

Polysilicon Nanowire with Liquid Gate Control for pH Sensing

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ABSTRACT

Polysilicon nanowire based sensors have garnered great potential in serving as highly sensitive, label-free and real-time sensing for broad range of applications, that include but not limited to pH values, DNA molecules, proteins and single viruses. In this research, two distinct types of polysilicon nanowires are fabricated, one has an array of nanowires with a 100 nm width and the other is a single nanowire with 100 nm width. Top-down fabrication method is utilized to fabricate the polysilicon nanowire from silicon wafer using the conventional photolithography and reactive ion etching processes. The fabricated polysilicon nanowire have an approximately 100 nm in width, is then undergo surface modification, which is the nanowire is immersed into a 2% 3-aminopropyltriethoxysilane (APTES) to create a molecular binding chemistry, which results in amino (NH₂) and silanol (SiOH) groups at the nanowire surface. Since the surface of the polysilicon is hole-dominated (p-type material), it responds well to changes in pH values. In this research, pH sensing is performed based on several types of standard aqueous pH buffer solutions (pH 2, pH 4, pH 7, pH 10 and pH 12) to demonstrate the electrical response of the sensor. At low pH, NH₂ group is protonated, resulting in high proton ion acts as a positive gate. At high pH, SiOH group is deprotonated, resulting in bringing negative charges at the polysilicon nanowire surface and acts as a negative gate voltage. The sensitivity of the polysilicon nanowire attained was 207.1 fS/pH for array nanowire and 8.91 fS/pH for single nanowire, which shows excellent properties for pH sensing.

Keywords: Polysilicon Nanowire, Ph Sensing, Liquid Gate Control, Nanolithography.

1. INTRODUCTION

Power of hydrogen (pH) is a numeric scale to specify the acidity and basicity of an aqueous solution. Solutions with a pH less than 7 are acidic, meanwhile solutions with a pH greater than 7 are alkaline. PH measurements are important in agronomy, medicine, biology, chemistry, agriculture, food science, environmental science, cosmetic, chemical engineering, nutrition, and water purification. The pH scale is measured between 0 to 14 where 0 is the most acidic and 14 is the most alkaline. The concept of pH was first introduced by the Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory in 1909 [1] and was revised to the modern pH in 1924 to be used as a definition and measurement for electrochemical cells. The exact meaning of the "p" in "pH" is disputed, but according to the Carlsberg Foundation, pH stands for "power of hydrogen". The most accurate pH-measuring tool has been developed such as colorimeter or spectrophotometer and electronic pH meter which uses glass electrode. There are many methods that are used to measure the pH level such as optical methods and electronic methods [2-4]. The optical method uses colorimeter or spectrophotometer, which involves an absorbent universal indicator paper consists of various mixture. This mixture consists of specific organic

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material that changes color when in different pH level. The applications field for optical measurements of pH measurements, whether visual or photometric is very limited. If the solution to be measured is cloudy or has an inherent color, the measurements will be unreliable. Some measurement solutions also contain chemical bonds, which destroy the color indicators through oxidation or reduction and produce incorrect results. Meanwhile, electronic method are using pH meter, which uses the electrical potential of pH-sensitive electrodes as a measurement signal [5]. The pH meter gave much more accurate number of pH level. The downside of the pH meter is that it's not very cost effective and the probe needed to be clean regularly to avoid any contamination that can interfere with the result. Most probes also have a glass probe with is easily damage if exposed to high corrosive chemicals [6]. To the best of our knowledge, the development of polysilicon nanowire for the pH sensing has not been comprehensively studied. Because of the potentials and important applications of the pH sensor to monitor the number of free hydrogen ions (H^+) in a substance, we report herein a polysilicon nanowire with liquid gate control for pH sensing. Our polysilicon nanowire worked, as a sensing element of the device is sandwiched between the drain (D) and the source (S) electrodes. The fabricated polysilicon nanowire is then surface modified and characterized for electrical performance. In addition, the pH sensitivities of polysilicon nanowire array and single nanowire are demonstrated.

2. EXPERIMENTAL

2.1 Top-Down Fabrication Method

In this research, a top-down fabrication method was used to develop the polysilicon nanowire pH sensor. All the processes were carried out starting from the silicon wafer until the pH sensor device. The key process steps required to fabricate polysilicon nanowire are sample preparation, nanowires design, conventional photolithography and anisotropic etching process and then followed by morphological inspection to determine the quality of the polysilicon nanowire, specifically the uniformity, diameter and shape. The top-down fabrication method of polysilicon nanowire is briefly illustrated in Figure 1.

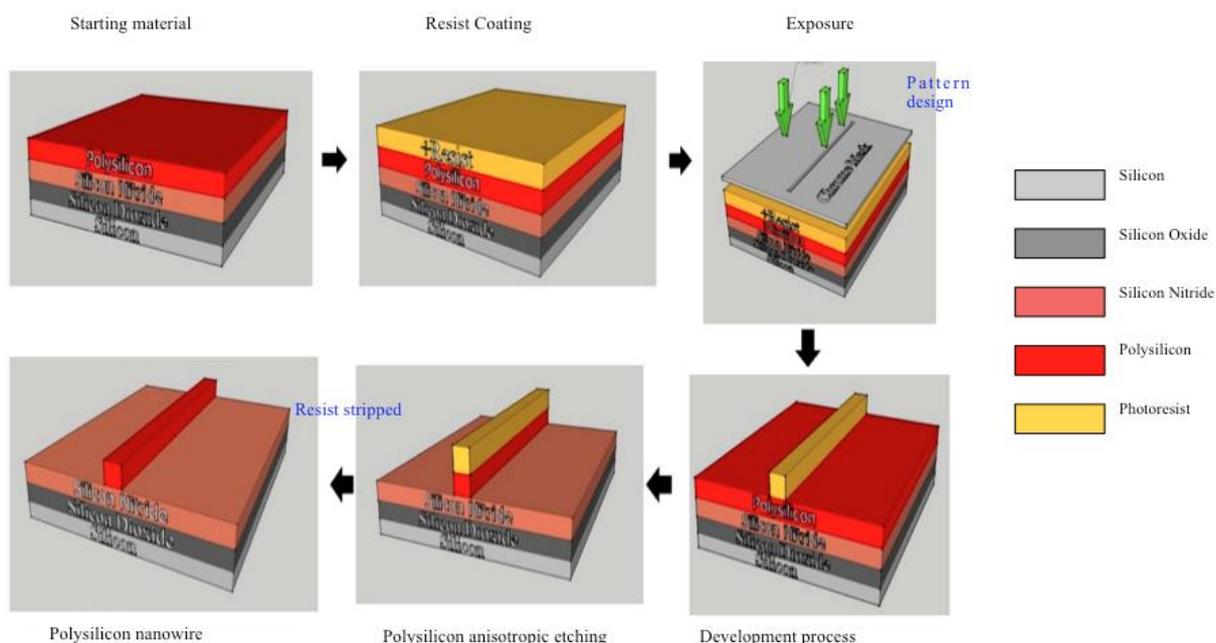


Figure 1. Top-down fabrication method of the polysilicon nanowire.

The sample preparation starts with the cleaning of wafer (Si-SiO₂-Si₃N₄-Polysilicon layers) using standard RCA 1 solutions to eliminate contaminants and followed by soaking in diluted hydrogen fluoride (HF) to eliminate native oxide [4]. Then the wafer (Si-SiO₂-Si₃N₄-Polysilicon layers) was cut into small pieces measuring 2cm by 2cm (sample). The sample is then coated with positive resist using a spin coater at 5500 rpm for 20 seconds. Now, the sample is ready for conventional photolithography steps to fabricate the polysilicon nanowire. The 300 nm thick layer of positive resist is subsequently coated on the polysilicon layer, then soft bake for 90 seconds at 90°C to drive off the solvent and solidify the film by using a hotplate. The coated sample was exposed to UV light through a chrome mask (we previously reported the pattern/mask of the nanowire elsewhere [3,7]) for 10 seconds and then, the exposed sample was developed using RD6 resist developer for 35 seconds depend on the pattern design. After development process, the sample was inspected using optical microscopy for control resist profile problems. Next, the sample is ready to anisotropic etching of polysilicon for 7 seconds and followed by resist stripping process. Finally, the polysilicon nanowire was obtained on the Si₃N₄ layer. The feature sizes and etch profile of the polysilicon nanowire was determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). It should be noted that the polysilicon nanowire was formed in this step in a good anisotropic profile [3].

2.2 Metal Contact Pads Development

The aluminum (Al) contact pads were developed using lift- off method [3,8] to allow electrical measurements on fabricated polysilicon nanowire. The larger Al contact pads for the D and S were connected to each end of the fabricated polysilicon nanowire. First, a negative resist was spin coated on the fabricated polysilicon nanowires at 3000 rpm for 25 seconds and then followed by pattern transfer using conventional lithography through a chrome pad mask. Next, Al was deposited onto the sample patterned using a thermal evaporator and finally the negative resist was stripped and the wafer rinsed using acetone/isopropanol (IPA). Figure 2(a) and 2(b) illustrate the polysilicon nanowire with Al contact pads for further connection to the outer circuits.

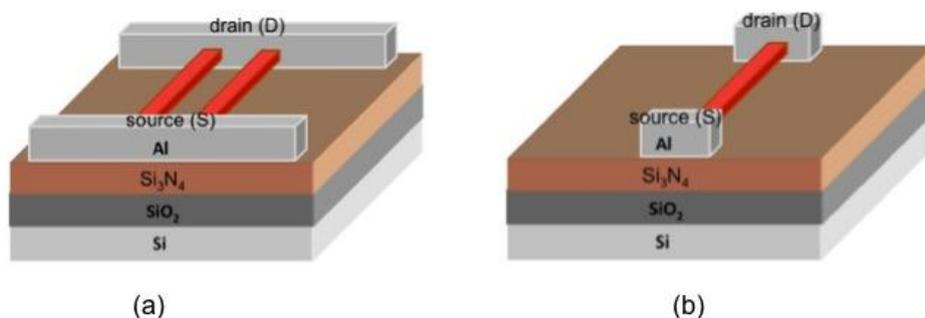


Figure 2. Polysilicon nanowire (a) array and (b) single wire with Al contacts at S and D.

2.3 Surface Modification

The surface modification began by cleaning the surface of nanowire using DI water and IPA. Next, to obtain surface-exposed amine groups on the surface of the nanowires, the polysilicon nanowire (array and single) was dipped in 2% 3-aminopropyltriethoxysilane (APTES (v/v)) in a mixture of 95% ethanol and 5% water for 2 hours at room temperature and then followed by cleaning process using ethanol for 3 times to remove any unreacted APTES and dried at 120°C for 10 minutes on a hot plate. Figure 3 illustrates the surface modification by APTES for polysilicon nanowire array.

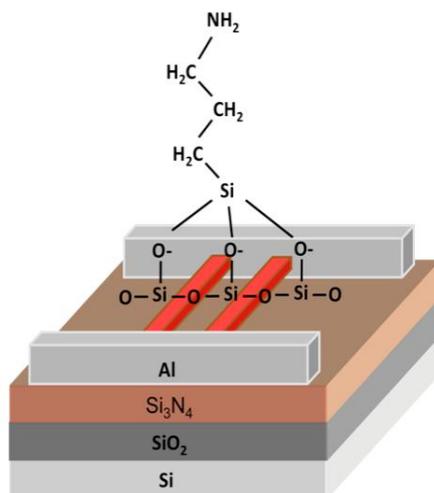


Figure 3: Surface modification by 3-aminopropyltriethoxysilane.

2.4 Electrical Measurements

The electrical measurement was conducted after the modification was done on the surface of polysilicon nanowire using KEITHLEY 6487 picoammeter/voltage source. During the pH measurement process, different pH buffer solutions (pH 2, pH 4, pH 7, pH 10 and pH 12) were dropped carefully using a micropipette onto the modified polysilicon nanowire and then the electrical measurements were performed using direct current (DC), voltage swept from 0 V to 1 V to quantify the electrical contact behavior and resistances with the two terminal, drain (D) and source (S) of the Al electrodes. After each value of the pH solutions was tested, the sample was cleaned with DI water and filter paper. The blower was used to dry the sample and to make sure that there was no dust on the sample. Sample was kept stationary with the probe needle location to avoid inaccurate results. Furthermore, sample was tested without any vibration or noisy environment to avoid poor results. All the measurements were carried out at ambient temperature.

3. RESULTS AND DISCUSSION

3.1 Morphology Characterization of the Polysilicon Nanowire

The morphology of the polysilicon nanowire was investigated using SEM and AFM, as they provide direct visualization of the quality of the nanowire (their shape, size and uniformity). The images were shown in Figure 4(a) and 4(b), respectively. The width of the polysilicon nanowire is approximately 100 nm. The images show that width is formed with normal development profile with desirable resolution, good pattern placement and good uniformity. For further information on morphology of the polysilicon nanowire, we previously reported the top-down nanofabrication method of the polysilicon nanowire elsewhere [7-8].

3.2 Electrical Characterization of Polysilicon Nanowire

The quality of the polysilicon nanowire was characterized electrically by measuring the current-voltage (I-V) characteristic between the S and D electrodes before investigating with different pH buffer solutions. The I_{ds} - V_{ds} characterization of polysilicon nanowire (dry and with an APTES surface modified) for array and single were plotted as shown in Figure 5(a) and 5(b), respectively. Both sensors exhibited an ohmic behavior (a linear relation between the current and voltage). This characteristic is in agreement with the previous research reported by the

researchers [3, 9-11]. After the surface modification using the APTES, the I_{ds} measured (at $V_{ds} = 1$ V) for polysilicon nanowire array and single nanowire were 700 pA and 85 pA, respectively. It was observed that the increase of nanowire numbers raises the amount of I_{ds} . As shown in both graphs, the I_{ds} after an APTES surface modified was much higher than the I_{ds} measured before the modification was made (dry). This finding is in agreement with the previous research reported by the Vo *et al.*, [12]. After modified the nanowire surface with APTES, a change in the current could be found for all the sensors. It was suggesting that, chemical passivation of the nanowire surfaces using different chemical functional groups can alter the band gap of nanowire [12]. The surface termination by amino (NH_2) reduced the band gap of the nanowire, thus allow for electrical conductivity. This electrical characterization confirmed that the fabricated polysilicon nanowire has excellent properties and great potential for further developments.

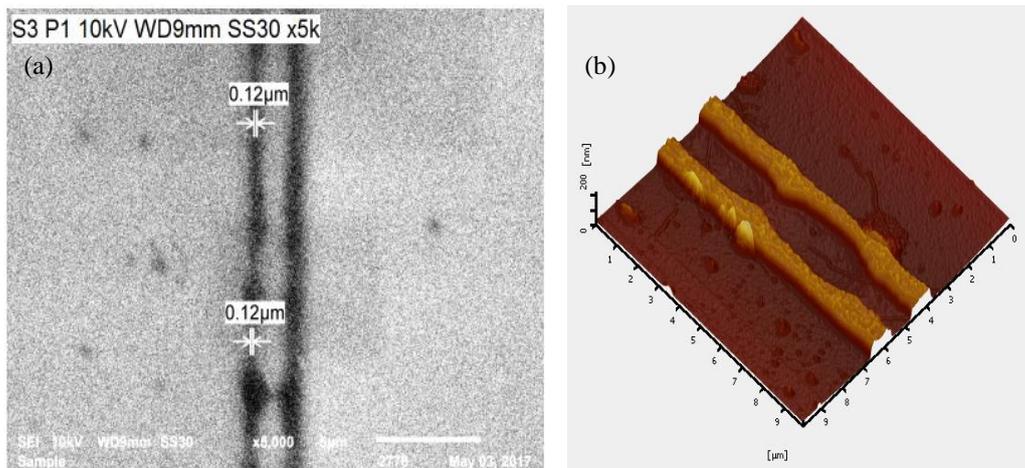


Figure 4. Polysilicon nanowire: (a) SEM image and (b) AFM topography.

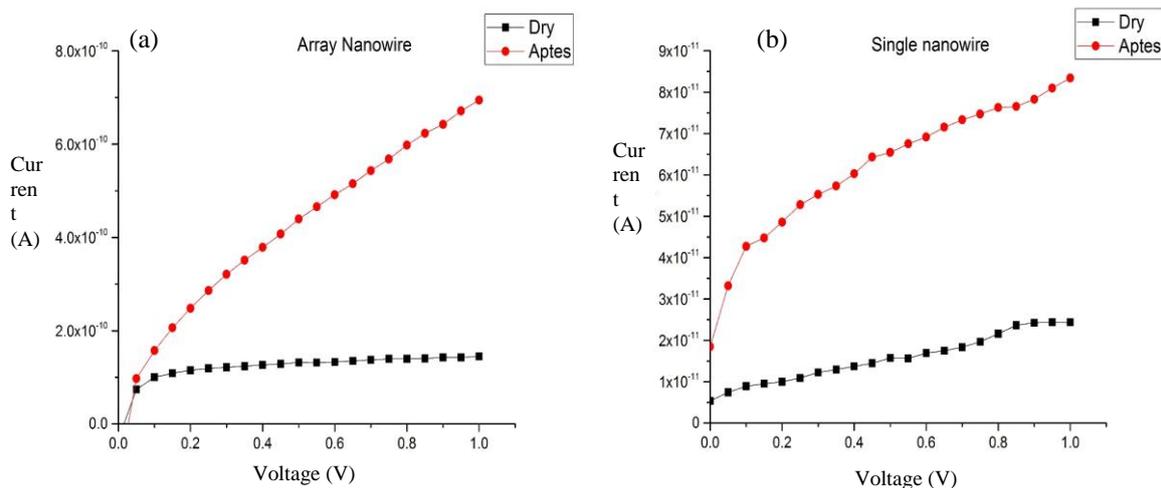


Figure 5. I_{ds} - V_{ds} characterization of polysilicon nanowire: (a) array and (b) single nanowire.

3.3 Analytical Performance of PH Sensing on Polysilicon Nanowire

To detect different pH levels, the polysilicon nanowire surface was modified with the APTES and then dropped with pH buffer solution onto the surface. These detection steps are called liquid gate control. A drain-source voltage, (V_{ds}) applied to the polysilicon nanowire will allow I_{ds} to

flow from the D to the S. The density of charge carriers in the nanowire is then modulated by the liquid gate, which in turn affects the current of the polysilicon nanowire. In addition, the APTES that are covalently linking on the polysilicon surface results in deprotonation and protonation of the silanol and amino groups [13], as shown in Figure 6.

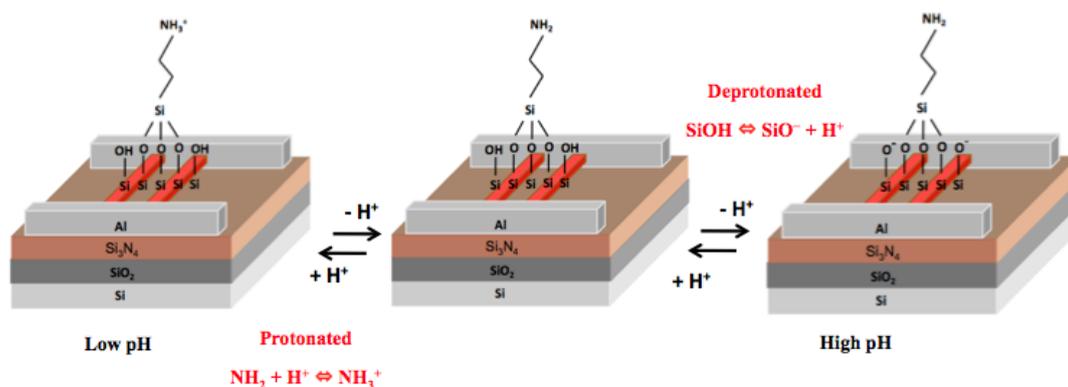


Figure 6. APTES modified polysilicon nanowire surface for pH level detection.

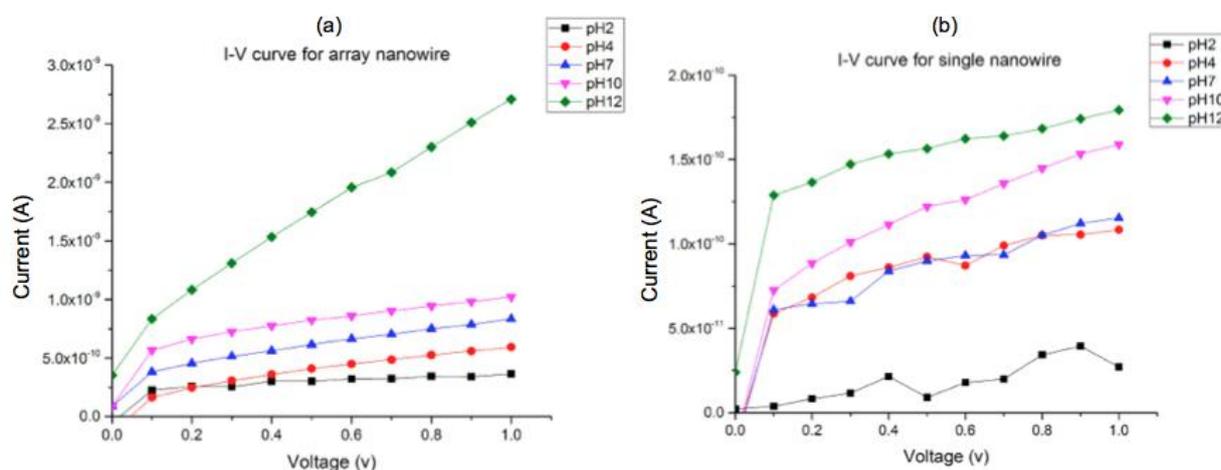


Figure 7. The I_{ds} - V_{ds} characteristic of polysilicon nanowire at different pH buffer solution (pH = 2,4,7,10,12): (a) array and (b) single nanowire.

Figure 7(a) and 7(b) show the I_{ds} - V_{ds} characteristic of polysilicon nanowire at different pH buffer solution (pH = 2, 4, 7, 10, 12) for nanowire array and single nanowire, respectively. For acidic solution (pH < 7), amino (NH_2) group is protonated to NH_3^+ , resulting in high proton ion (H^+) charges on the surface, which depletes hole carriers in the polysilicon [14]. Meanwhile for alkaline solution, silanol ($SiOH$) group is deprotonated, resulting in an increase of negative charges at the nanowire surface [14]. We also explored the pH sensitivity of the polysilicon nanowire for array and single by measuring a change in the conductance of the polysilicon nanowire according to the different pH buffer solution as shown in Figure 8(a) and 8(b), respectively.

It was observed that in both graphs, the sensitivity of the polysilicon nanowire attained was 207.1 fS/pH for array nanowire and 8.91 fS/pH for single nanowire, which show excellent properties for pH sensing. The results demonstrate that pH sensitivity increases with increasing number of nanowires (array as compared to a single nanowire). In addition to sensitivity, when the modified polysilicon nanowire was investigated in solutions with pH 2 to pH 12, it exhibited stepwise increases in conductance. This trend is in excellent agreement with the previous research reported by the Adam *et al* [15].

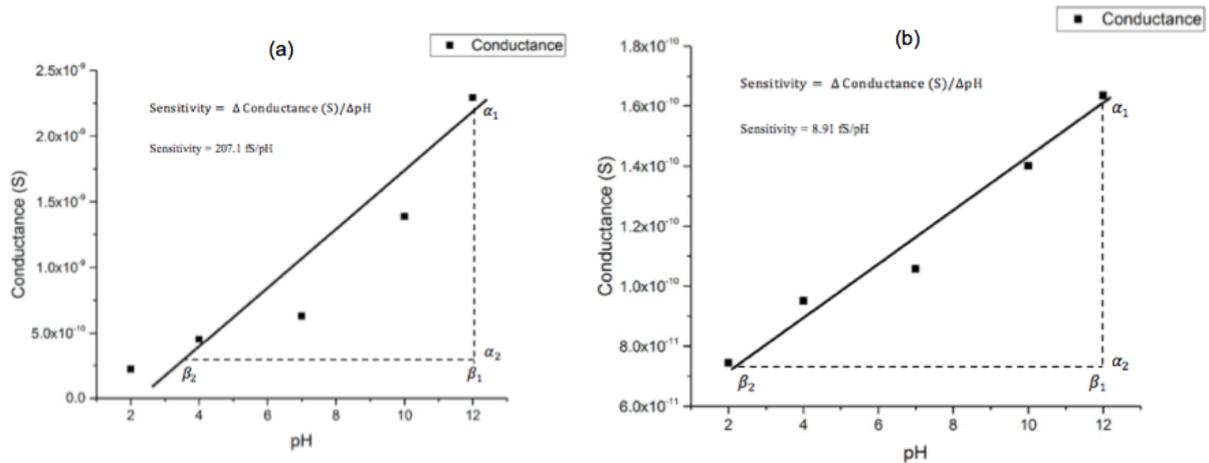


Figure 8: pH sensitivity of the polysilicon nanowire: (a) array and (b) single nanowire.

4. CONCLUSION

This research has demonstrated the polysilicon nanowire array and single nanowire with liquid gate control for pH sensing. With different pH values, the polysilicon nanowire is effortlessly protonated and deprotonated in the testing solutions. The 100 nm polysilicon nanowire exhibited a linear pH response with a sensitivity of 207.1 fS/pH for array nanowire and 8.91 fS/pH for single nanowire. It is noticed that increasing sensitivity is observed for higher numbers of nanowires. Our finding shows that sensors are able to detect the number of free hydrogen ions (H^+) in a substance and have the ability to work as a sensitive pH sensor. Thus, we expect this pH sensor to be beneficial for food, environment and medical applications.

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