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Fabrication of Silicon Nanowires Array Using E-beam Lithography Integrated with Microfluidic Channel for pH Sensing

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Abstract: Silicon nanowires based biosensors have garnered great potential in serving as highly sensitive, label-free and real-time response biosensing application. These biosensors are useful in detecting pH, DNA molecules, proteins and even single viruses. In this paper, we report the geometrical characteristics and performance of silicon nanowires array for pH level detection. The nanowires are designed for 40 nm, 50 nm and 60 nm diameter sizes. Top-Down Nanofabrication (TDN) is utilized in the development of resist mask and nanowires formation from silicon on insulator (SOI) wafer involving scanning electron microscope (SEM) based electron beam lithography (EBL). The smallest silicon nanowires structure achieved is 40 nm width and 30 nm height. The corresponding source and drain are fabricated *via* two aluminum (Al) electrodes on top of the silicon nanowires array using conventional lithography process. A 100 µm microfluidic channel is attached on the silicon nanowires for the sample solution transportation. pH level detection are performed based on several types of standard aqueous pH buffer solutions (pH 4, pH 7, pH 10 and pH 12) to test the electrical response of the sensor. Morphological and electrical responses have been proposed to verify the characteristics of the silicon nanowires array based pH sensor.

Keywords: Array, E-beam lithography, microfluidic channel, pH sensor, silicon nanowires.

INTRODUCTION

In recent years, the applications of silicon nanowires have attracted a lot of attention because of their applications in food industry, medical diagnosis, environmental monitoring, and many other areas [1-4]. Silicon nanowires surface can be sensitive to charge species combined with their high surface to volume ratio, hence preferable for high sensitivity pH sensor fabrication. The ability of such sensors was first demonstrated for pH detection by Bergveld in 1970 [5, 6]. A fundamental p-type silicon nanowires device was developed as a sensor by changing the silicon oxide surface with 3-aminopropyltriethoxysilane (APTES) [7], which results in amino (NH_2) and silanol (SiOH) groups at the nanowire surface [8]. Both groups are used as receptors for hydrogen ions which experience protonation and deprotonation reactions. There are now many different methods for fabrication of silicon nanowires. They are commonly placed into two categories namely bottom-up and top-down approaches [9-11]. In this work, the top-down approach is chosen to form the resist mask and fabricate the nanowires using scanning electron microscope (SEM) based electron beam lithography (EBL). EBL has played an important role in the development of nanostructure physics and is able to offer high resolution capabilities of this technology via versatile pattern formation and direct writing approach [10, 12]. The EBL utilized ma-N 2400 Series as the negative tone e-beam resist. The ma-N2400 Series negative tone e-beam resist consists of two components: a bisazide as photoactive compound and a phenolic resin (novolak) as polymeric bonding agent [13, 14]. The top-down nanofabrication consists of several steps, such as sample preparation, the software and pattern design, EBL system, inductively coupled plasma-reactive ion etching (ICP-RIE), SEM imaging and atomic force microscope (AFM) characterization [10, 15]. The fabricated silicon nanowires arrays are then functionalized and characterized for electrical performance.

EXPERIMENTAL

Materials

Silicon on insulator (SOI) wafer was purchased from Soitec with a silicon device layer of 50 nm. Commercially available pH buffer solution of pH 4, pH 7, pH 10 and pH 12 were purchased from QREC, Selangor, Malaysia. All buffer solutions were certified by the National Institute of Standards and Technologies (N.I.S.T. Malaysia) and were ready to be used at room temperature. The ma-N2405 negative resist and developer were purchased from Microresist Technology GmbH. 3-aminopropyl triethoxysilane (APTES, 99%) was purchased from Sigma-Aldrich, which functions as a facilitator to immobilize biomolecules on the SiOH group. All other chemical and solvent used in this fabrication process were purchased from Futurrex and Mallinckroot baker. Deionized water (18 MΩ cm) from an ultrapure water Milipore system is used for the rinsing process.

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Mask Design

The overall mask design for silicon nanowires array sensor consists of three mask designs, such as nanowires array design, pad mask and microfluidic channel mask as shown in Fig. (**1a**). The nanowires array were designed in various scale sizes (40 nm, 50 nm and 60 nm) using RAITH ELPHY Quantum GDSII Editor developed by Raith GmbH as shown in Fig. (**1b**). The AutoCAD was utilized to design the pad mask (Fig. **1a**) and microfluidic channel mask (Fig. **1c**), then prepared by printing onto the chrome mask glass surface. Chrome mask was used for better photo masking and to transfer structure onto device layer.

Fabrication of Silicon Nanowires Array

The top-down nanofabrication process of silicon nanowires array is briefly illustrated in Fig. (**2**). In this process, SOI wafer with 200 nm of buried oxide and a 50 nm top silicon layer were utilized as the substrate of the device (Fig. **2a**). The process was initialized *via* cleaning procedure using standard RCA 1 for 10 minutes at 70°C to remove organics or particles on the wafer surface. The wafer was then dipped into BOE for 10-15 seconds to remove a native oxide. After RCA 1 process, the wafer was dipped into standard RCA 2 for 10-15 minutes at 80°C and followed by a bake on the hotplate at 90°C for 60-90 seconds to remove the residual water or any moisture. Then, the wafer was cooled down to room temperature for about two to three hours before proceeding with resist coating process. Next, the wafer was cut into small pieces of 2 cm by 2 cm. ma-N2405 negative resist was spin coated using a photoresist spinner at 3000 rpm for 30 seconds to get approximately 100 nm resist films (Fig. **2b**). The resist was baked (Fig. **2c**) at 90°C for 90 seconds in order to harden the resist by evaporating any remaining solvents. The ma-N2405 negative resist was patterned by exposure using SEM based E-beam Lithography method. Exposures on ma-N2405 negative resist were done with a single pixel line (SPL) step size of 10 nm, a 20 nm area step size, a 75 pA beam current, an area dose of 200 uC/cm2, a SPL dose of 600 pC /cm and operating at an accelerating voltage of 20 KV (Fig. **2d**). The patterned ma-N2405 negative resist was developed using ma-D 532 developer for 40 seconds to wash away the unwanted resist (Fig. **2e**). The next step was hard bake at 90°C for 90 seconds in order to improve the resist adhesion to the developed wafer and becoming more resistant to etch process. An ICP-RIE plasma etch step (Fig. **2f**) was subsequently used to remove the silicon layer (Fig. **2g**). Afterwards, the patterned ma-N2405 negative resist was stripped using acetone. It should be noted that the silicon nanowires array was formed in this step in a good anisotropic profile (Fig. **2h**). The fabrication process was completed after the formation of aluminum pads (Fig. **2i**) using lift-off method and microfluidic channel (Fig. **2j**) was bonded on the center of silicon nanowires array for fluidic transport of the pH solution. The advantage of using microfluidic channel is to have a precise delivery for various chemicals for surface modifications, buffer solutions and bio-molecules at small volume. Apart from that, the microfluidic channel also helps to protect the Al electrodes pad from short-circuiting the sensing current.

Surface Modification of Silicon Nanowires Array

The purpose of surface modification was to prepare a suitable platform at the silicon nanowires array for bio-molecules detection. Silicon nanowires array can selectively trap the target molecule and further convert the action of binding to the electrical signal through strong affinity between the analyte and the receptor immobilized on silicon. 3-aminopropyl triethoxysilane (APTES, 99%), which functions as a facilitator to immobilize biomolecules on the SiOH group were used in this study. The surface modification was started by cleaning the surface of silicon nanowires array by using DI water, IPA and dried for 5 minutes. After cleaning process, the silicon nanowires array surface were functionalized with 2% APTES (v/v) in a mixture of 95% ethanol and 5% water for 2 hours at room temperature and rinsed with ethanol for 3 times.

Morphology Characterization and Electrical Measurements

The morphology of silicon nanowires array was investigated using SEM (JOEL JSM 6460LA). The geometrical characteristic of silicon nanowires array was measured using AFM system (SPI 3800N). The electrical character-

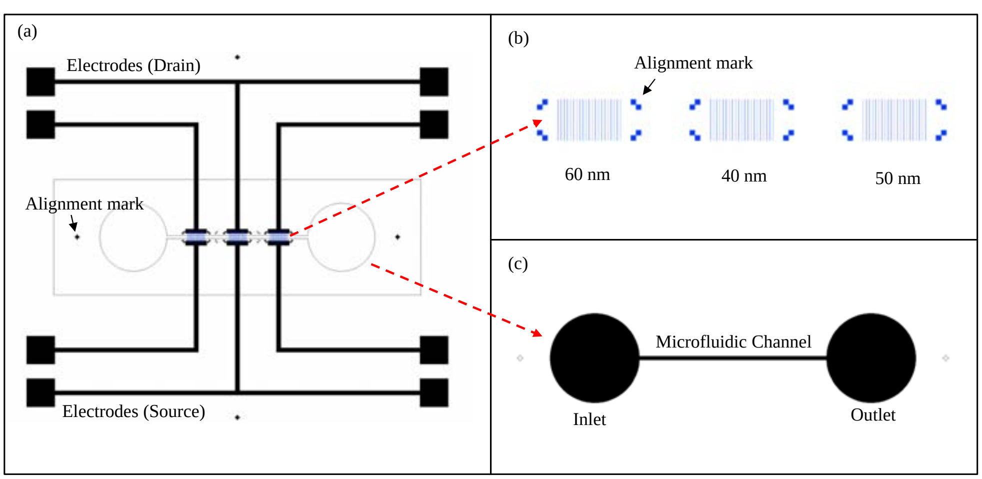

Fig. (1). (**a**) The overall mask design for silicon nanowires array sensor which has the drain and source electrode pad, (**b**) close-up view of nanowires array in various scale sizes and (**c**) 100 μm microfluidic channel mask design.

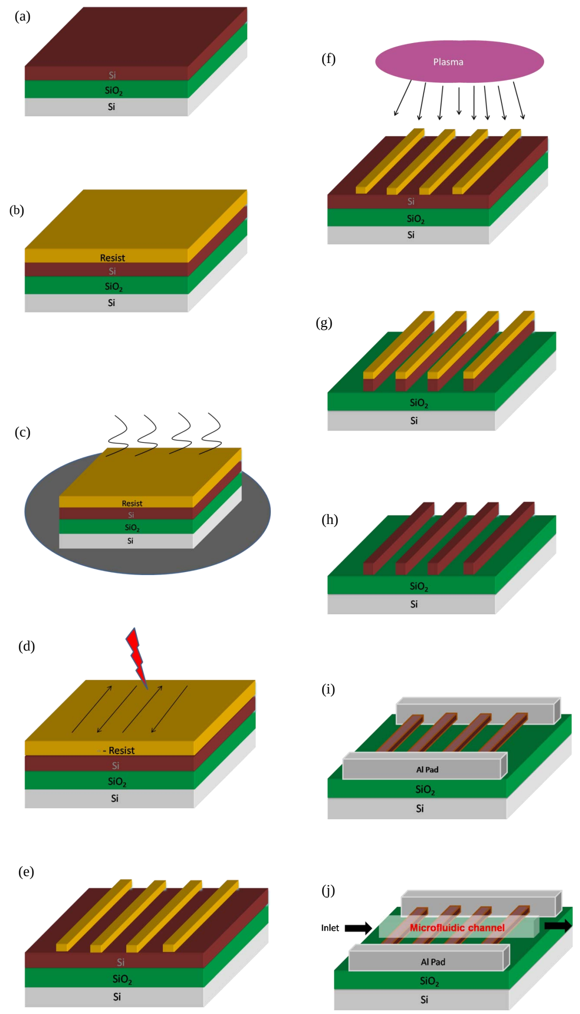

Fig. (2). Schematic diagram for the top-down nanofabrication process steps of silicon nanowires array sensor with integrated microfluidic channel.

istic of the fabricated silicon nanowires array was measured using KEITHLEY 6487 picoammeter/voltage. Electrical measurements were performed using direct current (DC) to quantify the electrical contact behavior and resistances with a two terminal, drain (D) and source (S) Al electrodes.

RESULTS AND DISCUSSION

Morphology and Geometrical Characterizations

A typical SEM image of silicon nanowires array is shown in Fig. (**3a**). The dimension of the silicon nanowires array is 40 nm width. The image shows that width is formed with normal developed, good uniformity, best resolution and good pattern placement. Fig. (**3b**) shows the close-up view of silicon nanowires. Besides normal developed, there was several resist profile problems involved during exposure and development process due to uncontrolled parameters plus the defects that may occur during all previous process. Three types of resist profile problems are under-development, incomplete development and over-development as pointed out by Nuzaihan M.N.M., *et al.* [16]. These resist profile problems can negatively affect the subsequent etch process. Over-development caused the features to appear narrower and poorly-defined. There are two possible outcomes for the developed sample that fails develop inspection: scrap or rework. Sample rework was done by stripping the resist off the sample surface, then setting the sample back into the sample preparation. One of the geometric characterizations of the silicon nanowires was carried out using the AFM. This is an instrument that can be used to map and measure surface features. Fig. (**4a**) shows that the width of silicon nanowires is 40 nm and the height is approximately 30 nm. Based on the results, the top width of the silicon nanowires is smaller than its based width as shown in Fig. (**4b**). The possibility is due to the limitation of the AFM physical probe which is not ideally sharp. As a consequence, the AFM image does not reflect the true sample topography, but represents the interaction of the nanowire and probe [17].

Electrical Characterizations

I-V characteristics of the silicon nanowire show the behavior of simple linear ohmic resistors with a conductance level in the range of a few tens to a few hundreds of nS [18]. For this experiment, silicon nanowires arrays with different width of 40 nm, 50 nm and 60 nm were characterized in air at room temperature as shown in Fig. (**5a**). Fig. (**5b**) shows the average resistance values of silicon nanowires with 40 nm, 50 nm and 60 nm were 6.3 GΩ, 5.2 GΩ and 4.6 GΩ, respectively. It is shown that, the resistance of the wire is inversely proportional to its width. As the wire gets smaller

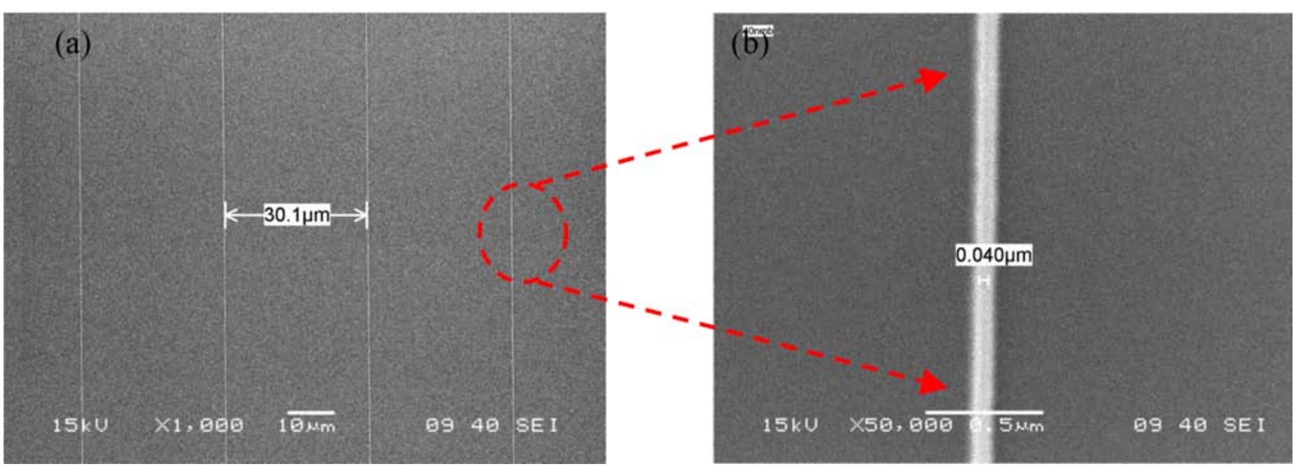

Fig. (3). SEM images (**a**) of silicon nanowires array and (**b**) the close-up view of 40 nm silicon nanowire.

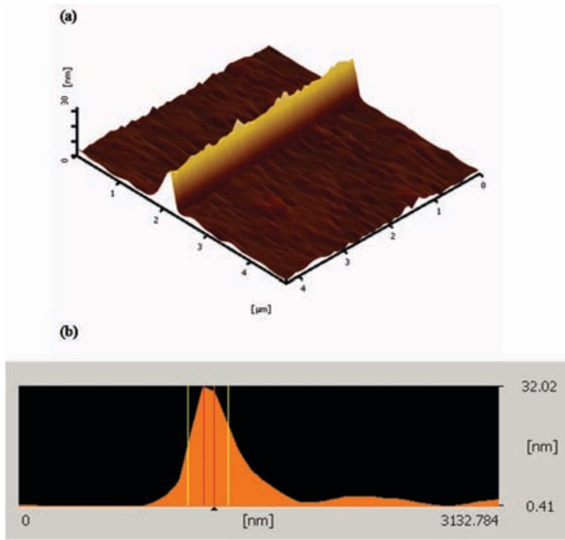

Fig. (4). AFM topography (**a**) of silicon nanowire and (**b**) the dimension of 40 nm width with the height of approximately 30 nm silicon nanowire.

(a) (b)

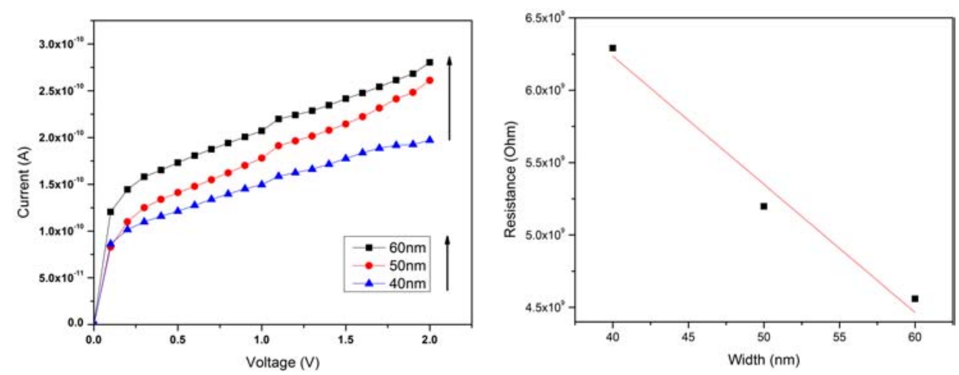

Fig. (5). (**a**) Electrical property of silicon nanowires array. I_{ds}-V_{ds} curve shows p-type behavior for 40, 50, 60 nm. The arrow highlights the direction from small to high width of silicon nanowires. (**b**) The average resistance values of silicon nanowires array dependent on the width of wire.

in size, the electrical resistance becomes higher due to the increased surface-area-to-volume ration [19]. The electrical conductivity for 40 nm, 50 nm and 60 nm was 2.4 pS, 2.8 pS and 3.4 pS, respectively. It is shown that, the smallest wire has much smaller conductance than bigger wire due to the large surface effects of smaller wire [19]. The electrical characterization confirmed that the proposed fabrication process produced high quality and performance silicon nanowires array with great potential for further developments.

Electrical Responses of pH Level on Silicon Nanowires Array Sensor

The I_{ds}-V_{ds} characteristic of 40 nm silicon nanowire array at different pH buffer solution (pH = 4, 7, 10, 12) are shown in Fig. (**6**). The characteristic shows increasing trend with the current/voltage and increasing trend with pH values. These trends are in agreement with the previous findings reported by Yi Cui *et al*. [20]. The resistance showed (Fig. **7**) the highest value (R = 718 MΩ) for pH 4 and the lowest value (R = 280 MΩ) for pH 12. At low pH (pH<7), amino (NH_2) group is protonated to NH_3^+ [20], resulting in high proton ion (H^+) charges on the silicon surface according to the reaction $NH_2 + H^+ \Leftrightarrow NH_3^+$ and acts as a positive gate [20], which depletes hole carriers in the p-type silicon

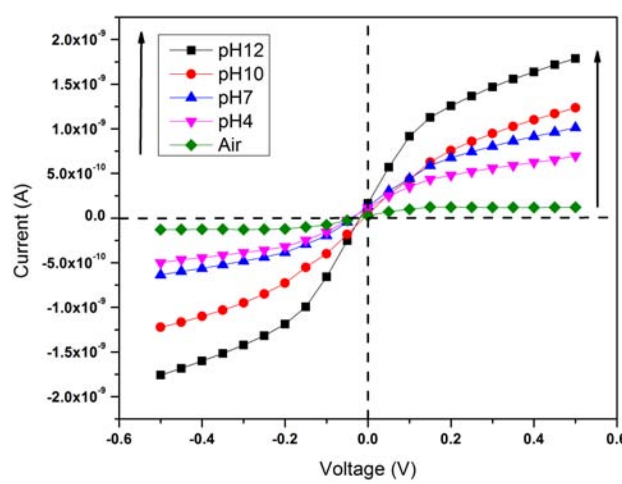

Fig. (6). Source-drain current (I_{ds}) versus source-drain voltage (V_{ds}) plots at different pH level for a typical p-type silicon nanowires array.

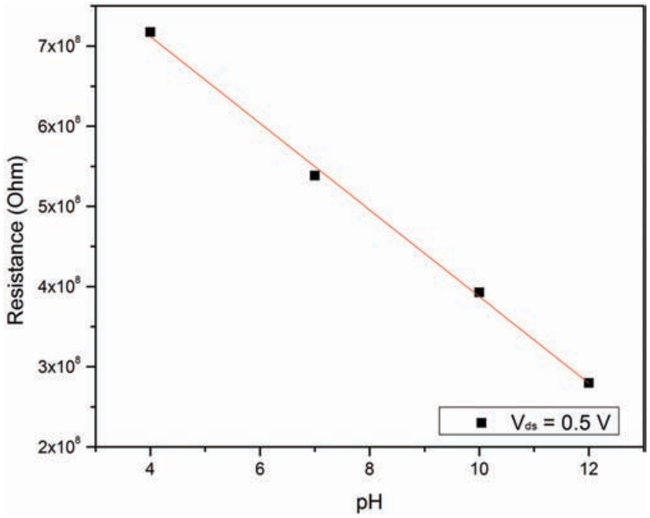

Fig. (7). The silicon nanowires array sensor shows the highest resistance value at low pH and the lowest resistance value at high pH.

nanowires and decreases the conductance (Fig. **8**). At high pH (pH>7), conductance is increased (Fig. **8**) due to silanol (SiOH) group is deprotonated to SiO^-, resulting in bringing negative charges at the silicon nanowire surface according to the reaction $SiOH \Leftrightarrow SiO^- + H^+$ and acts as a negative gate voltage [20]. The result shows that the silicon nanowires array works well as chemical sensor based upon the concentration of surface charge around the silicon nanowires. The pH sensitivity of the silicon nanowires array was determined by measuring a change in the conductance of the silicon nanowires array according to the pH buffer solution. Thus the sensitivity of the sensor can be expressed by the following equation:

$$\text{Sensitivity} = \Delta \text{ Conductance (S)} / \Delta \text{ pH} \tag{1}$$

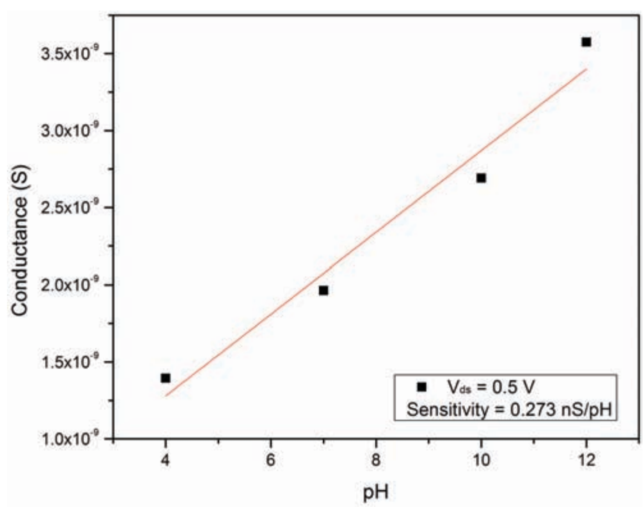

Fig. (8). Change of electrical conductance by different solution pH level. The sensor shows a linear relationship between pH level and electrical conductance of the silicon nanowires array with an approximate sensitivity of 0.273 nS/pH.

The pH sensitivity was calculated from the curve plotted in Fig. (**8**). The sensor shows a linear relationship between electrical conductance and pH level of the silicon nanowires with an approximate sensitivity of 0.273 nS/pH. These results are comparative and good agreement with the study reported by Yi Cui *et al.* [20], Park, I *et al.* [19], Lehoucq *et al.* [21] and Chen *et al.* [22], which show that the silicon nanowires exhibited a satisfactory linear response with pH. The pH sensitivity achieved by them were 100 nS/pH, 79.4 ns/pH, 5 nS/pH and 5 nS/pH, respectively. This proves that our device achieved much better and higher sensitivity in pH level detection. We have verified that our silicon nanowires array sensor works as a chemical and we believe such platform can be generalized for the detection pH with the proper small variations range of 0.1 pH unit, which is currently under investigation.

CONCLUSION

The Top-Down Nanofabrication (TDN) is utilized in the development of silicon nanowires array with integrated microfluidic channel and then tested as chemical sensors. This SEM based EBL produced the smallest and repeatable silicon nanowires array structure of 40 nm. In terms of sensing functionality, the silicon nanowires array has demonstrated the potential sensing in the pH level detection. The 40 nm silicon nanowires array sensor exhibited a linear pH response with a sensing sensitivity of 0.273 nS/pH.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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