial pH_B} = -2.3 \frac{kT}{q} \cdot \alpha \quad (2-22)$$

when

$$\alpha = \frac{1}{\frac{2.3kTC_{dif}}{q^2 \beta_{int}} + 1} \quad (2-23)$$

Depending on the intrinsic buffer capacitance C_{dif} , the parameter α is a dimensionless sensitivity parameter that varies between 0 and 1. If $\alpha=1$, the ISFET has a so-called Nernstian sensitivity of precisely-59.2mV/pH at 298K, which is also the maximum achievable sensitivity.

To use SiO₂ 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 Si₃N₄[9],[10] Al₂O₃[11],[12] and SnO₂. [13]

2.3 Drift

This phenomenon can be considered by two aspects, the trap of hydrogen-bearing species, and the hydration of the insulator surface after immersed in pH solution by the binding sites when they transport through the insulator. That is influence on drift is generally smaller than the latter. This result can be found in the measurement data of the research. This phenomenon is slow, continuous, change of

threshold voltage of an ISFET and it is difficult to identify the cause of this phenomenon, which could be either a surface or a bulk effect, or both. There are a number of possible reasons causes of drift. [14]

- (1) Injection of electrons from the electrolyte at strong anodic polarizations created negative space charge inside sensitive film.
- (2) Some surface effects, such as the rehydration of a surface that is partially dehydrated and ion exchange involving OH^- ions.
- (3) Variation of the surface state density (D_{it}) at the Si/SiO_2 interface which means the drift dependence of diffusion mechanism.
- (4) Drift of sodium ion under the influence of the insulator field. Given an effective diffusion coefficient D_{eff} , it is clear that a bulk redistribution of sodium which has left a trap near the edge of the SiO_2 .



2.3.1 Dispersive Transport

Dispersive transport was brief reviewed in[15] and should be characterized by a power-law time delay of mobility or diffusivity of the form $t^{\beta-1}$, $0 < \beta < 1$. In amorphous material, dispersive transport may arise from hopping transport, multiple-trap transport, or trap-controlled hopping transport.[16] Regardless of the specific dispersive mechanism involved, dispersive transport leads to a characteristic power-law time decay of diffusivity which can be described by:

$$D(t) = D_{00}(\omega_0 t)^{\beta-1} \quad (2-24)$$

where D_{00} is a temperature-dependent diffusion coefficient which obeys an Arrhenius relationship, ω_0 is the hopping attempt frequency, and β is the dispersion parameter satisfying $0 < \beta < 1$. Dispersive transport leads to decay in density of

sites/traps occupied by the species undergoing transport. This decay is described by the stretched-exponential time dependence given by:

$$\Delta N_{S/T}(t) = \Delta N_{S/T}(0) \exp[-(t/\tau)^\beta] \quad (2-25)$$

where $\Delta N_{S/T}(t)$ is the area density (unit of cm^{-2}) of sites/traps occupied, τ is the time constant combined with structural relaxation, and β is the dispersion parameter.

2.3.2 Expression for Drift

The hydration lead to the chemical composition of the sensing layer, it is reasonable to assume that the dielectric constant of the hydrated surface layer differs from that of the sensing oxide bulk. The overall insulator capacitance, which is determined by the series combination of the surface hydration layer and the underlying sensing film, will exhibit a slow, temporal change. When drift phenomenon occurs at the surface of an activity-biased ISFET, the gate voltage will simultaneously exhibit a change to keep a constant drain current. The change of the gate voltage can be written as

$$\Delta V_G(t) = V_G(t) - V_G(0) \quad (2-26)$$

Since the voltage drop inside of the semiconductor is kept a constant, $\Delta V_G(t)$ becomes:

$$\Delta V_G(t) = [V_{FB}(t) - V_{FB}(0)] + [V_{ins}(t) - V_{ins}(0)] \quad (2-27)$$

where V_{FB} is the flatband voltage and V_{ins} is the voltage drop across the insulator.

V_{FB} and V_{ins} are given by the following expression:

$$V_{FB} = E_{ref} + \chi^{sol} - \Psi_0 - \frac{\Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS}}{C_{OX}} \quad (2-28)$$

$$V_{ins} = \frac{-(Q_B + Q_{inv})}{C_{OX}} \quad (2-29)$$

where the Q_{inv} is the inversion charge. If the pH, temperature, and the ionic strength of the solution are held constant, E_{ref} , Φ_{Si} , Ψ_0 , and χ^{sol} can be neglected, so the drift can be rewritten as:

$$\Delta V_G(t) = -(Q_{OX} + Q_{SS} + Q_B + Q_{inv}) \left[\frac{1}{C_i(t)} - \frac{1}{C_i(0)} \right] \quad (2-30)$$

In this study, the gate oxide of the fabricated ISFET was composed of two layers, a lower layer of thermally-grown SiO_2 of thickness, t_L , and an upper layer of sputter-grown ZrO_2 of thickness, t_U . $C_i(0)$ is the effective insulator capacitance given by the series combination of the thermally-grown SiO_2 capacitance, ϵ_L/t_L , and the sputter-grown ZrO_2 capacitance, ϵ_U/t_U . $C_i(t)$ is analogous to $C_i(0)$, but an additional hydrated capacitance at the oxide-electrolyte interface must be considered, and the sputter-grown ZrO_2 capacitance is now given by $\epsilon_U/[t_U - t_{HL}]$. The series combinations of the capacitance are illustrated in Fig.2-6. Therefore, the drift is given by:

$$\Delta V_G = -(Q_{OX} + Q_{SS} + Q_B + Q_{inv}) \left[\frac{\epsilon_U - \epsilon_{HL}}{\epsilon_U \epsilon_{HL}} \right] t_{HL}(t) \quad (2-31)$$

From the equation, we know that drift of gate voltage ΔV_G if the substrate type was different, it depends on the Q_{inv} and Q_B . Other terms at eqns.2-29 can be appropriate as constant values no matter what the substrate is. According to this assumption, it is possible to eliminate the drift or hold the drift to be a constant at any other pH aqueous solution through the CMOS ISFET. By applying dispersive transport theory, an expression for $t_{HL}(t)$ is given by [15]

$$t_{HL}(t) = t_{HL}(\infty) \left\{ -\exp \left[-(t/\tau)^\beta \right] \right\} \quad (2-32)$$

with

$$t_{HL}(\infty) = \frac{D_{00}\omega_0^{\beta-1}\Delta N_{S/T}(0)}{A_D\beta N_{hydr}} \quad (2-33)$$

where A_D is the cross-sectional area, and N_{hydr} is the average density of the hydrating species per unit volume of hydration layer. Hence, combination of eqns.2-24 to eqns.2-30 the gate voltage drift can be expressed by the following equation:

$$\Delta V_G(t) = -(Q_{OX} + Q_{SS} + Q_B + Q_{inv}) \left[\frac{\varepsilon_U - \varepsilon_{HL}}{\varepsilon_U \varepsilon_{HL}} \right] t_{HL}(\infty) \{1 - \exp[-(t/\tau)^\beta]\} \quad (2-34)$$

From this equation, we can expect that if the time of gate oxide immersing in the test-solution is long enough, the gate voltage drift will approach a constant value which is greatly dependent on the hydration depth, $t_{HL}(\infty)$.



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Chapter 3

Experiment and Measurement

3.1 Introduction

The ISFET is similar to conventional MOSFET. The difference between MOSFET and ISFET structure is the process of gate electrode. This chapter introduces the process flow and structure of ISFET. (Fig.3-1)

Step1:

1. RCA clean.
2. Wet oxide growth 6000Å, 1050°C, and 65mins.

Step2:

3. Mask^{#1} to define Source/Drain region.
4. BOE wet etching of silicon dioxide.
5. Dry (Screening) oxide growth 300 Å, 1050°C, 12mins.
6. Source/Drain implantation, Dose=5E15 (1/cm²), Energy=25Kev.
7. Source/Drain annealing, 950°C, 30mins.

Step3:

8. PECVD Oxide deposition 1 μm.

Step4:

9. Mask^{#2} to define contact hole and gate region.
10. BOE wet etching of silicon dioxide.
11. Dry oxide growth 100 Å, 850°C, 60mins.

Step5:

12. Mask^{#3} to define the sensing layer region.

13. Sensing layer (ZrO_2) deposition by Sputtering. 300 Å.

14. ZrO_2 sintering 600°C, 30mins.

Step6:

15. Mask#4 to define the contact and solid reference electrode region.

16. Al deposition by Sputtering 5000 Å.

Step7:

17. Backside Al evaporation 5000 Å.

18. Pt and Al sintering 400°C, 30mins

Step8:

19. Coating the polymer-based material as REFET sensing layer.

3.2 The step illustration

In step1, RCA clean is for cleaning up the surface, to make the growing equality of Wet Oxide better.

In step2, the area defined source-drain grow a layer of 100Å screen oxide to protect the surface when ion-implantation. After ion-implantation, high potential doping ion destroy the structure of lattice on silicon, and repair it by the way of anneal.

In step3, then using PECVD grow oxide 1 μm as insulation to prevent buffer solution effect the device when ISFET immersed in the solution.

In step4, decide the gate oxide region, and then use BOE etching oxide. It grows better quality gate oxide 100Å by using dry oxide.

In step5, define the sensing layer region for growing 300Å ZrO_2 cause the sensitivity of metal oxide higher, which is about 57mv/pH.

In step6, define electrode region for deposition 5000Å Al.

In step7, finished Backside Al evaporation 5000Å is the primary process of

ISFET.

In step8, ISFET coated polymer is REFET sensing layer since polymer lower sensitivity efficiently.

3.3 Measurement system

To investigate the characteristics of polymer structure as sensing layer, we used the HP4156 as measurement tool and system (shown in Fig.3-2) to measure I-V curve for pH-ISFETs. In order to get correct result of measurement, the entire measurement procedures were executed in a dark box to prevent the electromagnetic wave and light influence.[1] The measured pH values are 1,3,5,7,9,11,13, and the pH buffer solution were supplied by Riedel-deHaen corp.

In order to measure Na^+ ions, so must to prepare the NaCl solution. The NaCl salts are electronic grade and solution are prepared in DI water with different concentration. When preparation of NaCl solution, it have to know the solubility of NaCl at room temperature is about 37g NaCl per 100g water.

3.3.1 Current-Voltage (I-V) measurement set-up

A HP-4156 semiconductor parameter analyzer system were setup to measure the I-V characteristic curves, in which include $I_{\text{DS}}-V_{\text{GS}}$ and $I_{\text{DS}}-V_{\text{DS}}$ curve at controlled temperature. When dropping the buffer solution, must be careful. Because the sensing region is too small, it could easily generated air bubbles at interface. In order to measure exact values for difference solution, every pH solution is immersed for the same time before measurement.

In order to obtain exact values, at first we measure $I_{\text{DS}}-V_{\text{DS}}$ to observe the linear

region. Next, we define the I_{DS} as constant to measure $I_{DS}-V_{GS}$. In this operate condition, it can find the characteristics of pH-ISFET. It can find the pH sensitivity from $I_{DS}-V_{GS}$ curve of maximum transconductance. Beside, we can see that with different buffer solution the reference electrode voltage is shifted and shifted voltage per pH value is sensitivity, shown in Fig.3-3.

3.3.2 Current-Voltage (I-V) measurement set-up with drift

In order to measure drift phenomenon of pH-ISFETs with the same buffer solution and the same condition samples period of seconds, minutes and hours. After seven hours, we can compare drift phenomenon of all samples. This detection principle is in a similar manner to that of the pH measurement and is shown in Fig.3-4.



3.4 References

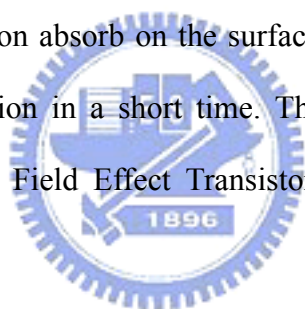
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Chapter 4

Results and Discussions

4.1 Introduction

This experiment use a high polymer, it is a hydrophobic material which can reduce H ion in a large number, the shortage is vulnerable to buffer solution in the sensing film, so we utilize a way that Nafion entrapment PR to produce REFET(Reference Electrode Field Effect Transistor). Since Nafion is a proton exchange membrane, it can protect PR for this feature and it become the mechanism of proton exchange to make ion absorb on the surface of PR steadily in fear of peel for the attack of buffer solution in a short time. This experiment discusses a best REFET (Reference Electrode Field Effect Transistor) in different structure and in various viewpoints.



4.2 Comparison of different structure's feature

The experiment utilizes different approach of entrapment to measure the comparison of its structure's feature. It use $ZrO_2/PR/Nafion$ and $ZrO_2-mix(PR+Nafion)$ two different structure's approach of entrapment, and get the common conclusion that sensitivity of both reduce from 56mV/p in ZrO_2 sensing layer to 5mV/pH and 8.3mV/pH(Fig 4-2)(Fig4-3).

The main reason is the entrapment PR (FH6400) can reduce the sensitivity efficiently, and it can get different material's site-binding from Gouy-Chapman-Stern

Theory model[2] and Site-binding model[3], which traps the number of ion are also different. In addition, ZrO₂[4] is the material of high K and the sensitivity of metal oxide to H ion is higher, and PR is a PVC high polymer material that is not easy to absorb H ion, so it higher than ψ_{PR} in ψ_{ZrO_2} , the sensitivity can reduce largely about 85%.

However, the performance of two structure on Drift since structure of ZrO₂/PR/Nafion inferior to the structure of PR mix Nafion (Fig.4-5) (Fig.4-6)(Fig.4-7), buffer solution trough Nafion make the surface area that ions absorb to PR larger than the surface area of mingle one from the analysis of triple structure, and if uncovered PR immerse in buffer solution directly, it will easy to peel by the attack of solution quickly. Hence, the main reason that tripe layer structure is not stable as the mix one is the surface area of PR molecule contact with buffer solution larger than the surface area of mix one, so it is easy to attack by buffer solution.

4-3 The comparison of PR-mix-Nafion deposition on different structure

The comparison of this experiment utilize two different base on different Sensing film, ZrO₂ and SiO₂(Fig.4-8), and the material of both of them mix PR and Nafion coast on sensing film to get the sensitivity are 8.3mV/pH and 13.3mV/pH respectively. The sensitivity measured in previously ZrO₂ and SiO₂ experiment are about 55mV/pH and 32.5mV/pH(Fig.4-3)(Fig.4-9). It concludes from site-binding model[1] and experiment data that the main reason affect sensitivity is "hydrophobic" from PR material cause H⁺ ions uneasy to absorb, so the H ion mainly absorb on the surface of PR and it not connect with the sensing layer in bottom. Nevertheless, the structure

base on SiO₂ is inferior to ZrO₂ on the improvement of sensitivity and stability of drift (Fig.4-10),it perhaps because interface of SiO₂ and PR is not as well as the interface of ZrO₂ and PR.

4-4 The comparison of different PR-mix-Nafion proportion's feature

This experiment utilize PR mix Nafion in different proportion, there are concentration 5 : 1 and 1 : 1 on sensing-layer entrapment ZrO₂. Among the result that 0.01ml PR mix 0.01ml Nafion entrapment ZrO₂, it can observe the sensitivity from the 54.16mV/pH in the begging reduce to 8.3mV/pH(Fig.4-3), the other is the result that 0.05ml PR mix 0.01ml Nafion entrapment ZrO₂ reduce from 54.16mV/pHr to 4.16mV/pH(Fig.4-13). From this phenomena, it can detect the concentration of PR affect directly to the sensitivity of REFET and it further prove PR is the main reason of reducing sensitivity in 4-3.

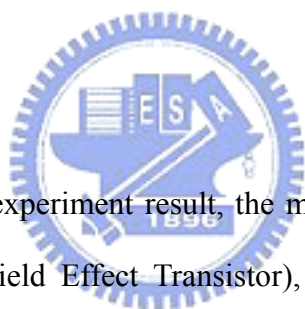
The performance of Drift (Fig.4-6)(Fig.4-14) can get the two sample's stability (PR1:Nafion1) is superior to (PR5:Nafion1) in the four hours later, the possible cause from the proportion of Nafion of the former higher than the later one. It mean the PR area entrap Nafion larger than the later, so it is uneasy to attack by the solution and cause PR peeling. In conclude, the sensitivity in (PR5:Nafion1) (Fig.4-15) is small and the time for stable of reliability is short, an the other vice versa.

4-5 The comparison of different proportion's durability and repeatability

This experiment utilizes two structures in 4-4 (Fig.4-12) continue to do long time durability test, the first stage is measure sensitivity by doing four hours DRIFT

experiment to the measured sample respectively, and the second stage repeat the first stage experiment again. In this research, it observed the experiment of the structure can't bear doing long term measure immersed the solution, and the feature of sensitivity and drift measured in the four hours can be made as a REFET(Reference Electrode Field Effect Transistor). Also, it observed that the feature of the two kind of mix proportion on sensitivity and drift in the measure of second stage already peel almost wholly for the long time attack in the buffer solution to make the mixing layer of PR and Nafion of the sample be invalid. It is realized in this experiment the only fine REFET (Reference Electrode Field Effect Transistor) of the structure in the four hours short time is unappreciable to do the long time measure.

4.6 Conclusion



To integrate the above experiment result, the mix layer of Nafion and PR is a good (Reference Electrode Field Effect Transistor), it could reduce H^+ Sensitivity from 57.5mV/pH to 8mV/pH. It use easy approach of entrapment to make Nafion do for the entrapped PR steadily through the mechanism of proton exchange, and it observed in the experiment the OXIDE and ZrO_2 of the bottom of PR is not associated directly with the SENSITIVITY, the main effect reason is PR which is not easy for the absorbing of H ion.

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Chapter 5

Future work

From this experiment, it can realize that use the deposition feature of Nafion to entrap material of PR on a good sensing film and it get the feature of PR from the test result. It can utilize the approach of entrapment to combine other substance (like protein, enzyme...etc) in the future, and ISFET develop BIO-SENSOR in further.



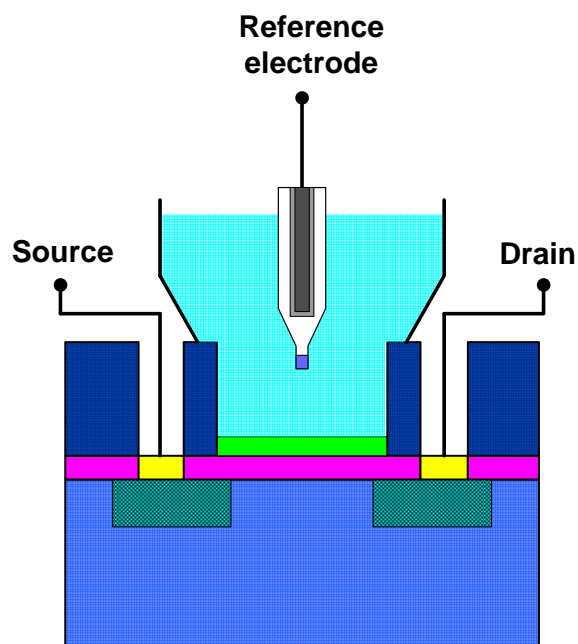


Fig. 1-1 ISFET Cross-Section Structure



Sensing membrane	Test range(pH)	Sensitivity(mV/pH)	Reference
ZrO ₂	1-13	57.5	2
Si ₃ N ₄	1-13	46-56	3
Al ₂ O ₃	1-13	53-57	4
Ta ₂ O ₅	1-13	56-57	5
SnO ₂	2-10	58	3

Table 1-1 Sensitivities and test range for different sensing membranes.

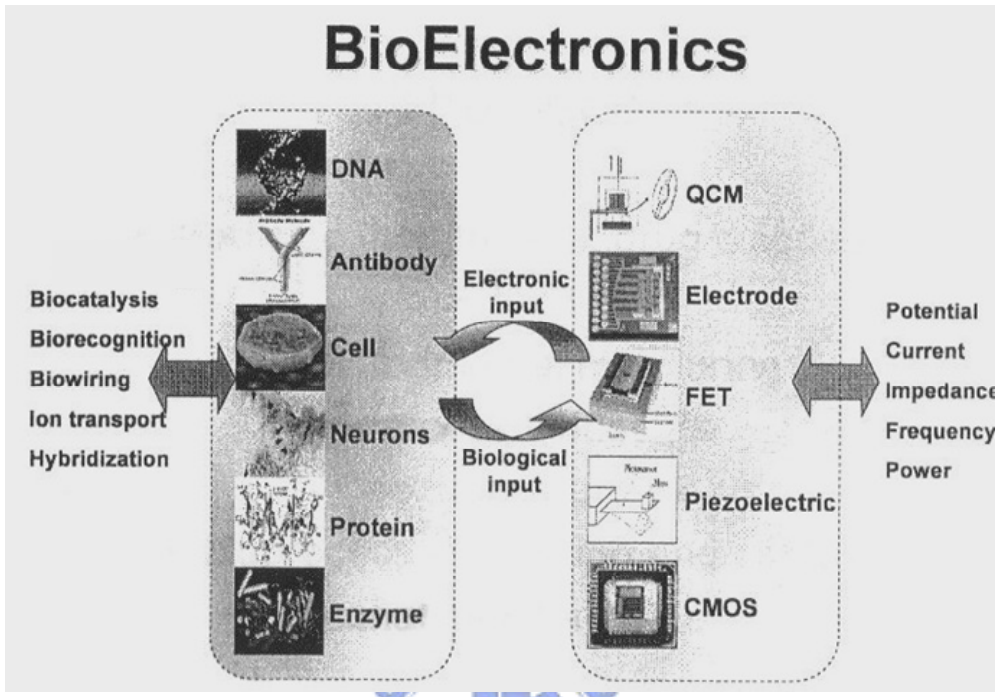


Fig. 1-2 important platform of Bio-sensors

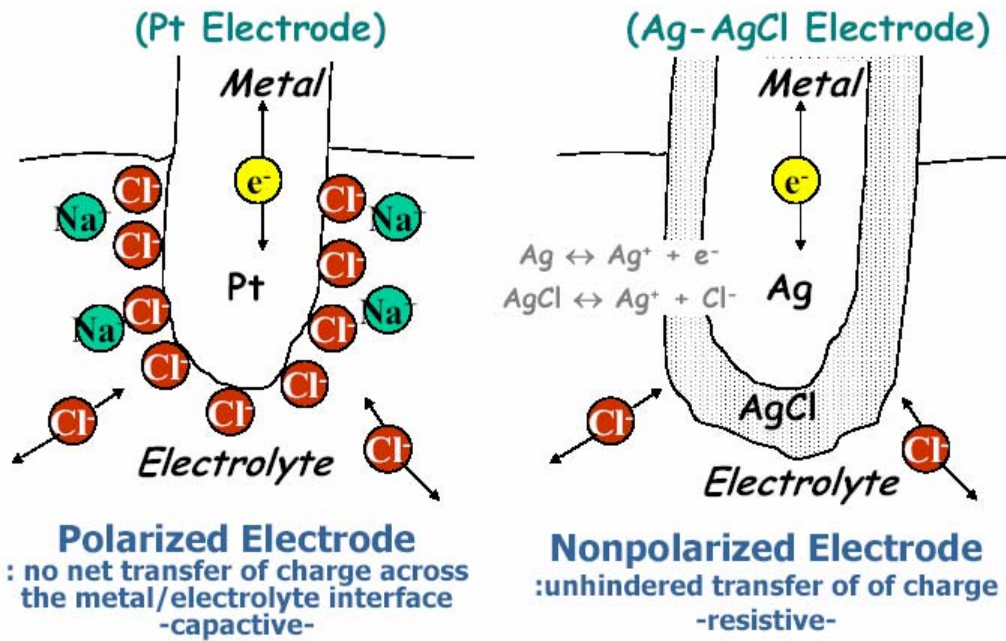


Fig.1-3 electrode structure

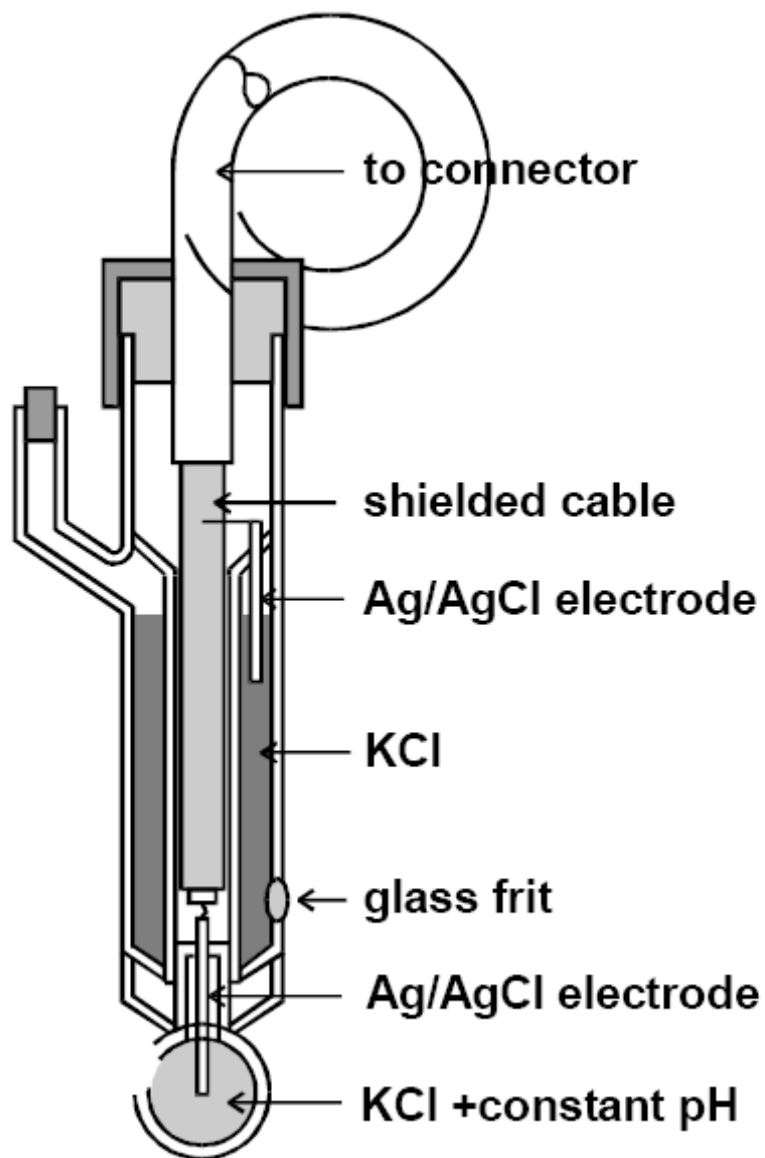


Fig. 1-4 Conventional glass electrode

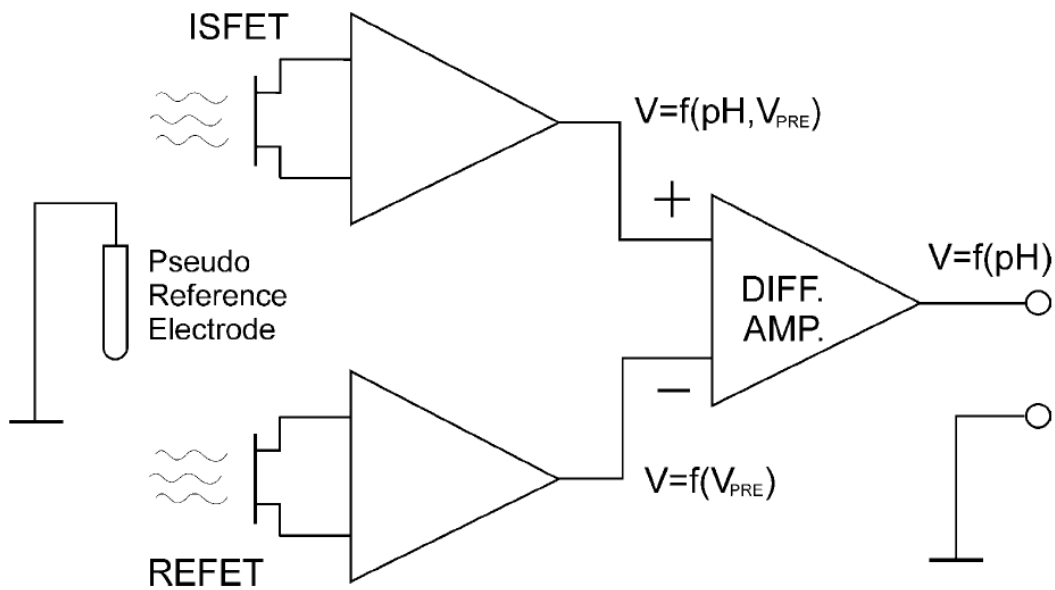


Fig. 1-5 using solid-state technology in measurement system

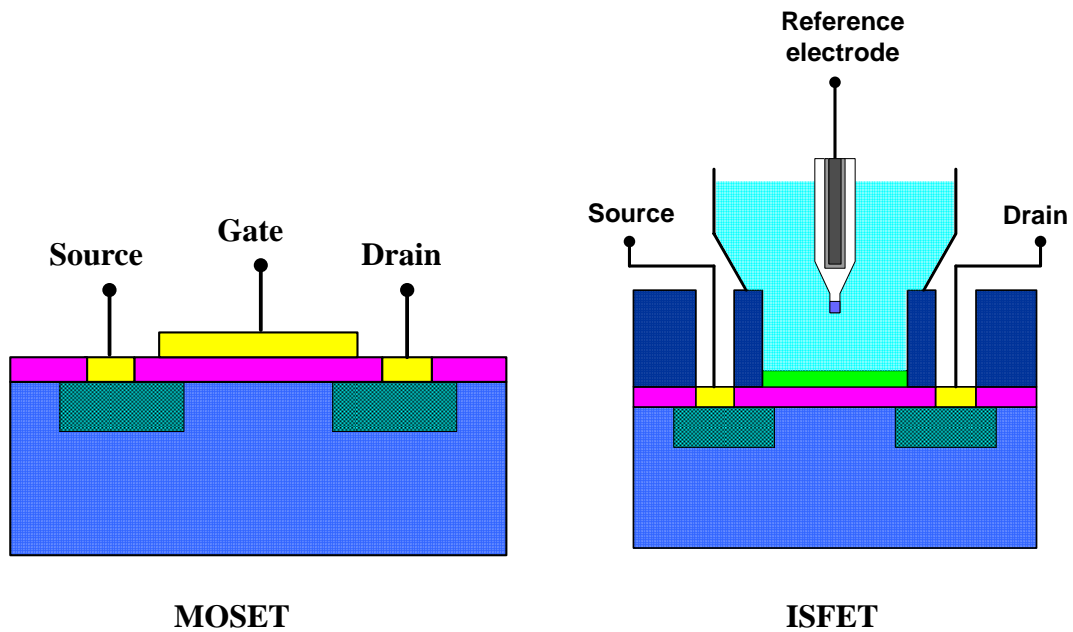


Fig 2-1 Structure of MOSFET and ISFET

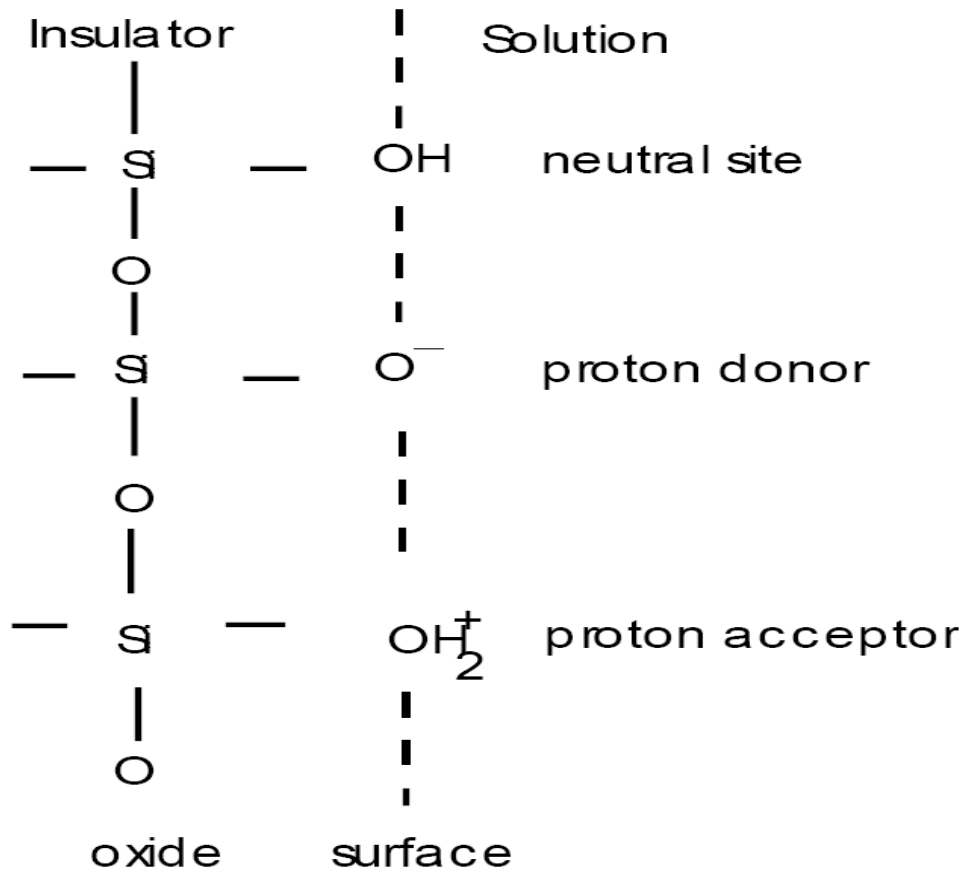


Fig 2-2 Site-binding model

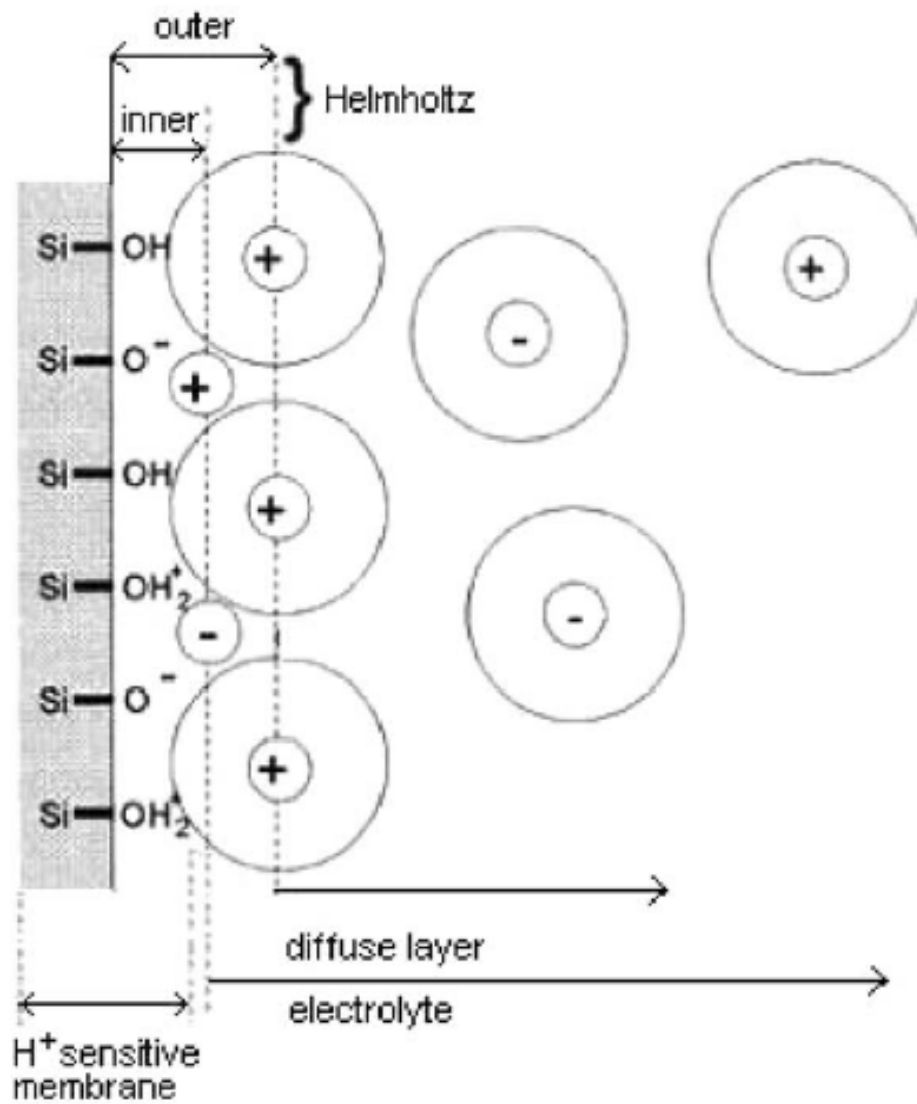


Fig.2-3 Silicon dioxide and electrolyte interface

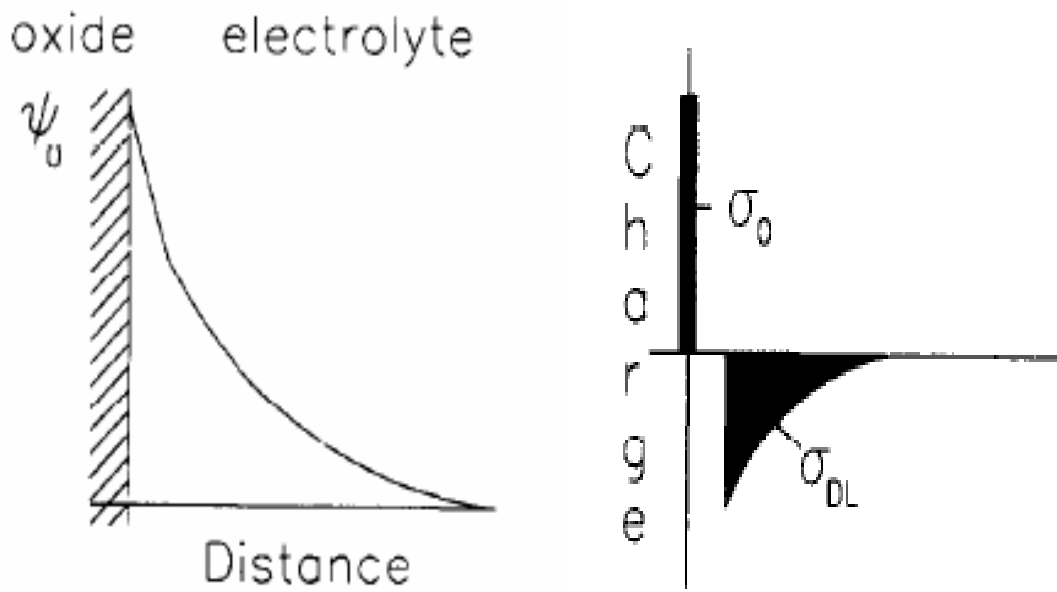


Fig.2-4 Potential profile and charge distribution at an oxide electrolyte solution interface.

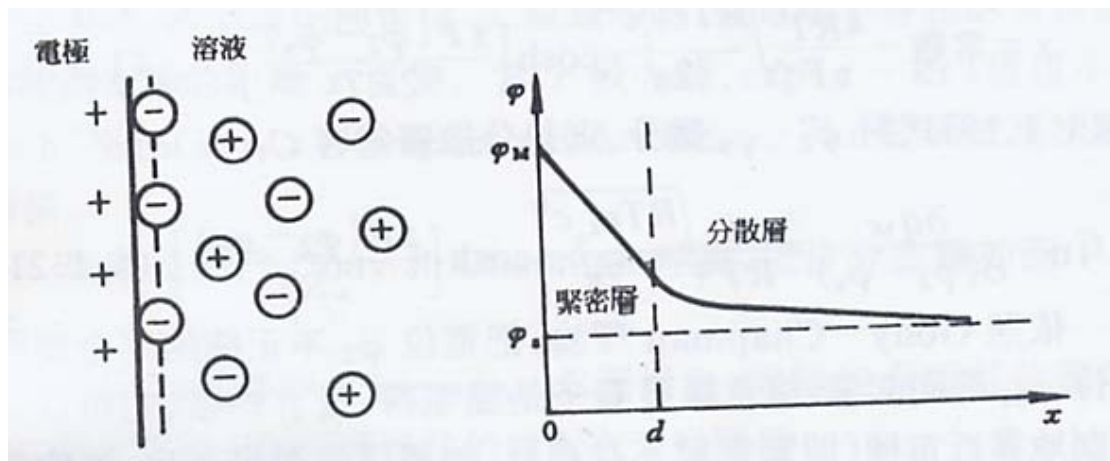


Fig. 2-5 Gouy-Chapman-Stern model

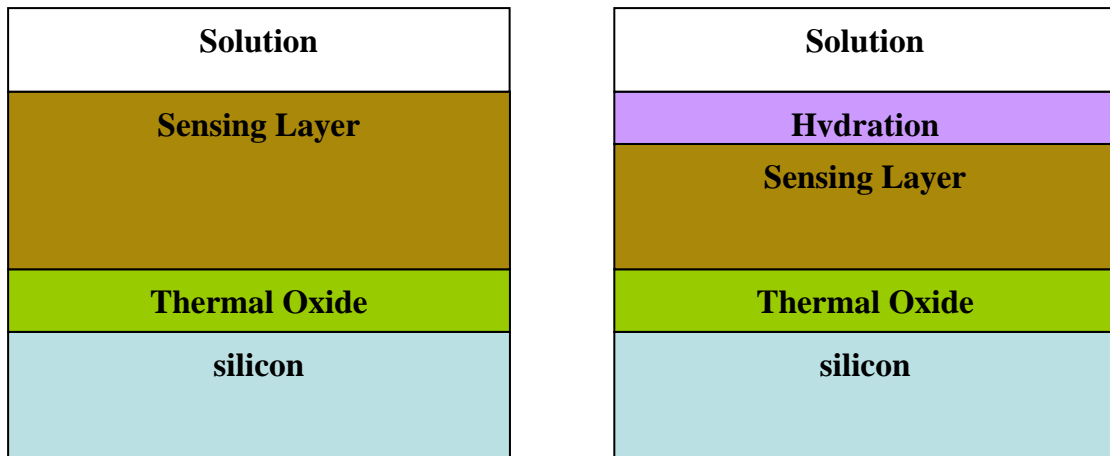
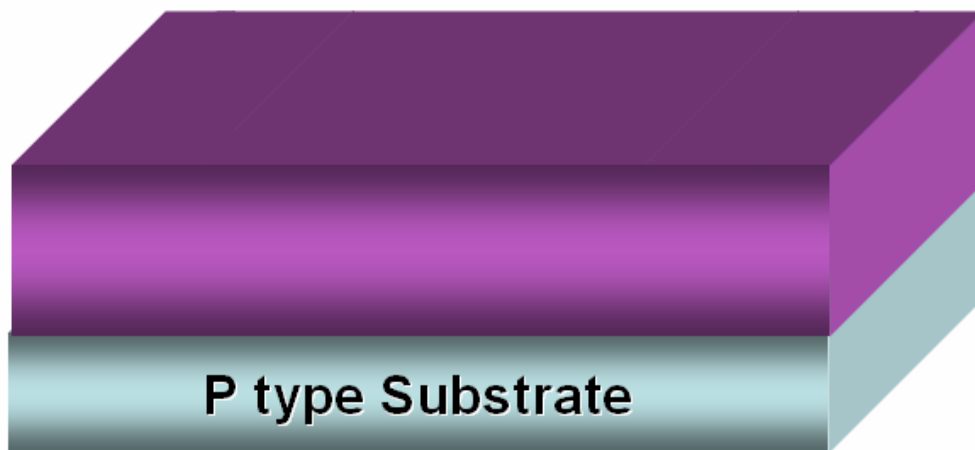
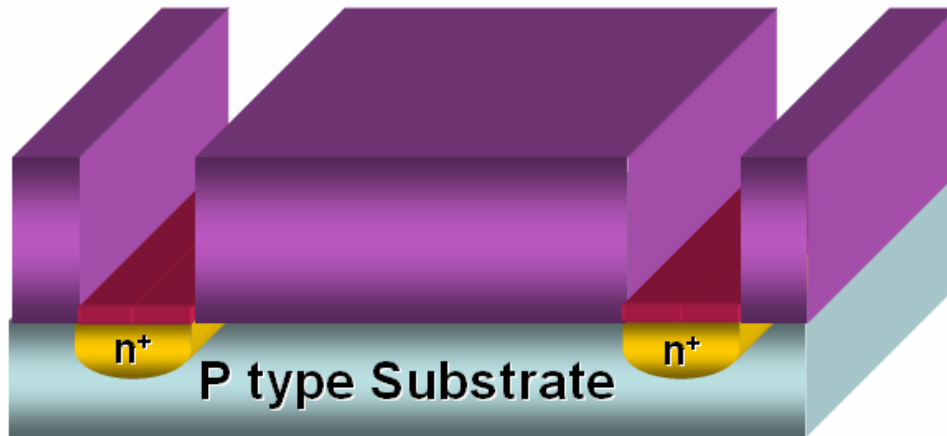


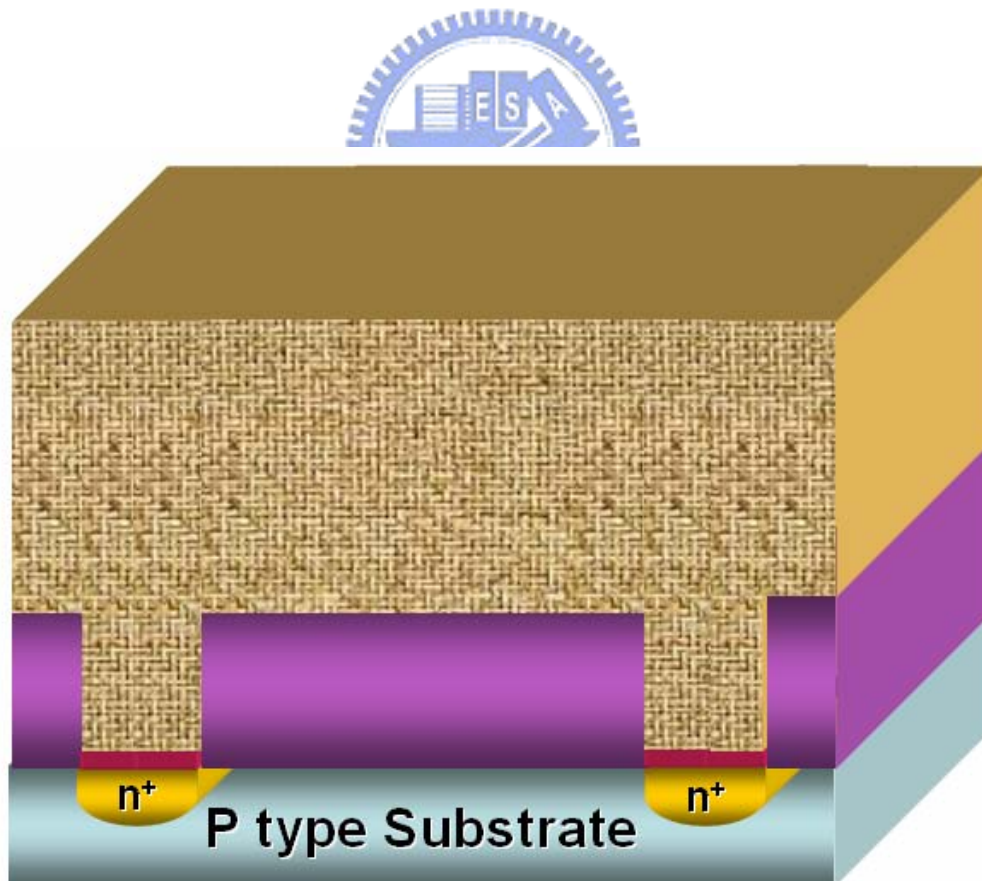
Fig.2-6 Series combination of the (a) initial (b) hydrated insulator capacitance



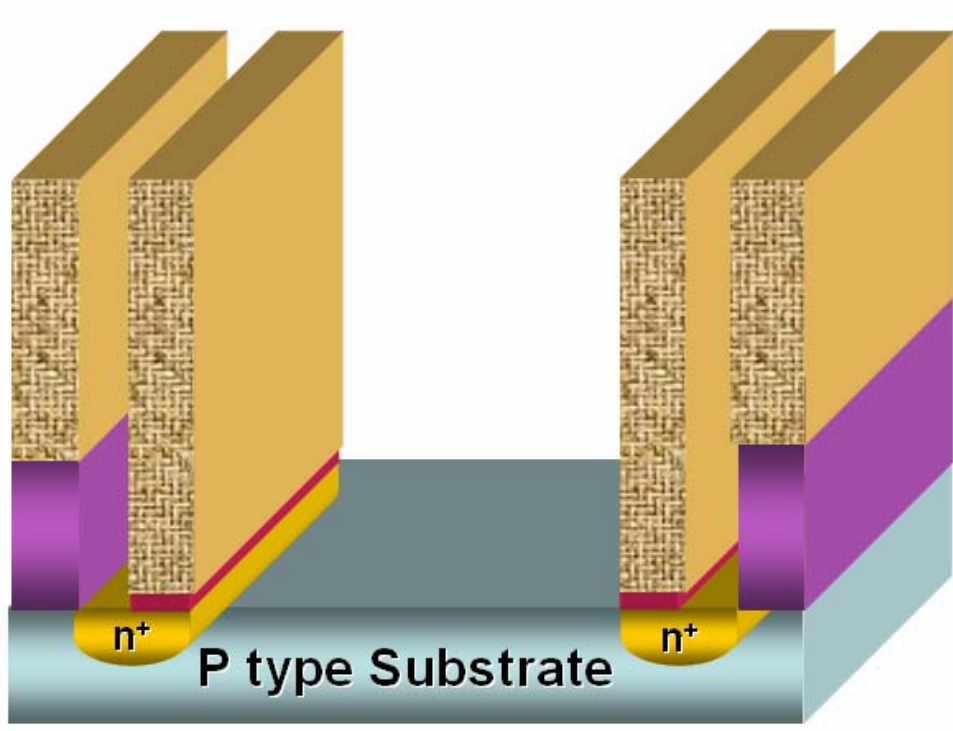
Step1



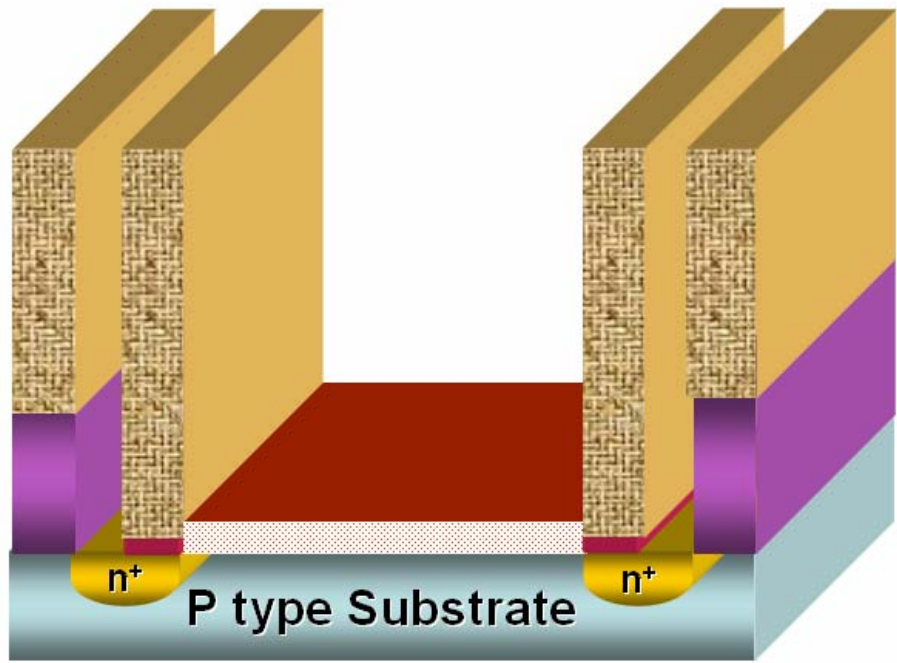
Step2



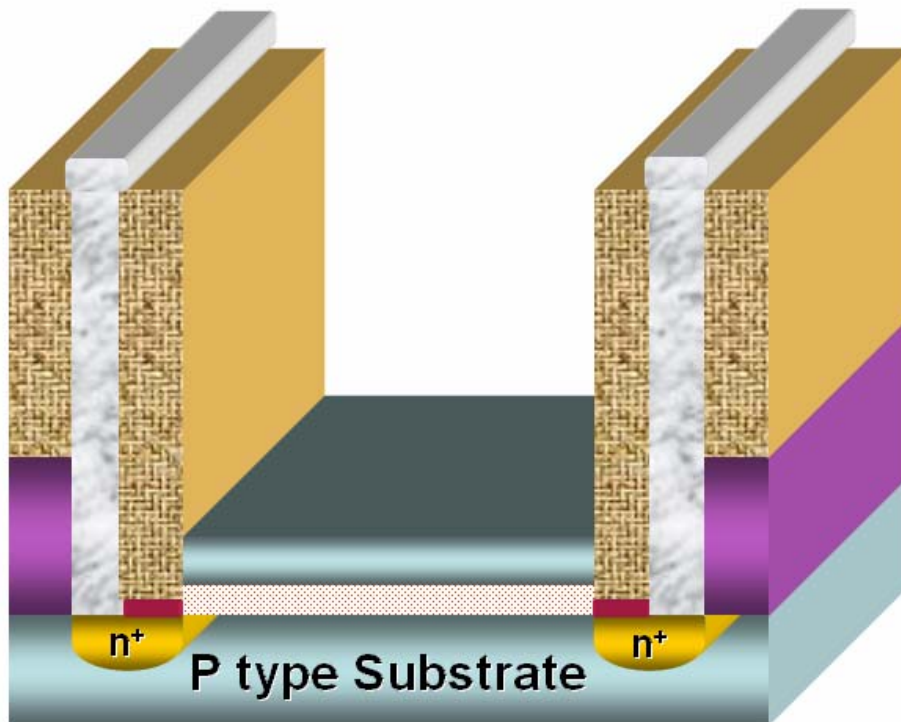
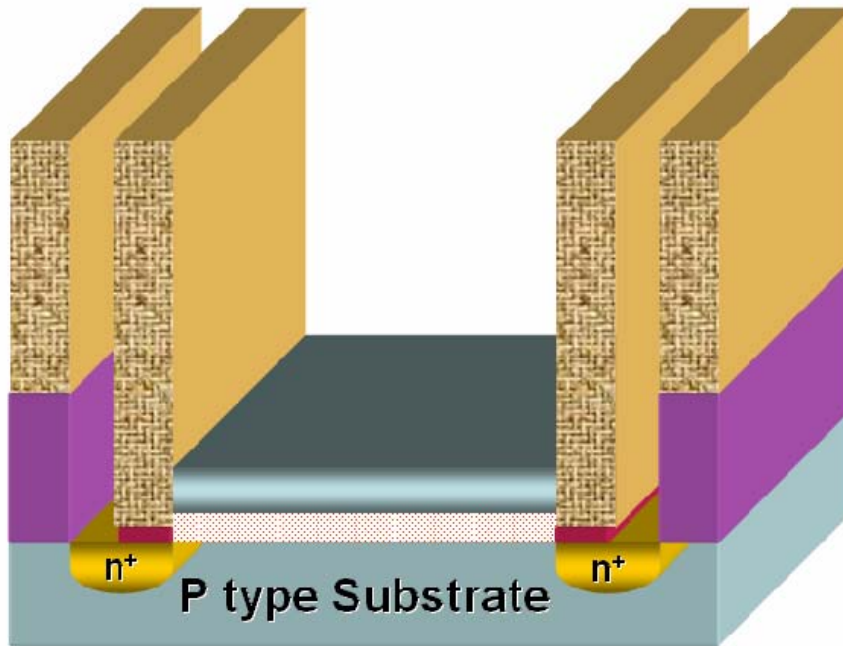
Step3



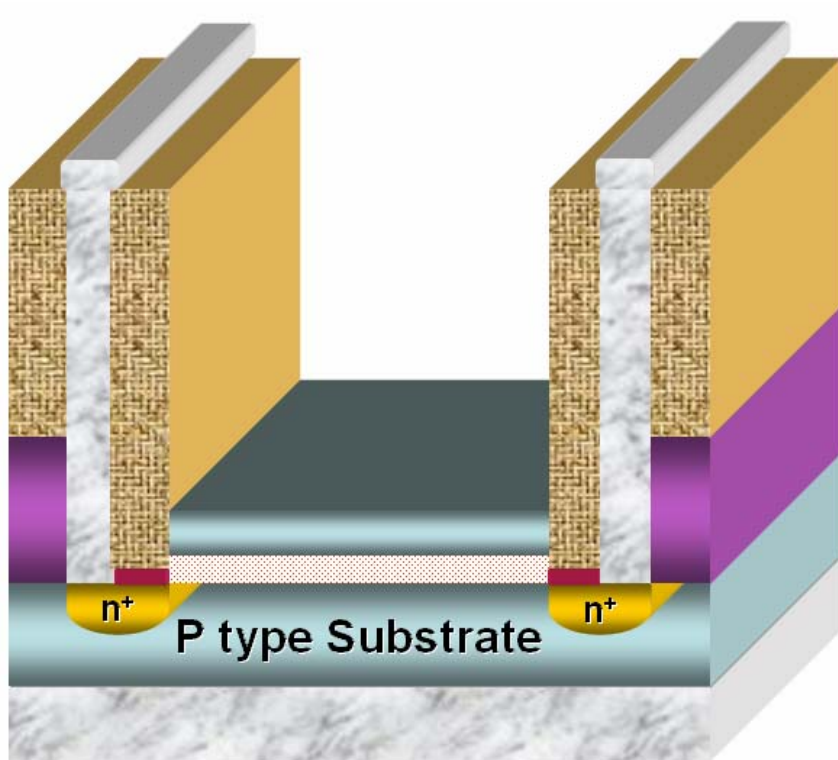
Step4



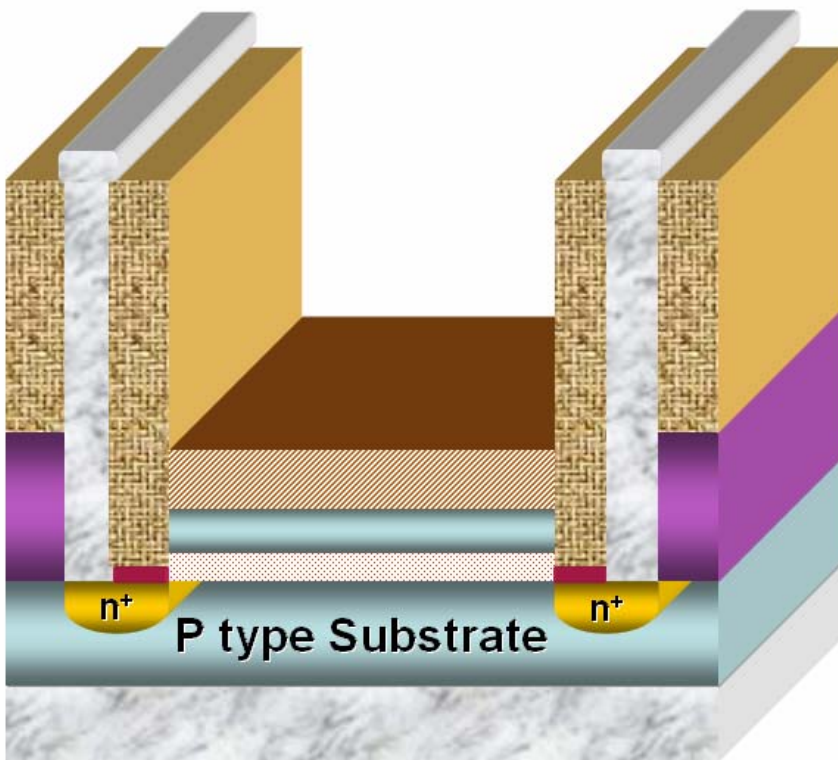
Step5



Step7



Step8



Setp9

Fig. 3-1 Fabrication Process Flow

parameters of ZrO ₂ sputter
power : 110 W
Ar / O ₂ : 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}

Table 3-1 ZrO₂ Sputtering parameters

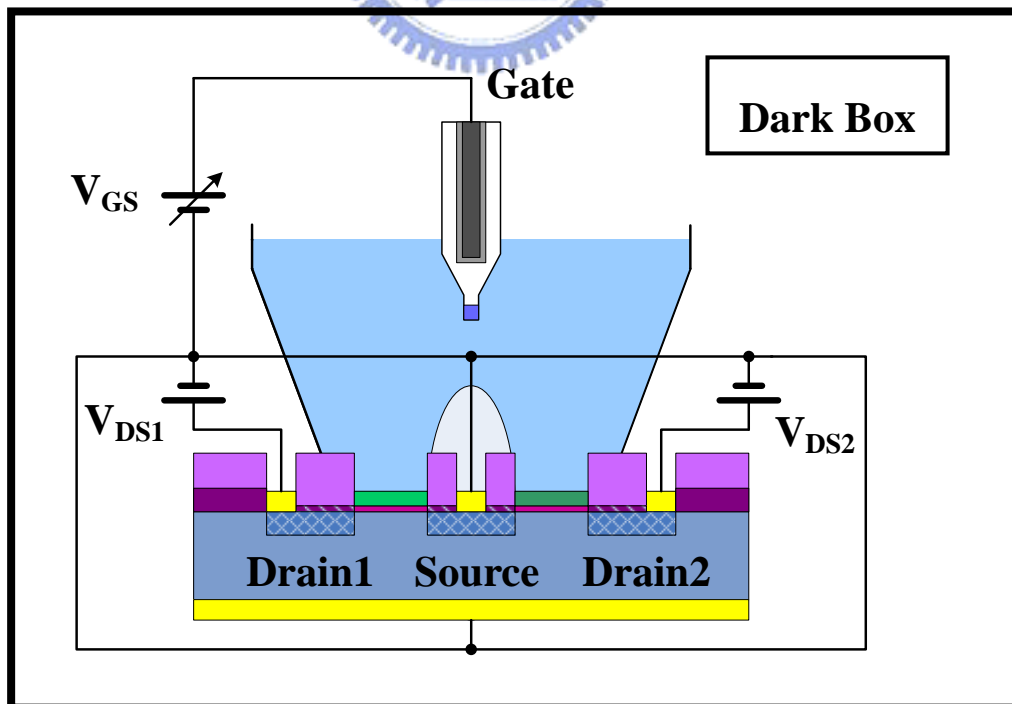


Fig 3-2 Measurement set-up

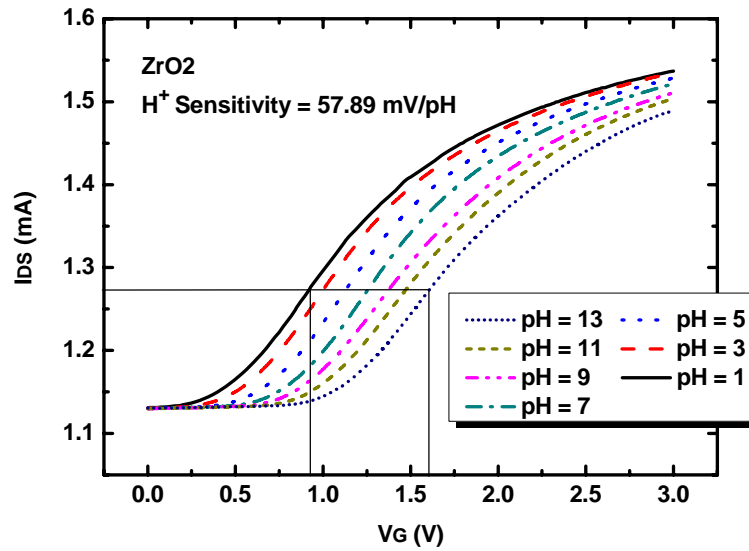


Fig 3-3 Extraction method of sensitivity

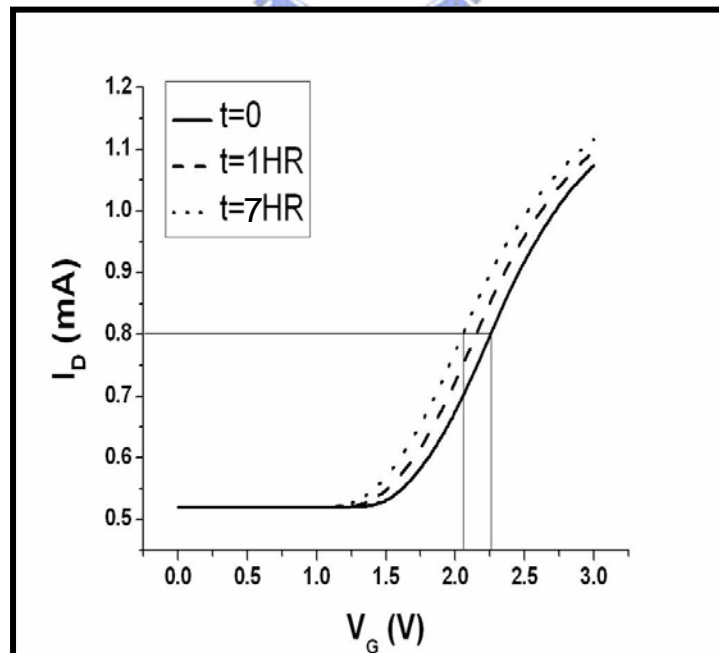


Fig 3-4 Extraction method of drift

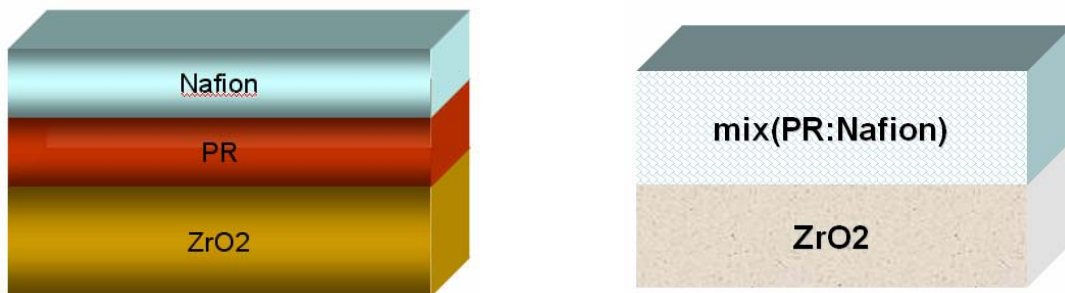


Fig.4-1 The comparison between enclosure and entrapment

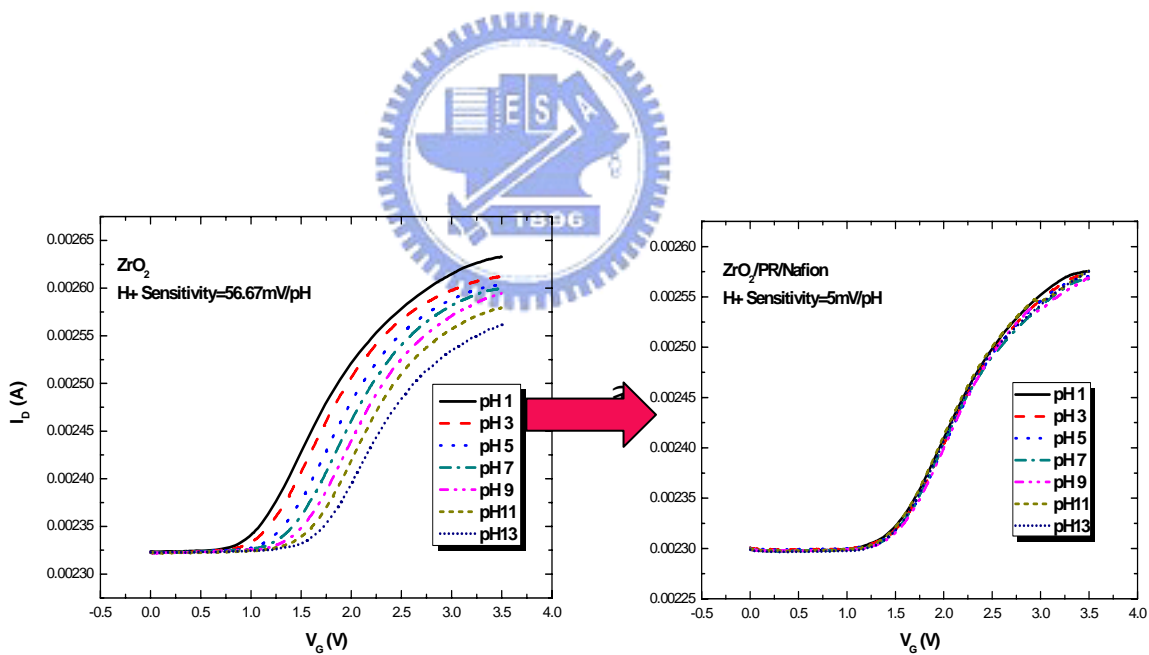


Fig.4-2 The variety of ZrO₂ sensitivity to H⁺ after coated with PR/Nafion

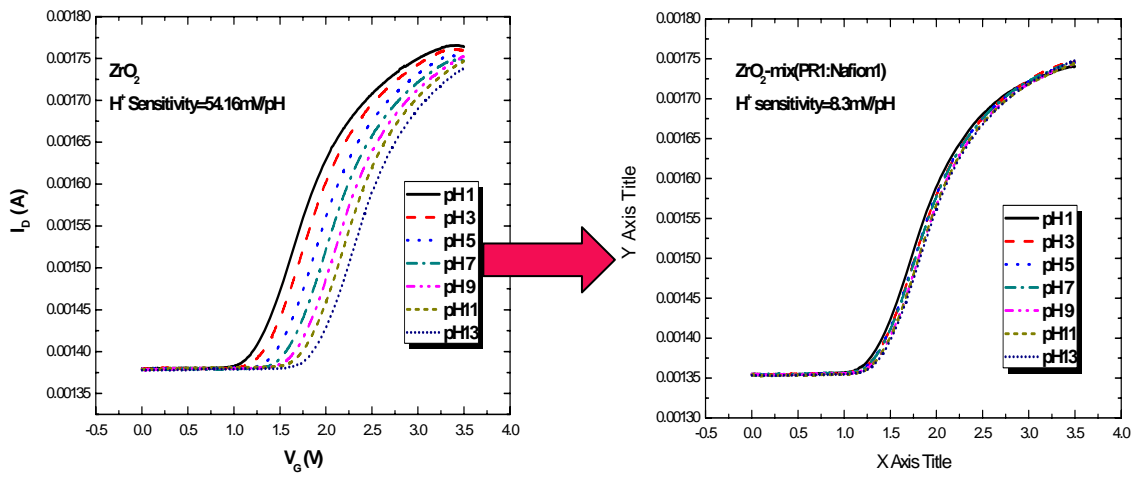


Fig. 4-3 The variety of ZrO₂ H⁺ sensitivity after coated with PR :Nafion=1:1

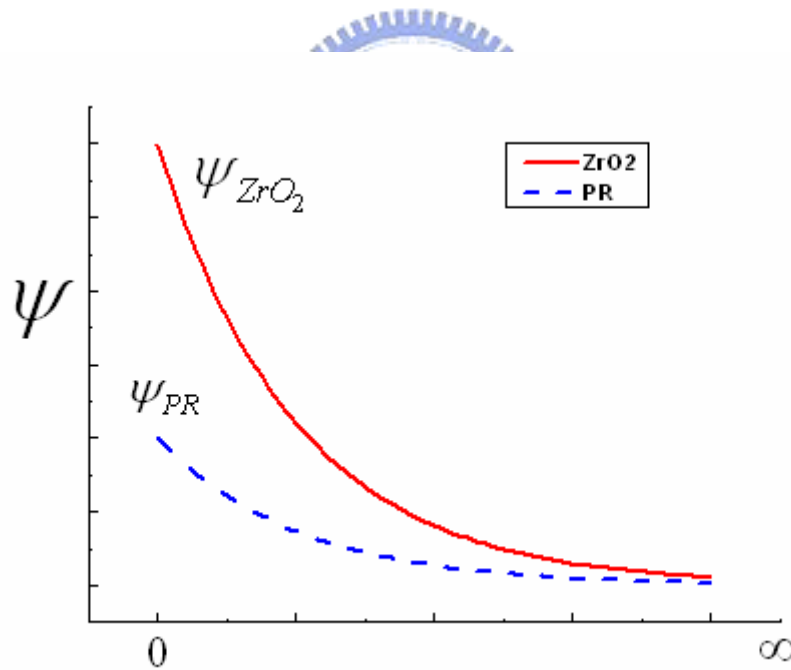


Fig. 4-4 The comparison of surface potential between ZrO₂ and SiO₂

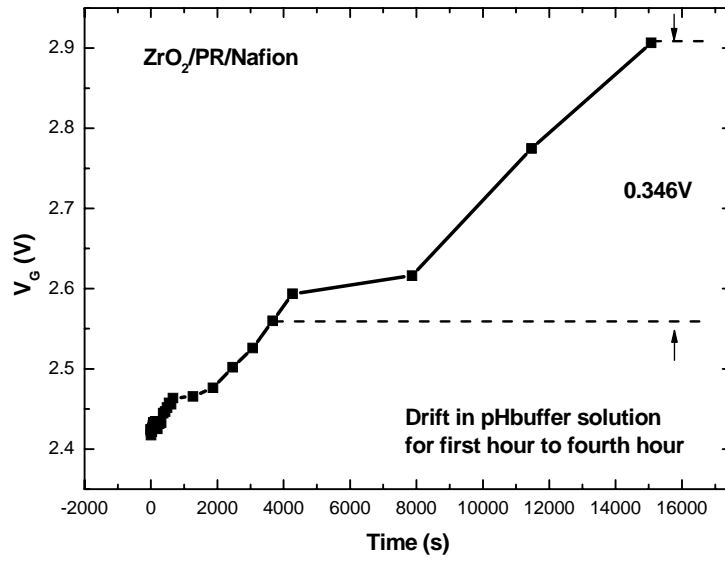


Fig4-5 Time to drift in pH buffer solution of ZrO₂/PR/Nafion-REFET for 4 hours

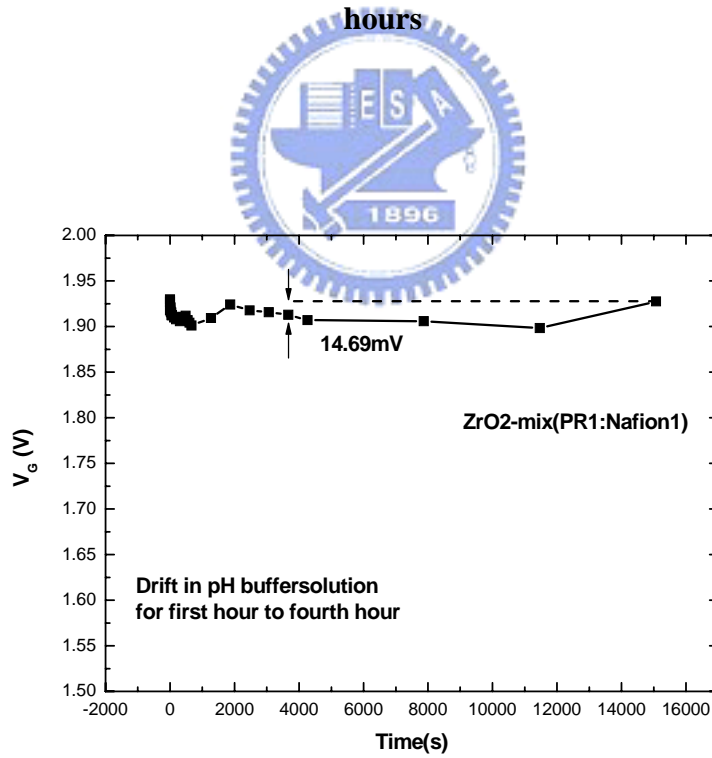


Fig4-6 Time to drift in pH buffer solution of ZrO₂-mix(PR1:Nafion1)-REFET for 4 hours

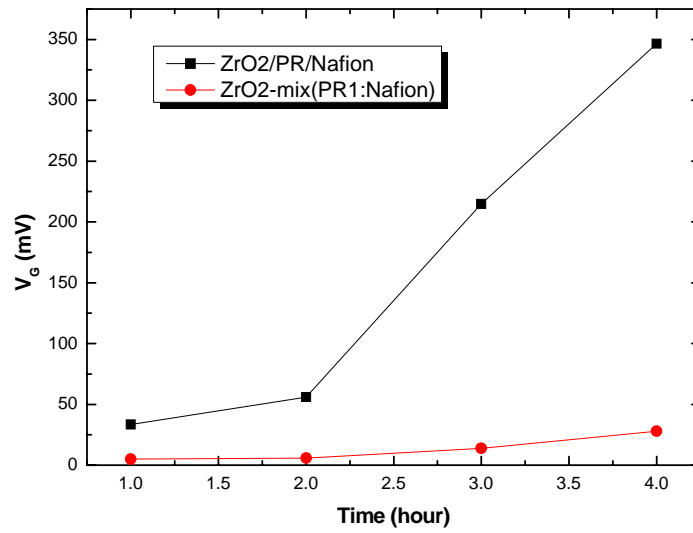


Fig4-7 The drift phenomenon in different structure

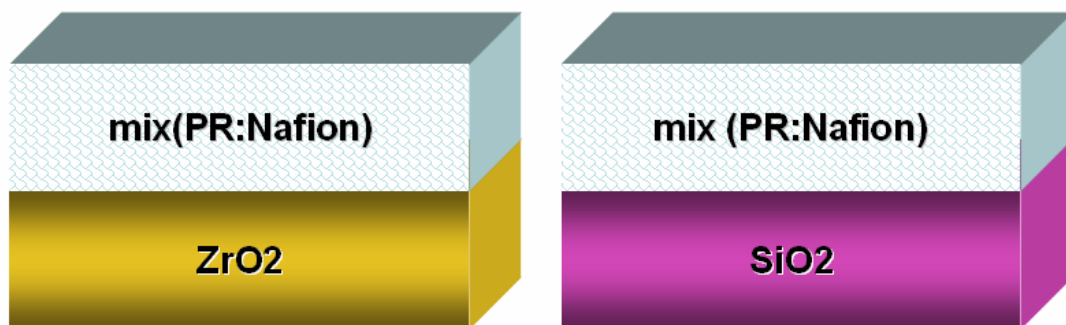


Fig.4-8 Compare in different sensing-layer

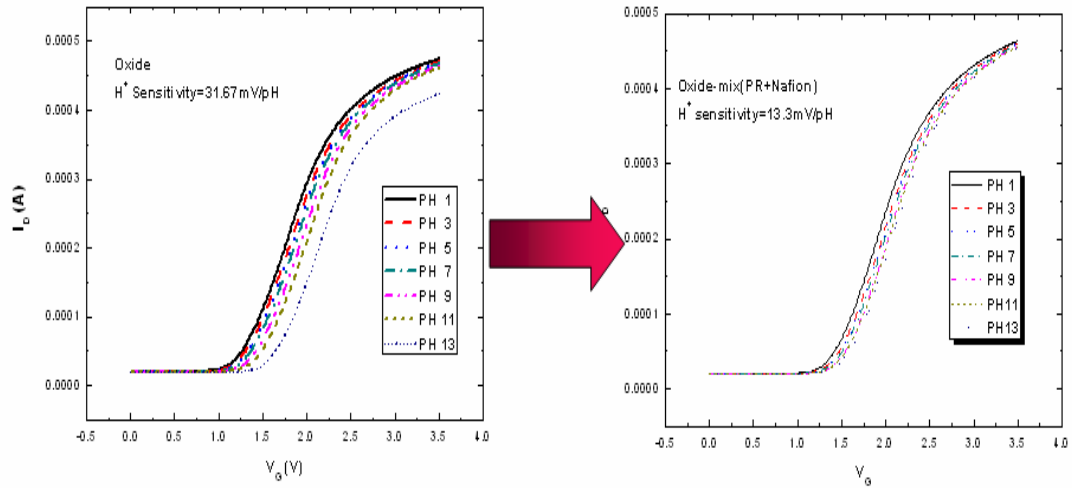


Fig. 4-9 The variety of SiO₂ H⁺ sensitivity after coated with PR and Nafion

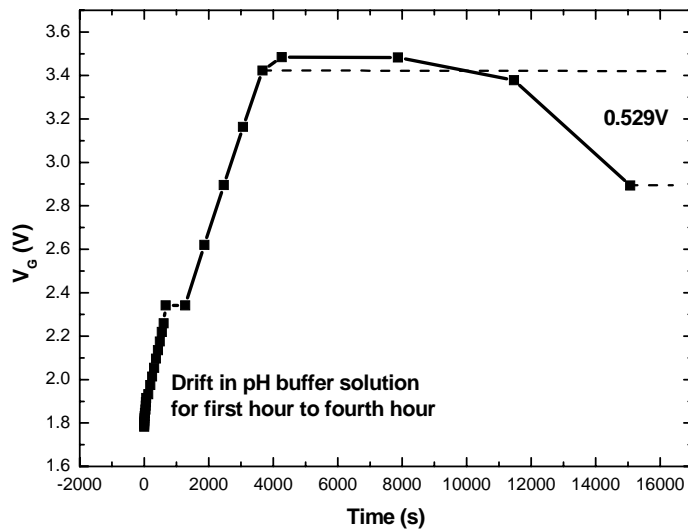


Fig4-10 Time to drift in pH buffer solution of SiO₂-mix(PR1:Nafion1)-REFET for 4 hours

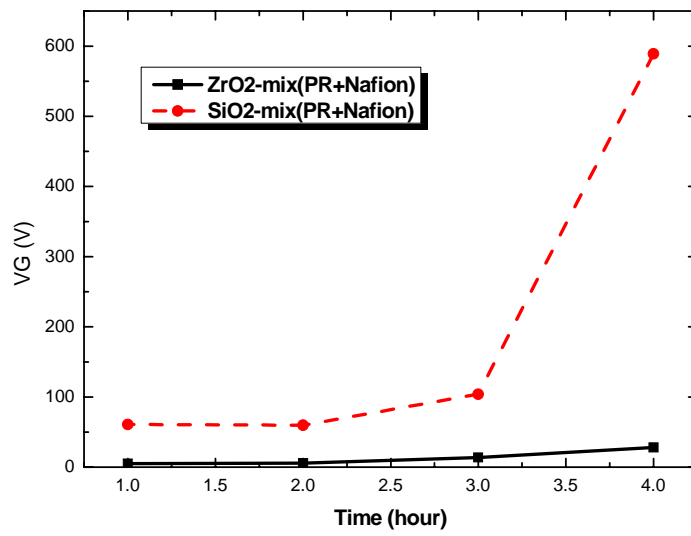


Fig4-11 The drift phenomenon in different sensing-layer

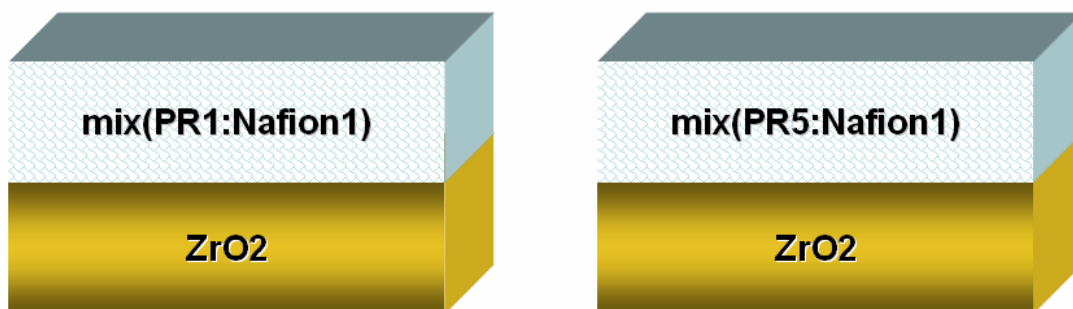


Fig4-12 The comparison between different proportions of PR and Nafion

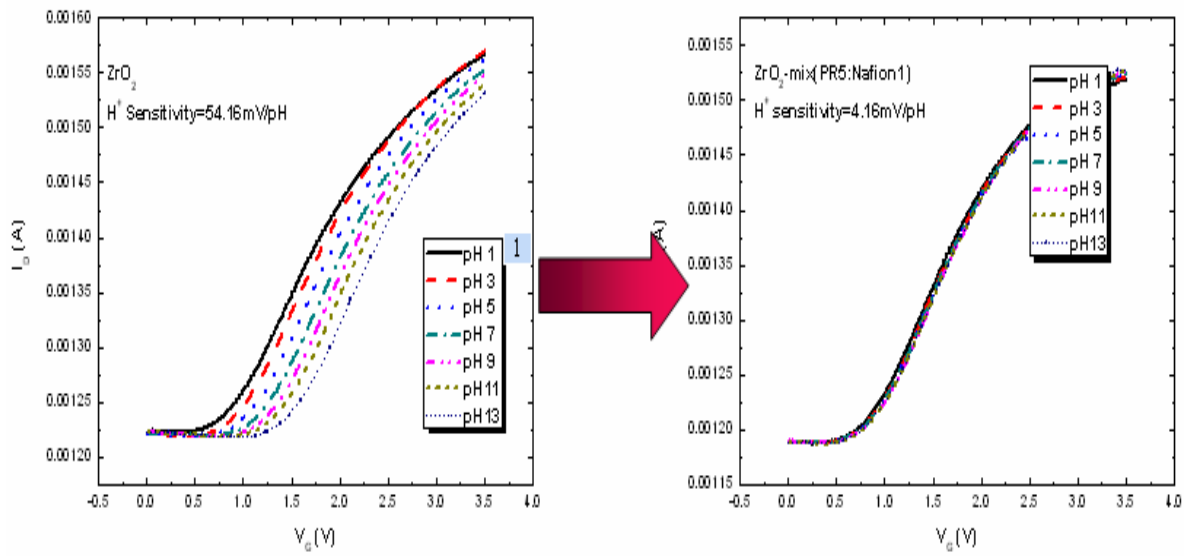


Fig4-13 The variety of SiO₂ H⁺ sensitivity after coating with PR:Nafion=5:1

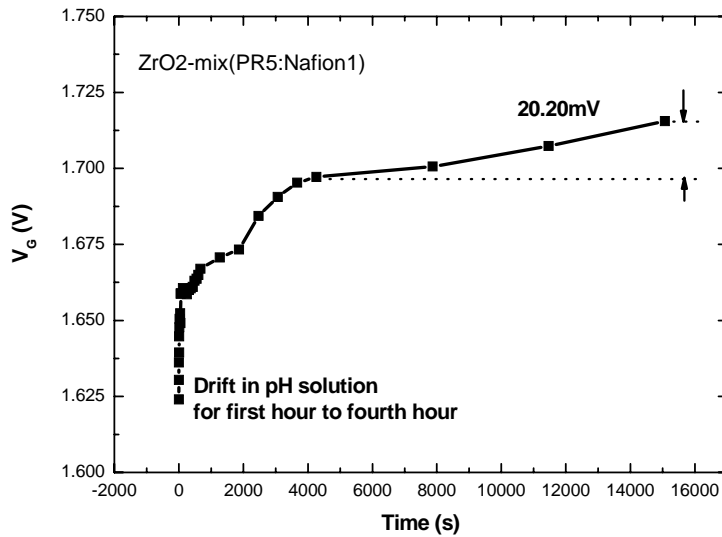


Fig4-14 Time to drift in pH buffer solution of ZrO₂-mix(PR5:Nafion1)-REFET for 4 hours

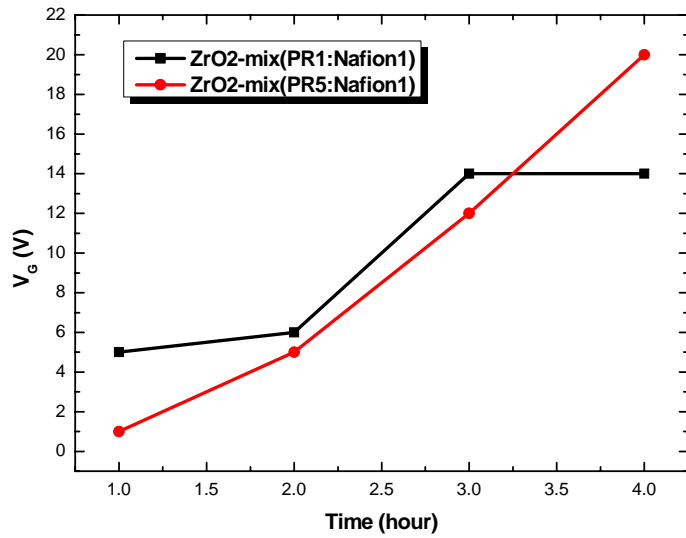


Fig4-15 The drift phenomenon in different proportions of PR:Nafion

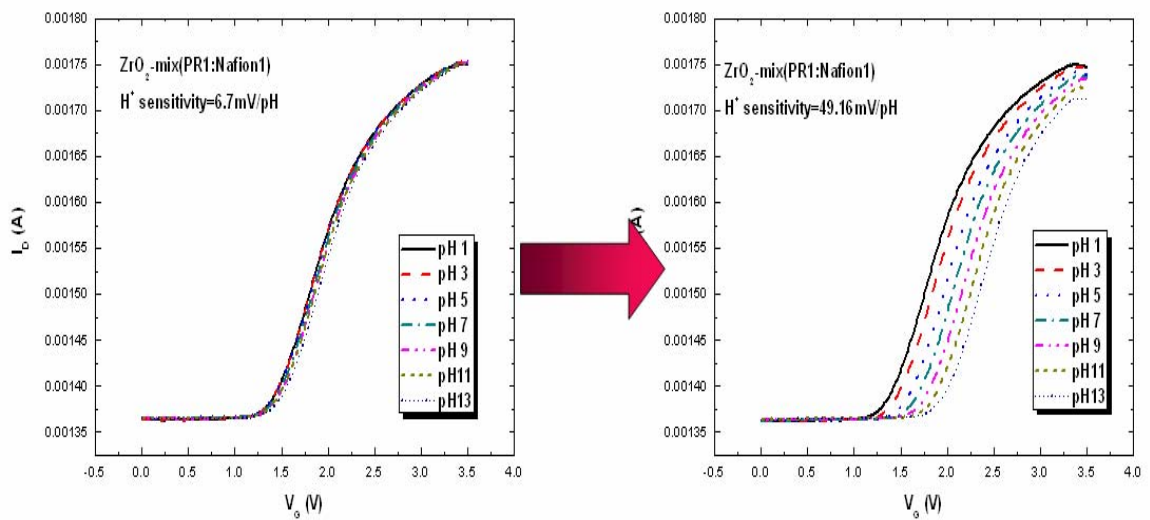


Fig4-16 Sensitivity variety from 1st to 2nd measurement of ZrO₂-mix(PR1:Nafion1)

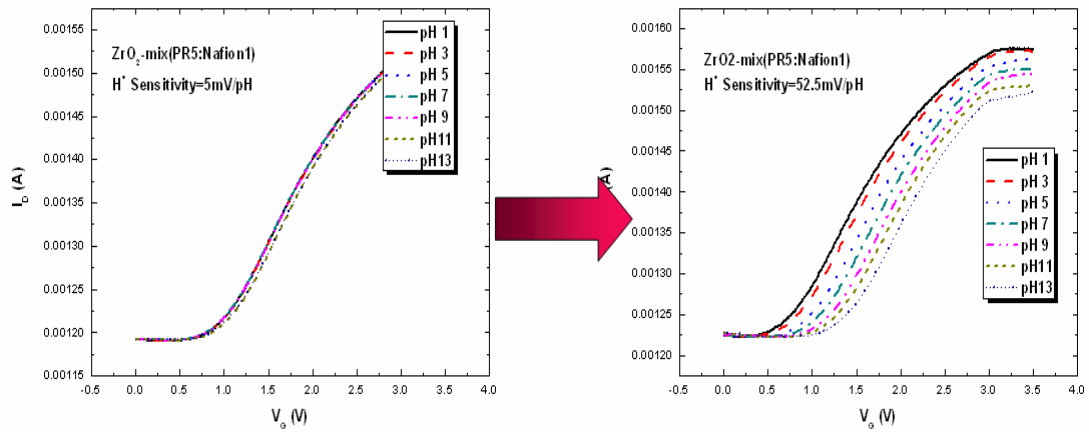


Fig4-17 Sensitivity variety from 1st to 2nd measurement of ZrO₂-mix(PR5:Nafion1)

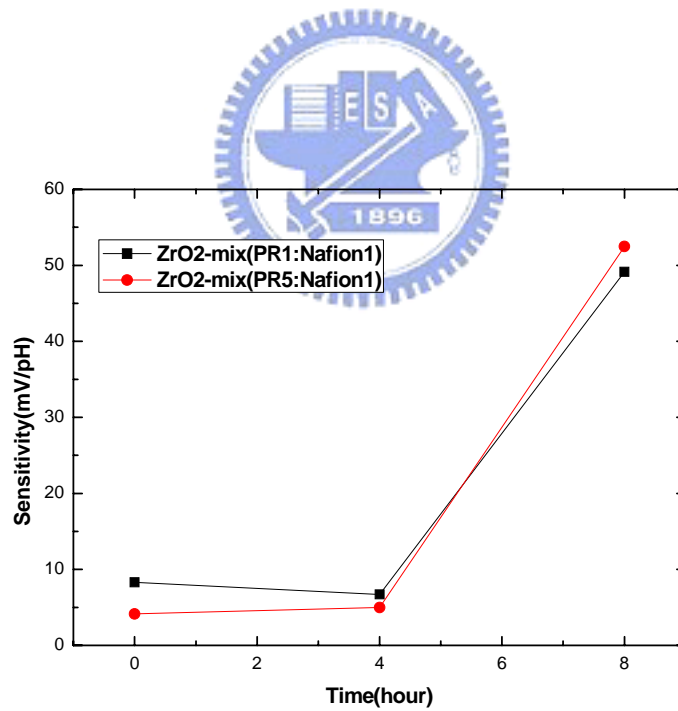


Fig4-18 The variety of sensitivity in 8 hours

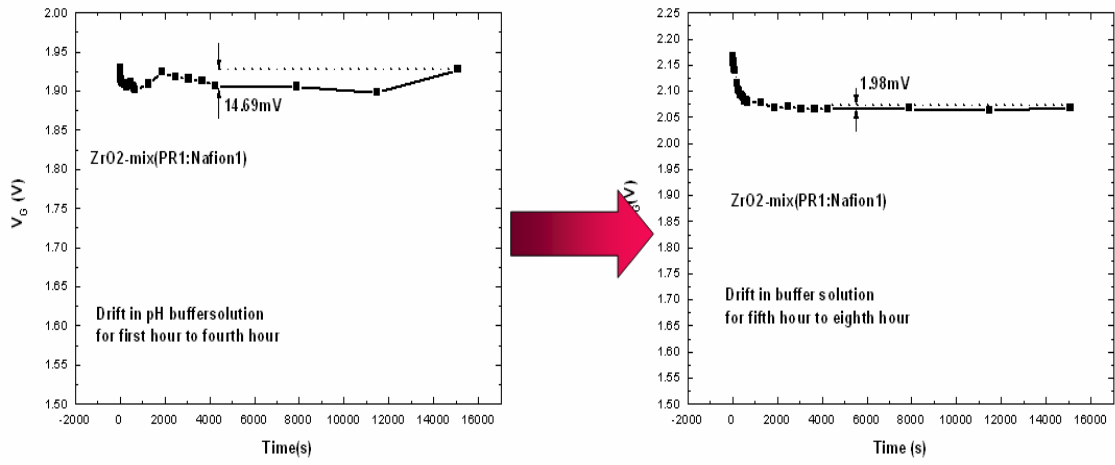


Fig4-19 Drift variety from 1st to 2nd measurement of ZrO2-mix(PR1:Nafion1)

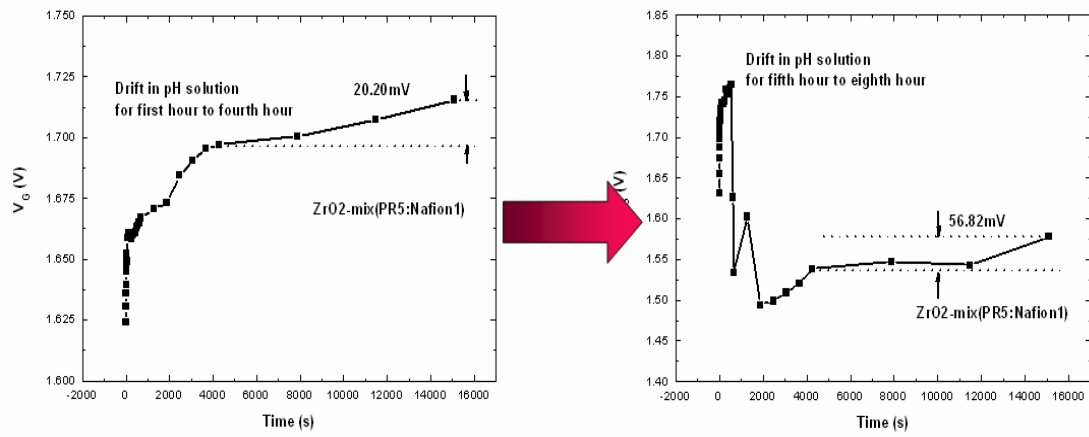


Fig4-20 Drift variety from 1st to 2nd measurement of ZrO2-mix(PR5:Nafion1)

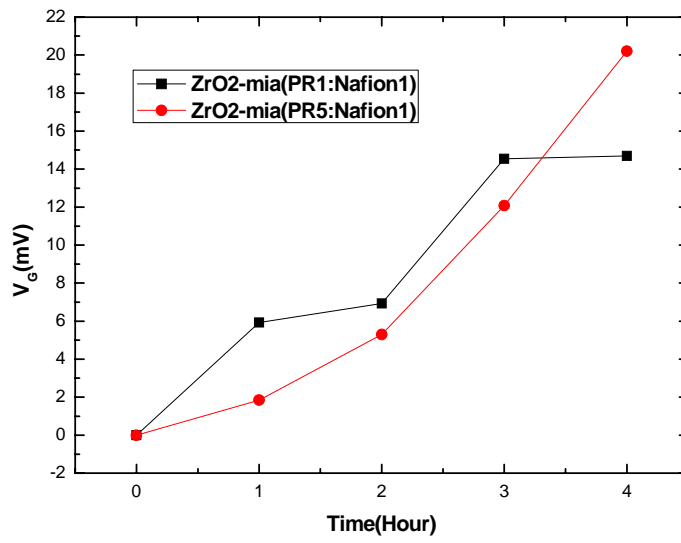


Fig.4-21 Drift v.s. time in 4hours

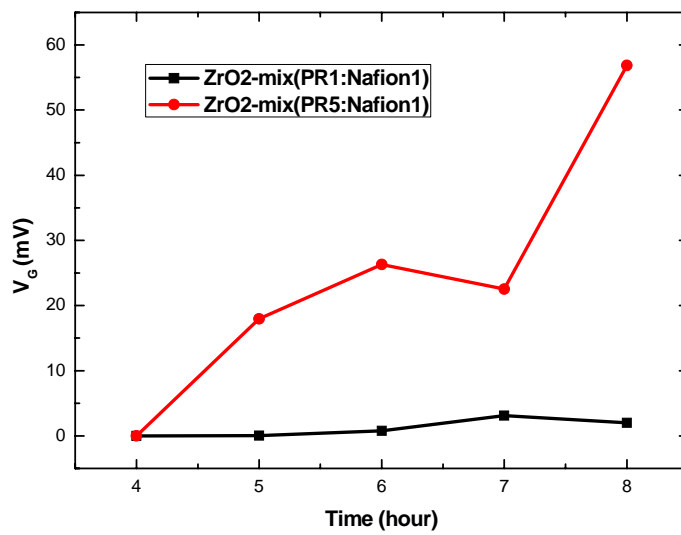


Fig.4-22 Drift v.s. time between 4th to 8th

簡歷

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(民國 88 年 9 月~民國 92 年 6 月)

國立交通大學微電子奈米科技產業研發碩士專班

(民國 95 年 2 月~民國 97 年 2 月)

碩士論文：以NafionTM/PR包埋結構作為參考場效電晶體之感測層研究

The study of NafionTM/PR entrapment structure as REFET Sensing film

