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Design, Fabrication and Testing of CNT Based ISFET for NANO pH Sensor Application: A Preliminary Study

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***Abstract*—In recent years, there has been increasing interest in monitoring and controlling of pH. It has become an important aspect of many industrial wastewater treatment processes. At the same time, the demand for smaller electronic devices used for various industrial and commercial applications has greatly increased. Micro and nano materials, such as Carbon Nanotubes (CNTs), are known for their excellent electrical and mechanical properties, as well as for their small size, therefore they are good candidates to manufacture micro or nano electronic devices. These devices can be used for pH control. However, this cannot be achieved unless CNTs with metallic or semiconducting band structures can be successfully deposited and separated. In these processes, microchip fabrication and deposition of CNTs using Dielectrophoresis (DEP) are involved. Comparing with some traditional pH sensors, which mainly consist of Ion-Sensitive Field Effect Transistor (ISFET), signal operational amplifier and Analog Digital Convert (ADC), Nano pH sensor with CNTs may provide more benefits owing to their unique properties. For example, 70-80% of multi-walled CNTs (MWCNTs) are metallic and have high current density, which means this kind of micro device has a linear relationship of I-V characteristic and can produce signal strong enough to make operational amplifying circuits unnecessary. In addition, to manufacture smaller devices more functional becomes possible as CNTs are tiny and compact.**

I. Introduction

CARBON Nanotubes (CNTs) closely resemble hollow graphite fibers that exist in entangled bundles of tens to hundreds. These come in two different forms: multi walled carbon nanotubes (MWCNT) and single walled carbon nanotubes (SWCNT). SWCNTs and MWCNTs range in diameter from 1-10 nm and 10-50 nm respectively. About 70-80% of SWCNT tend to contain semiconducting properties, whereas 70-80% of MWCNT tend to contain metallic properties [1]. CNTs have also been known to contain remarkable electrical, mechanical, and thermal properties [2]. Metallic CNTs can be used as connecting wires for Micro-Electro-Mechanical Systems (MEMS) and Nano-Electro-Mechanical Systems (NEMS) because of their size and low resistance, while semi-conducting CNTs can be used for nano transistors [3]. In order to determine the band structure, dielectrophoresis (DEP) is applied.

DEP is a process through which neutral particles, such as CNTs, can be translated through a suspending medium in a non-uniform electric field which is generated between a pair of electrodes. DEP is used to separate, trap, and sort cells, bacteria and so on. DEP technique for aligning CNTs has been used in [1-2, 4-5]. Although there are many other techniques that may achieve the same results, DEP is the preferred method. The theory and methodology have been well documented and the method is widely used for the manipulation of particles on the micro and nano scale. However, DEP can only be applied to carry out alignment of CNTs bundle. Atomic Force Microscopy (AFM) will be necessary if people are dealing with single CNT alignment.

So far, biomedical engineers have exploited primarily the possibilities of the chip technology to develop silicon-based sensors, which has been incorporated in the tip of a catheter since 1970. This technology should provide the clinicians with cheap sensors on electronic micro chips, which would become continuously cheaper and cheaper, even with improved characteristics. Moreover the reproducibility of sensor characteristics should be highly improved compared to the usually piecewise-assembled sensors existing up to that time, due to the replication procedure on which the silicon technology relies. Therefore, many of the first papers on silicon sensors appeared in biomedical engineering literature, for example with respect to the development of ion sensors. Ion-Selective Field-Effect Transistor (ISFET) pH sensor [6] is one of the most well-known examples. Furthermore, with more and more study on CNTs, we believe CNTs with metallic properties may have a huge potential to produce more compact devices for pH measurement applications based on ISEFT. In this paper, CNT deposition and alignment is introduced through DEP to verify if they are metallic or semi-conducting by I-V characteristic analysis. If the characteristic is linear, the CNTs can be regarded as metallic, whereas, if it is non-linear, they are semi-conducting. So far, CNT based ISFET for pH control application has not yet been explored. If this is made possible, it will be a significant contribution for applications in various

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areas, including medicine, biology and industry.

II. CNT BASED ISFET

A. Introduction to MOSFET

An ISFET is generally used to measure ion concentrations in solutions; when the ion concentration, such as pH, changes, the current through the transistor will change accordingly. Here, the solution is used as the gate electrode. A voltage between substrate and oxide surfaces arises due to an ions sheath. Actually, an ISFET's source and drain are constructed similarly as a Metal-oxide Semiconductor Field-Effect Transistor (MOSFET) [7]. The basic structure of a MOSFET is formed by adding two heavily doped n^+ regions to the MOS capacitor on p-type Si as shown in Fig.1. When the gate voltage V_G exceeds its threshold voltage, then an inversion layer is formed at the SiO_2/Si interface. The n^+-source region can supply electrons to the inversion region without depending on the thermal generation rate as required for the MOS capacitor. An n^+-drain region should be added so that electrons can flow from source to the drain through the inversion layer when a positive drain voltage V_D is applied. This electron flow constitutes the drain current I_D. Current into the drain is taken as a positive current and the positive gate voltage controls the number of electrons in the inversion layer and hence controls the drain current.

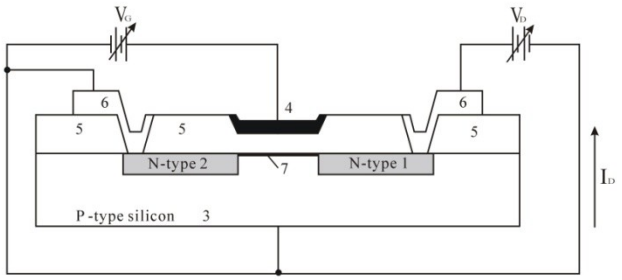


Fig.1. Schematic diagram of an MOSFET: 1 drain; 2 source; 3 substrate; 4 gate; 5 insulator; 6 metal contacts; 7 inversion layer.

B. CNT Based ISFET

Although an ISFET is very similar to a MOSFET, there are still some differences. As shown in Fig.2, the metal gate is replaced by the metal of a reference electrode, whilst the target liquid in which this electrode is present makes contact with the bare gate insulator. Both of them have the same equivalent circuit. Then, devices with this structure can be applied to pH measurement [6]. However, the objective of this paper is to enhance the inversion layer with CNTs as NANO wire to conduct electrons between the drain and source, the drain current might be much greater under the same gate voltage. Fig.3 illustrates the potential application of both SWCNTS and MCNTs in an ISFET structure pH measurement device. If this is verified, then we can make these devices compact and cheap earning to CNT's unique mechanical and electronic properties, such as high current carrying capabilities. As it is known, most of MWCNTs possess metallic conductive properties, which means they can provide us with a linear I-V curve when these CNTs are used as nano-wires. In the rest of this paper, a means of testing conductivity property is introduced.

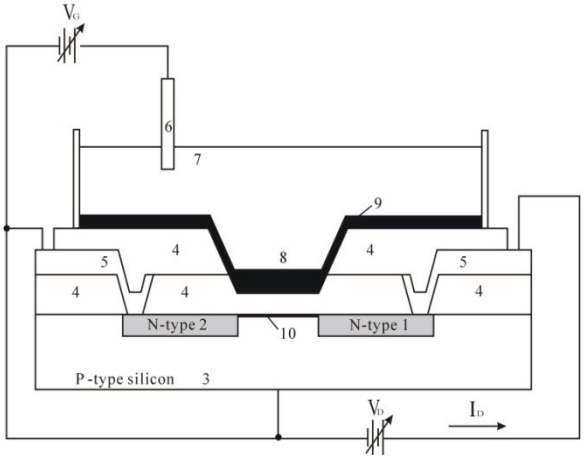


Fig.2. Schematic diagram of a composite gate, dual dielectric ISFET: 1 drain; 2 source; 3 substrate; 4 insulator; 5 metal contacts; 6 reference electrode; 7 solution; 8 electroactive membrane; 9 encapsulant; 10 inversion layer.

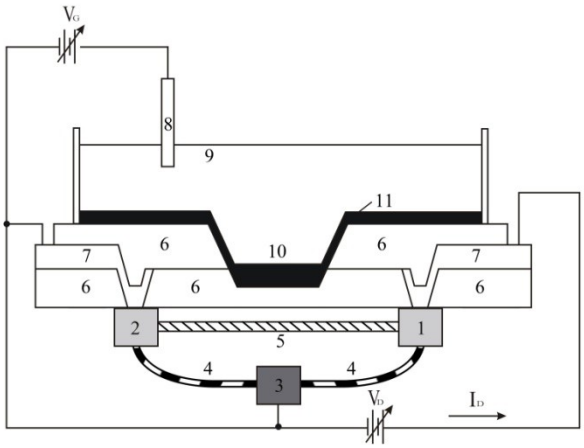


Fig.3. CNT based ISFET: 1 N-doped drain; 2 N-doped source; 3 P-type silicone substrate; 4 SWCNT as transistor; 5 MWCNT as nano-wire; 6 insulator; 7 metal contacts; 8 reference electrode; 9 solution; 10 electroactive membrane; 11 encapsulate

III. CHIP STRUCTURE AND WIRE BONDING

The micro chip is originally made up of four layers from bottom up: silicon wafer, 300Å of silicon dioxide, 200Å of chromium and 3000Å of gold. The fabrication flow is illustrated in Fig. 4 & 5, and after it is done, the electrodes on the chips are achieved as shown in Fig. 6 and ready to carry out CNT deposition and alignment.

For the electrode fabrication, a mask is first designed for the desired chips. Using AutoCAD, a template of the mask is

drawn. Triangular electrodes coming to an angle of 30 degrees with electrode gaps ranging from 2-30 microns are designed. 24 micro-chips are fitted on a circular diameter of 125 mm. The finished microchips consist of four layers (from bottom up): the 125 mm diameter silicon wafer, 300 Å of silicon dioxide, 200 Å of chromium, and 3000 Å of gold. To apply the different layers, the steps are as follows:

First, by thermal oxidation, the silicon dioxide layer, acting as an insulator, is first applied to the wafer. Referring to the Silicon Thermal Oxide thickness calculator [8], the time needed to stay in the furnace as well as the temperature of the furnace can be determined. The crystal orientation and the active dopant concentration of the wafer in addition to the type of furnace being used are needed to determine these parameters. A time of one hour and two minutes at 900 degrees in the dry furnace is applied to achieve the desired thickness of 300 Å of silicon dioxide. The next step is to apply the chrome and gold layers.

Both the chrome and gold layers can be completed through the evaporation. At the beginning, the chrome layer is set as an adhesion layer for the gold. The process is then repeated for the gold layer.

The photolithography process consists of four basic steps: application of the resist, exposure to the mask, development and inspection of the wafer. The chosen thickness of the resist is 2.5 microns and the material needed is AZ4110 at 1000rmp. The Eaton coater is used to apply the resist. After the resist is achieved, the wafer is soft heated on the hot plate at 110°C for 120 seconds and then put onto a cool plate at 45°C for 30 seconds. To expose the resist, the Suss is used where the wafer is placed on the aligner chuck with the mask aligned overhead. Exposure time is calculated as the ratio of energy to intensity. Energy is calculated by 35 multiplied by the resist thickness and the intensity is found recorded in the log book. The alignment gap is set at 65 microns. After the energy and alignment gap are entered into the system, the resist is exposed. At the development wet bench, the develop time is set at 90 seconds. Once developed, the cassette is dump rinsed and then put in SRD. A microscope is used for the inspection at the top, bottom, side to side, and center to make sure lines are sharp and no other deformations.

At the acid wet bench, the unwanted metal is etched away. The wafer is immersed in the first gold etch (GE8148), and then the chrome etch (CEP-200). The wafer remains in the gold until the unwanted gold has been removed. After the gold etch is finished and the wafer is rinsed, the wafer is placed in the CEP-200 to reach the oxidized layer.

At last, the resist is then removed by dousing it in the resist strip. A blanket exposure of three times the exposure time is completed and followed with the development process. The wafer is set in AZ300T at 90 degrees for 10 minutes. The microchips are then diced and wires can be soldered to the gold pads so that the AC power can be applied.

For wire bonding, since the traditional method of soldering can damage micro chips easily, conductive epoxy should be used to stick wires onto Au pads. In this experiment, the two parts of conductive epoxy are equally mixed together, and then we put a little of the mixture on the pads, finally the pads can be stuck to the wires. In order to make the epoxy firm enough to bond the wires, the chip is heated at 130ºC for about 1 hour on a heat plate as shown in Fig. 7.

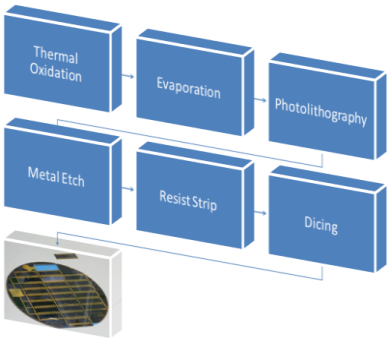


Fig.4. Flowchart of micro chip fabrication process.

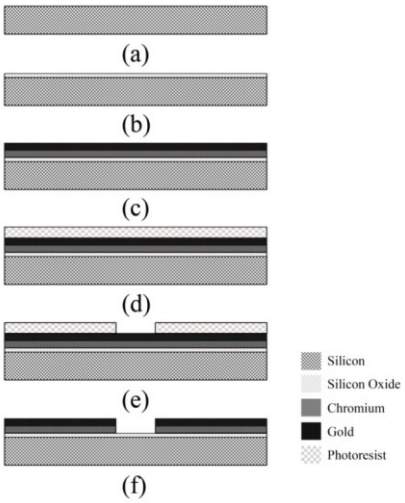


Fig.5. Fabrication process of micro electrode: (a) silicon substrate; (b) 300Å silicon-dioxide by thermal oxidation of silicon wafer; (c) both chromium and gold are deposited on the silicon dioxide surface by evaporation; (d) cover the surface by photoresist layer; (e) photoresist is patterned and exposed; (f) the micro electrodes are fabricated.

Fig.6. Top-view of one pair electrode from microscope.

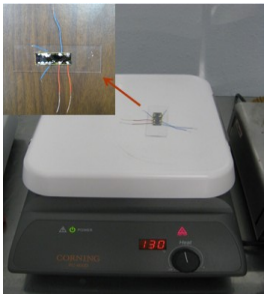


Fig.7. Heating plate for wire-bonding.

IV. CNT Solutions And DEP Forces

At the beginning, the stock solution is a mixture of 0.5mg MWCNTs, 3µl surfactant (Nanospere®) and 5ml DI water. The surfactant is helpful to accelerate the dissolution but it is not enough. A sonicate process is necessary to make CNTs suspend uniformly. The sonicator used here is shown in Fig. 8. Before sonicating, the tank should be filled with water and the cuvette of stock is fixed on the top while the cuvette body should be below the water level in the tank. Then after the sonicator has been working for about 7 minutes, the CNTs in the stock are suspended uniformly. Eventually, 5X, 10X and 50X solutions are obtained by diluting the stock by 5 times, 10 times and 50 times with CNT concentration of 0.02g/l, 0.01g/l and 0.002g/l respectively as shown in Fig. 9.

As it is known, AC power supply is necessary to generate DEP forces between two electrodes. Thus, here we use a function generator to provide a Sine power function with 1.5MHZ frequency and 30V P-P voltage. The function generator is shown in Fig. 10, and there is also an oscilloscope to monitor the power function generated. Then CNT deposition and alignment can be realized through DEP forces in the operational platform of a microscope. In Fig. 11, two cables from the function generator provide the electrodes with AC power through connecting to the wires bonded on the pads.

Fig.8. The sonicator.

Fig.9. CNT solutions after diluting.

Fig.10. Function generator and oscilloscope to generate DEP forces.

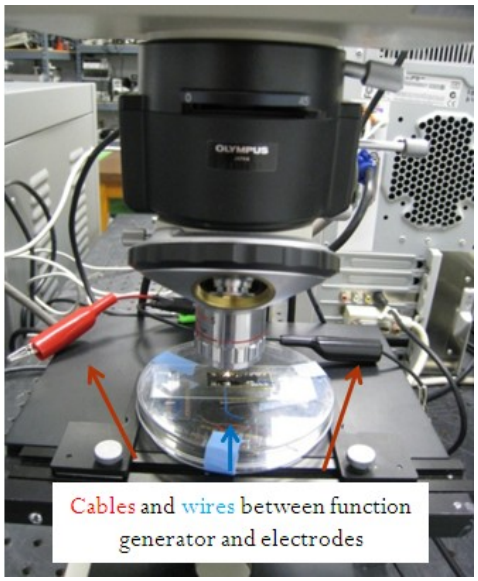
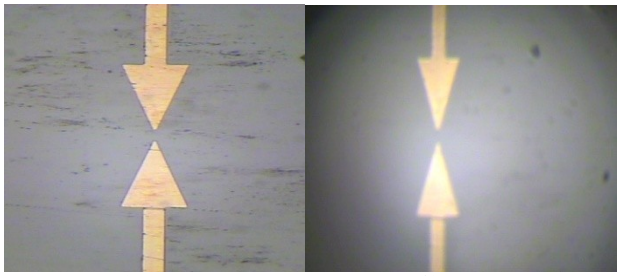


Fig.11. Operational platform in microscope.

V. Experimental Results

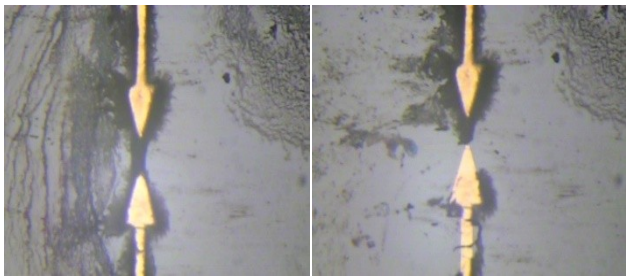
A. I-V Curve Measurement

For testing I-V characteristics, the gap distance is about 30 microns, and a pipette, whose sucking range is from 0.5 to 10µl, is used to deposit a 1.5µl CNT droplet from the 10X solution onto the gap. Fig. 12 illustrates the electrode before and after the droplet is deposited observed. Next, the function generator is turned on and DEP forces are formed between the electrodes. The equipment should be turned off immediately after the CNT "babble" disappears. Fig. 13 shows the result of CNT alignment: there is a nano wire consisting of MWCNTs connecting the two electrodes.



(a) (b)

Fig.12. Electrodes observed by the camera: (a) before deposition; (b) after deposition.



(a) (b)

Fig.13. (a) Electrodes after alignment is done; (b) cleaned by acetone.

In Fig.13 (b), the resistance of the nano wire is measured by a multimeter, 1.215kΩ. Fig. 14 describes the experimental setup of the I-V curve measurements. In this experiment, a DC power generator is used to supply DC potential from 0 to 10V with 1V increments and the corresponding current values are measured by a multimeter. Then these voltage and current values are recorded and the record is repeated until there are three groups of data available. As shown in Fig. 15, the current values in blue are not from any of the three groups but the averaged current values. The curve in red in the comparison is generated by linear curve fitting based on the eleven individual and discrete coordinates from the measurement. The red line is taken as the reference to tell if the I-V values represent a linear or non-linear characteristic. Through comparing, we can conclude that the MWCNTs have metallic properties.

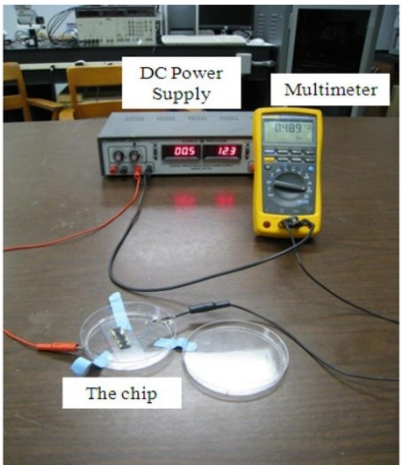


Fig.14. Experimental setup for I-V measurement.

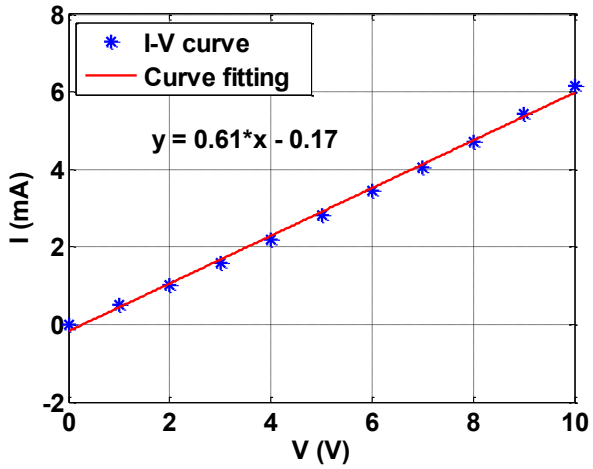
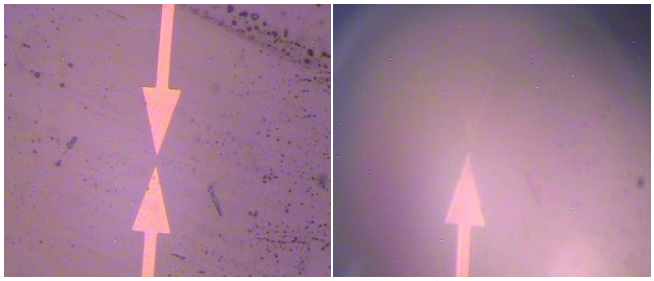


Fig.15. Experimental result of I-V curve characteristic measurement I.

From Fig.13 we find that 1.5µl of the 10X solution contains too many CNTs. Therefore, another experiment is done in the same way but with a 1.5µl droplet of the 50X solution. Fig.16 shows another pair of electrodes which has the same gap as the last one does. Fig.17 illustrates the electrodes after CNT alignment is done with the same sine function. It is difficult to see the nano-wire in this case as the concentration is much lower than before. However, the electrodes are connected which can be proved by measuring the resistance. The resistance is about 245.5kΩ and another I-V curve can be drawn as shown in Fig.18. Based on this result, we can also verify that the CNTs have metallic properties.



(a) (b)

Fig.16. Another pair of electrode with CNT deposition of 50X solution: (a) before; (b) after

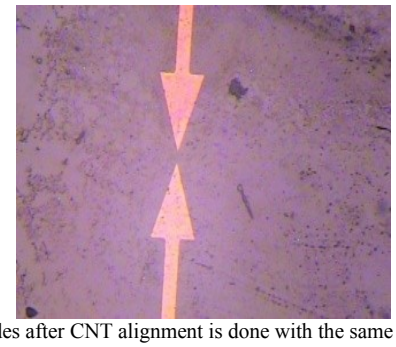


Fig.17. Electrodes after CNT alignment is done with the same AC power.

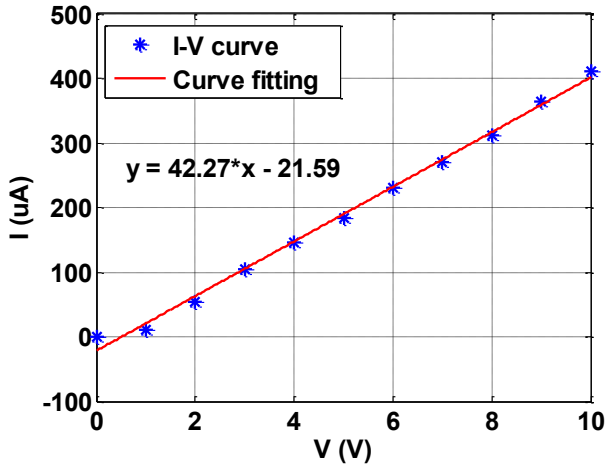


Fig.18. Experimental result of I-V curve characteristic measurement II.

B. Scanning Electron Microscope Aid

The Scanning Electron Microscope (SEM) is a type of electron microscope that images the sample surface by scanning

it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample, producing signals that contain information about the sample's surface topography, composition and other properties, such as electrical conductivity. Therefore, SEM is adopted to examine how the CNT alignment is done. Fig.19 is the scanning image of the first pair of electrodes with CNTs deposited and aligned, which also gives the measurement of the gap distance, 27.9μm. As shown in Fig.20, these MWCNTs are not aligned perfectly linearly. That could be caused by several factors, including the P-P voltage, frequency of the AC power for DEP and so on. More tests will be done in order to achieve an optimized model for alignment.

In the future, in order to improve the experimental results, an alcohol solution will be used to dissolve the MWCNTs instead of DI water, since the surfactant, which causes the surface of the electrodes to look dirty, is not necessary. In addition, besides the sonicate, a centrifugal process for obtaining CNT solutions is also helpful to obtain better experimental results. For example, it becomes possible to deposit, separate and align single CNT as a nano-wire by AFM manipulation. Furthermore, the peak to peak voltage of the AC function for DEP process is going to be lowered, which can protect the electrode better from break and crack. Finally, the current electrodes will be replaced by others with much smaller gap distance, such as 1-2 microns.

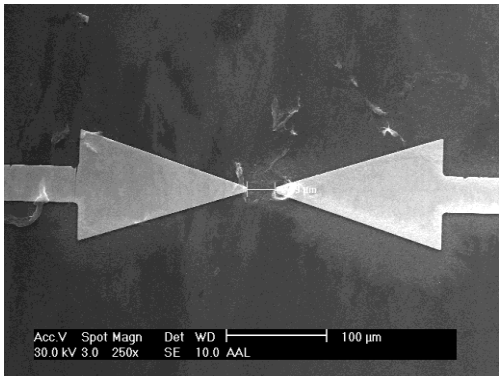


Fig.19. Electrode scan and gap measurement by SEM.

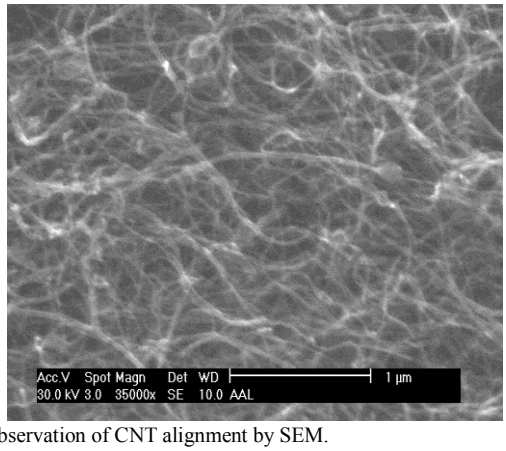


Fig.20. Observation of CNT alignment by SEM.

VI. Conclusion

In this paper, we have proposed a novel idea for developing CNT based NANO pH sensor based on ISFET. CNTs with metallic properties have significant potential to take the place of the inversion layer in ISFET working as the conductive media owing to its unique advantages, such as high current carrying capacity, compact and cheap. Moreover, testing of CNTs I-V characteristic has been done in order to verify if they are metallic or semi-conductive. According to the experimental results, we can tell whether the CNTs have metallic or semi-conducting properties. The metallic CNTs can be used as nano-wires connecting the source and drain, while the semi-conducting ones are developed for nano-transistors. Overall, this novel idea on development of nano pH sensor based on CNTs has potential for commercialization.

Acknowledgment

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