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碩士論文

多晶矽奈米線薄膜電晶體之研製與應用於酸鹼 感測器之研究 Fabrication, Characterization, and pH Sensors

Application of Poly-Si Nanowire Thin Film Transistors

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中華民國九十九年七月

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摘要

我們成功的發展出一套簡單與低成本的技術,來製作奈米線場效電晶體。藉 由此種元件,我們可以得到一個接近理想狀態的酸鹼感測器(57.1mV/pH)。此外, 我們可以不需藉由任何額外的外接電路,即可觀測出酸鹼溶液所造成的即時電性 變化,同時,此項元件還能多次重覆使用。

另外,我們也比較了奈米線與一般的平面場效電晶體電特性上的差異,以及 感測的敏感度表現。我們發現,相較於傳統電晶體的次臨界擺幅(1333 mV/dec), 奈米線改進的幅度相當大(297 mV/dec)。此外,對於感測器方面,奈米線所產生 的電流敏感度(12.78%/pH)也比傳統電晶體(5.46%/pH)的表現為好。而這些特性 也間接證明了本實驗室所製作出的奈米元件特性優異,非常適合用於感測器方 面。

Fabrication, Characterization, and pH Sensors

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Abstract

In this thesis, we've successfully developed a simple and low-cost method to fabricate thin film transistors with nanowire channels. By employing the fabricated devices equipped with a SiO₂ sensing pad for pH sensing application, a high sensitivity (57.1mV/pH) is obtained, which is close to the ideal value (60mV/pH). Besides, real-time drain current response corresponding to the variation of pH value in the test solution is demonstrated without using any external circuit. Reproducibility of such capability is also confirmed in this work.

We've also investigated and compared the basic and pH sensing characteristics of the nanowire structures and conventional planar devices. The subthreshold swing of the nanowire structures (297 mV/dec) is much better than that of the planar ones (1333 mV/dec). Furthermore, the current response sensitivity of nanowire (12.78%/pH) is also better than that of the planar (5.46%/pH) one. These characteristics evidence the superiority of the nanowire device for sensor application.



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Contents

Abstract		i
Acknowledge	ement	iv
Contents		V
Table Captio	ons	vii
Figure Capti	ions	viii

Chapter	r 1 Introduction	1
1-1	An Overview of Nanowire Technology	1
	1-1-1 Bottom-Up Approach	2
	1-1-2 Top-Down Approach	3
1-2	Introduction of Sensor Devices	4
	1-2-1 Introduction of ISFET	4
1-3	Motivation	5
1-4	Organizations of the Thesis 1896	7

Chapter	2 Devic	e Structures, Fabrication and Characteristic Analysis	8
2-1	Proc	ess Flow and Structure of NW Devices	8
2-2	Proc	ess Flow and Structure of Planar Devices	11
	2-2-1	Planar Device with Thin Channel	11
	2-2-2	Planar Device with Thick Channel	12
2-3	Mea	surement Setups and Electrical Characteristics of the Fal	oricated
	Devi	ces	13
	2-3-1	Measurement System	13
	2-3-2	Theory and Model of Threshold Voltage Variation	13
	2-3-3	Comparisons of Basic Electrical Characteristics	16
Chapter	3 Analy	visis of the Characteristics of pH Sensors	21

Chapter 3	Analysis of the Characteristics of pH Sensors	21
3-1	Microfluidics Settings and Measurement Methods	21

3-2	The	Theory of pH Sensors	
3-3	Anal	ysis of pH Sensing Characteristics	25
	3-3-1	The Sensitivity of Different Structures	25
	3-3-2	Effects of Antenna Pad Area	27
	3-3-3	Effects of Antenna Pad Materials	

Chapter 4	Conclusion and Future Work	
4-1	Conclusion	31
4-2	Future Work	32
References	S	
Tables	••••••	42
Figures		43
Vita		86



Table Captions

Chapter 2

Chapter 3



Figure Captions

Chapter 1

Fig. 1-1.	Schematic representation of a general ISFET device
Fig. 1-2.	Schematic diagram of a nanowire channel device43

Chapter 2

Fig. 2-1.	(a) The layout and (b) cross-sectional view of NWTFT44
Fig. 2-2.	(a) Deposition of dummy gate and (b) definition of dummy gate (c)
	Deposition of α -Si and (d) SPC (e) Source/Drain ion implantation
	and (f) definition of Source/Drain (g) Removing dummy gate and (h)
	Deposition of gate oxide (i) Deposition of gate poly and (j) gate ion
	implantation (k) Annealing
Fig. 2-3.	SEM of the sidewall spacer nanowire46
Fig. 2-4.	Dimension of the nanowire
Fig. 2-5.	(a) Deposition of in-situ-doped n+ poly-Si and (b) definition of
	Source/Drain (c) Deposition of α -Si and (d) SPC (e) Definition of the
	channel and (f) deposition of the gate oxide (g) Deposition of gate
	poly and (h) gate ion implantation (i) Definition of the gate and
	annealing47
Fig. 2-6.	(a) Deposition of α -Si and (b) SPC (c) Definition of Source/Drain
	and (d) deposition of gate oxide (e) Deposition of gate poly and (f)
	gate ion implantation (g) Definition of the gate and (h) Source/Drain
	ion implantation (i) Annealing49
Fig. 2-7.	(a) Diagram of ΔQ_{DEP} within depletion region. (b) Electrical field

change	in	den	letion	region	indı	iced]	hv	ΛO_{DED}		51	
unangu	111	սսր	icuon	region	muu	iccui	U y	$\Delta Q DEP$	· • • • • • • • • • • • • • • • • • • •	21	•

- Fig. 2-11. Schematic representation of grain size in (a) thin and (b) thick channel after SPC.
- Fig. 2-12.Mobility variation of the three types of structures with (a) Al and (b)Si as pad materials. Error bars represent standard deviations......58
- Fig. 2-13. $I_D V_G$ curves of fifteen NW devices for (a) thick planar, (b) thin

planar, and (c) NW structures with Al as pad material......59

- Fig. 2-16. Standard deviation of V_t versus $1/(WL)^{1/2}$ for thick planar, thin

	planar, and NW devices
Fig. 2-17.	Mean values of S.S. for thick planar, thin planar, and NW devices
	with (a) Al and (b) Si as pad materials. Error bars represent
	standard deviations64

Chapter 3

Fig. 3-1.	The components of the base of the microfluidic channel system65
Fig. 3-2.	The PDMS microfluidic component65
Fig. 3-3.	The plastic used to press the PDMS microfluidic. An inlet and an
	outlet tubes are connected to the microfluidic for flowing the test
	solution during testing
Fig. 3-4.	Schematic representation of the setting for constructing the
	microfluidic channel system
Fig. 3-5.	(a) An overview and (b) close look of the sensing equipment66
Fig. 3-6.	Structural formula of PDMS67
Fig. 3-7.	Schematic representation of the testing configuration using
	nanowire devices equipped with an antenna sensing pad67
Fig. 3-8.	Controllable syringe pump68
Fig. 3-9.	An example illustrating the response of drain current to the
	injection of a new test solution with different pH value68
Fig. 3-10.	Subthreshold characteristics of a nanowire device tested in solutions
	with various pH values69
Fig. 3-11.	Schematics for deriving shift in threshold voltage from the shift of
	drain current69
Fig. 3-12.	Schematic representation of the site-binding model70

Fig. 3-13.	The variation of the reduced current response ratio versus pH for
	the three types of test structures71
Fig. 3-14.	The variation of the V_{t} response versus pH for the three types of test
	structures71
Fig. 3-15	(a) The real-time measurement obtained from a nanowire device. (b)
	The real-time measurement obtained from a planar device with a
	thin channel. (c) The real-time measurement obtained from a
	planar device with a thick channel72
Fig. 3-16.	\boldsymbol{V}_t response versus pH for three devices with various antenna pad
	areas74
Fig. 3-17.	Current response ratio versus pH for three devices with various
	antenna pad areas
Fig. 3-18.	The real-time Id measurements of nanowire devices with antenna
	pad area of (a) $30x60 \ \mu m^2$, (b) $100x100 \ \mu m^2$, and (c) $200x500 \ \mu m^2$. 76
Fig. 3-19.	Sensitivity of the nanowire devices with Al ₂ O ₃ antenna pad material
	of various area
Fig. 3-20.	The I_D - V_G curves measured at different pH solutions with antenna
	pad area of (a) 50x100 (b) 100x100, (c) 100x200, and (d) 100x500
	μm ² 79
Fig. 3-21.	Current response ratio versus pH for the four devices with various
	antenna pad areas80
Fig. 3-22.	The real-time measurement of nanowire devices with antenna pad
	area of (a) 50x100 (b) 100x100, (c) 100x200, and (d) 100x500 μm^2 . 82
Fig. 3-23.	Test procedure for (a) acid and (b) basic solution with a loop time of
	21 min (1260 s) with 7 min per step, respectively
Fig. 3-24.	Measured Id as a function of time for (a) acid and (b) basic solution. x_i

Fig. 3-25.	Vt response for devices with Al ₂ O ₃ antenna pad tested at different
	steps for (a) acid and (b) basic solution. The arrows indicate the test
	sequence



Chapter 1

Introduction

1-1 An Overview of Nanowire Technology

In order to achieve low subthreshold swing (S.S.), high switching speed, high Ion / Ioff ratio and outstanding gate controllability in nano-scale devices, nanowire technology has been in active development in order to solve these problems which have plagued the conventional planar scheme. In general, when a stripe structure with its cross-sectional dimension or feature size smaller than 100 nm, it could be called nanowire (NW). In recent years, one-dimensional structures, such as NWs and nanotubes, have gradually emerged and played an important role in the development of advanced electronic devices and the relevant applications. Si NWs have been recognized as ideal building blocks for nano scale electronics. A clever and simple scheme to fabricate NWs without resorting to complex and costly fabrication facilities has also been proposed [1]. Since NWs have very small volume and large surface-to-volume ratio, they have been adopted for a variety of applications, including nano complementary metal-oxide-semiconductor (CMOS) transistors [2-4], NW thin-film transistors (TFTs) [5], memory devices [6,7], light-emitting diodes (LEDs) [8], and biochemical sensors [9,10]. For electronic devices like MOS transistors, NWs can improve gate controllability and suppress short channel effects [2]. For memory devices, the use of NW as the channel can potentially reduce programming and erasing time. And for biochemical sensors, their high surface-to-volume ratio and excellent gate-controllability can reduce S.S., enabling a much better sensitivity.

Usually, based on the fabrication sequence, the preparation of NWs could be categorized into two types, one is "top-down", and the other is "bottom-up", as described in the following section.

This approach typically employs deposition methods to form the NWs directly. For this purpose, nowadays many deposition methods have been developed, including laser ablation catalyst growth [11], chemical deposition catalyst growth [12], solid-liquid-solid [13] and oxide-assisted catalyst-free method [14]. The first two methods are based on vapor-liquid-solid (VLS) mechanism, which is carried out with metal nanocluster catalyst as an active favorite site for absorbing gas-phase reactants, and then the cluster becomes a site for growing the NW as the supersaturation state is reached. Afterwards, these NWs are harvested and dispersed into a solution, and then the NWs are disposed on the substrate for device fabrication. There are several methods used to assemble and align the NWs, including microfluidic channel [15], electric-field-directed assembly [16] and Langmuir-Blodgett (LB) technique [17]. Although cheaper and more flexible for experimental purposes are the advantages of these approaches, there are still some concerns for the above scheme. For example, it is very difficult to align and position the NWs accurately, resulting in a significant variation in device characteristics.

1-1-2 Top-Down Approach

Different from the bottom-up approach, the top-down method has the capacity of **1896** precise positioning and good reproducibility, so this approach is very suitable for many kinds of mass fabrications. Although top-down approach has these attractive advantages, it still faces some issues. For instance, this approach often needs to employ advanced lithography techniques, such as e-beam [18], deep UV [19], nanoimprint [20-22], and so on, to generate the NWs patterns. These equipments are so expensive that many academic research units can't afford it. As a result, some skills which can be implemented and accomplished with conventional (and cheap) lithography tools, such as spacer patterning [23], thermal flow [24] and chemical shrink [25], have been proposed and developed to help generate NWs.

1-2 Introduction of Sensor Devices

Utilizing the metal-oxide-semiconductor field-effect transistor (MOSFET) as a sensor can be traced back to 1975 by Lundstrom *et al.*, who used the palladium-gated MOSFET to sense the hydrogen concentration (GASFET) [26]. Generally, in these days, the most popular way for sensing applications is fluorescent labeling. Nevertheless, there still exist some problems, such as non-real-time detection, non-uniform labeling for tagging molecules and easy signal quenching. Some approaches have been developed and used as an alternative to address these problems, such as surface plasmon resonance (SPR) [27], nano cantilevers [28] and ion sensitive field effect transistors (ISFETs) [29]. In this thesis, we fabricated and studied the **1896** operation of ISFETs. The development of sensor devices is reviewed below.

1-2-1 Introduction of ISFET

The first paper on ISFET was published in 1970 by Bergveld [30]. The ISFET operates like an MOSFET but with its gate in the form of a reference electrode inserted in a solution covering the gate oxide (SiO₂), as shown in Fig. 1-1. The surface of the gate oxide serves the role of the sensing site, on which the ions in the solution can be received and bonded. SiO₂ material was first applied in ISFET [30]. To have a

higher sensitivity, other materials were explored and reported, like Al_2O_3 [31], Ta_2O_5 [32], Si_3N_4 [33], WO_3 [34], SnO_2 [35]. When the ions were bonded with the dielectric surface, the surface potential of the material would be changed, so the channel conductance of the FET device would vary accordingly. Generally, as more positive ions are presented in an aqueous solution than the negative ones, they will induce more native carriers (e.g., electrons) in the channel and hence increase the conductance of an n-type FET device.

1-3 Motivation

In the past, the pH-meter was generally made of glass electrode, which would make the equipment bulky and the users need to lug it to the places where measurements are performed. In addition, glass is breakable and fragile so careful handling adds to the cost. To solve these problems, some alternative structures have been developed, like ISFET. As compared with former techniques, ISFET has many advantages. First, it only needs a little media to expose. This favors the construction of a small and portable test system. Second, its application is not restricted to pH sensing but also some other fields of bio sensors. Third, since ISFET has a structure almost the same as planar MOSFETs, it is easy to achieve mass production with low cost [36, 37].

Although conventional ISFET has those advantages, it is not flawless. For instance, in most cases it uses the planar device structure built on a bulk substrate, and could suffer from the problems of subthreshold leakage currents, which will lead to a higher S.S. and therefore a lower sensitivity. This phenomenon will be discussed in this thesis later. To achieve high sensitivity and better response to the detection, in this thesis we utilize a NW-FET to sense pH value. As mentioned above, due to the large surface-to-volume ratio, NWFET possesses higher I_{on} / I_{off} ratio and is sensitive to the surface condition. Accordingly, we can utilize the output current difference to differentiate the change of the pH value. Because it is fully compatible with silicon processes with low-temperature thermal cycles during fabrication, the NW approaches can be easily integrated with CMOS circuitry. To fabricate the device, tight control over a number of structural parameters, such as the dimensions of the NW structures, is needed. In this study we proposed and developed a novel method adopting sidewall spacer method to form NWs TFT. The structure is shown in Fig.1-2 [38]. Such NW sensors have been implemented with a micro-fluid scheme suitable for pH testing environment.

1-4 Organizations of the Thesis

In this thesis, we will show the relationship between the different type of structures, including planar and NW FETs, and the characteristics of pH measurements. In this chapter we have already introduced NW technology and the sensing structures. Then in Chapter 2, we will briefly describe the fabrications of "planar thick", "planar thin" and "NW" structures. Besides, we will describe measurement methods, equipments and the relating theorem and characteristic in detail with the device. In Chapter 3, we will describe sensing measurement equipments and methods. Besides, the sensitivity and the characteristics of pH measurement with respect to the different size of sensing area and structures will be **1896** discussed. Finally, we will summarize the conclusion of this thesis and suggestions for future work.

Chapter 2

Device Structures, Fabrication and Characteristic Analysis

As discussed in Chapter 1, in order to have high sensitivity, we have to reduce the S.S.. To achieve this purpose, we have recently developed a method to fabricate tiny NW as the channel of the devices [38]. The method is simple and low cost. To illustrate the effectiveness of NW channel, in this thesis three structures were fabricated and characterized. Two of them are with planar channel structures and the last one is with NW channel structure. In each of the structures, two kinds of sensing materials were employed, including aluminum oxide (Al₂O₃) and silicon oxide (SiO₂). In this chapter, we will describe the process flows of these devices and the measurement settings

2-1 **Process Flow and Structure of NW Devices**

The top-view of the NW device is shown in Fig. 2-1(a). Fig. 2-1(b) is a cross-sectional view of the device along Line $\overline{aa'}$ in Fig. 2-1(a). A series of schematic diagrams illustrating the NW fabrication flow are shown in Figs. 2-2(a) to

(k). All devices used in this work were fabricated on 6-inch silicon wafers. First, we capped the wafers with 1500 Å silicon nitride (Si₃N₄) at 780 $^{\circ}$ C by the low pressure chemical vapor deposition (LPCVD) system. Then, we deposited a layer of 1000 Å TEOS oxide at 700 °C by LPCVD (Fig. 2-2(a)). Next, the oxide was patterned by standard I-line lithographic and plasma etching steps (Fig. 2-2(b)) to form a dummy structure. A 1000 Å -thick amorphous-silicon (α -Si) layer was then deposited at 560 °C by LPCVD (Fig. 2-2(c)). Next an annealing step was performed at 600 $^{\circ}$ C in N₂ ambient for 24 hours to transform the α -Si into poly-Si (Fig. 2-2(d)). Afterwards, the source/drain (S/D) implant was performed by P^{31+} implantation with dose of 5×10^{15} cm⁻² and energy of 15 keV (Fig. 2-2(e)). An I-line lithographic step was then performed to generate S/D photoresist patterns, and the exposed poly-Si layer was then etched by a reactive plasma etching step to define the S/D regions. During the step, we could control the over-etching time to simultaneously form the poly-Si NW spacers along the two sides of the dummy structure in a self-aligned manner with respect to the S/D and gate (Fig. 2-2(f)). Note that, due to the low implantation energy, the NW channels remained undoped after their formation. Figure 2-3 shows the SEM image of the sidewall NW channels and the dummy structure. Diluted HF etching was carried out in the subsequent step to remove the dummy structure (Fig. 2-2(g)). Next, we deposit 300 Å -thick TEOS oxide to serve as the gate oxide at 700 °C by LPCVD

(Fig. 2-2(h)). Then, a 1000 Å -thick poly-Si was deposited at 620 °C by LPCVD to serve as the top gate electrode (Fig. 2-2(i)). Afterwards, the top gate implant was performed by P^{31+} implantation with a dose of 5×10^{15} cm⁻² and energy of 35 keV (Fig. 2-2(j)). Next we used the I-line lithographic and stander plasma etching to define the gate electrode. Then in order to reduce the S/D and gate resistance, the devices were treated with a rapid thermal annealing (RTA) at 900 °C for 60 seconds (Fig. 2-2(k)). The devices were then covered with an ONO stack consisting of 2000 Å -thick TEOS oxide, 1000 Å -thick silicon nitride, and 1000 Å -thick TEOS oxide, all deposited by LPCVD. The inserted nitride was used to enhance the water-repellent property of the devices during sensing test. After the formation of contact holes, we split the wafer into two groups with different pad materials filling in the contact holes, namely, aluminum, and *in-situ* doped n⁺ poly-Si. These materials were subsequently defined to serve as the test pads for device characterization. Finally, all devices received a forming gas sintering step at 400 °C for 30 minutes. Figure 2-4 shows the cross-sectional SEM image of the NW structure. From this image, we can observe that the channel height and thickness are approximately 40 nm and 50 nm, respectively, and the shape is almost triangular.

2-2 Process Flow and Structure of Planar Devices

For comparison with the NW structures, we've also fabricated the planar devices

with various channel thickness.

2-2-1 Planar Device with Thin Channel

The top view of the "planar-thin" devices is also shown in Fig. 2-1(a). The cross-section views formed after different steps of fabrication along Line \overline{bb} " in Fig. 2.1(a) are shown in Figs. 2-5(a) to (i). First, the 6-inch wafers were capped with a 1500 Å silicon nitride and a 500 Å *in-situ* doped n° poly-Si (Fig. 2-5(a)). After standard I-line lithography and plasma etching to define the S/D regions (Fig. 2-5(b)), we deposited a 100 Å -thick amorphous silicon layer (Fig. 2-5(c)). Then, an annealing step was performed at 600 °C in N₂ ambient for 24 hours to transform the α -Si into poly-Si (Fig. 2-5(d)). The channel was then defined by another I-line and plasma etching steps (Fig. 2-5(e)). Note that the S/D thickness is much thicker than the channel in order to reduce the parasitic resistance. Next, a 300 Å -thick TEOS was deposited to serve as the gate oxide (Fig. 2-5(f)), then a 1000 Å -thick gate poly-Si layer was subsequently deposited (Fig. 2-5(g)). Afterwards, the top gate implant was

performed by P^{31+} implantation with dose of 5×10^{15} cm⁻² and energy of 35 keV (Fig. 2-5(h)). After the gate formation, an RTA annealing with 900 °C for 30 seconds was performed to reduce S/D and gate resistance (Fig. 2-5(i)). The subsequent fabrication flow was the same as that used in NW device fabrication.

2-2-2 Planar Device with Thick Channel

The top view of this structure is the same as that shown in Fig. 2-1(a). The fabrication steps with the cross-section views along Line \overline{bb} in Fig. 2-1(a) are shown in Figs. 2-6(a) to (i). To begin with, a 1500 Å thick silicon nitride layer was first capped on Si wafer surface, followed by the deposition of an α -Si layer of 500 Å (Fig. 2-6(a)). After the annealing step performing at 600 °C in N₂ ambient for 24 hours to transform α -Si into poly-Si (Fig. 2-6(b)), the active region is formed (Fig. 2-6(c)). Then, we deposited a 300 Å thick TEOS oxide as the gate oxide (Fig. 2-6(d)), and a 1000 Å thick poly-Si layer as the gate material (Fig. 2-6(e)). Afterwards, the top gate implant was performed by P³¹⁺ implantation with dose of 5×10^{15} cm⁻² and energy of 35 keV (Fig. 2-6(f)). In the subsequent step, we used I-line photolithographic and plasma etching steps to define the gate region (Fig. 2-6(g)), then performing a P³¹⁺ implant with dose of 5×10^{15} cm⁻² and energy of 35 keV to dope the S/D and gate (Fig

2-6(h)). Dopant activation was done by performing RTA at 900 $^{\circ}$ C for 30 seconds (Fig. 2-6(i)). The subsequent processes were the same as that used in fabricating devices with thin channel.

2-3 Measurement Setups and Electrical Characteristics of the Fabricated Devices

2-3-1 Measurement System

All electrical characteristics of the devices characterized in this thesis were measured by an automated system consisting of switching system-708A, Model 4200 Semiconductor Characterization System (Model 4200-SCS) with built-in software, and Keithley Interactive Test Environment (KITE).

2-3-2 Theory and Model of Threshold Voltage

Variation

Because of the device scaling, the dopant counts in channel region of modern nano-scale CMOS devices may fall less than a few hundreds. In this situation, random dopant distribution in depletion region is one of the possible reasons to induce V_t variation [39]. Generally, the Vt can be represented by

$$V_t = V_{FB} + \phi_S - \frac{Q_{DEP}}{C_{OX}}, \qquad (2-1)$$

where V_{FB} is the flat band voltage, ϕ_s is the surface potential between oxide and channel, Q_{DEP} is the charge within the depletion region, and C_{OX} is the capacitance of gate oxide per unit area. From the formula, we can see that the last term is related to the dopant distribution, so it represents an impact factor to affect the V_t. According to Takeuchi's model [40], V_t shift (ΔV_t) can be described as

$$\Delta V_t = \frac{\Delta Q_{DEP}}{C_{OX}} \times \left(1 - \frac{x_0}{W_{DEP}}\right)$$
(2-2)

In order to simplify the model, he assumed that all the parameters are constant, except the dopant distribution. This formula is based on scheme shown in the Fig. 2-7(a) which assumes that additional charges (ΔQ_{DEP}) at the position (x_0) along X-axis **1896** within maximum depletion width (W_{DEP}) will cause the surface potential and V_t shifts. The solid line in Fig. 2-7(b) represents the original electric field distribution in the depletion region induced by substrate doping (N_{SUB}) without any additional charge and the surface electrical field is E₀. When ΔQ_{DEP} is added, there will be a potential drop at x_0 . In order to balance this phenomenon, the surface electric field will be enhanced by ΔE , and the electric field distribution is modified as shown by the dashed line. Such modification affects the surface potential and makes V_t change.

In order to calculate the V_t shift, we can first approximate ΔQ_{DEP} by

Poisson's statistics [41], so

$$\Delta Q_{DEP} = \frac{q \cdot \sqrt{N_{SUB} \left(x\right) \cdot L \cdot W \cdot \Delta x}}{L \cdot W}, \qquad (2-3)$$

where W is the channel width and L is the channel length. By substituting Eq. (2-3) into Eq. (2-2), and integrating all the contribution of ΔQ_{DEP} in the depletion region from x = 0 to x = W_{\text{DEP}}, we obtain

$$\Delta V_t = \frac{q}{C_{OX}} \times \sqrt{\frac{N_{EFF} \cdot W_{DEP}}{3 \cdot L \cdot W}}, \qquad (2-4)$$

where N_{EFF} is a weighted average of $N_{SUB}(x)$ defined as

$$N_{EFF} = 3 \cdot \int_{0}^{W_{DEP}} N_{SUB}(x) \cdot (1 - \frac{x}{W_{DEP}})^{2} \cdot \frac{dx}{W_{DEP}} \quad . \tag{2-5}$$

We can see in Eq. (2-4) that ΔV_t is inversely proportional to the L and W which are **1896** related to the dimensions of the devices, and proportional to the W_{DEP} which is related to the sharped thickness for devices with a fully depleted sharped

to the channel thickness for devices with a fully-depleted channel.

In this study, no intentional channel doping was performed in the poly-Si channel. Nevertheless, the trapping sites located in or near the grain boundaries may play a similar role to that of random dopants in the bulk CMOS devices. This is because their charge state is affected by the gate bias and may affect V_t. This means we can adopt the above theory and replace the parameter N_{SUB} with N_{TRAP} to analyze the fluctuation in device characteristics. The relationship between random "trap"

effect and the deviation of the V_t will be discussed in the end of this section.

2-3-3 Comparisons of Basic Electrical Characteristics

Figs. 2-8(a) to (f) show typical I_D-V_G curves of the three types of structures and two different pad materials. From the curves, we can see the slopes of the "planar-thick" device in the linear region are the smallest, and those of the NW's are the largest. It means that if we use NW, the largest current difference can be obtained in a small change in V_G. This is one of the reasons why we want to use the NW structures for sensor applications. To compare the characteristics more clearly, we utilize the S.S. that is defined as below: $S.S. = \left[\frac{\partial(\log I_D)}{\partial V}\right]^{-1} (mV/dec). \qquad (2-6)$

We can find that the mean S.S. of the NW is much smaller than that of the planar ones. It is because NW channel has the largest surface-to-volume ratio, and the gate is more effective in control the turning on and off of the channel. Besides, the off-state leakage is dramatically reduced with ultra-thin channel thickness, as compared with the planar device with thick channel.

Moreover, from the figures, we can see the on/off ratio of the NW devices is the

largest (~10⁶) among the devices, while the planar devices with thick channel is the worst. This is because of the off leakage currents of the thick planar devices which is much larger than the other two structures as mentioned above. The gate is difficult to control the deeper portion of channel which is responsible for the off-state leakage. Figs. 2-9(a) and (b) show the I_D -V_G curves of different structures and pad materials. We can clearly see that the NW structure has the best performance among the test devices.

We also compare the mobility performance of the devices by measuring the field-effect mobility which is defined as, $E = \frac{L \cdot G_m}{W \cdot C_{OX} \cdot V_D}$ (cm²/V-s), (2-7)

where C_{ox} is the gate oxide capacitance per unit area, W is the channel width, and G_m stands for the transconductance given by,

$$G_m = \frac{\partial I_D}{\partial V_G} \Big|_{V_D = const.}$$
 (2-8)

Figs. 2-10(a) and (b) present the mobility of the three types of devices with various pad materials. We can see that the mobility of the NW and thick planar devices are larger than that of the thin planar ones. One of the possible reasons is the small grains size contained in the ultra-thin (~ 100 Å) channel of the thin planar devices. In this case the top and bottom α -Si/dielectric interfaces are so close that the SPC process

would be limited by the heterogeneous nucleation process at the interfaces and the grain size thus shrunk Figs. 2-11(a) and (b) are the schematic drawings to explain the phenomenon. For the case when the channel thickness is thin, as shown in Fig. 2-11(a), the grains size will be limited by the thickness, so mobility and the conduction current will suffer from more scattering with the grains boundaries than the case with a thick channel. Besides, although the original α -Si film thickness of NW devices (1000 Å) is two times larger than that of the planar thick (500 Å), the mobility is not much bigger. This is attributed to the fact that the portion of the final NW channel is near the side wall of the dummy structure, and generally the grains size near the interface is smaller than the outer part, thus the benefit of an increased grain size with increasing thickness is not significant. Figs. 2-12(a) and (b) are the variation of the mobility. We can see the mean value of the mobility is the best for NW even though the channel thickness is the smallest.

Next, we compare the deviation of threshold voltage among the different structures. Figures 2-13(a) to (f) are the I_D -V_G curves of fifteen devices measured from the three types of structures with various pad materials. The channel length of the devices was 2 μ m, the channel width is 0.4 μ m for planar and 65 nm for NW, and the channel thickness is 500, 100 and 400 Å for "planar-thick", "planar-thin" and "NW", respectively. First, from the diagrams, we can clearly see that the variation is

the worst for the thick planar devices, while the NW devices are the best. Figs. 2-14(a) to (c) and Figs. 2-15(a) to (c) are the mean V_t from different structures and pad materials with channel length of 1 μ m, 2 μ m and 5 μ m, respectively. V_t is defined as V_G at $I_D = W/L \times 10$ nA. The error bar in the figures represents the standard deviation in V_t . We can find the deviation shows the identical trend. That is, when the channel length increases, the deviation decreases. As mentioned before, discrete random dopant (or trap) in the depletion region of the channel plays a main role in affecting the threshold voltage deviation. Then, according to Eq. 2-4, the ΔV_t will be proportional to W_{DEP}, and inversely proportional to L and W. It seems that this phenomenon that we discovered can be well explained by the effect. In order to verify this assumption, we plot ΔV_t versus $1/\sqrt{LW}$ in Fig. 2-16. It means that the ΔV_t for this effect will be only affected by W_{DEP}, and proportional to it. First, we compare the thick and thin planar devices. Since the channel thickness of the fabricated devices is pretty thin (only 500 Å even for the "thick" planar split), W_{DEP} is assumed to be the channel thickness. Because the thickness of thick planar devices is thicker than the thin planar ones, we can see the ΔV_t of planar thick is bigger. It means that there are more ΔQ_{DEP} as the channel becomes thicker, so the ΔV_t is larger. On the other hand, the channel in NW is of triangular column, so we can't directly use the channel thickness to represent the W_{DEP}. But we still can use the following formula to find out

the average W_{DEP}:

$$Q_{DEP} = -qN_{TRAP}(W_{DEP} \cdot L \cdot W) = -qN_{TRAP}V_{CHANNEL} = -qN_{TRAP}(W_{DEP(\text{average})}W_{COVERED}L), (2-9)$$

where $V_{CHANNEL}$ is volume of the channel, $W_{DEP(average)}$ is the average depletion width and $W_{COVERED}$ is the gated channel width. Because it is fully depleted, the last term of the original formula can be represented by the volume of the channel. Then, we can utilize the channel surface area that is covered by gate to calculate the average W_{DEP} . And we can find that the W_{DEP} of NW is around 80 Å which is smaller than the thin planar ones, so we can get the smallest slope for NW in Fig. 2-16. In other words, NW has the best control over the threshold voltage variation.

We also compare the Δ S.S. among the different structures. Figures 2-17(a) and (b) 1896 show the mean value of S.S. and Δ S.S. of the test samples. The channel length of all samples is 2 µm. Again it can be seen that the thick planar device has the largest Δ S.S., and NW has the smallest deviation. As mentioned before, NW has the largest surface to volume ratio, which can increase gate coverage within finite channel region. The smallest mean value and standard deviation of S.S. with the NW split reflect this trend. Finally, Table 2-1 summarizes of the conclusions in Chapter 2.

Chapter 3

Analysis of the Characteristics of pH Sensors

3-1 Microfluidics Settings and Measurement Methods

The electrical measurement equipment for pH sensors is the same as that mentioned in Sec. 2-3. The microfluidic channel system which houses the test devices is composed of a base (Fig. 3-1), a microfluidic channel made of polydimethylsiloxane (PDMS) (Fig. 3-2), and a plastic mold used to press the PDMS (Fig. 3-3). Construction of these components is shown in Fig. 3-4, and the final views are shown in Figs. 3-5(a) and (b). The chemical constitution of PDMS is shown in Fig. 3-6. Normally we can clean the material using acetone only. Major advantages of the PDMS approach are summarized in Table 3-1. For those merits, it becomes one of the most attractive materials for microfluidic device.

All the pH solutions were deployed by using phosphate buffered saline (PBS)(10mM, pH7.4, 13mM Na₂HPO₄, 2.26mM KH₂PO₄). NaOH was used to make it more basic, while H₃PO₄ was used for opposite purpose. The glass electrode pH meter was used to measure and help calibrate the pH value of the solutions that we

intended to test. The reference electrode material was silver. Figure 3-7 is the schematic illustration of the test configuration equipped with the poly-Si NW devices.

When starting experimental measurements, we injected the test solution into the microfluidic system via an inlet tube (see Fig. 3-3). The solution was then flowed through the microfluidic channel of the PDMS microfluidics where the sensing pad of the test device was located, and was then flowed out via the outlet tube (see Fig. 3-3). To make the flow stable, a string pump (Fig. 3-8) was used for automatic injection. During the measurement solutions with various pH values were injected sequentially and we could measure the real-time drain current characteristics (i.e., Id vs. time) at a fixed V_G condition operated in subthreshold region. The set V_G was determined in the beginning of the test by first measuring the I_D - V_G curve. Throughout the test V_d was set at 0.5 V. For real-time characterization, evolution of drain current measured under the appropriate V_G with the flowing solution of varying pH values was recorded. However, as the pH of the test solution was changed to a new value, it needed a period of time to become stable. A typical example is given in Fig. 3-9. As can be seen in the figure, as the pH is varied from 9 to 10, a drop in drain current occurs and takes several hundreds of seconds to reach the steady state. The difference between the new stable Id and the previous stable one is then recorded and used as an indicator to reflect the capability of the test device in sensing the pH value of the test solution.
In addition, we can also derive the shift in V_t from the drain current difference. Figure 3-10 shows the subthreshold characteristics of a test device measured in solutions with pH ranging from 7 to 10. It can be seen that a change in pH results in a parallel shift in the I-V curves and thus S.S. remains the same. From this we can, based on the relation shown in Fig. 3-11, derive the shift in V_t from the drain current difference. Based on the scheme, V_t shift is used as another indicator for analyzing the sensitivity of the testers.

3-2 The Theory of pH Sensors

Variation in pH value of the test solutions is responsible for the variation of sensing signal. According to its definition, pH can be expressed as

$$pH = -\log[H^+]_b, \qquad (3-1)$$

where $[H^+]_b$ is the bulk concentration of H^+ ions in the solution. It implies that sensors can detect the change of pH because of the variation in the concentration of H^+ ions.

The most plausible reason to explain why sensors can detect the variation of $[H^+]_b$ is based on the site-binding model. The model was first introduced in 1974 by Yates *et al.* [42] to describe the properties of an oxide/aqueous electrolyte interface. In the site-binding model, the oxide surface contains sites in three forms: $A - O^-$, $A - O^-$

OH, and A – OH_2^+ , as shown in Fig. 3-12. The neutral A – OH sites are characterized

by the equilibrium constants K_a and K_b, and can be written as the following equations,

$$A - OH \xleftarrow{K_a} A - O^- + H^+, \tag{3-2}$$

$$A - OH + H^+ \xleftarrow{K_b} A - OH_2^+, \tag{3-3}$$

$$K_a = \frac{[A - O^-][H^+]_s}{[A - OH]}, \qquad (3-4)$$

$$K_{b} = \frac{[A - OH_{2}^{+}]}{[A - OH][H^{+}]_{s}},$$
(3-5)

where $A - O^-$, A - OH, and $A - OH_2^+$ are the negative, neutral and positive surface sites, respectively, K_a and K_b are the equilibrium constants, and $[A - O^-]$, [A - OH]and $[A - OH_2^+]$ are the numbers of the surface sites per unit area. Note that $[H^+]_s$ is the concentration of the H^+ ions in solution near the surface, and the relationship between $[H^+]_s$ and the bulk concentration $[H^+]_b$ can be written by the Boltzmann equation,

$$[H^{+}]_{S} = [H^{+}]_{b} \cdot \exp(\frac{-q\psi_{0}}{KT}), \qquad (3-6)$$

where ψ_0 is the pH-dependent surface potential, K is the Boltzmann constant, q is the elementary charge, and T is the absolute temperature. The surface potential is actually correlated with the net surface charge density,

$$\sigma_0 = ([A - OH_2^+] - [A - O^-])$$
(3-7)

According to Eq. 3-2 and 3-3, for instance, if σ_0 at pH 7 is zero, we know that for an acid, the predominant concentration of H⁺ ions will cause the reaction to generate $A - OH_2^+$. In other words, $[A - OH_2^+]$ is more than $[A - O^-]$, so by Eq. 3-7 the surface potential will be positive. Conversely it is negative in a basic solution. Because of the change of surface potential with varied pH value of the test solution, we can see the change of electrical characteristics.

In this study, we employed two types of sensing pad materials, namely, Al and Si. Naturally, the surface of the materials forms a native oxide layer which becomes practical sensing site of the sensing antenna connected to the sensor devices. Through the conductive solution, we can apply a voltage to the antenna pad through a probe immersing inside the test solution without practically contacting the electrode. Owing to the change of surface potential caused by the reactions mentioned above, the effective gate voltage will be enhanced or decreased. This change reflects on a modification of the output currents (I_D) which is recorded and analyzed.

3-3 Analysis of pH Sensing Characteristics

3-3-1 The Sensitivity of Different Structures

In this experiment, the test solution starts at pH 3 and then pH 3-5-7-9 in

sequence. The V_D set during the measurements is 0.5 V. First we define a parameter,

"reduced current response ratio", as follows:

Reduced current response ratio =
$$\frac{I_{D3} - I_{DX}}{I_{D3}} \times 100\%$$
, (3-8)

where I_{D3} is the drain currents at pH 3 (i.e., the initial drain current), and I_{DX} is the drain currents at pH X (X = 3, 5, 7, 9). Fig. 3-13 shows the reduced current response ratio as a function of the pH value for NW and planar devices having a SiO₂ sensing layer. In this plot the antenna area is $30 \times 60 \ \mu m^2$. We can observe that, among the test devices, the NW structure has the strongest response for the variation of pH, and the planar device with thick channel is the worst. With the fitting lines included in the figure, we can see the reduced current response sensitivity of NW devices is 2.5 times higher than that of the thick planar device. This is because the NW sample has the best S.S. as have been shown in Section 2-3. This means that a small change in surface potential of the sensing pad will cause a larger change of drain currents or, in other words, a greater response. This demonstrates the effectiveness of utilizing the NW structures as a sensor. Figure 3-14 shows the V_t shift derived from the results shown in Fig. 3-13. Again, the NW device exhibits better sensitivity than the planar counterparts. Figures 3-15 (a) \sim (c) show the real-time drain current measurements of the test devices.

3-3-2 Effects of Antenna Pad Area

Here we will discuss the relationship between the exposed area of sensing layer and pH sensitivity. In a set of experiments, the testing starts by placing the test device in the test solution with pH 3, followed by injecting various test solutions with a pH sequence of 3-5-7-9. Here we use the V_t at pH 3 as the reference voltage to calculate and get the shift in V_t at each stage with respective to that with pH 3. Figure 3-16 shows the enhanced V_t response for three NW devices with various sensing (antenna) areas as a function of pH, and the material of the sensing layer is SiO₂. We can find an increase in antenna area tends to increase the sensitivity. In the figure, the sensitivities are 57.1, 50.8, and 45.2mV/pH for pad area of 200x500, 100x100, and 30x60 μ m², respectively. According to Eq. 3-7, we know that the surface potential is decided by the number of $A-OH_2^+$ and $A-O^-$ sites. The above trend can thus be attributed to the fact that a larger pad can provide more binding sites and therefore renders a bigger change in the amount of charges bonded to the sensing pad as the pH of the test solutions is varied. Figure 3-17 is the reduced current response ratio as a function of pH for the three devices. This is due to the fact that, in this indicator, the current has been normalized to the initial current level. However, as it is transformed into the V_t, the effect of sensing pad area on the sensitivity becomes clear, as shown in Fig.3-16. Figures 3-18(a) to (c) show the real-time drain current measurements performed on the devices.

3-3-3 Effects of Antenna Pad Materials

Figure 3-19 shows the sensitivity of NW devices with Al₂O₃ sensing pad of different sensing pad area. In the measurements, the pH value of the test solution started at 7, and with a sequence of 7-8-9-10. Here we used the V_t at pH 7 as the reference voltage, and then calculated and obtained the shift in V_t as the pH of the test solution is changed. In this figure we can find the sensitivity of devices with Al₂O₃ as the sensing material still shows a positive correlation with antenna pad area. Besides, from Figs. 3-20(a) to (d), we can easily see the value of the V_t shift becomes apparent when the antenna pad is larger. Figure 3-21 is a figure showing the current response ratio for these devices at different pH. We can discover the current response of Al_2O_3 surpasses that of SiO₂ shown in Fig. 3-17. This in turn results in the greatly enhanced sensitivity of devices with Al₂O₃ sensing pad shown in Fig. 3-19 over that with SiO₂ shown in Fig. 3-16. One interesting finding shown in Fig. 3-19 is the extremely high sensitivity (> 120 mV/pH) exhibited by the NW devices with Al_2O_3 sensing material. These values are two times larger than the theoretical limit of 60 mV/pH at room

temperature proposed by P. Bergveld [43]. Figures 3-22(a) to (d) are the results of real-time measurements performed on these devices. Although such high sensitivity is intriguing and could be of importance for practical application, origins for the phenomenon are still unknown and need additional efforts to investigate and disclose.

Other test procedures are shown in Figs. 3-23 (a) and (b), respectively, for probing the hysteresis characteristics of the tester with an Al_2O_3 sensing pad in a loop time of 1260 s. The real-time diagrams obtained from the tests are shown in Figs. 3-24(a) and (b). The shift in V_t in each stage during testing with respect to the V_t at pH 7 at time zero for the acid- and basic- cycles are shown in Figs.3-25 (a) and (b), respectively. In these figures it can be seen that the two datum points recorded at pH 7 do not coincide actually, indicating the occurrence of hysteresis. We can see the difference of point *a* and *b* is 10.9 mV, which is smaller than the difference (22.2 mV) of point b' and c'. This means the hysteresis in acid is smaller than that in basic solutions. There are two possible reasons to explain this phenomenon. The first one was brought up by L. Bousse et al [45]. The explanation is that the dominant ion species H^+ in acid solutions is smaller and lighter than the OH⁻ ions in basic solutions, so it is easier and faster for H⁺ to go through the sensing material. It can thus reduce the total reaction time. So we will find the hysteresis in acid is smaller in basic solutions. Another plausible reason is owing to the higher sensitive of the tester exhibiting in basic solutions than acid ones. So in limited time period, it is more difficult for the testing in basic than in acid to return the original current state.



Chapter 4

Conclusion and Future Work

4-1 Conclusion

In this thesis, we have developed a simple method to fabricate poly-Si NWTFTs. In the device fabrication sidewall spacer etching technique was used to define the NW patterns, and no advanced or expensive lithographical tools like e-beam writer was involved. We've also utilized the fabricated NWTFTs as a test vehicle for sensing pH of chemical solutions. In this scheme, the NW channel was connected to an antenna test pad with varied area and pad material. For comparison purpose, planar devices were also fabricated and compared. Among the test devices, NW structures exhibit the best performance in terms of lowest leakage current, smallest S.S. and highest on/off currents ratio, owing to the high surface-to-volume ratio and tiny channel dimensions. For device variation issue, the standard deviation of V_t is shown to be inversely proportioned to \sqrt{WL} and proportional to the depletion width. Because of the superior gate controllability, NW devices also present the tightest control over V_t and S.S. variations.

For the pH measurements, because of the characteristic steep S.S., we can easily

see that the NW structures have the best sensitivity as compared with planar devices. In addition, the results show that the relationship between sensitivity and the sensing pad area is positive. Regarding the sensing pad materials, our results indicate that Al₂O₃ has better sensitivity than SiO₂. Moreover, the sensitivity of the test devices with Al₂O₃ sensing pad can be much larger than the limitation of 60 mV/pH at room temperature, predicted in previous theory [43], although details about origins of this phenomenon remain unclear. We've also measured the hysteresis characteristics of pH testing. The results indicate the hysteresis in acid is smaller than that in basic. This is attributed to the smaller size and lighter mass of H⁺, the major reactants in acid, over that of OH⁻ in basic solution. As a result, H⁺ ions move more quickly and reduce the response time within reaction. Therefore, the hysteresis in acid is smaller than that in basic.

4-2 Future Work

In this thesis, we found the sensitivity transcended the theoretical limit value (60mV/pH) at room temperature when using Al_2O_3 as the antenna pad material. Nevertheless, such phenomenon was not seen as SiO_2 was used as the sensing material. Certainly it needs more efforts to clarify the associated mechanisms. Examination of additional types of sensing materials is also important. The environmental noise is always an annoying factor in experiments. In order to improve the quality of experiments, the construction of an advanced testing environment and equipment with high precision and automatic measurement procedure is essential.



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Tables

Structures Characteristics	Planar Thick (Al)	Planar Thin (Al)	Nanowire (Al)	Planar Thick (Si)	Planar Thin (Si)	Nanowire (Si)
on/off ratio	~ 104	~105	~10 ⁶	~5x104	~105	~5 x10⁵
Mobility (cm²/ V-s)	23.35	<mark>6.6</mark> 3	24.71	18.59	6.66	25.26
Vt (V)	4.97	3.91	1.27	4.38	4.27	1.61
ΔVt (V)	0.44	0.17	0.11	0.35	0.18	0.09
S.S. (mV/dec.)	1301.06	1163.81	317.41	1305.97	1224.92	331.99
ΔS.S. (mV/dec.)	711.31	238.49	113.37	574.85	277.69	106.44

 Table 2-1 summarize of the electrical characteristics for the devices.



Table 3-1 Advantages of PDMS for microfluidic system.

1. Easy to fabricate
2. Can endure critical pH value
3. Bio & chemical compatibility
4. Cheap
5. Transparent (Easy to see the flow of fluid, and we can make

sure the fluid is circulation.)

Figures



Fig. 1-2. Schematic diagram of a nanowire channel device.

Silicon Nitride Si Substrate

Poly-Si _____ NW Channel



Fig. 2-1. (a) The layout and (b) cross-sectional view of NWTFT.



Fig. 2-2. (a) Deposition of dummy gate and (b) definition of dummy gate.



Fig. 2-2. (c) Deposition of α-Si and (d) SPC.



Fig. 2-2. (e) Source/Drain ion implantation and (f) definition of Source/Drain.



Fig. 2-2. (g) Removing dummy gate and (h) Deposition of gate oxide.



Fig. 2-2. (i) Deposition of gate poly and (j) gate ion implantation.





Fig. 2-3. SEM of the sidewall spacer nanowire.



Fig. 2-4. Dimension of the nanowire.



Fig. 2-5. (a) Deposition of in-situ-doped n+ poly-Si and (b) definition of Source/Drain.



Fig. 2-5. (c) Deposition of α-Si and (d) SPC.



Fig. 2-5. (e) Definition of the channel and (f) deposition of the gate oxide.



Fig. 2-5. (g) Deposition of gate poly and (h) gate ion implantation.



Fig. 2-5. (i) Definition of the gate and annealing.



Fig. 2-6. (a) Deposition of α-Si and (b) SPC.



Fig. 2-6. (c) Definition of Source/Drain and (d) deposition of gate oxide.



Fig. 2-6. (e) Deposition of gate poly and (f) gate ion implantation.



Fig. 2-6. (g) Definition of the gate and (h) Source/Drain ion implantation.



Fig. 2-6. (i) Annealing.



Fig. 2-7. (a) Diagram of ΔQ_{DEP} within depletion region. (b) Electrical field change in depletion region induced by ΔQ_{DEP} .



Fig. 2-8. Transfer characteristic of thick planar devices with (a) Al and (b) Si as pad materials.



Fig. 2-8. Transfer characteristic of thin planar devices with (c) Al and (d) Si as pad materials.





Fig. 2-8. Transfer characteristic of NW with (e) Al and (f) Si as pad materials.



Fig. 2-9. Comparing with the transfer characteristic of the three types of structures with (a) Al and (b) Si as pad materials.



Fig. 2-10.Mobility of the three types of structures with (a) Al and (b) Si as pad materials.



(a)

Fig. 2-11.Schematic representation of grain size in (a) thin and (b) thick channel after SPC.

57



Fig. 2-12. Mobility variation of the three types of structures with (a) Al and (b) Si as pad materials. Error bars represent standard deviations.


Fig. 2-13.I_D-V_G curves of fifteen NW devices for (a) thick planar, (b) thin planar, and (c) NW structures with Al as pad material.







Fig. 2-14. Mean values of V_t for (a) thick planar, (b) thin planar, and (c) NW structures with Si as pad material. Error bars represent standard deviations.



Fig. 2-15. Mean values of V_t for (a) thick planar, (b) thin planar, and (c) NW structures with Al as pad material. Error bars represent standard deviations.





(a)

Structure Types

Fig. 2-17. Mean values of S.S. for thick planar, thin planar, and NW devices with (a) Al and (b) Si as pad materials. Error bars represent standard deviations.



Fig. 3-1. The components of the base of the microfluidic channel system.



Fig. 3-2. The PDMS microfluidic component.



Fig. 3-3. The plastic used to press the PDMS microfluidic. An inlet and an outlet tubes are connected to the microfluidic for flowing the test solution during testing.



Fig. 3-5. (a) An overview and (b) close look of the sensing equipment.



Fig. 3-6. Structural formula of PDMS.



Fig. 3-7. Schematic representation of the testing configuration using nanowire devices equipped with an antenna sensing pad.



Fig. 3-8. Controllable syringe pump.



Fig. 3-9. An example illustrating the response of drain current to the injection of a new test solution with different pH value.









Fig. 3-13. The variation of the reduced current response ratio versus pH for the three types of test structures.



Fig. 3-14. The variation of the V_t response versus pH for the three types of test structures.



Fig. 3-15(a). The real-time measurement obtained from a nanowire device.



Fig. 3-15(b). The real-time measurement obtained from a planar device with a thin channel.





pH Value

Fig. 3-16.V_t response versus pH for three devices with various antenna pad areas.



Fig. 3-17.Current response ratio versus pH for three devices with various antenna pad areas.















Fig. 3-20. The I_D -V_G curves measured at different pH solutions with antenna pad area of (a) 50x100 (b) 100x100, (c) 100x200, and (d) 100x500 μ m².







Fig. 3-22. The real-time measurement of nanowire devices with antenna pad area of (a) 50x100 (b) 100x100, (c) 100x200, and (d) 100x500 μm².



Fig. 3-23.Test procedure for (a) acid and (b) basic solution with a loop time of 21 min (1260 s) with 7 min per step, respectively.



Fig. 3-24. Measured Id as a function of time for (a) acid and (b) basic solution.



Fig. 3-25. Vt response for devices with Al₂O₃ antenna pad tested at different steps for (a) acid and (b) basic solution. The arrows indicate the test sequence.

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Fabrication, Characterization, and pH Sensors Application of Poly-Si Nanowire Thin Film Transistors