

國立交通大學

電子工程學系 電子研究所碩士班

碩士論文

以Polyimide高分子材料和Nafion<sup>TM</sup>作為REFET感測層  
之研究

The study of polyimide/Nafion<sup>TM</sup> structure as  
sensing films for REFET application

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中華民國九十七年七月

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# 以Polyimide高分子材料和Nafion<sup>TM</sup>作為REFET感測層 之研究

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離子感測場效電晶體 (ISFET) 最早是由 P.Bergveld 在 1970 年所提出的，其結構是將傳統的金氧半場效電晶體中的金屬閘極以待測溶液與參考電極所取代之。元件的電性會隨著溶液的不同而產生變化，同時我們也可藉由電性的變化來判定溶液的性質，我們在此以酸鹼離子感測器做探討。

本論文以找到最好的 REFET 為目標，在本篇論文中我們使用高分子聚合物 Polyimide 和 Nafion 兩種材料，利用不同的組合結構覆蓋在 ZrO<sub>2</sub>-pH-ISEFT 的閘極絕緣層上，來修飾原本對氫離子有高靈敏度的 ZrO<sub>2</sub>-pH-ISEFT 變成一個對氫離子靈敏度極低的參考電晶體(REFET)，這個使用 Nafion 與 Polyimide 混合物的參考電晶體(REFET) 可以有很低的靈敏度 7.5 mV/pH，為了確認此結構對 pH 緩衝液的抵抗力，我們也對此混合物結構對做閘極電壓漂移的研究，六小時的量測

結果顯示，閘極電壓漂移為 1.28mv/hr，最後我們將 REFET/ISFET 使用虛電極(Pt) 量測結果顯示可以有 54.47 mV/pH。



# The study of polyimide/Nafion<sup>TM</sup> structure as sensing films for REFET application

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## ABSTRACT

The logo of National Chiao Tung University is a circular emblem with a gear-like border. Inside the circle, there is a stylized building and the year '1896' at the bottom. The word 'ABSTRACT' is printed in bold, black, uppercase letters across the top of the logo.

The ion-sensitive field effect transistor (ISFET) was first introduced by P.Bergveld in 1970. The metal gate is replaced by a reference electrode and the electrolyte. The electric characteristics are changed by different kinds of electrolyte, and we can distinguish the properties of electrolyte. In this study we examine pH-ion-sensitive field effect transistor.

The present paper takes finding the best REFET as a goal. We use high polymer Polyimide and the Nafion two kinds of materials in this paper. The different membrane has been coated on over the ZrO<sub>2</sub> gate insulator surface of an ISFET. We apply the Nafion mixed Polyimide structure to modify the ISFET sensing layer and successfully make the high H<sup>+</sup> sensitivity ZrO<sub>2</sub>-pH-ISFET become a low H<sup>+</sup> and Na<sup>+</sup> sensitivity REFET. From the experimental results, the H<sup>+</sup> sensitivity of ZrO<sub>2</sub>-pH-ISFET can be decreased to 7.5 mV/pH. We want to test this structure chemistry resistibility. We study the drift phenomenon in this structure. In the

measurement with of 6 hours the gate voltage drift was 1.28mv/hr. When in differential ISFET/REFET with QRE (Pt) measurement, the H<sup>+</sup> sensitivity will be 54.47 mV/pH .



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誌于 2008.07 林昇宇

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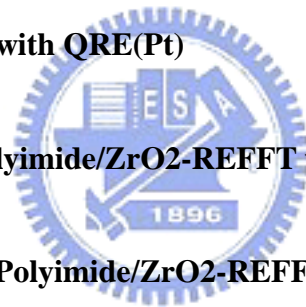
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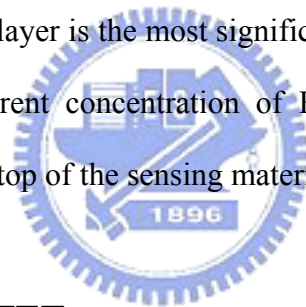


# Chapter 1

## Introduction

### 1.1 Introduction to ISFET

ISFET was proposed more than 30 years ago. In 1970 Bergveld published the Ion-sensitive-field-effect-transistor (ISFET) paper [1]. The ISFET device is similar to the conventional MOSFET except that the metal/poly gate is replaced by sensing layers, and the sensing layers are exposed to the solution directly. The most of the advantages of ISFET are small size making multiple sensors on a chip, fast response, mass producible, and cheap cost possibility. And the manufacturing process is similar to the MOSFET. The sensing layer is the most significant part in ISFET. The different pH solution makes the different concentration of H<sup>+</sup>-ion. The H<sup>+</sup>-ions from the electrolyte accumulate on the top of the sensing material.



### 1.2 The problems of ISFET system

In practical application of ISFET, a standard reference electrode is required to provide a reference electric potential. However, the size of the standard reference electrode is relative big, it is not suitable for applications, especially when the sample is little.

How to detect a correct and consistent pH value is always the direction of research. Besides adopting materials that have good linearity, sensitivity, and stability, there are two important subjects in measurement that provide alternative ways to obtain a reliable pH value. One is the design of a stable reference electrode, the other is the introduction of a REFET.

### 1.3 Reference electrode

An ideal reference electrode for use as the ISFET gate terminal should provide [2]

- a) an electrical contact to the solution from which to define the solution potential;
- b) an electrode/solution potential difference ( $E_{ref}$ ) 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 the reference electrodes in miniaturized dimensions [3,4]. The on-chip fabrication of a reference electrode with IC-compatible techniques would make ISFET suitable for biomedical sensing because of the low cost, small size and rigidity.



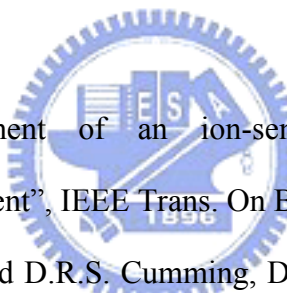
### 1.4 Reference FET

An ideal reference ion-sensitive field-effect transistor (REFET) is a FET that is insensitive to ions in pH measurement [3], but identical to the ISFET in terms of transconductance, thermal response, etc. The differential measurement between an ISFET and a REFET thus eliminates the variations of the environment, such as temperature, light, instable reference electrode/solution contact potential, etc. This can be achieved by coating an ISFET with a polymer membrane to prevent the hydrogen ions from reaching the insulator surface.

## 1.5 Motivation of this work

In order to attain diminution for ISFET, we want to find some thing which can replace ISFFET's glass electrode. One is use solid state electrode, and another is REFET. But 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. This study use polymer as sensitivity to compare with Drift, and it make a better REFET.

## 1.6 References

- 
- [1] P. Bergvled, "Development of an ion-sensitive solid-state device for neurophysiological measurement", IEEE Trans. On Bio-Med. Eng. (1970) 70-71
- [2] P.A. Hammond, D. Ali and D.R.S. Cumming, Design of a single-chip pH sensor using a conventional 0.6- $\mu\text{m}$  CMOS process, IEEE Sens. J. **4** (2004) 706-712.
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- [4] I.Y. Huang and R.S. Huang, Fabrication and characterization of a new planar solid-state reference electrode for ISFET sensors, Thin Solid Films **406** (2002) 225-261.
- [5] A. Errachid, J. Bausells and N. Jaffrezic-Renault, A simple REFET for pH detection in differential mode, Sens. Actuators B **60** (1999) 43-48.

## Chapter 2

### Theory Description

#### 2.1 Definition of pH

The term pH is derived from a combination of p for the word power and H for the symbol of the element hydrogen [1]. In aqueous solution, the following equilibrium exists between the water (H<sub>2</sub>O), the acid (H<sup>+</sup>) and the alkali (OH<sup>-</sup>):



pH is one of the most common chemical and biomedical measurements. The degree of the pH is the solution of ionization which can supply how much hydrogen ions (H<sup>+</sup>), not the concentration of the solution itself. The definition in pH is expressed as

$$pH = -\log a_{\text{H}^+} = -\log \gamma[\text{H}^+] \quad \text{Eq. 2-2}$$

where  $a_{\text{H}^+}$  is the hydrogen ion activity,  $\gamma$  is the activity coefficient which equals to 1 when diluted solution, and  $[\text{H}^+]$  is the molar concentration of solvated protons in units of moles per liter. In practice, pH depends on a number of factors, such as the concentration of the added acid and its dissociation constant [2].

#### 2.2 The method for pH detection

Traditionally, the methods for the measurement of pH values include indicator reagent, pH test strips, metal electrode and glass electrode. There are some drawbacks on the other methods, except for glass electrode. Such as, indicator reagent can show different colors at different solvent, but it only exhibit a range of pH not the accuracy value; As pH test strips immersed in the test liquid, they show a particular color



corresponding to the pH of the solution. These are similar to indicator reagent; The hydrogen electrode method is a golden standard for all methods of pH measure. The activity of the hydrogen ions is determined by potentiometric measurement using a standard hydrogen electrode and a reference electrode. In order to ensure a saturated layer of hydrogen adsorbed at the platinum surface, hydrogen gas is continuously bubbled around the platinum electrode. However, this method is not suitable for daily use due to the inconvenience of handling hydrogen gas [4]. Because of some limitations in practical applications of the first three methods, the glass electrode becomes the most widely used method for the pH measurement, and it is considered to be the standard measuring method.

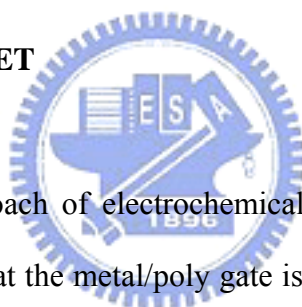
The glass electrode is most widely used for pH measurement due to ideal Nernstian response independent of redox interferences, short balancing time of electrical potential, high reproducibility and long lifetime. However, glass electrode has several drawbacks for many industrial applications. Firstly, they are unstable in alkaline or HF solutions or at temperatures higher than 100°C. Also, they exhibit a sluggish response and are difficult to miniaturize. Moreover, they cannot be used in food or in in vivo applications due to their brittle nature [3]. There is an increasing need for alternative pH electrodes [4].

New trends of pH measurements such as optical-fiber-based pH sensor, mass-sensitive pH sensor, metal oxide sensor, conducting polymer pH sensor, nano-constructed cantilever-based pH sensor, ISFET-based pH sensor and pH-imaging sensor. In this study, we will discuss what problems in practical applications of ISFETs and how to improve them

## 2.3 The theory of ISFET

Since ISFET was the first reported by Bergveld, research on new material of sensing thin and fabrication process to improve the sensitivity and stability has been continuously proposed [5-7]. At the same time, the mechanism of the pH response of pH ISFET has also been studied extensively [6-12]. Electrochemical measurement of pH utilizes devices that transduce the chemical activity of the hydrogen ion into an electronic signal, such as an electrical potential difference or a change in electrical conductance. The followings are the theoretical foundations which are mostly adopted to characterize the ISFET.

### 2.3.1 From MOSFET to ISFET



The ISFET is a new approach of electrochemical measurement of pH, which is similar to MOSFET except that the metal/poly gate is replaced by sensing layers, and the sensing layer is immersed in aqueous solution. Because of it can not directly supply on the aqueous, therefore the reference electrode is adopted to connect with sensing layer. The reference electrode not only supply stable voltage but also can connect the circuit with sensing layer to make a loop. It can trace back to the history of the development of ISFET, it is not difficult to find out the similarities between ISFET and MOSFET. In general MOSFET is Metal-Insulator-Semiconductor structure, ISEFT is Electrolyte-Insulator-Semiconductor structure. The most obvious characteristic is the similarity between their structures. For this reason, the best way to comprehend the ISFET is to understand the operating principle of a MOSFET first.

When MOSFET is operated in the so-called ohmic or non-saturated region, the drain current  $I_D$  is given by:

$$I_D = \frac{C_{OX}\mu W}{L} \left\{ (V_{GS} - V_T) - \frac{1}{2} V_{DS} \right\} V_{DS} \quad \text{Eq. 2-3}$$

where  $C_{OX}$  is the gate insulator capacitance per unit area;  $\mu$  is the electron mobility in the channel;  $W/L$  is the width-to-length ratio of the channel;  $V_{GS}$  is gate to source voltage;  $V_{DS}$  is drain to source voltage and  $V_T$  is the threshold voltage.  $V_T$  can be described by following expression:

$$V_T = V_{FB} - \frac{Q_B}{C_{OX}} + 2\phi_F \quad \text{Eq. 2-4}$$

where  $V_{FB}$  is the flat-band voltage;  $Q_B$  is the depletion charge in the silicon substrate, and  $\phi_F$  is the potential difference between the Fermi level and intrinsic Fermi level. The degree of  $\phi_F$  is dependent on the doped concentration.  $V_{FB}$  can be described by following expression:

$$V_{FB} = \frac{\Phi_M - \Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS}}{C_{OX}} \quad \text{Eq. 2-5}$$

where  $\Phi_M$  is the work function of the gate metal;  $\Phi_{Si}$  is the work function of silicon;  $Q_{OX}$  is the charge in the oxide and  $Q_{SS}$  is the surface state density at the oxide-silicon interface. Substitution of Eq. (2-4) in Eq. 2-5, the general form of the threshold voltage of a MOSFET can be described by following expression:

$$V_T = \frac{\Phi_M - \Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS} + Q_B}{C_{OX}} + 2\phi_F \quad \text{Eq. 2-6}$$

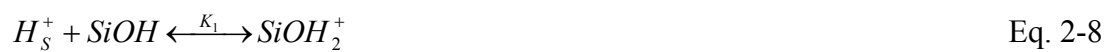
In the case of ISFET, the metallic gate is taken off. So that, the term  $\Phi_M$  and  $\Phi_{Si}$  are no longer to considered on the ISFET. At Fig. 2-1 illustrates, it can observe the similarities and differences between MOSFET and ISFET. When immersed in a aqueous solution, it must occur surface potential at the oxide-solution interface. The surface potential must take in into account. Hence the threshold voltage become the following expression:

$$V_T = E_{ref} + \chi^{sol} - \Psi_0 - \frac{\Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS} + Q_B}{C_{OX}} + 2\phi_F \quad \text{Eq. 2-7}$$

where  $E_{ref}$  is the constant potential of the reference electrode;  $\chi^{sol}$  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  $\Psi_0$ , it is the kernel of ISFET sensitivity to the electrolyte pH which is controlling the dissociation of the oxide surface. In order to obtain an accuracy pH value, to investigate a high pH sensitivity ISFET on the electrode-electrolyte interface is necessary.

### 2.3.2 The Response of pH at the Oxide-Electrolyte Interface

The surface of any metal oxide always contains hydroxyl groups, in the case of silicon dioxide SiOH groups [13]. These groups consist of donate and accept a proton from the solution. Therefore, as ISFET sensing layer like SiO<sub>2</sub> contact an aqueous solution, the change of pH will change the SiO<sub>2</sub> surface potential. These reactions can be expressed by:



where  $H_S^+$  represents the protons at the surface of the oxide.

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:

$$a_{H_S^+} = a_{H_B^+} \exp \frac{-q\Psi_0}{KT} \quad \text{Eq. 2-10}$$

or

$$pH_S = pH_B + \frac{q\Psi_0}{2.3KT} \quad \text{Eq. 2-11}$$

where  $a_{H^+}$  is the activity of  $H^+$ ;  $q$  is the elementary charge;  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The subscripts B and S refer to the bulk and the surface, respectively.

There are two important parameters which are related to ISFET sensitivity,  $\beta_s$  and  $C_s$ .  $\beta_s$  is the symbol of the surface buffer capacity, the ability of  $\beta_s$  as the oxide surface to deliver or take up protons, and  $C_s$  is the differential double-layer capacitance, of which the value is mainly determined by the ion concentration of the bulk solution via the corresponding Debye length.

$$\frac{\Delta\sigma_0}{\Delta pH_s} = -q\beta_s \quad \text{Eq. 2-12}$$

where  $\sigma_0$  is the surface charge per unit area.  $\beta_s$  is called the intrinsic buffer capacity because it is the capability to buffer small changes in the surface pH ( $pH_s$ ), but not in the bulk pH ( $pH_B$ ).

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

$$\sigma_{DL} = -C_i\Psi_0 = -\sigma_0 \quad \text{Eq. 2-13}$$

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,  $C_s$ :

$$\frac{\Delta\sigma_{DL}}{\Delta\Psi_0} = -\frac{\Delta\sigma_0}{\Delta\Psi_0} = -C_s \quad \text{Eq. 2-14}$$

As a result, combination of Eq. 2-12 to 2-14 lead to an expression for the sensitivity of the the electrostatic potential change in  $a_{H_s^+}$  :

$$\frac{\Delta\Psi_0}{\Delta pH_s} = \frac{\Delta\Psi_0}{\Delta\sigma_0} \frac{\Delta\sigma_0}{\Delta pH_s} = \frac{-q\beta_s}{C_s} = \frac{\Delta\Psi_0}{\Delta(pH_B + \frac{q\Psi_0}{2.3KT})} \quad \text{Eq. 2-15}$$

Rearrange Eq. 2-15 gives a general expression for the sensitivity of the electrostatic potential to changes in the bulk pH [13]:

$$\Delta\Psi_0 = -2.3\alpha \frac{kT}{q} \Delta pH_B \quad \text{Eq. 2-16}$$

with

$$\alpha = \frac{1}{\frac{2.3kTC_s}{q^2\beta_s} + 1} \quad \text{Eq. 2-17}$$

The parameter  $\alpha$  is a dimensionless sensitivity parameter that varies between 0 and 1, depending on the intrinsic buffer capacity,  $\beta_s$ , of the oxide surface and the differential capacitance  $C_s$ . We can get the maximum value  $\alpha$  so that the sensitivity become -59.2 mV/pH at 298K which is called Nernstian sensitivity. Therefore, the intrinsic buffer capacity  $\beta_s$  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  $\text{SiO}_2$  from MOSFET does not fulfil the requirements of a high vale of  $\beta_s$ . The pH sensitivity is low depending also on the electrolyte concentration through  $C_s$ . Therefore other films such as  $\text{ZrO}_2$  were introduced to increase the values of  $\beta_s$ . 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.

## 2.4 Drift Phenomenon

Drift phenomenon is while ISFET expose to an aqueous solution for a long time, shift of ISFET gate voltage after a proper time from the response of the ISFET device. It has been reported by Dun et al. [18]. According to Hein and Egger [19], two types of drift have to be distinguished, the storage drift (irreversible shift without any applied voltages) and the long-term drift (irreversible shift under operating conditions). The initial drift means the drift after 3 h from the response starting [20]. The former's influence on drift is generally smaller than the latter. This result can be found in the previous work [3, 14-16] and also in the measurement data of this research. The phenomenon called drift is a slow, continuous, change of the threshold voltage of an ISFET in the same direction. It is difficult to identify the cause of this phenomenon, which could be either a surface or a bulk effect, or both. There are some possible reasons causes of drift [17].

(1) Variation of the surface state density ( $D_{it}$ ) at the Si/SiO<sub>2</sub> interface which means the drift dependence of diffusion mechanism.

(2) Some surface effects, such as the rehydration of a surface that is partially dehydrated and ion exchange involving OH<sup>-</sup> ions.

(3) 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<sub>2</sub>.

(4) Injection of electrons from the electrolyte at strong anodic polarizations created negative space charge inside sensitive films.

Dun et al. [18] recognized that the drifts of Si<sub>3</sub>N<sub>4</sub> and Ta<sub>2</sub>O<sub>5</sub> gate ISFET both change toward the output voltage increasing. This condition is the same as that some

negative charges ( $\text{OH}^-$ ) rise on the sensitive surface.

The great part of people most supported the drift phenomenon are the cases (1) and (2). There are two models such as the site-binding model and the gel model, which are classified according to the location where the mechanism of pH-sensitivity is presumed to occur. These models can help us to have a further understanding of the transport of mobile ions. Nonetheless, these two models are only the characteristics of ions transport in the insulator, while the physical model for the gate voltage drift is going to be presented in the next section.

#### 2.4.1 Dispersive Transport

Dispersive transport was brief reviewed in [3] and it is observed in a broad class of disordered materials. In an amorphous material, dispersive transport may arise from hopping motion through localized states (hopping transport), trap-limited transport in the presence of traps possessing an exponential energy distribution (multiple-trap transport), or a combination of the aforementioned transport mechanisms (trap-controlled hopping transport) [21]. Regardless of the specific dispersive mechanism involved, however, dispersive transport leads to a characteristic power-law time decay of diffusivity [22] which can be described by

$$D(t) = D_{00}(\omega_0 t)^{\beta-1} \quad \text{Eq. 2-18}$$

where  $D_{00}$  is a temperature-dependent diffusion coefficient which obeys an Arrhenius relationship,  $\omega_0$  is the hopping attempt frequency, and  $\beta$  is the dispersion parameter satisfying  $0 < \beta < 1$ . Dispersive transport leads to a decay in the density of sites/traps occupied by the species undergoing transport. This decay is described by the stretched-exponential time dependence given by



$$\Delta N_{S/T}(t) = \Delta N_{S/T}(0) \exp[(-t/\tau)^\beta] \quad \text{Eq. 2-19}$$

where  $\Delta N_{S/T}(t)$  is the area density (units of  $\text{cm}^{-2}$ ) of sites/traps occupied,  $\tau$  is the time constant associated with structural relaxation, and  $\beta$  is the dispersion parameter.

## 2.4.2 Expression for Drift

In general, the surface of a sensing film is known to undergo a relatively slow conversion to a hydrated  $\text{SiO}_2$  layer or contain oxygen atoms during contact with an aqueous solution [23-28], Since hydration leads to a change of the chemical composition of the sensing film surface, it is reasonable to assume that the dielectric constant of the hydrated surface layer differs from that of the sensing film 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 actively-biased ISFET, the gate voltage will simultaneously exhibit a change to keep a constant drain current. The change in the gate voltage can be written as:

$$\Delta V_G(t) = V_G(t) - V_G(0) \quad \text{Eq. 2-20}$$

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

$$\Delta V_G(t) = [V_{FB}(t) - V_{FB}(0)] + [V_{ins}(t) - V_{ins}(0)] \quad \text{Eq. 2-21}$$

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:

$$V_{FB} = E_{ref} + \chi^{sol} - \Psi_0 - \frac{\Phi_{Si}}{q} - \frac{Q_{OX} + Q_{SS}}{C_{OX}} \quad \text{Eq. 2-22}$$

$$V_{ins} = \frac{-(Q_B + Q_{inv})}{C_{OX}} \quad \text{Eq. 2-23}$$

where  $Q_{inv}$  is the inversion charge. If the temperature, pH, and the ionic strength of the solution are held constant,  $E_{ref}$ ,  $\chi^{sol}$ ,  $\Psi_0$ , and  $\Phi_{Si}$  can be neglected, so the drift can be

rewritten as:

$$\Delta V_G(t) = -(Q_{OX} + Q_{SS} + Q_B + Q_{inv}) \left[ \frac{1}{C_i(t)} - \frac{1}{C_i(0)} \right] \quad \text{Eq. 2-24}$$

In this study, the gate oxide of the fabricated ISFET was composed of two layers, a lower layer of thermally-grown SiO<sub>2</sub> of thickness,  $x_L$ , and an upper layer of sputter-grown ZrO<sub>2</sub> of thickness,  $x_U$ .  $C_i(0)$  is the effective insulator capacitance given by the series combination of the thermally-grown SiO<sub>2</sub> capacitance,  $\epsilon_L/x_L$ , and the sputter-grown ZrO<sub>2</sub> capacitance,  $\epsilon_U/x_U$ .  $C_i(t)$  is analogous to  $C_i(0)$ , but an additional hydrated layer of capacitance make  $C_i$  always smaller than  $C_i$ ,  $\epsilon_{HL}/x_{HL}$ , at the oxide-electrolyte interface must be considered, and the sputter-grown ZrO<sub>2</sub> capacitance is now given by  $\epsilon_U/[x_U - x_{HL}]$ . The series combinations of the capacitances are illustrated in Figure 2-3. Therefore, the drift is given by

$$\Delta V_G(t) = -(Q_{OX} + Q_{SS} + Q_B + Q_{inv}) \left( \frac{\epsilon_U - \epsilon_{HL}}{\epsilon_U \epsilon_{HL}} \right) x_{HL}(t) \quad \text{Eq. 2-25}$$

From this equation, we observed that drift of gate voltage  $\Delta V_G$  if the substrate type was different, it might to be positive or negative value. Because of the value of  $\Delta V_G$  is positive or negative, it is depend on the  $Q_{inv}$  and  $Q_B$ . Other terms at Eq.(2-25) can be appropriate as constant value no matter what the substrate is. According to this assume 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  $x_{HL}(t)$  is given by [1]

$$x_{HL}(t) = x_{HL}(\infty) \left\{ 1 - \exp[-(t/\tau)^\beta] \right\} \quad \text{Eq. 2-26}$$

**with**

$$x_{HL}(\infty) = \frac{D_{00} \omega_0^{\beta-1} \Delta N_{S/T}(0)}{A_D \beta N_{hydr}} \quad \text{Eq. 2-27}$$

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. Thus, combination of Eq. 2-20 to 2-27

the gate voltage drift can be expressed by the following formula:

$$\Delta V_G(t) = -(Q_{OX} + Q_{SS} + Q_B + Q_{inv}) \left( \frac{\epsilon_U - \epsilon_{HL}}{\epsilon_U \epsilon_{HL}} \right) x_{HL}(\infty) \{1 - \exp[-(t/\tau)^\beta]\} \quad \text{Eq. 2-28}$$

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

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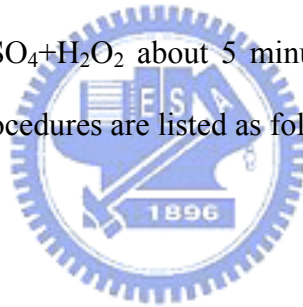
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## Chapter 3

### Experiment and Measurement

#### 3.1 ISFET and REFET fabrication Process flow

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 procedures are listed as follows:



1. RCA clean.

Wet oxide  $6000\text{\AA}$ ,  $1050^\circ\text{C}$ ,

2. Define Source/Drain region. (mask 1)

BOE wet etching of silicon dioxide.

3. Dry oxide growth  $300\text{\AA}$ ,  $1050^\circ\text{C}$ ,

4. Source/Drain implantation, Dose= $5E15(1/\text{cm}^2)$ , Energy= $25\text{Kev}$ .

5. Source/Drain annealing,  $950^\circ\text{C}$ , 60mins.

6. PECVD Oxide deposition  $1\mu\text{m}$ .

7. Define contact hole and gate region. (mask 2)

BOE wet etching of silicon dioxide.

8. Dry oxide growth  $100\text{\AA}$ ,  $850^\circ\text{C}$ ,

9. Define the sensing layer region. (mask 3)

Sensing layer ( $\text{ZrO}_2$ ) deposition by Sputtering.  $300 \text{ \AA}$ .

$\text{ZrO}_2$  sintering  $600^\circ\text{C}$ , 30mins.

10. Define the contact and quasi reference electrode region. (mask 4)

. Ti/Pt deposition by Sputtering  $150 \text{ \AA}$  /  $350 \text{ \AA}$ .

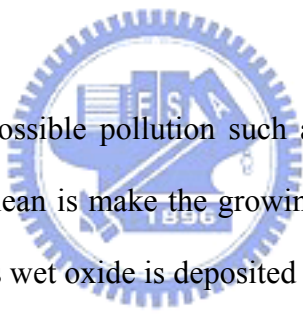
11. Backside Al evaporation  $5000 \text{ \AA}$ .

Pt and Al sintering  $400^\circ\text{C}$ , 30mins

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

## 3.2 Key steps illustration

### 3.2.1 Gate region formation



RCA clean is reduce the possible pollution such as particles, organics, diffusion ions and native oxide. RCA clean is make the growing equality of Wet Oxide better. The next step  $6000 \text{ \AA}$  thickness wet oxide is deposited as barrier layer for S/D implant. The density and the energy of S/D implant is  $5 \times 10^{15} \text{ (1/cm}^2\text{)}$  and  $25 \text{ KeV}$  with phosphorous dopant for n-type ISFET. After ion-implantation, high potential doping ion destroy the structure of lattice on silicon, and repair it by the way of anneal.

PECVD Oxide film about  $1 \mu\text{m}$  was deposited onto the original  $6000 \text{ \AA}$  thickness oxide, which protect the structure of a pH-ISFET blocking the ions diffuse when immersed in electrolyte. Thus, a stable electrical characteristic can be obtained.

Following the PECVD Oxide film deposition,  $100 \text{ \AA}$  thickness dry oxide was grown in a dry oven as gate oxide formed.

### 3.2.2 Sensing layer deposition

The ZrO<sub>2</sub> sensing film 300Å is growth by the sputter It has been proved the ZrO<sub>2</sub> film deposited by sputtering has good characteristics as a pH-ISFET sensing layer in our lab. ZrO<sub>2</sub> cause the sensitivity of metal oxide higher, which is about 58mv/pH.

Therefore, in this study we still use ZrO<sub>2</sub> as the sensing layer and research the the suitable REFET for it. The detailed parameters of sputter are listed in Table 3.1. The test structures of REFET are listed in Table 3.2.

### 3.3 Measurement Principle

The setup of the measurement system is illustrated in Fig. 3-2. ISFET and REFET were designed to share the same source terminal, and the drain-to-source voltage were biased at the same condition ( $V_{DS1}=V_{DS2}$ ). The drain currents of ISFET and REFET were set at a constant magnitude, therefore, if the pH of the solution varies, the gate voltage must adjust its magnitude to maintain the constant current. Consequently, the variation of the gate voltage exhibits the pH sensitivity of the sensing oxide. Fig. 3-3 illustrates the detection principle of pH. For the drift measurement, the detection principle is in a similar manner to that of the pH measurement and is shown in Fig. 3-4.

### 3.4 Measurement system

#### 3.4.1 Preparation of measurement

To investigate the characteristics of the ZrO<sub>2</sub> 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 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.

### **3.4.2 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 [5], the first equilibrium will achieve in a minute.

In order to obtain the sensitivity, at first we measure the  $I_{ds}$ - $V_{ds}$  to observe 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 the next buffer solution which was under test twice, and stay 1 min to avoid the effect of the buffer solution that was measured before. This step can make our 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

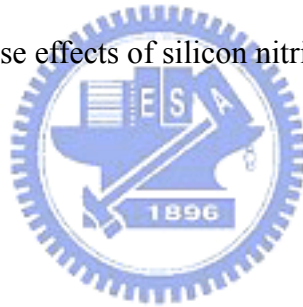


### **3.4.3 Drift measurement set-up**

The drift characteristics were measured with differential pH=7 value of aqueous solution and the same condition samples period of 30 seconds, 1 minute, 10 minutes and 1 hour. 33 sampling points in the time frame of 7 hours were observed for n-type and p-type ISFET with  $ZrO_2$ . The detection principle is in a similar manner to that of the pH measurement and is shown in Fig. 3-4.

### 3.5 References

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## Chapter 4

### Results and Discussions

#### 4.1 Introduction

According to chapter 2, the sensitivity of ISFET is related to the numbers of surface sites the more numbers of surface sites the larger sensitivity it has. To reduce the sensitivity, we use a high polymer. Polymer is a hydrophobic material which can reduce H ion in a large number. Finally, high/low sensitivities of membranes for ISFET and REFET are essential for getting higher resolution of pH measurement. This experiment discusses a best REFET (Reference Electrode Field Effect Transistor) in different structure.

In this study we fabrication of a REFET based on a polymer membrane. The membrane has been coated on over the  $ZrO_2$  and  $SiO_2$  gate insulator surface of an ISFET. The polymer membrane we use polyimide and Nafion . Nafion is a proton exchange membrane, it can protect polymer and it become the mechanism of proton exchange to make ion absorb on the surface of polymer steadily. We use three different membrane polyimide, Nafion/polyimide and Nafion mix polyimide.

#### 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 Polyimide,  $ZrO_2$ /Polyimide/Nafion and  $ZrO_2$ -mix(Ployimide+Nafion) three different structure's approach of entrapment, and get the common conclusion that sensitivity of both reduce from 58mV/p in  $ZrO_2$  (Fig.4-1) sensing layer to 12.5mV/pH (Fig.4-2) ,10mV/pH (Fig.4-3) and 9.75mV/pH (Fig.4-4) respectively.

The main reason is the entrapment Polyimide can reduce the sensitivity efficiently, and it can get different material's site-binding from Gouy-Chapman-Stern Theory model and Site-binding model, which traps the number of ion are also different. the sensitivity can reduce largely about 80%. But  $ZrO_2$ /Polyimide/Nafion and  $ZrO_2$ -mix (Polyimide+Nafion) membrane can not sense pH11 and pH13 . Accordingly we baked the membrane in order to solve this problem. After baked we observed the membrane can sense pH11 and pH13, and sensitivity of both reduce to 10mV/pH (Fig 4-5), 7.5mV/pH (Fig4-6) and 8.4mV/pH (Fig4-7) respectively. The main reason is the solvent in polyimide be volatilized. It made polyimide hardness and polyimide is not easy to absorb H ion. Table 4.1 lists the corresponding sensitivity values.

### 4.3 The comparison of deposition on different structure

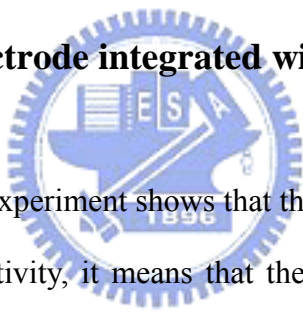
The comparison of this experiment utilize two different base on different Sensing film,  $ZrO_2$  and  $SiO_2$ , and the material of both of them mix Polyimide and Nafion coast on sensing film to get the sensitivity are 7.5mV/pH and 8.175mV/pH (Fig.4-9) respectively. The sensitivity measured in previously  $ZrO_2$  and  $SiO_2$  experiment are about 58mV/pH (Fig.4-1) and 37.5mV/pH (Fig.4-8). It concludes from site-binding model and experiment data that the main reason affect sensitivity is " hydrophobic" from Polyimide material cause H ion uneasy to absorb, so the H ion mainly absorb on the surface of Polyimide and it not connect with the sensing layer in bottom. Nevertheless, the structure base on  $SiO_2$  is inferior to  $ZrO_2$  on the improvement of sensitivity because interface of  $SiO_2$  and Polyimide is not as well as the interface of  $ZrO_2$  and Polyimide.

## 4.4 Drift Characteristics

Drift characteristics of REFET sensing layer structure for  $ZrO_2$ - pH -ISFET are shown in Fig. 4-10~4-15. Measurements were carried out in pH 7, and the duration of each measurement was about 7 hours. Average drift rate per hour was calculated by averaging the gate voltage drift in the last 6 hour, we discovered after baked membrane have low Drift.

The performance of two structure on Drift since structure of baked  $ZrO_2$ /Polyimide/Nafion inferior to the structure of baked Polyimide mix Nafion the results were 2.298, 1.284/hour respectively. Table 4.2 lists the corresponding Drift values.

## 4.5 Quasi-Reference Electrode integrated with REFET/ISFET



According to our previous experiment shows that the polymer-based materials make REFET have low sensitivity, it means that the surface potential is a constant value. In this experiment, we use  $ZrO_2$  membrane with QRE and the after baked NF-mix-polyimide/  $ZrO_2$  ISFET/REFET sensor array system, and  $ZrO_2$  membrane with QRE. And the after baked NF/polyimide-  $ZrO_2$  ISFET/REFET sensor array system, and  $ZrO_2$  membrane with QRE.

### 4.5.1 The bare Quasi-Reference Electrode integrated with REFET/ISFET

Fig. 4.16 shows three times the the sensitivity of  $ZrO_2$ -pH-ISFET measured by bare Quasi-Reference Electrode. We can see the gate voltage (VG) range of pH 1~13 value is very unstable, and the sensitivity linearity is very bad. This is the main problem of Quasi-Reference Electrode.

#### **4.5.2 The NF/ polyimide-ZrO<sub>2</sub> and NF-mix- polyimide/ZrO<sub>2</sub> Quasi-Reference Electrode**

Fig. 4.17 shows three times sensitivity of NF/polyimide- ZrO<sub>2</sub>-pH-REFET measured by Quasi-Reference Electrode. Fig. 4.18 shows three times the sensitivity of NF-mix-polyimide/ZrO<sub>2</sub>-pH-REFET measured by Quasi-Reference Electrode. We can see with the polymer coated, the gate voltage (VG) range of pH 1~13 value becomes better.

#### **4.5.3 The coplanar ISFET/REFET sensor array system with Quasi-Reference Electrode**

The sensor array system is composed by the coupled sensing membrane without polymer coated and with the polymer coated. Fig. 4.19 shows the sensitivity of differential ISFET/REFET with Quasi-Reference Electrode.

The linearity are much better than the bare Quasi-Reference Electrode. And the sensitivity is 54.47pH/mV and 49.56pH/mV. From the experimental results, the NF/polyimide-ZrO<sub>2</sub> and NF-mix-polyimide/ZrO<sub>2</sub> coplanar ISFET/REFET sensor array system seems to have the potential to solve the unstable problem of the Quasi-Reference Electrode. Table 4.3 lists the corresponding sensitivity values.

## 4.6 Conclusions

The results of this study show the Nafion and polyimide based membrane made a low sensitivity and made a low drift. When polyimide which after baked can have good sensitivity for pH1~13 and low drift. The sensitivity of ZrO<sub>2</sub>-pH-ISFET is 58mV/pH without any polymer modifying, but after treating with Nafion mix polyimide, the sensitivity can decrease to 7.5mV/pH. It means modifying by the Nafion mix polyimide material is a successful treating method for REFET. The process is simple and easy to fabricate. The unstable gate voltage (VG) range problem of Quasi-Reference Electrode is also solved by coplanar ISFET/REFET sensor array system. And we have the sensitivity of co-planar structure of ISFET/REFET are 54.47mV/pH by ZrO<sub>2</sub>/Polyimide/Nafion and 49.56mV/pH by ZrO<sub>2</sub>-mix(Polyimide+Nafion). This and the use glass electrode is similar. Used the Quasi-Reference Electrode to completed has been small.

A miniaturized ISFET/REFET pair with Quasi-Reference Electrode was demonstrated. It shows 54.47mV/pH sensitivity and 1.2841mV/hour drift with ZrO<sub>2</sub>/Polyimide/Nafion structure. The results are compatible with glass electrode.

Baking process steps are necessary for polyimide membrane, which can further obtain low sensitivity for pH1~13 and achieve lower drift.



## Chapter 5

### Future Work

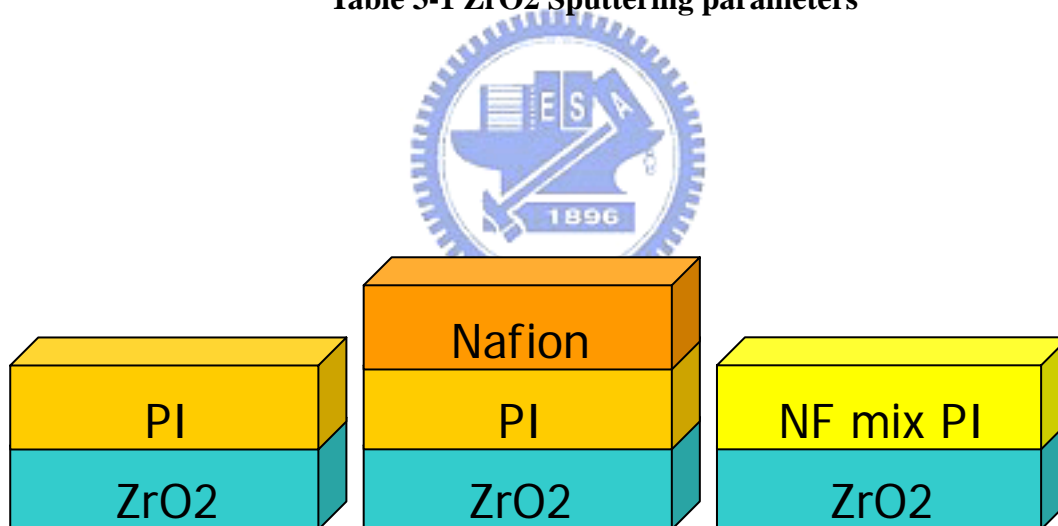
#### 5.1 Future Work

After this study, we find a REFET based on polyimide and Nafion membrane. This REFET is have a low sensitivity and low drift. But the coating process is not optimized in this experiment. So, the optimized coating method, including the influence of baking temperature or dropping manners, and the accurate thickness, needs to be studied further. The properties of these polymer materials and other new polymer stuffs are also need to be more understood. Final, we went to integrating differential electric circuit on chip.



<b>parameters of ZrO<sub>2</sub> sputter</b>
<b>power : 110 W</b>
<b>Ar / O<sub>2</sub> : 24 / 8 ( sccm )</b>
<b>Density : 6.51</b>
<b>Acoustic impedance : 14.72</b>
<b>Tooling factor : 0.533</b>
<b>Rate : 0.01 Å / s</b>
<b>pre sputter 60W for 10 min</b>
<b>Pressure : 7.6×10<sup>-3</sup></b>

**Table 3-1 ZrO<sub>2</sub> Sputtering parameters**



**Table 3-2 The test structures of REFET, NF=Nafion PI=polyimide**

Structures	Sensitivity(mV/pH)	SENDER RANGE
ZrO <sub>2</sub>	58	1~13
Polyimide/ZrO <sub>2</sub>	12.5	1~13
PLmixNF/ZrO <sub>2</sub>	9.75	1~9
PL/NF/ZrO <sub>2</sub>	10	1~9
baked PL/ZrO <sub>2</sub>	10	1~13
baked PImixNF/ZrO <sub>2</sub>	7.5	1~13
baked PI/NF/ZrO <sub>2</sub>	8.4	1~13

**Table4.1 Sensitivity in different test structures PI=polyimide NF=Nafion**

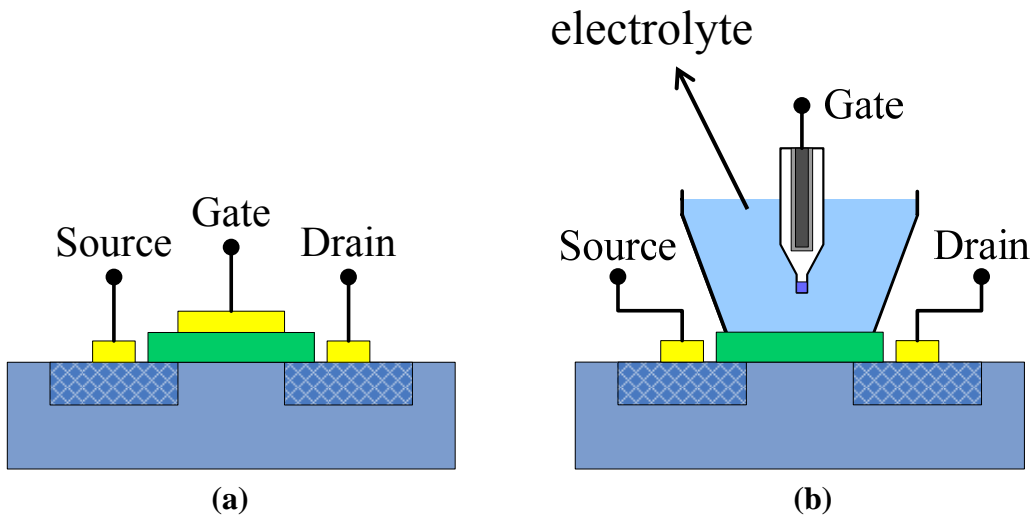
Structures	Drift(mv/hr)
ZrO <sub>2</sub>	0.6175
Polyimide/ZrO <sub>2</sub>	4.3575
PImixNF/ZrO <sub>2</sub>	3.7525
NF/PI/ZrO <sub>2</sub>	2.5
Baked PI/ZrO <sub>2</sub>	4.0533
Baked PImixNF/ ZrO <sub>2</sub>	2.298
Baked NF/PI/ ZrO <sub>2</sub>	1.2841

**Table4.2 Drift in different test structures PI=polyimide NF=Nafion**

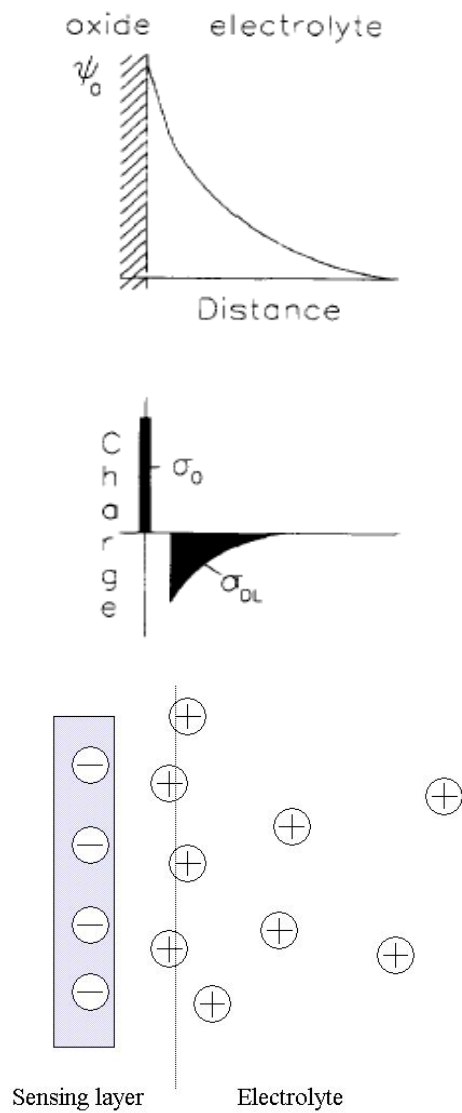
Structures	Sensitivity (mV/pH)	Drift (mV/hr)	Linearity
ZrO <sub>2</sub> with glass electrode	58	0.6175	0.9932
Baked NF/PI/ ZrO <sub>2</sub> -REFET/ ZrO <sub>2</sub> -ISFET	54.47	1.2841	0.9743
Baked PI mixNF/ ZrO <sub>2</sub> -REFET/ ZrO <sub>2</sub> -ISFET	49.56	2.298	0.96371

**Table 4.3 Sensitivity in different electrode PI=polyimide NF=Nafion**

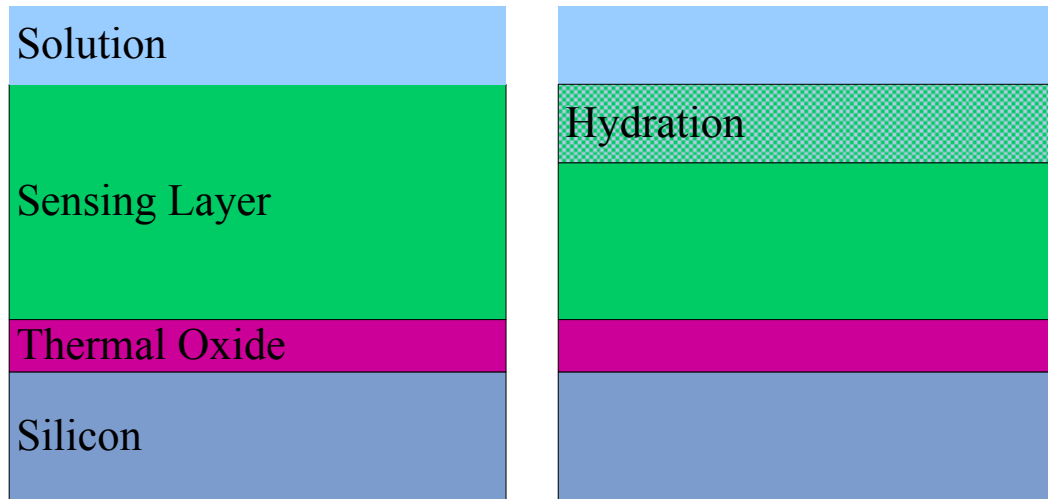




**Fig. 2-1 Schematic representation of (a) MOSFET, (b) ISFET**

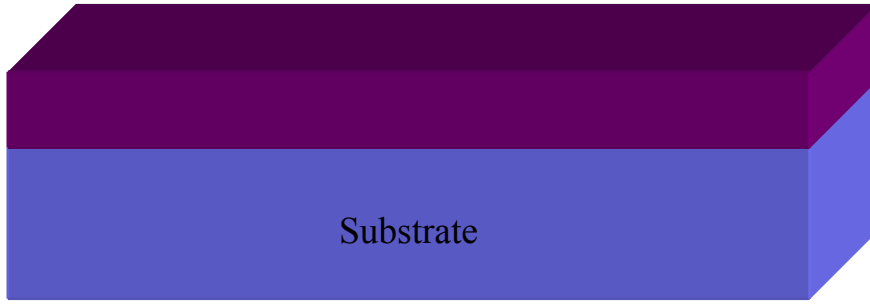


**Fig. 2-2 Potential profile and charge distribution at an oxide electrolyte solution interface**

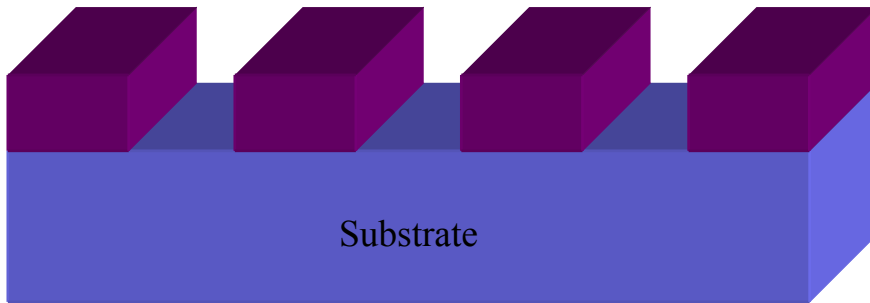


**Fig. 2-3 Series combination of the (a) initial (b) hydrated insulator capacitance**

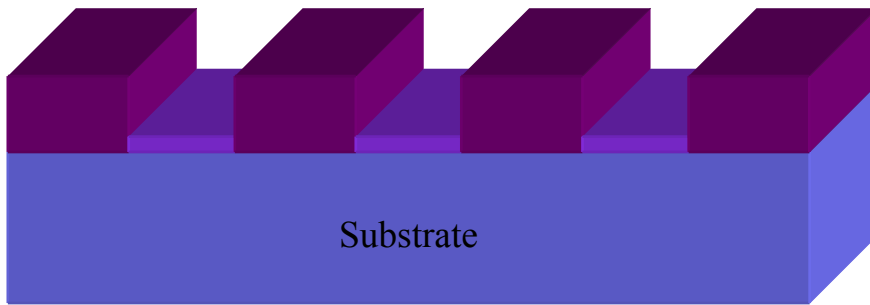




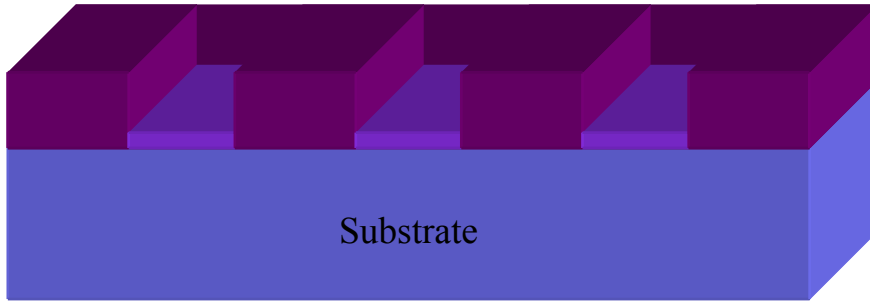
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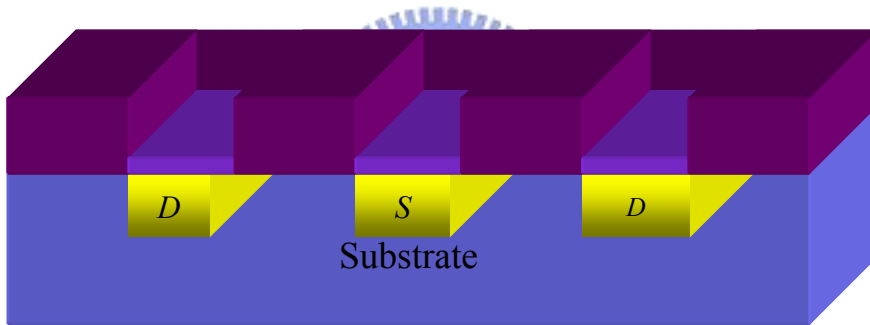
(2)



(3)

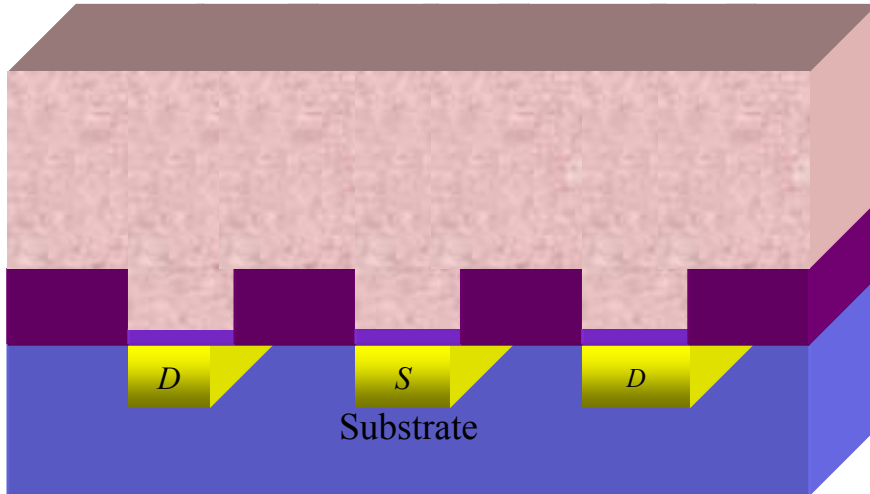


(4)

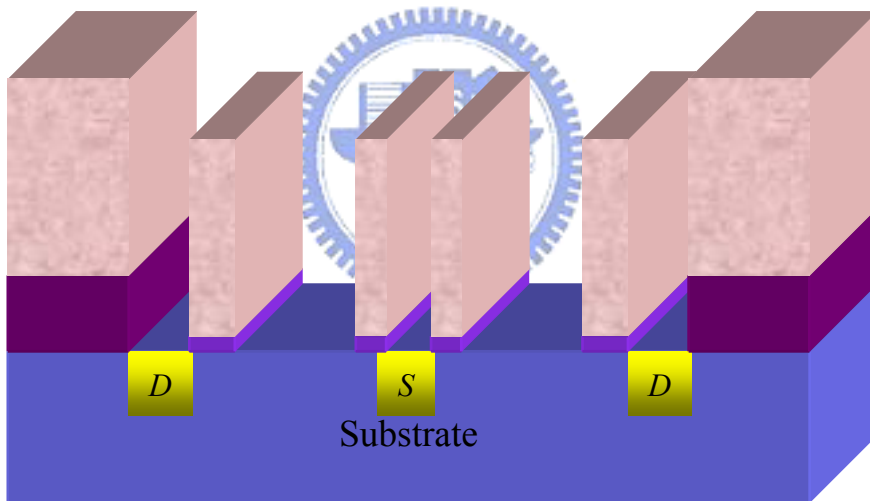


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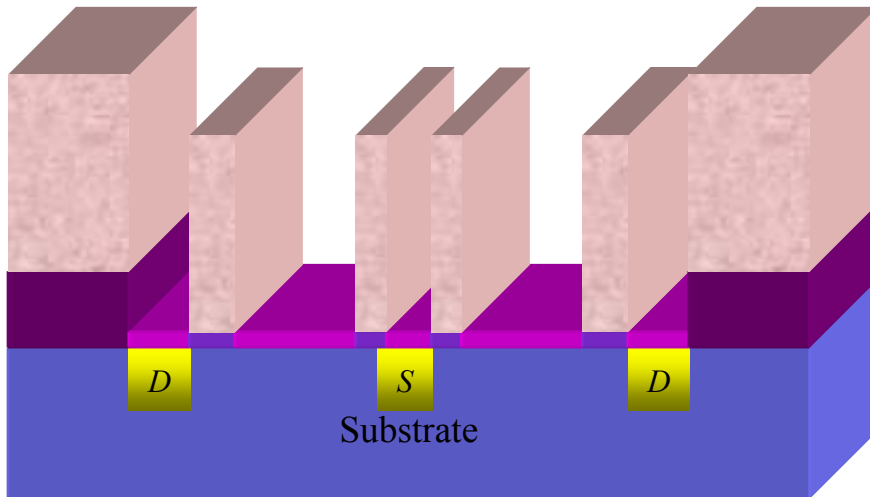




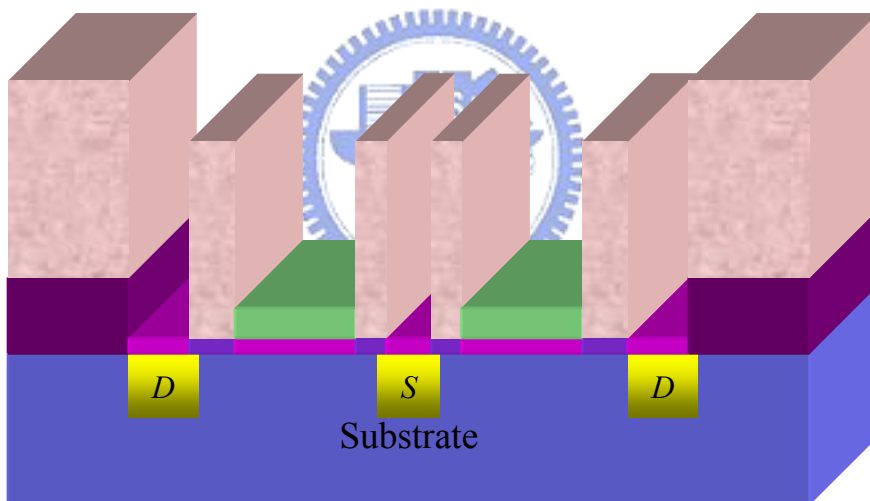
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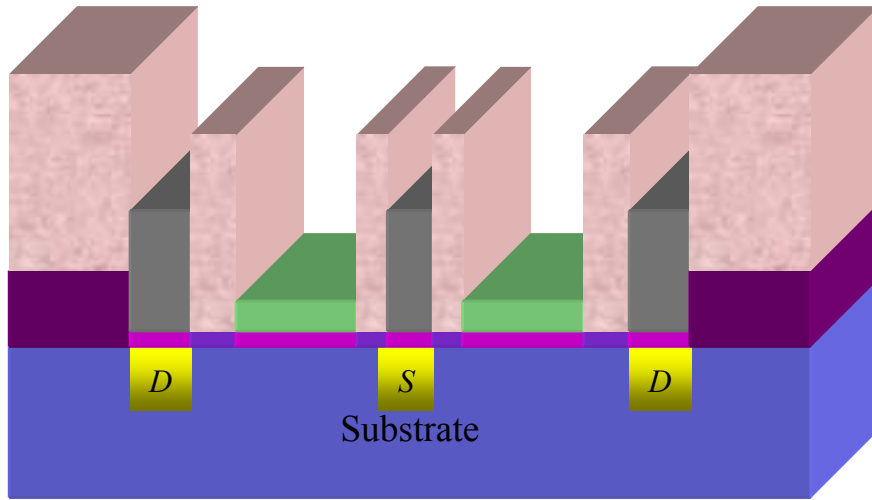
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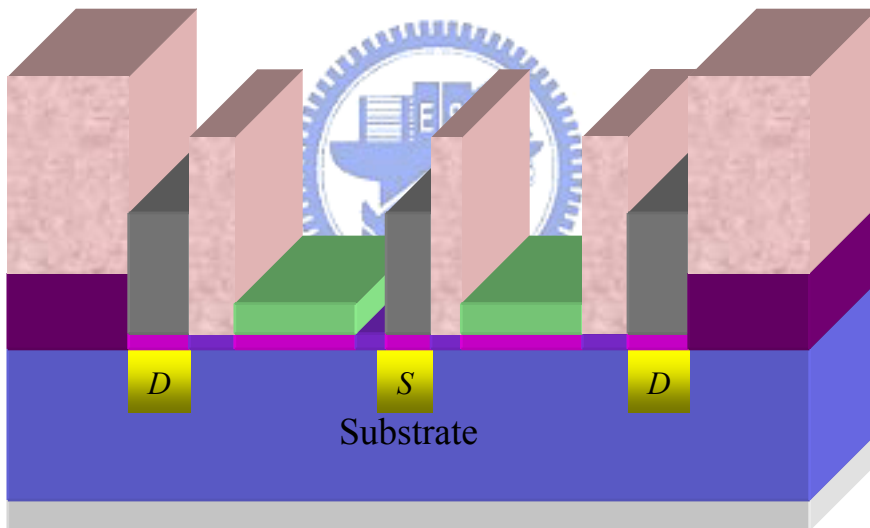
(8)



(9)



(10)



(11)

**Fig. 3-1 Fabrication process flow**

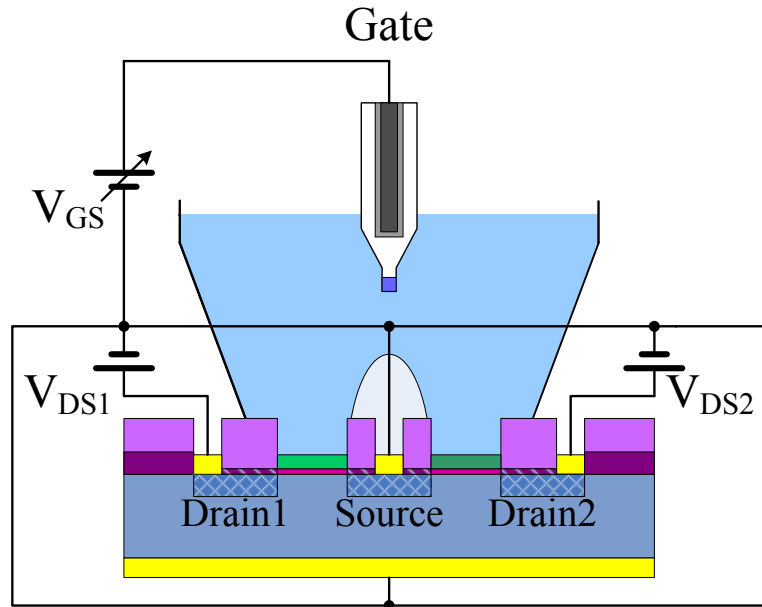


Fig. 3-2 Measurement setup

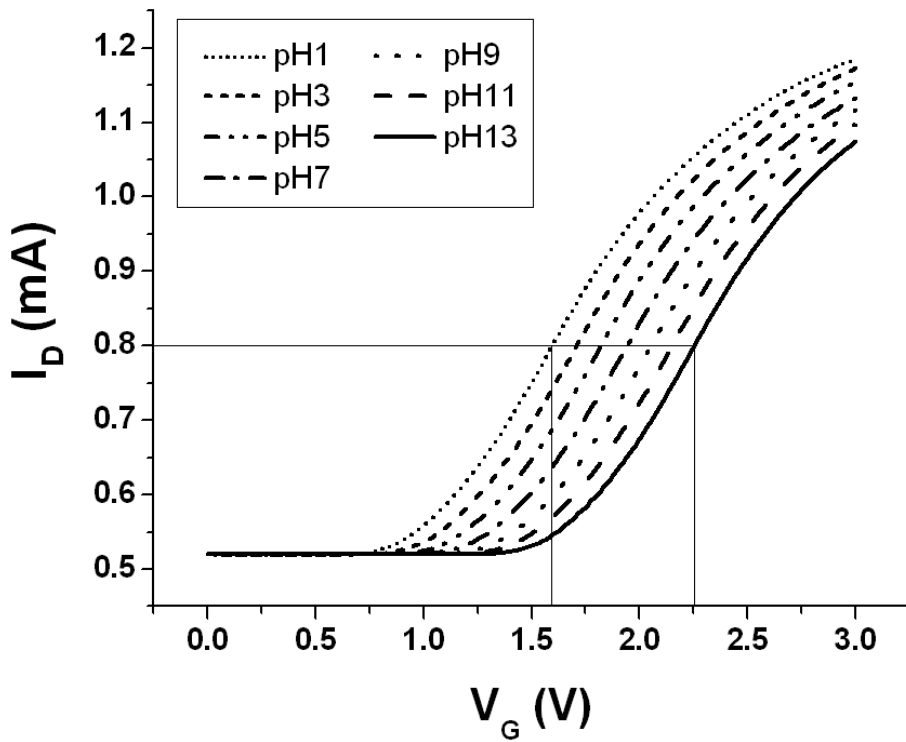


Fig. 3-3 Detection principle of pH sensitivity

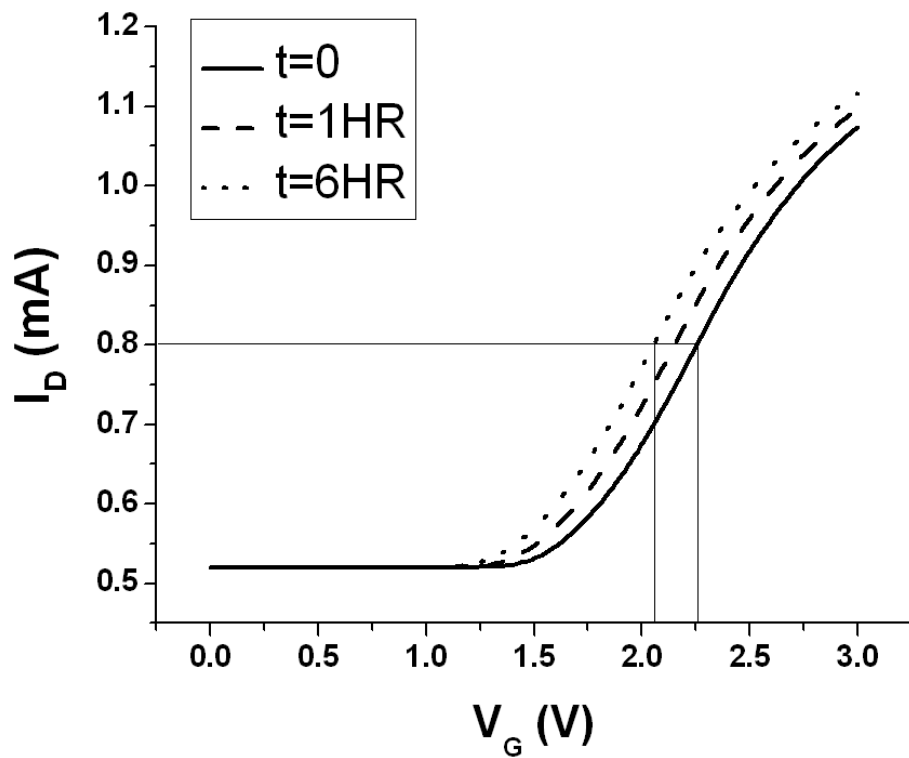
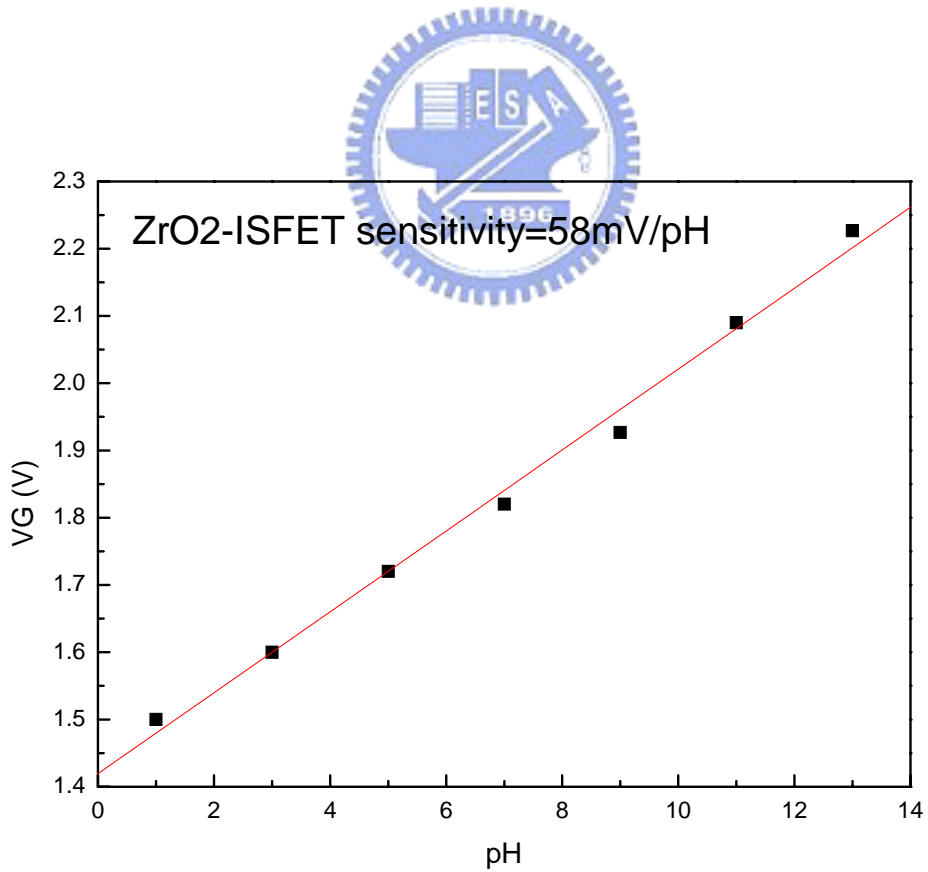
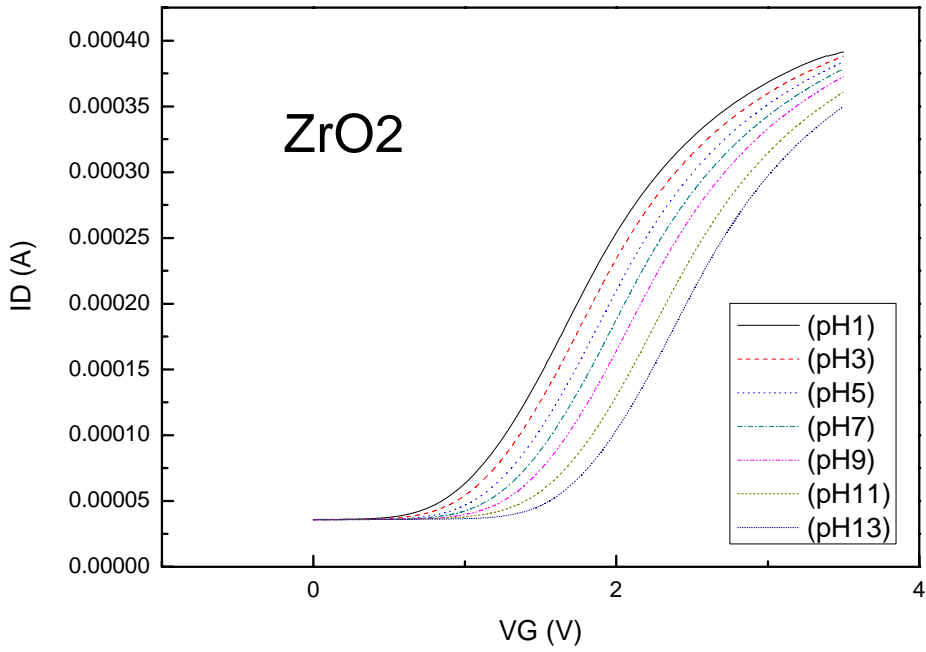
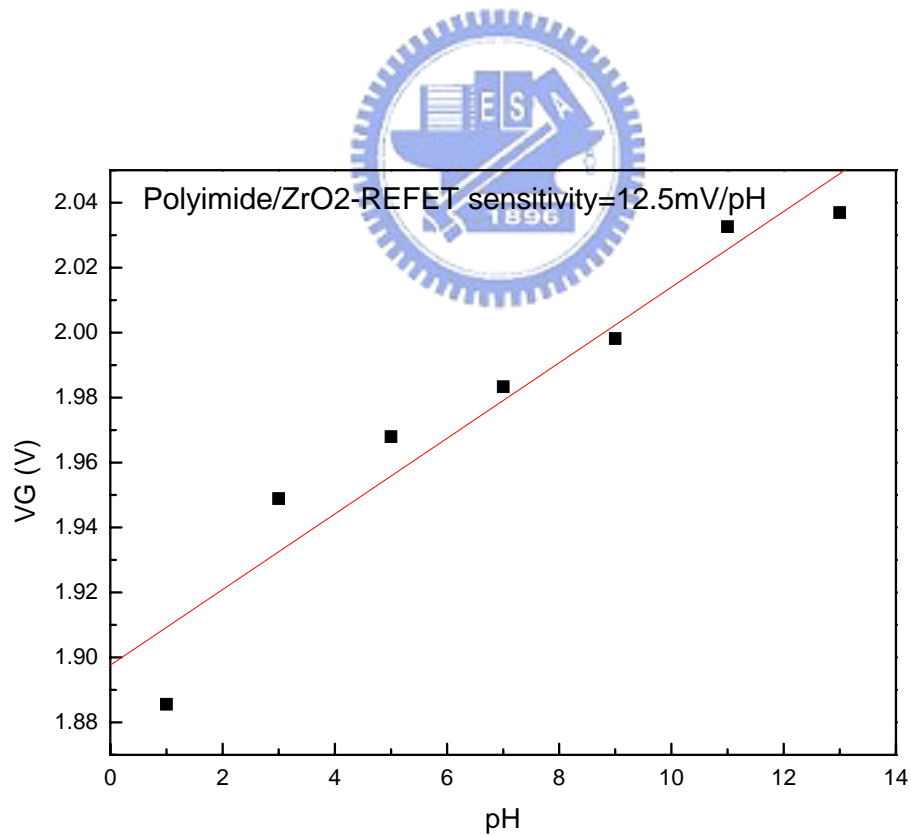
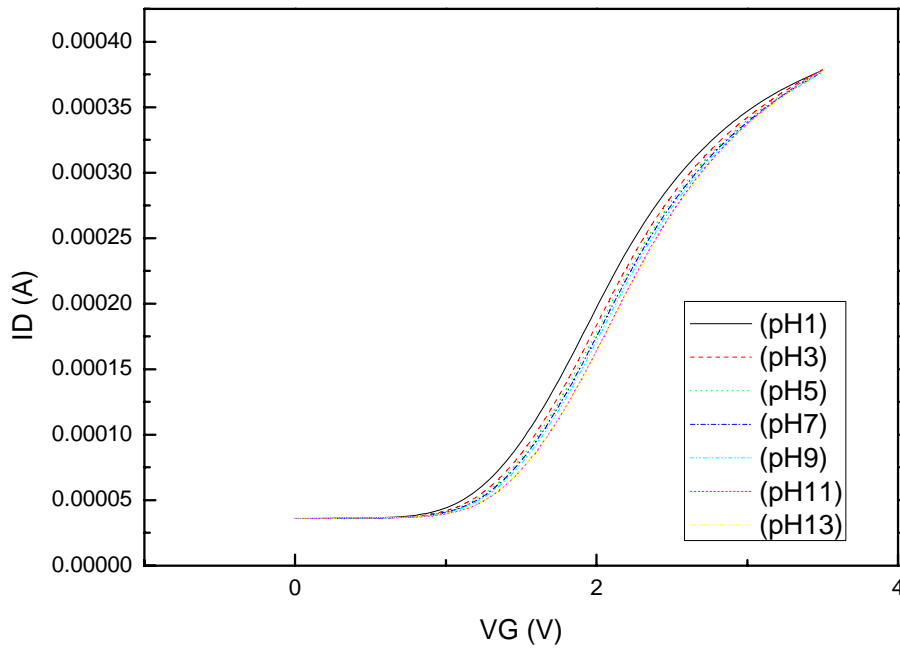


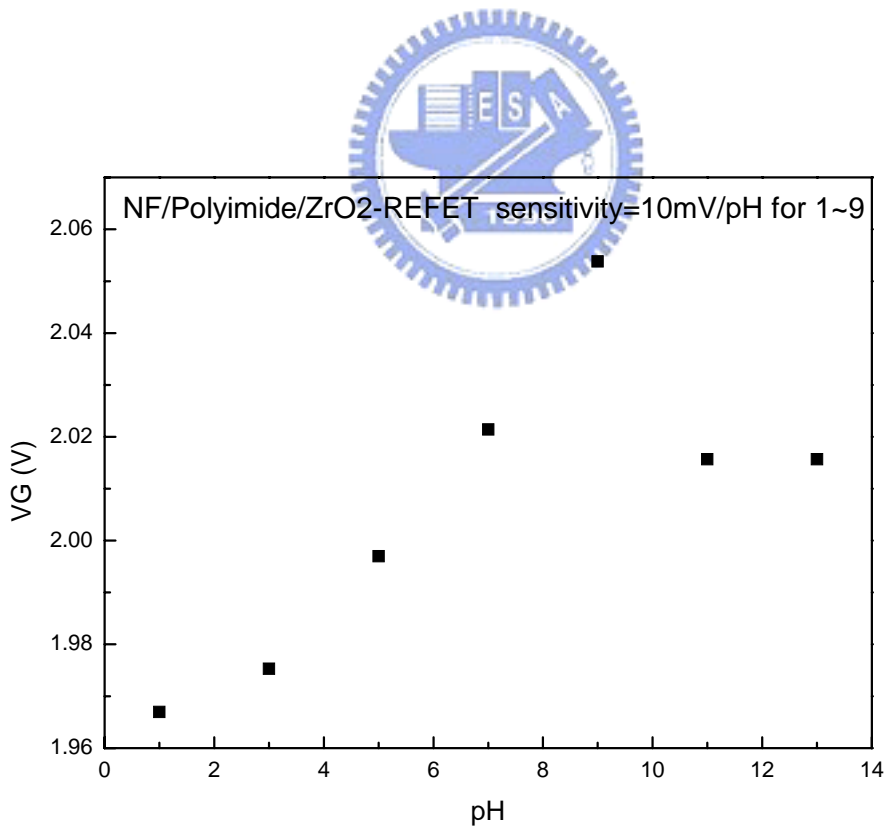
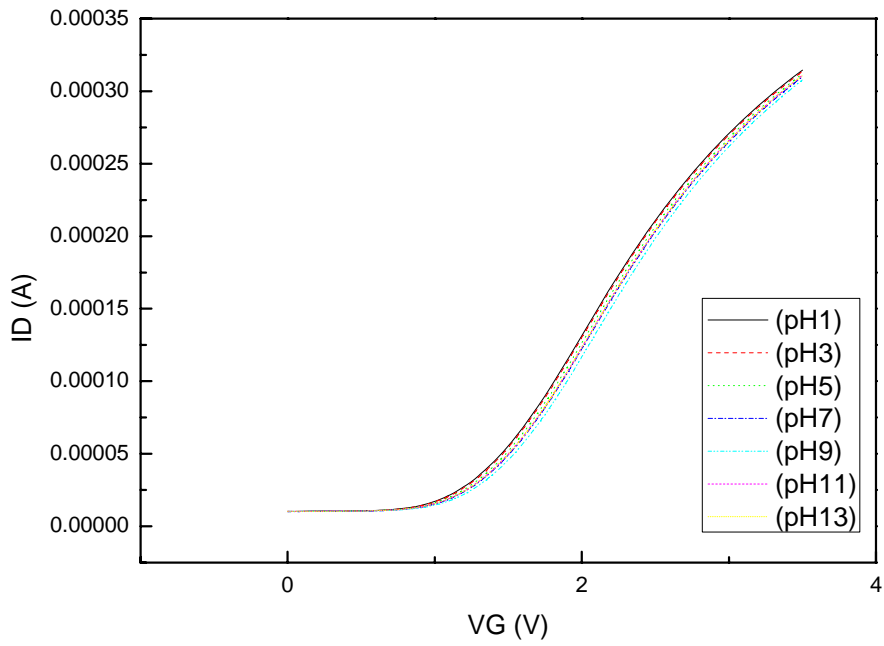
Fig. 3-4 Detection principle of drift



**Fig. 4-1 H<sup>+</sup> sensitivity of ZrO<sub>2</sub>-ISFET**

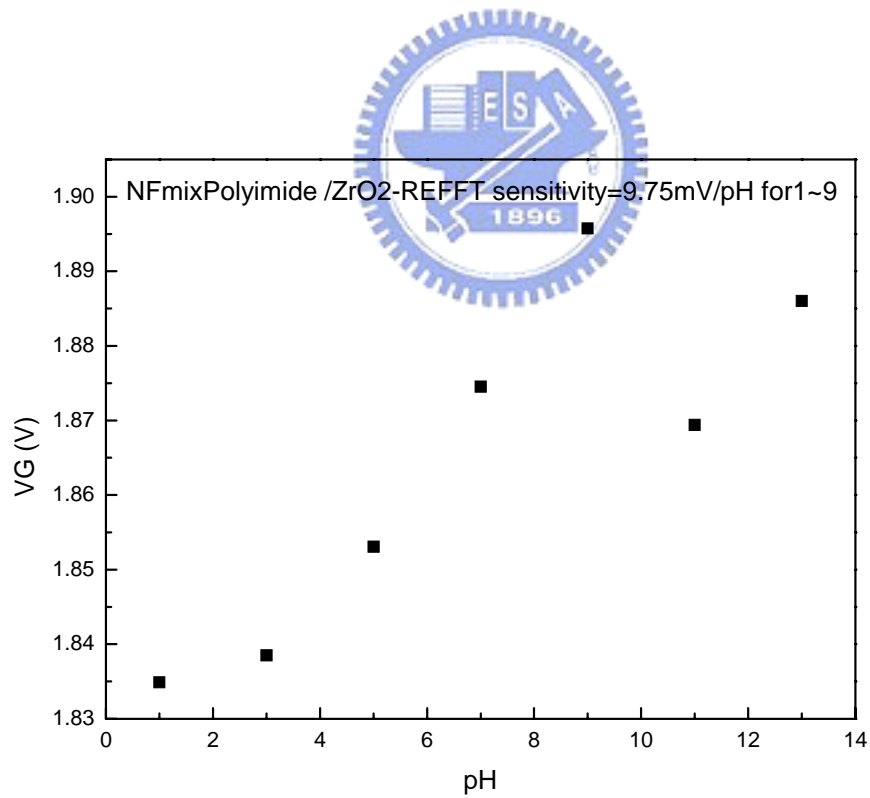
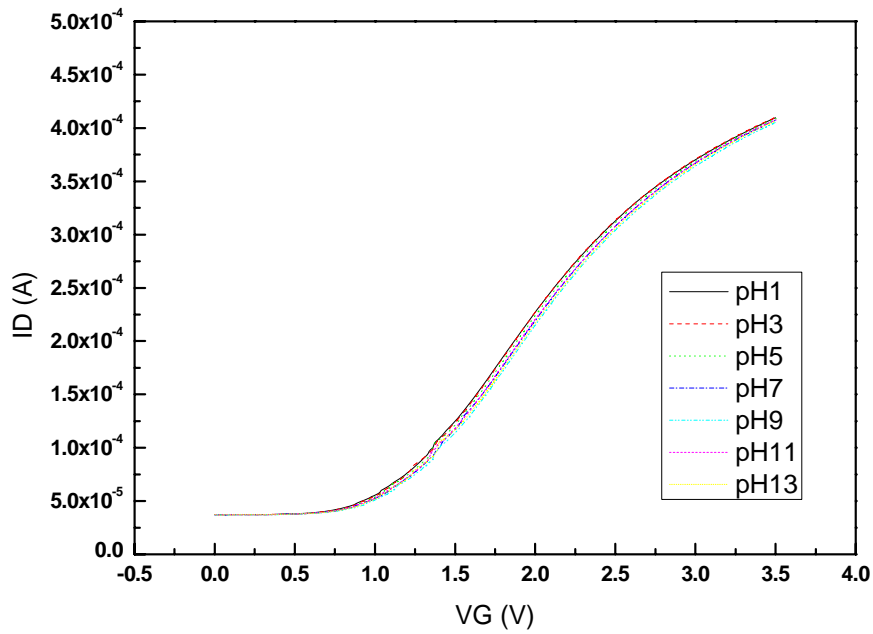


**Fig. 4-2 H<sup>+</sup> sensitivity of Polyimide/ZrO<sub>2</sub>-REFET**

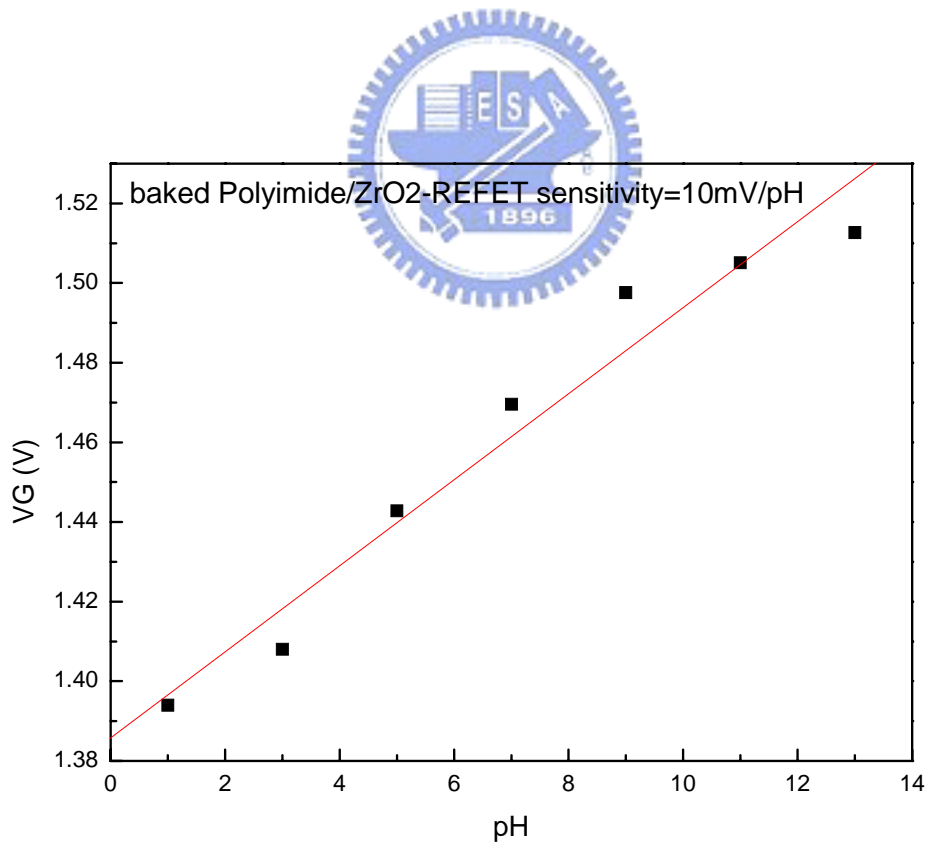
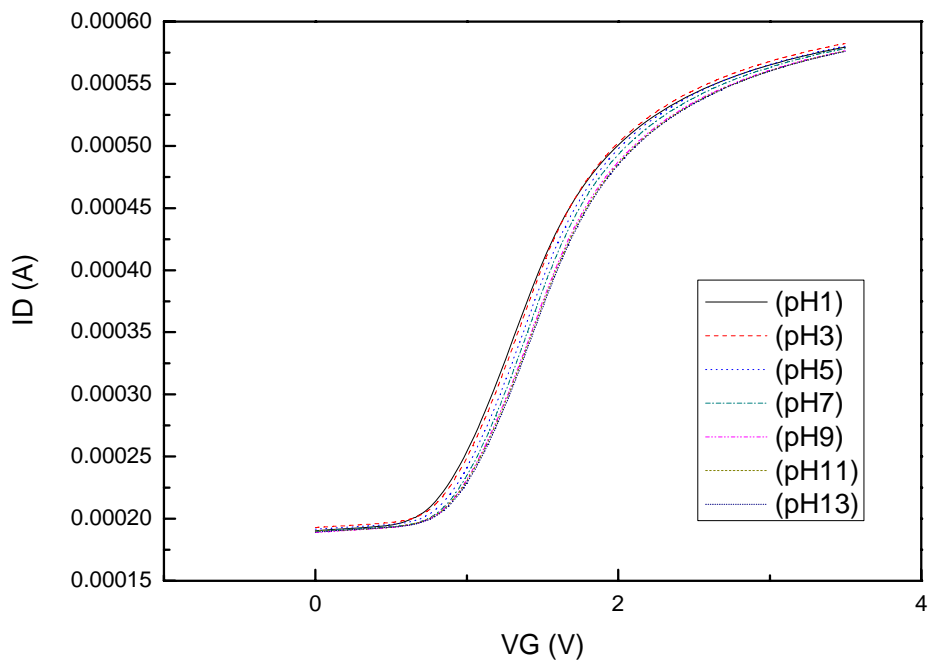


**Fig. 4-3 H<sup>+</sup> sensitivity of NF/ Polyimide/ZrO<sub>2</sub>-REFET**

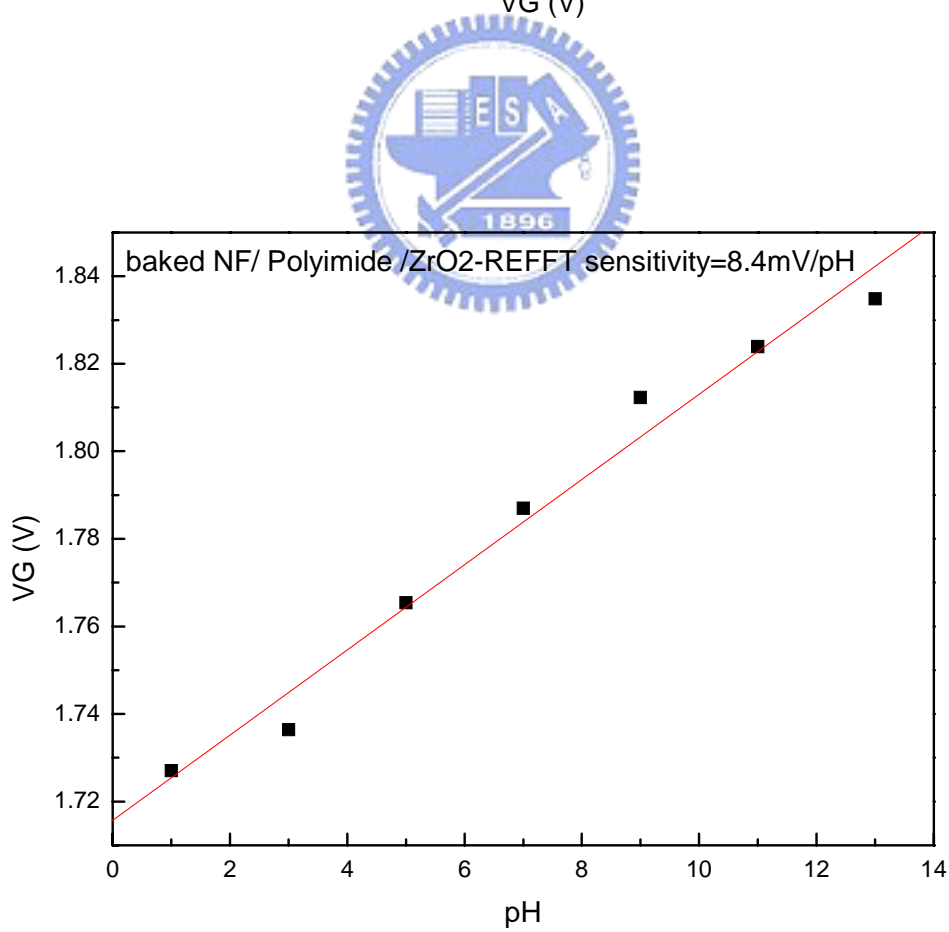
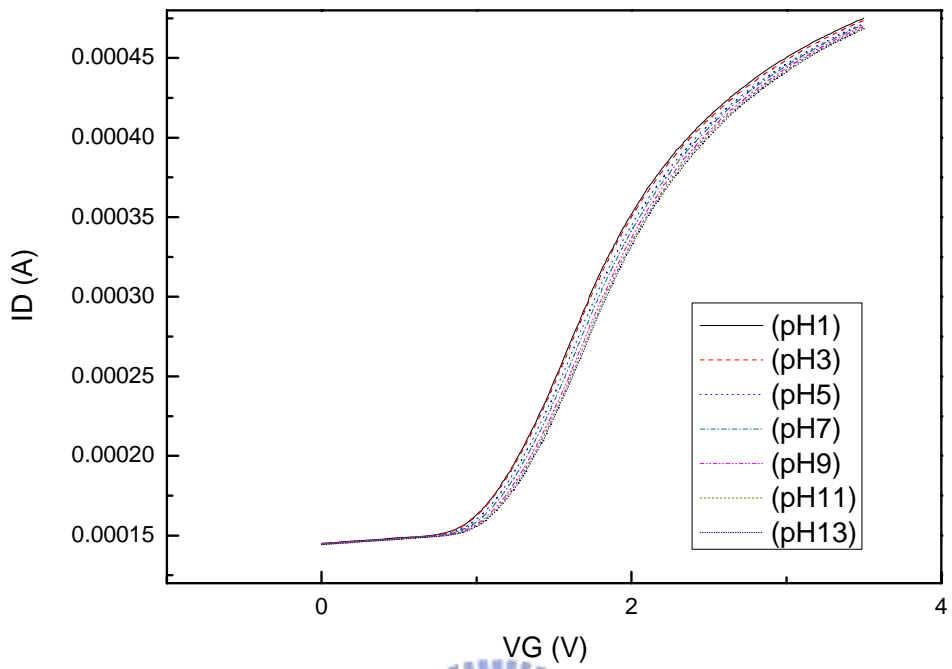




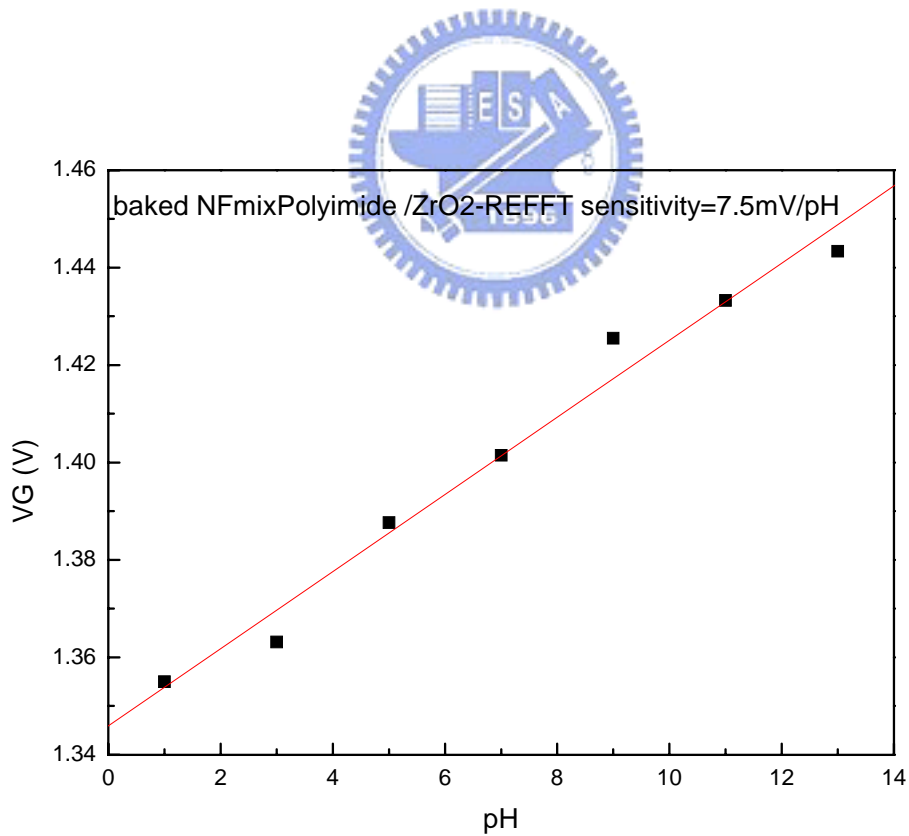
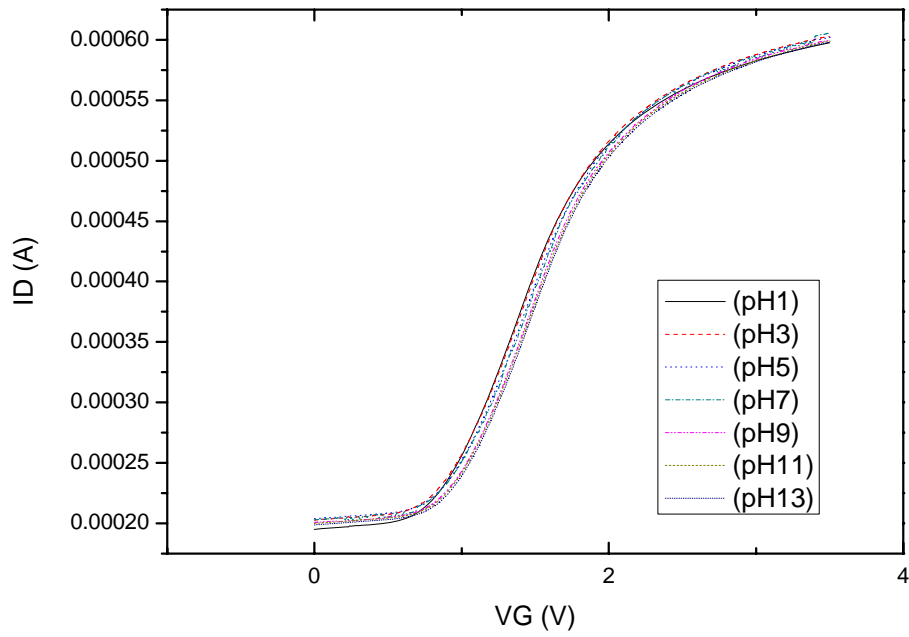
**Fig. 4-4 H<sup>+</sup> sensitivity of NFmixPolyimide/ZrO<sub>2</sub>-REFFT**



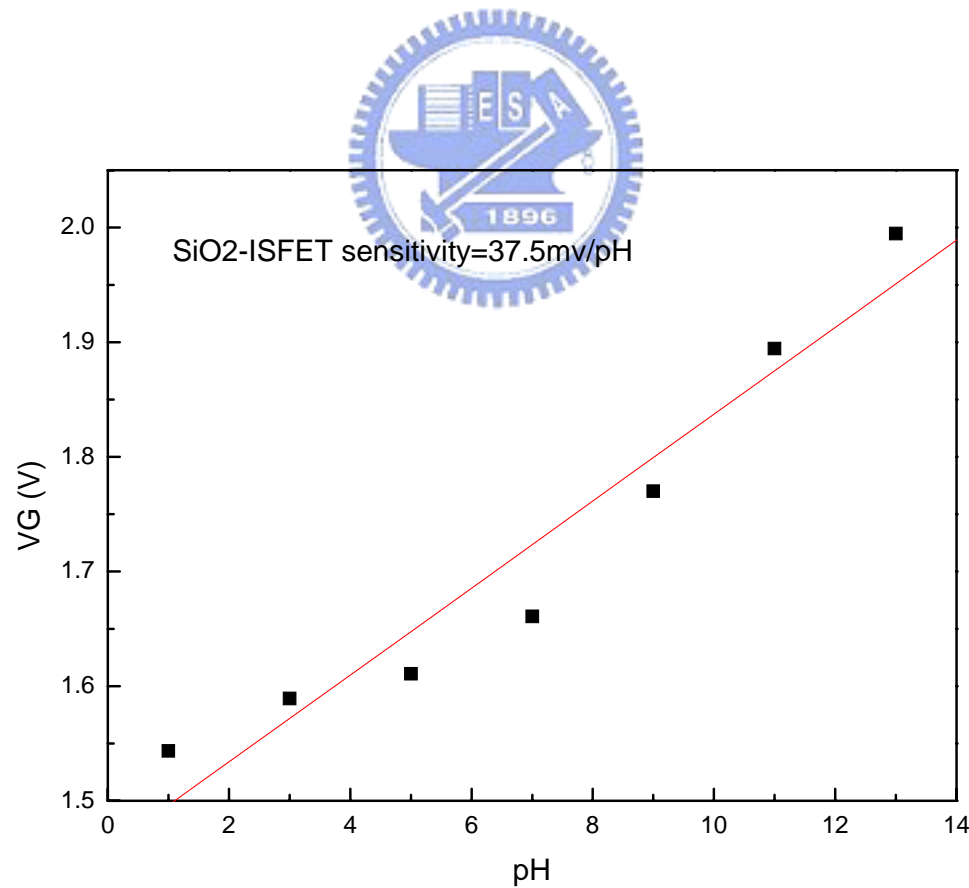
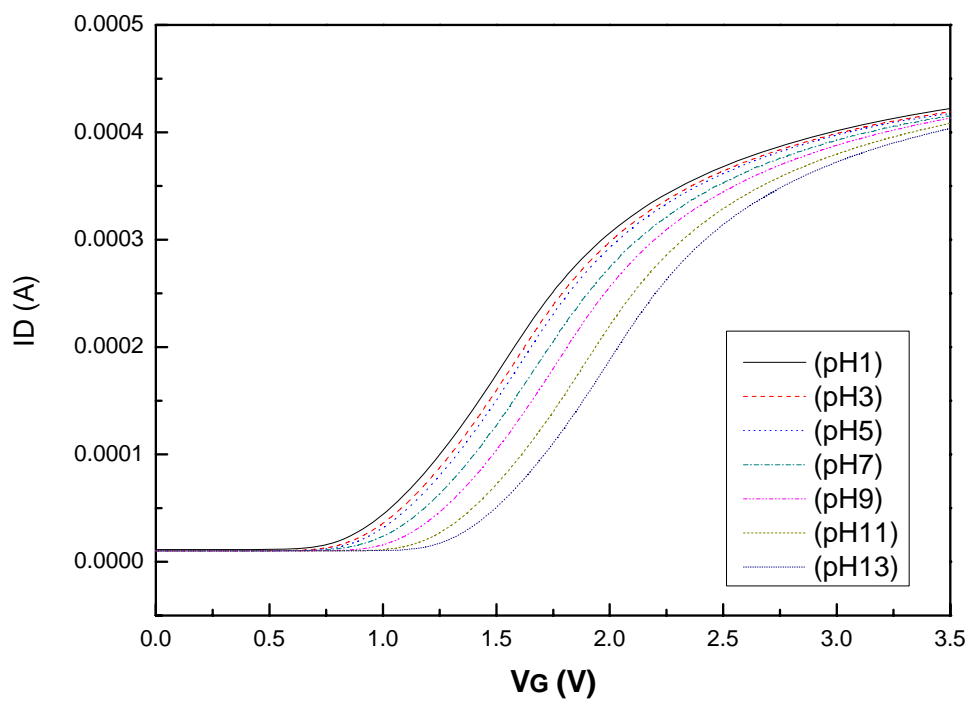
**Fig. 4-5  $H^+$  sensitivity of baked Polyimide/ $ZrO_2$ -REFET**



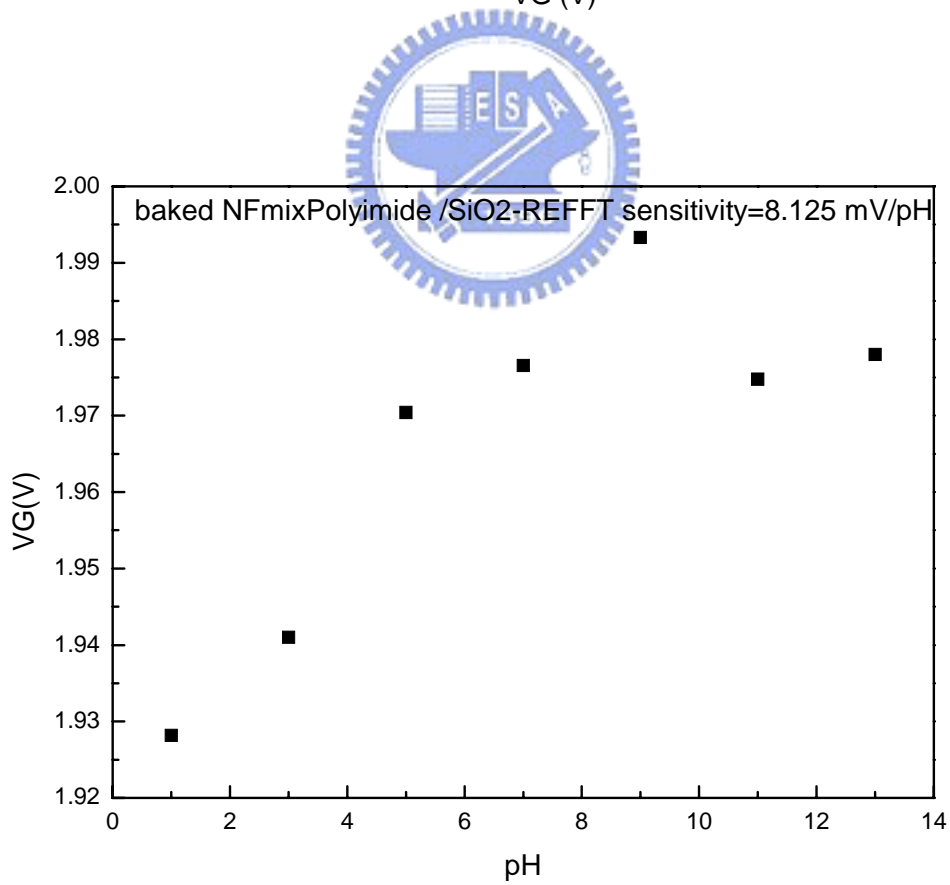
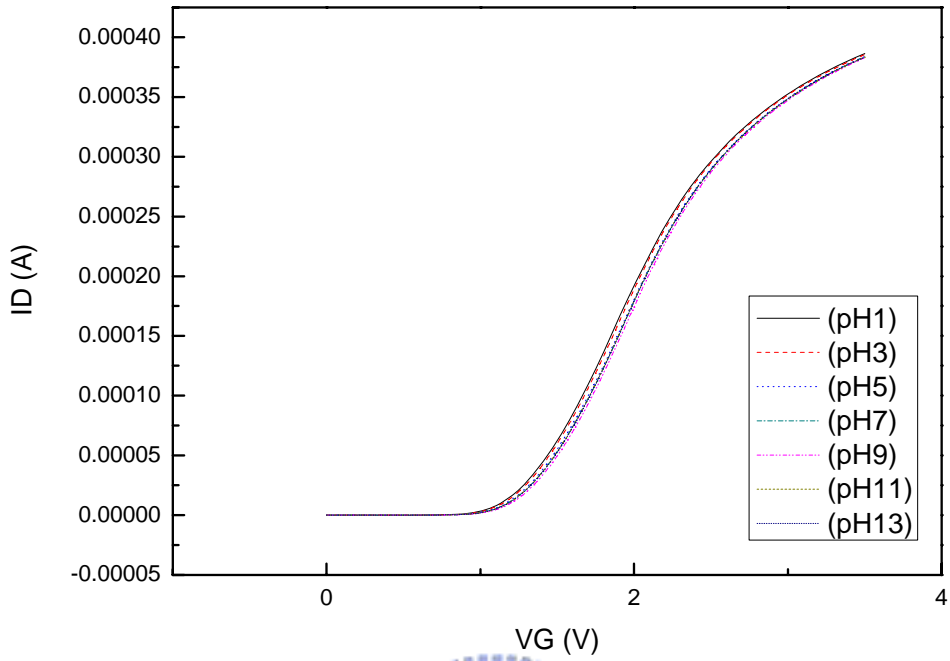
**Fig. 4-6 H<sup>+</sup> sensitivity of baked NF/Polyimide/ZrO<sub>2</sub>-REFFT**



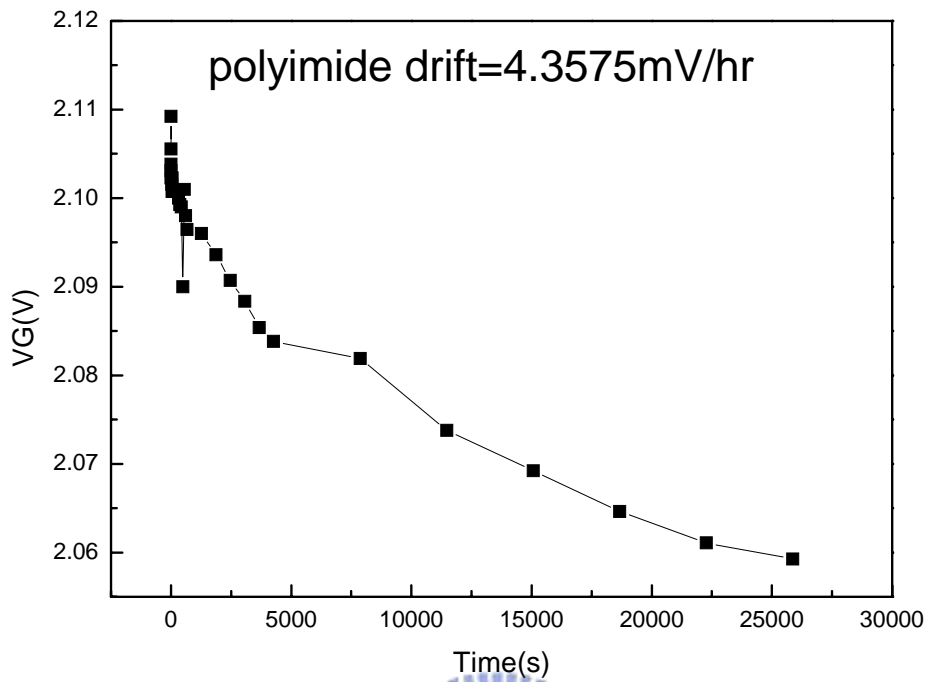
**Fig. 4-7 H<sup>+</sup> sensitivity of baked NFmixPolyimide/ZrO<sub>2</sub>-REFFT**



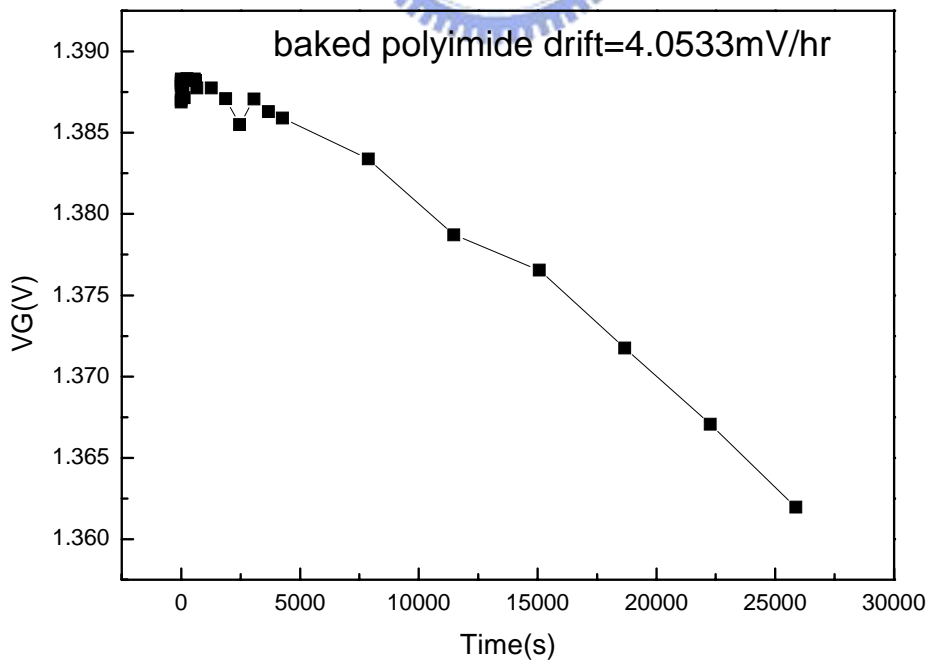
**Fig. 4-8 H<sup>+</sup> sensitivity of SiO<sub>2</sub>-ISFET**



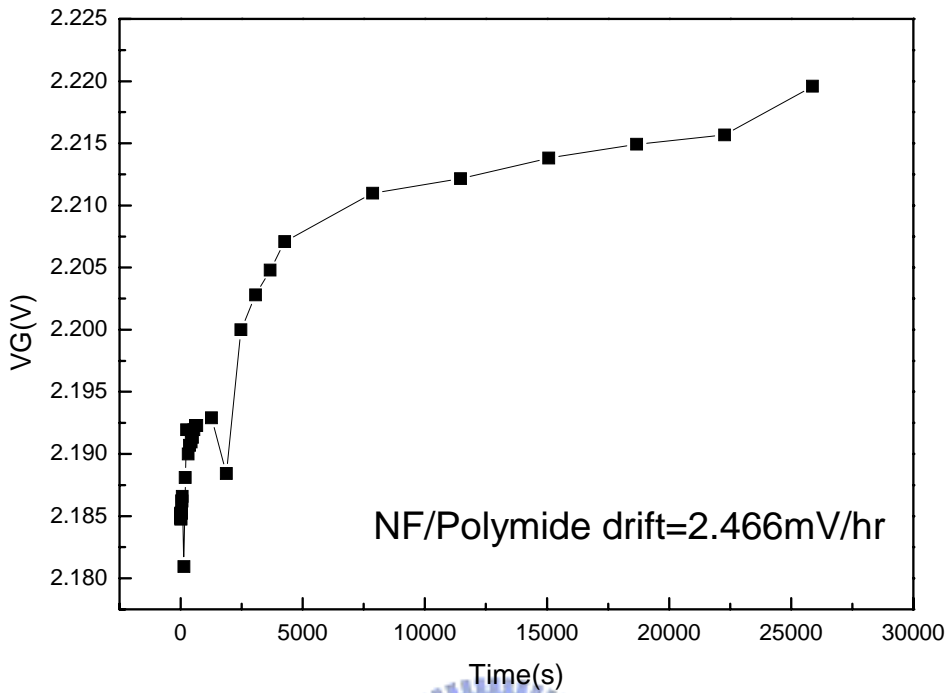
**Fig. 4-9 H<sup>+</sup> sensitivity of baked NFmixPolyimide/SiO<sub>2</sub>-REFFT**



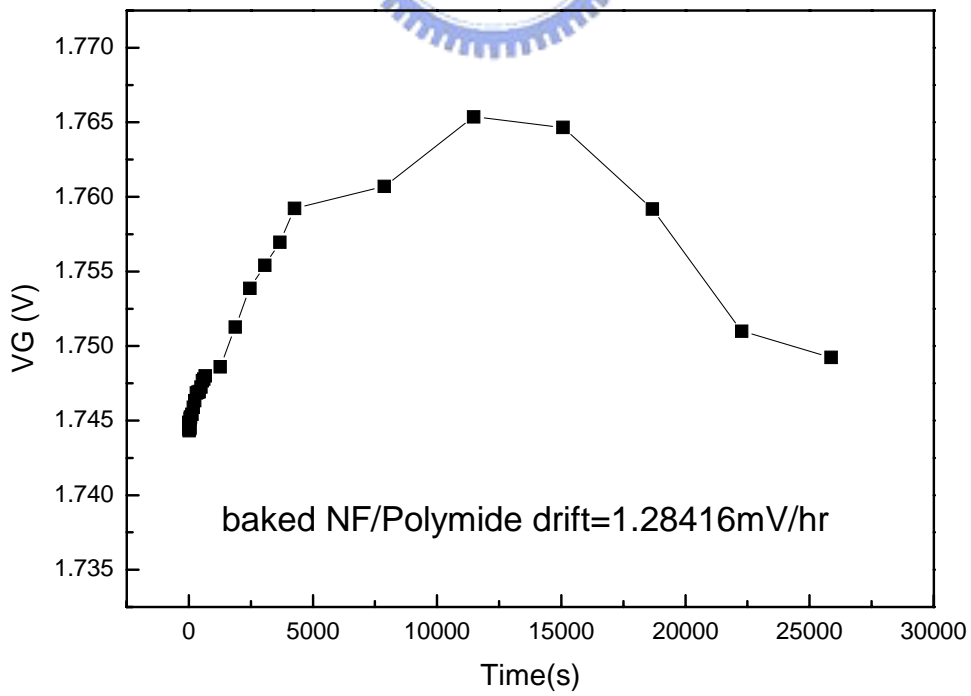
**Fig. 4-10 Drift of polyimide/ZrO<sub>2</sub>-REFET**



**Fig. 4-11 Drift of baked polyimide/ZrO<sub>2</sub>-REFET**



**Fig. 4-12 Drift of NF/polymide/ZrO<sub>2</sub>-REFET**



**Fig. 4-13 Drift of baked NF/Polymide/ZrO<sub>2</sub>-REFET**



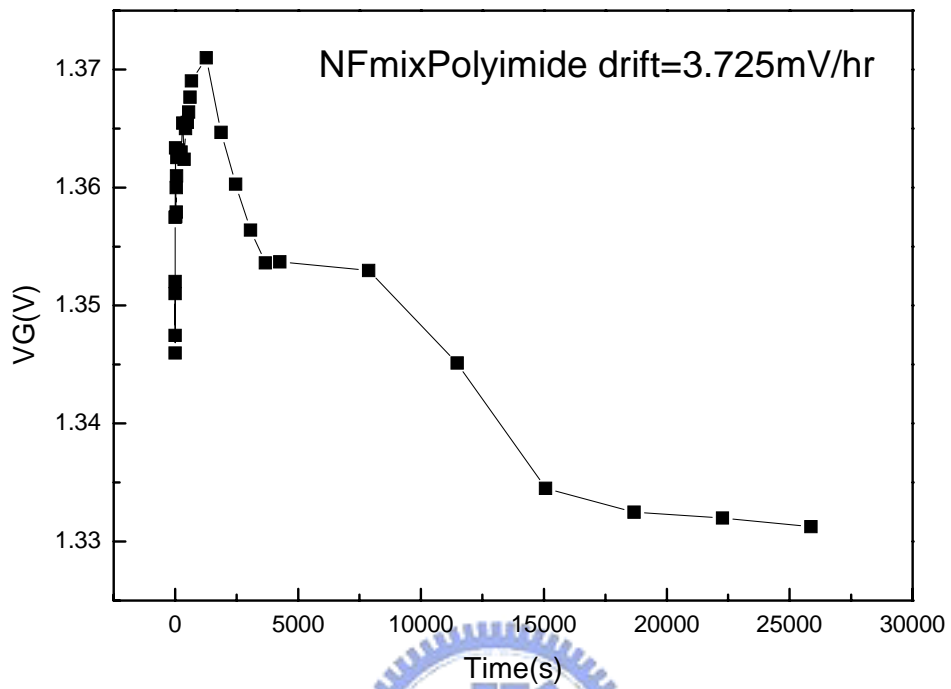


Fig. 4-14 Drift of NFmixPolyimide/ZrO<sub>2</sub>-REFFT

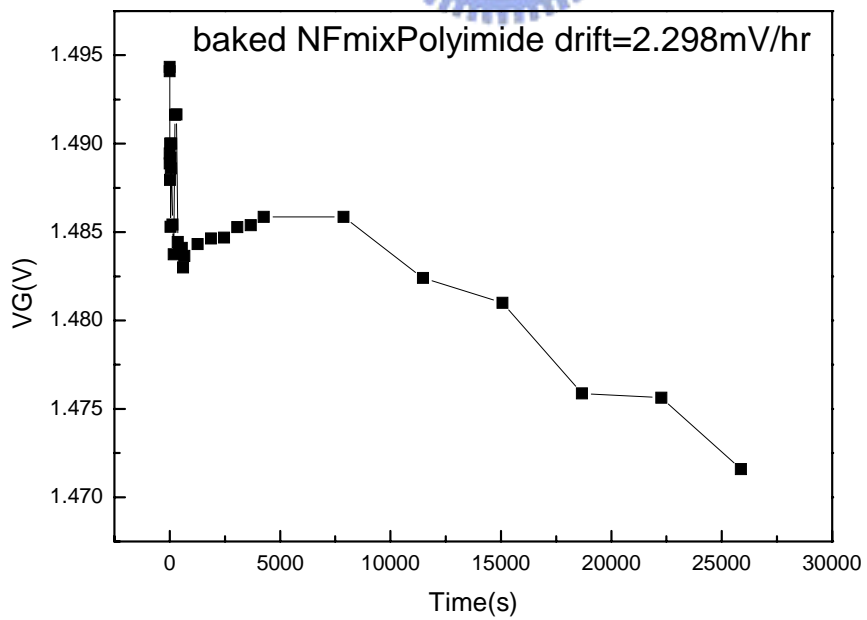
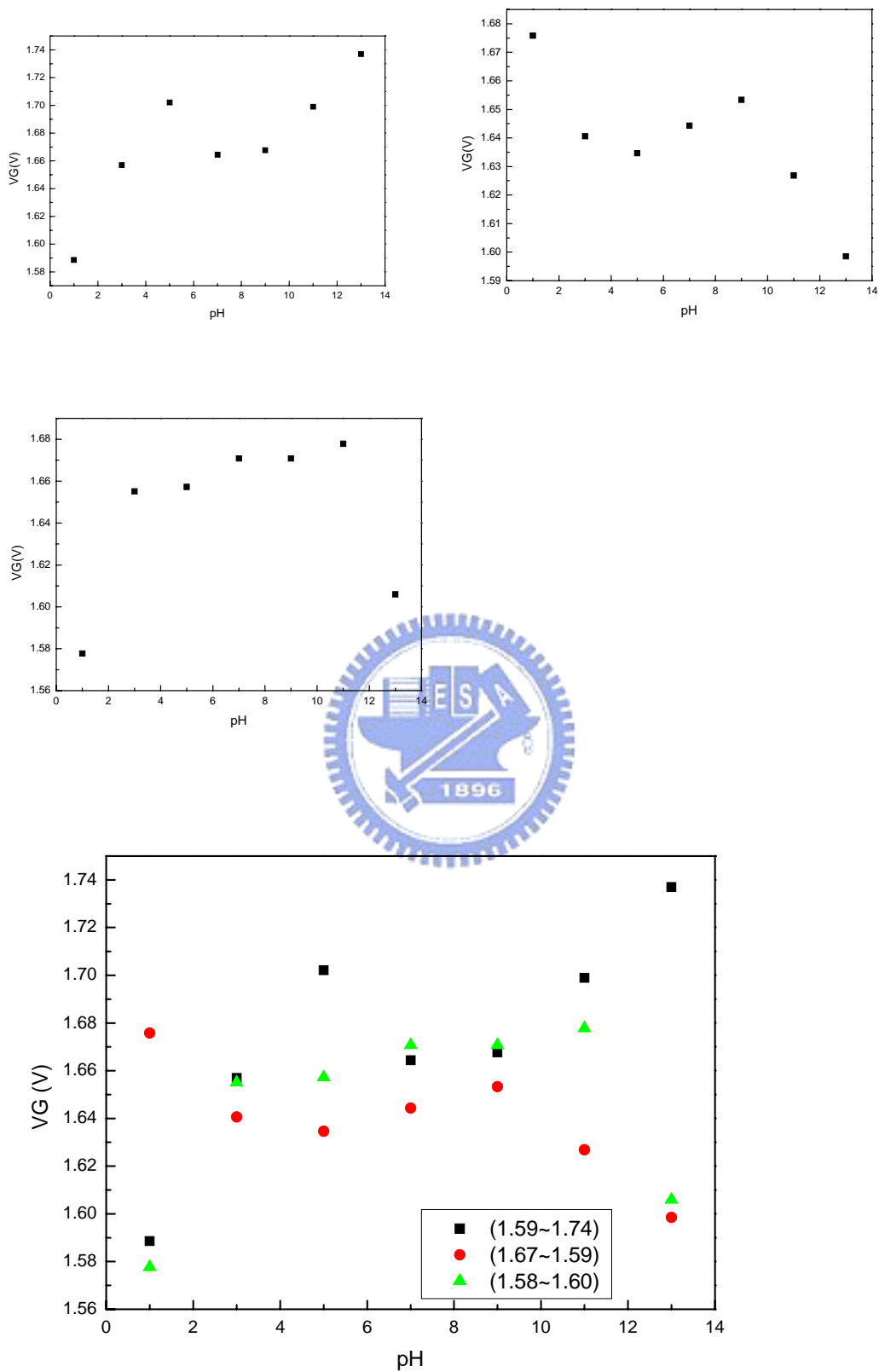
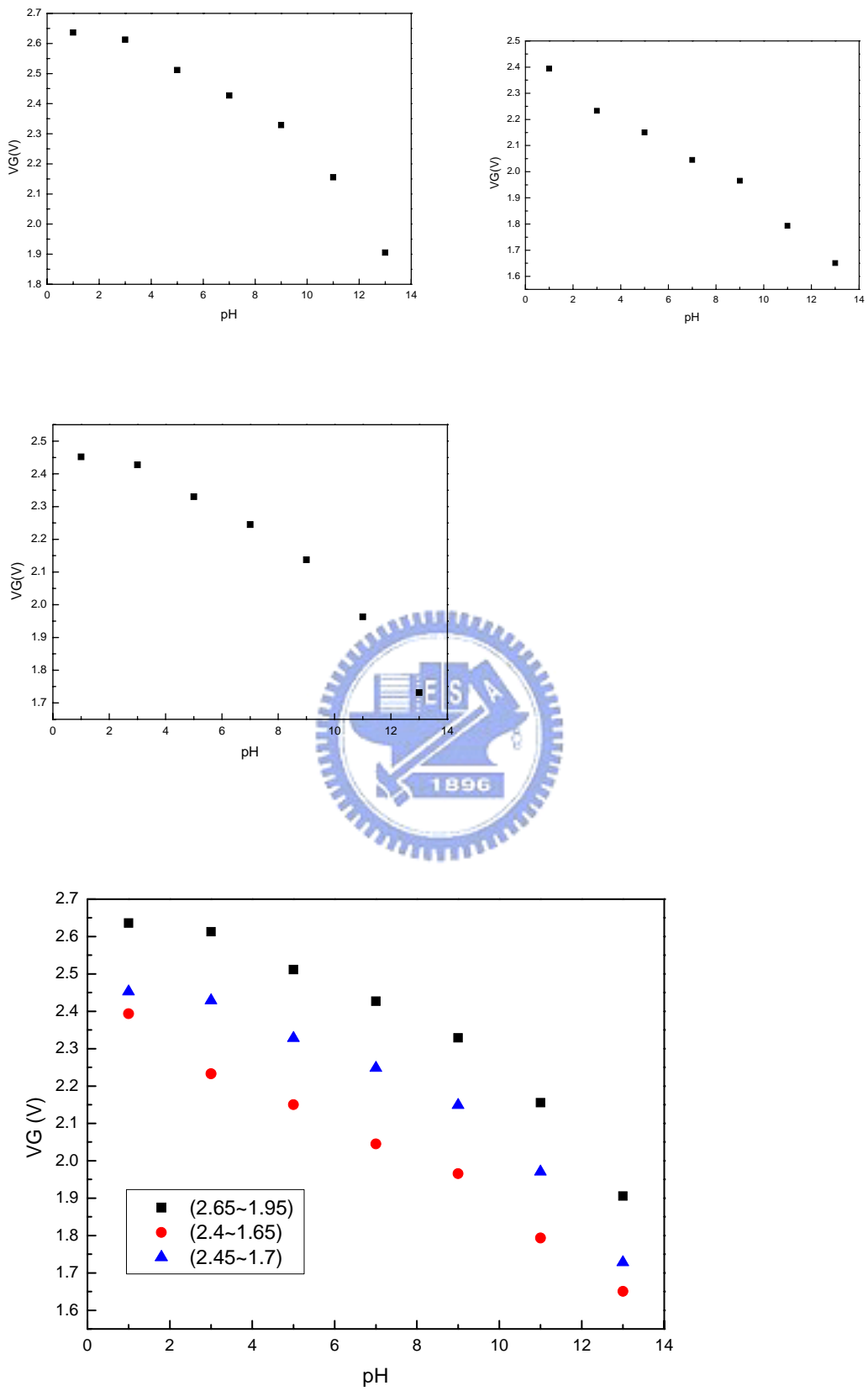


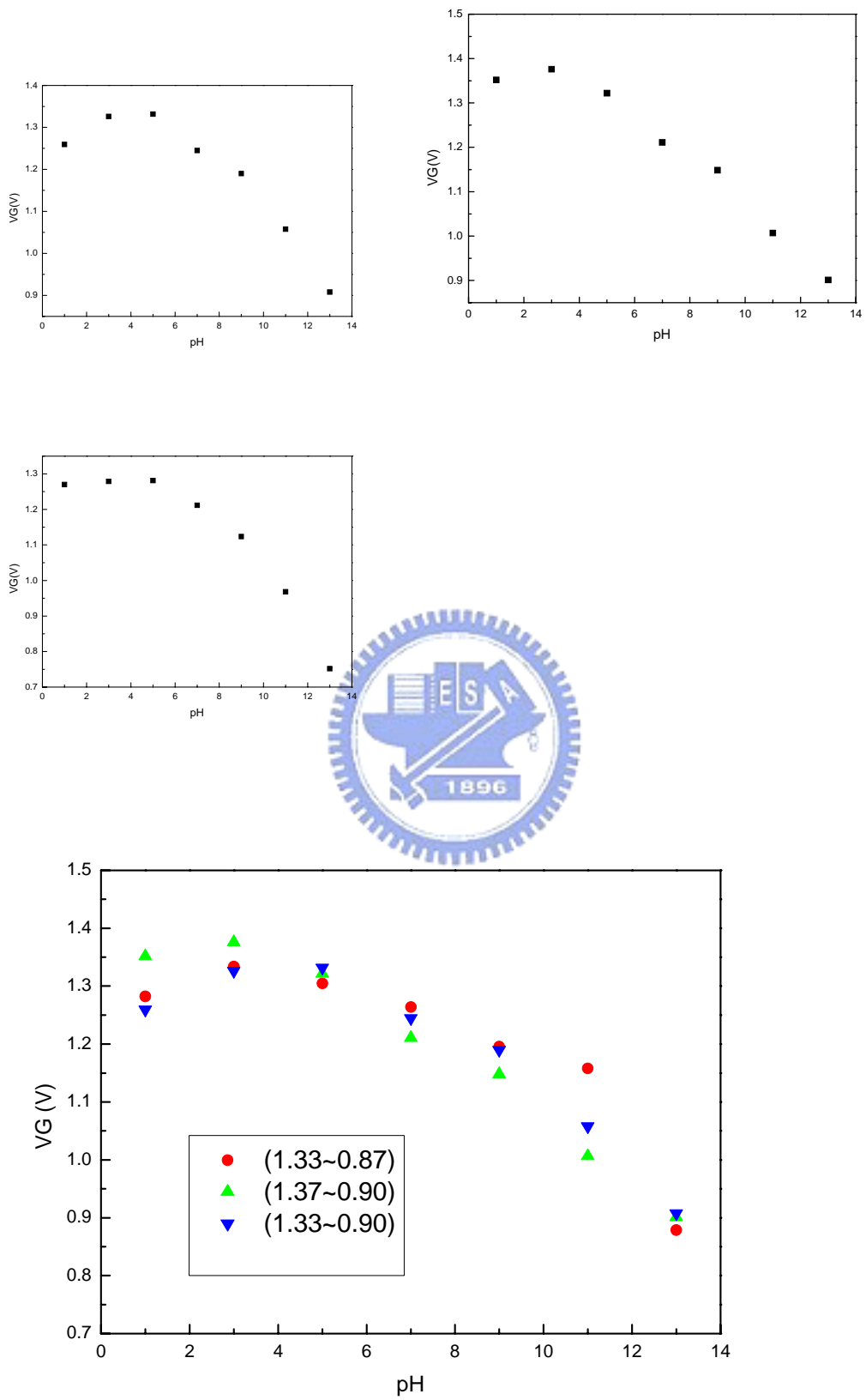
Fig. 4-15 Drift of baked NFmixPolyimide/ZrO<sub>2</sub>-REFFT



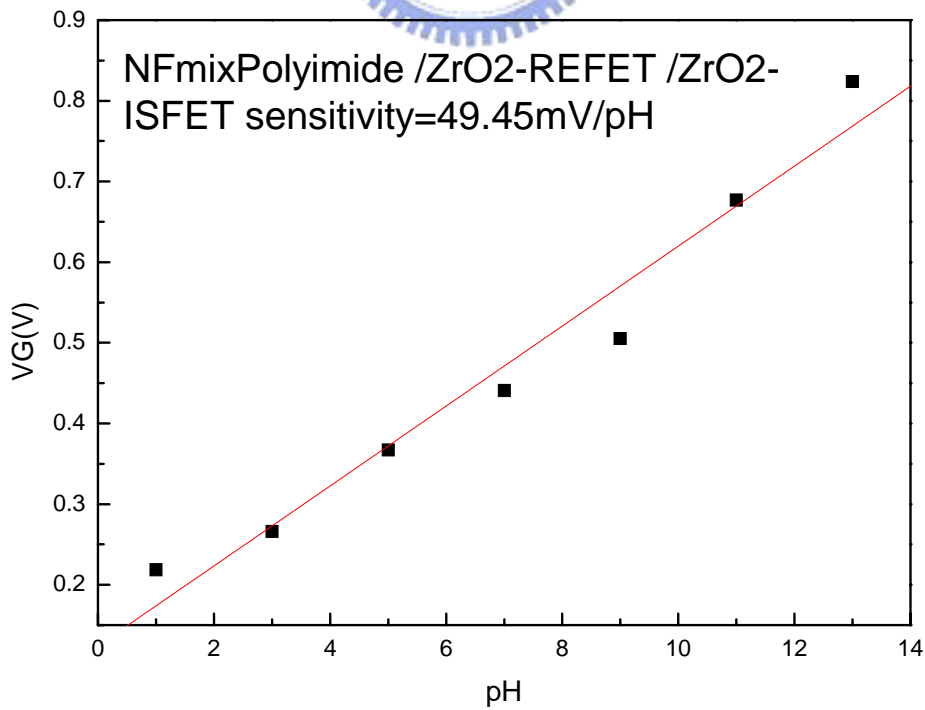
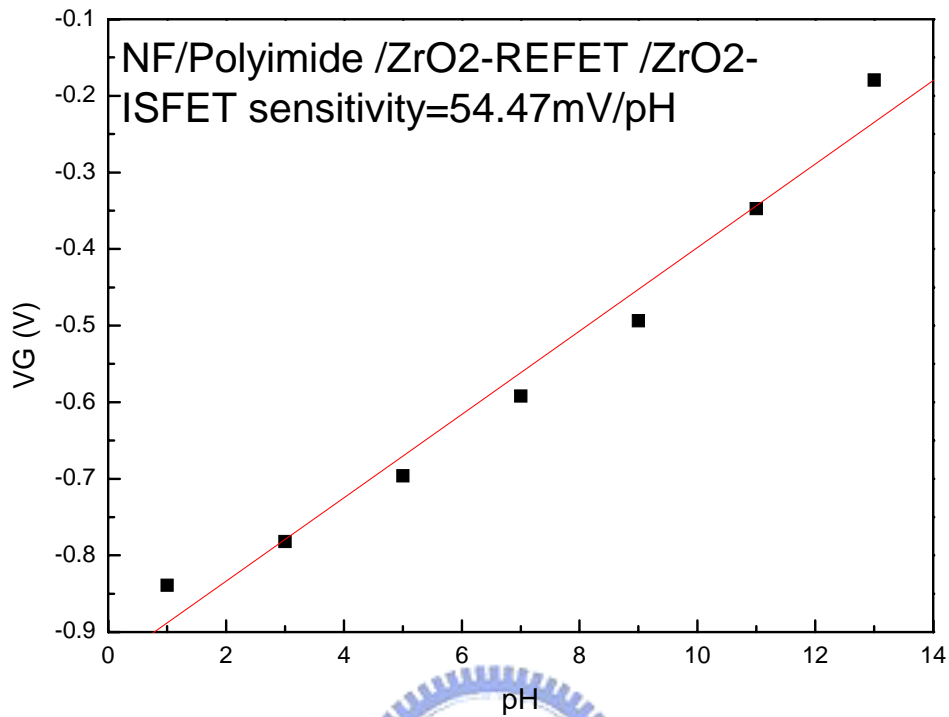
**Fig. 4-16 ZrO<sub>2</sub>-ISFET with QRE (Pt)**



**Fig. 4-17 Baked NF/Polyimide/ ZrO<sub>2</sub>-REFFT with QRE(Pt)**



**Fig. 4-18 Baked NFmixPolyimide/ZrO<sub>2</sub>-REFFT with QRE(Pt)**



**Fig. 4.19 ISFET/REFET differential with Quasi-Reference Electrode**

## 簡 歷

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國立交通大學電子工程研究所

碩士論文：

以Polyimide高分子材料和Nafion™作為REFET感測層之  
研究

The study of polyimide/Nafion™ structure as sensing  
films for REFET application