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Atomic Force Microscopy Based Nano Manipulation towards CNT-ISFET pH Sensing System

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***Abstract* - In this paper, we present a novel means by which nano manipulation can be realized on a field effect transistor (FET) surface. Using atomic force microscopy (AFM) tip as a manipulation tool, micro and nano scale channels are created between the gap of a pair of gold (Au) electrodes. Following a dielectrophoresis (DEP) process, carbon nanotubes (CNTs) are deposited and aligned perfectly inside the channels cut by the AFM. Then, the two electrodes are bridged and ready to be developed as an ion-selective field effect transistor (ISFET) structure that has the potential to work as a high-performance pH sensor. Owing to the unique electrical properties of CNTs, such as conductivity (either metallic or semiconducting) and great current carrying capacity (~1 TA/cm^3), there is a huge possibility that this CNT-based ISFET system is a much better replacement for the existing ISFET-based pH sensors. The pH sensing system will be much more compact, cheaper and reproducible, and no longer need outside amplifier circuits, which will have huge benefits in industry, biology as well as medicine.**

I. INTRODUCTION

Carbon Nanotubes (CNTs) closely resemble hollow graphite fibers that exist in entangled bundles of tens to hundreds. They 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 [1-3]. CNTs have also been known to possess remarkable electrical, mechanical, and thermal properties [4]. 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 semiconducting CNTs can be used for nano transistors [5].

Furthermore, 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 microchips, which would become continuously cheaper, even with improved characteristics. Moreover the reproducibility of sensor characteristics should be highly improved compared to the usually piecewise-assembled sensors, 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)-based pH sensor [6] is one of the most well-known examples, which has been already realized and applied to practice. With more study on CNTs, these nanotubes with metallic and semiconducting properties may have a huge potential to produce more compact and efficient devices for pH measurement application based on ISEFT structure. So far, CNT-based ISFET for pH control application has not yet been explored. However, after learning both CNTs and ISFET deeper, we believe a proper combination may have a huge potential to contribute more compact, cheaper but more efficient devices for pH measurement applications.

AFM was the first tool that can perform high resolution imaging and vacuum free working environment more than twenty years ago [7-8]. Nowadays, AFM has been playing a more important role in various research areas. This is not only because it can provide high resolution image in both air and liquid but also it can measure the mechanical properties, such as Young's Modulus [9-10]. Moreover, the AFM tips have been employed as an end effector of robots to realize the manipulation of nanoparticles or the modification of sample surface for many years [11-12]. Agilent 5500 ILM possesses a separate software package named PicoLITH which provides users with the tools necessary to perform nanolithography using an AFM tip. This enables users to either manipulate nanoparticles or scratch sample surfaces with a controllable parameter setting. Enlightened by such an advanced tool, this research work is aimed at scratching the silicon dioxide surface of the basic FET structure where the gap between a pair of gold microelectrodes varies. It is also in the location where the inversion layer is and this inversion layer is generated and used to transport the ions while the ISFET system is active. For instance, if there is a nanochannel inside which the nanotubes are aligned and connecting the electrodes, the drain current between the source and the drain should be much higher under the same gate voltage. Owing to their unique electrical properties, these channel-aligned nanotubes will work as a highway for the ions and has the potential to improve the system performance dramatically. Herein, we propose the idea, introduce the schematic and provide the preliminary testing and results in this paper.

II. CNT-BASED ISFET

A. ISFET

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

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change accordingly. Here, the solution is used as the gate electrode instead of the traditional metal gate. The voltage between substrate and oxide surfaces arises due to an ions sheath. An ISFET's source and drain are constructed similarly as a Metal-oxide Semiconductor Field-Effect Transistor (MOSFET) [13]. Although an ISFET is very similar to a MOSFET, there are still some differences. As shown in Fig.1, 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. Devices with this structure can be applied to pH measurement. However, the final objective of our work on Nano pH sensor is to enhance the inversion layer with CNTs as nano wires to conduct electrons between the drain and source. The drain current might be much greater under the same gate voltage. Furthermore, the semiconducting CNTs are able to be fabricated as transistors. If all of these are verified, then these devices could be fabricated, manufactured and cheap earning to one of CNTs unique electrical property, such as high current carrying capabilities.

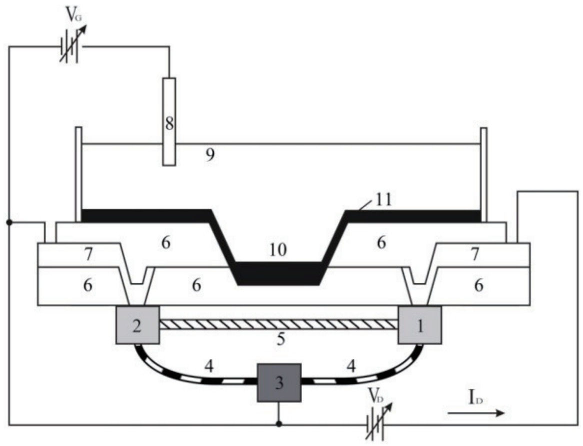

Fig. 1. Schematic of CNT-based ISFET: 1 N-doped drain; 2 N-doped source; 3 P-type silicone substrate; 4 SWCNT as transistor; 5 MWCNT as nano-wire; 6 insulator; 7 metal contacts; 8 reference electrode; 9 solution; 10 electroactive membrane; 11 encapsulate.

B. *FET Fabrication*

The basic FET structure is originally made up of four layers from bottom up: silicon wafer, 300Å of silicon dioxide, 200Å of chromium and 5000Å of gold, where the gold layer is thick enough to solder for wire bonding, and fabricated using surface micromachining techniques. The fabrication flowchart is illustrated in Fig. 2. For the electrode fabrication, a mask as shown in Fig.3 is first designed for the desired chips. Triangular electrodes with angle of 30, 60 and 90 degrees, with electrode gaps of different lengths are designed. 24 microelectrode chips are fitted on a circular silicon wafer with a diameter of 125 mm. The reason why we choose triangular variation is that triangular electrodes provide a wider zone of stronger DEP force and weaker hydrodynamic force than other variations, such as square and semicircular shaped, which do not allow particles to be easily released [14].

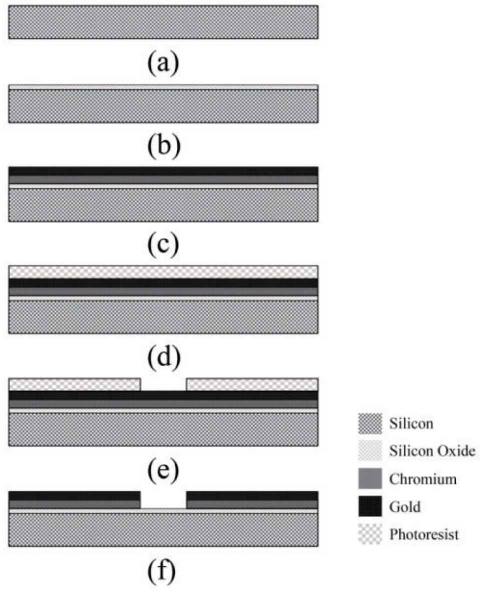

Fig. 2. Fabrication process of micro electrode: (a) silicon substrate; (b) 300Å silicon-dioxide by thermal oxidation of silicon wafer; (c) both chromium and gold are deposited on the silicon dioxide surface by evaporation and electro plating; (d) cover the surface by photoresist layer; (e) photoresist is patterned and exposed; (f) the metals are etched as patterned and the rest of photoresist is stripped off completely.

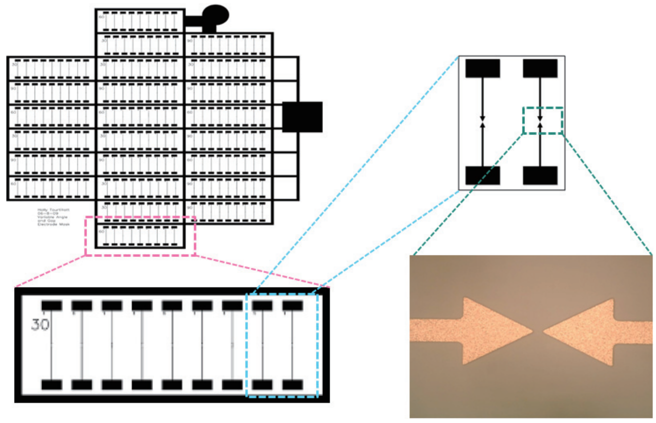

Fig.3. Mask design and Au microelectrodes on Si substrate as FET.

III. AFM-BASED NANO MANIPULATION

Since the basic FET structure has been fabricated and available on the chip, the AFM-based nanomanipulation process can readily be carried out. As shown in Fig. 3, a chip with nine pairs of gold microelectrode is scratched by a Diamond-Like-Carbon (DLC) coating AFM tip [15] at the location of the electrode gaps. Each pair of electrode has a 60° triangle shape with about 10µm gap and the DLC tip is of 48N/m spring constant and 190kHz resonant frequency. Prior to scratching the electrode surface, a topography scan of the area, which encloses the desired nanochannel is necessary. Figure 4 shows an AFM topography scan of the electrodes under contact imaging mode. This image is loaded into PicoLITH and ready to cut. In PicoLITH, the object can be drawn on the loaded image and the parameters for scratching are set: Force setpoint at 7.5V, which will maintain a constant mechanical force the AFM tip and the surface by maintaining a constant amount of deflection of the cantilever for the entire manipulation and has a range of -10.0V to 10.0V; times at 150, which is the number of times the object is traced by the tip and tip speed at 2µm/s. In this experiment, the object is drawn as a straight line between the two electrodes. By positioning the tip to the start point where the object starts, the scratching gets started. Figure 5 presents the 3-dimensional topography scan after scratching the electrode gap in Fig. 4. As we can see, there is a clear channel scratched between the two electrodes and the width and depth of the channel can be measured as shown in Fig. 6. On this chip, eight out of nine pairs of electrode gaps were cut except for the one in the middle (5th pair). Table I provides the details of the dimension measurement of the cut channels. These channels are embedded so they can be regarded as an enhanced inversion layers and we expect an improvement of the structure performance.

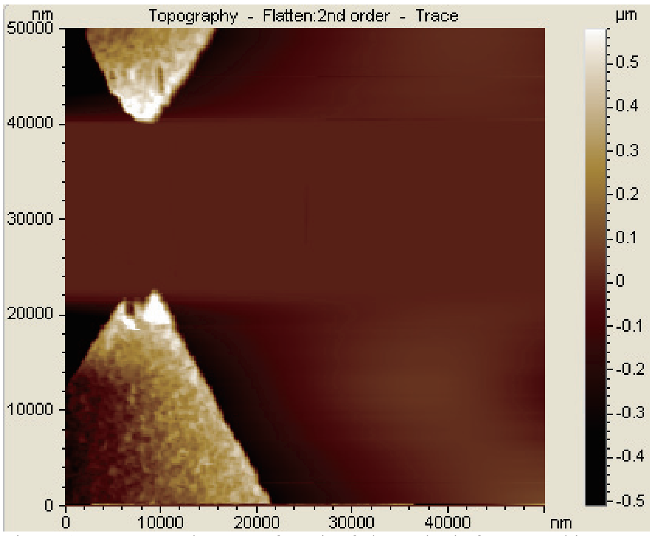

Fig. 4. AFM topography scan of a pair of electrodes before scratching.

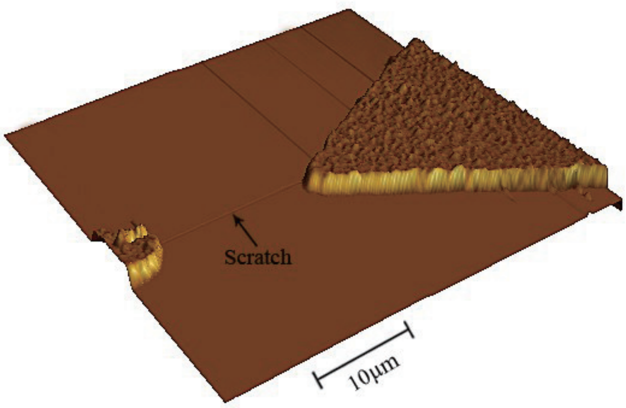

Fig. 5. 3D topography image of a pair of electrodes with scratched gap.

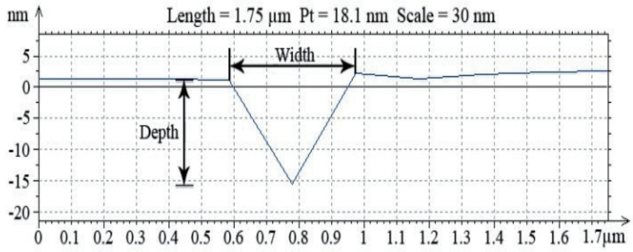

Fig. 6. Dimension measurement of the scratched nanochannel.

Table I
DIMENSION MEASUREMENT RESULTS OF SCRATCHED NANOCHANNELS

Elec. Pair #	Length (µm)	Width (µm)	Depth (nm)
1	17.32	0.58	2.8
2	21.88	0.39	2.10
3	18.16	0.59	4.90
4	18.75	0.59	9.10
6	21.09	0.78	3.40
7	17.97	0.39	4.21
8*	18.95	0.39	16.80
9	19.14	0.39	1.80
Average	19.16	0.513	5.64

* As shown in Fig. 5&6.

IV. CHARACTERIZATION OF ELECTRICAL PROPERTY

A. CNT Preparation

Two CNT-samples are prepared: 1.37mg SWCNTs dissolved in 1ml Deionized (DI) water with 2µl Triton; and 2.69mg MWCNTs dissolved in 1ml DI water with 5µl Nanosperse, and then sonicated for 1 hour. After the stocks are available, 5X, 10X and 20X dilutions are also prepared.

B. Wire Bonding

For wire bonding, since the traditional method of soldering can damage micro chips easily, conductive epoxy is used to stick wires onto the gold (Au) pads in order to interface the outer environment. In this experiment, the two parts of conductive epoxy are equally mixed together, and then we deposit a little of the mixture on the pads, finally the wires can be stuck to the pads. The epoxy will get firm enough to bond stably after being heated at 130ºC for about 1 hour on a heat plate. Eventually, we have wires ready coming from the metal pads to apply DEP forces in between the electrodes.

C. CNT Alignment

Dielectrophoresis (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 [16-17]. Figure 7 illustrates the experimental setup for CNT alignment by applying DEP forces. Function generator provides us with an AC power of 20V p-p and 1.5MHz, which will be verified by the oscilloscope. Then the chip is real-time observed by the optical microscope during the alignment. 1.5µl of 10X SWCNT dilution is dropped on the gap of the electrode pairs 1-4 while 1.5µl of 10X MWCNT dilution for the pairs 6-9. Then by connecting the electrodes to the function generator, DEP forces are generated in the gaps and the electrodes are bridged by the CNTs. Figure 8 shows the observations of the electrode gaps.

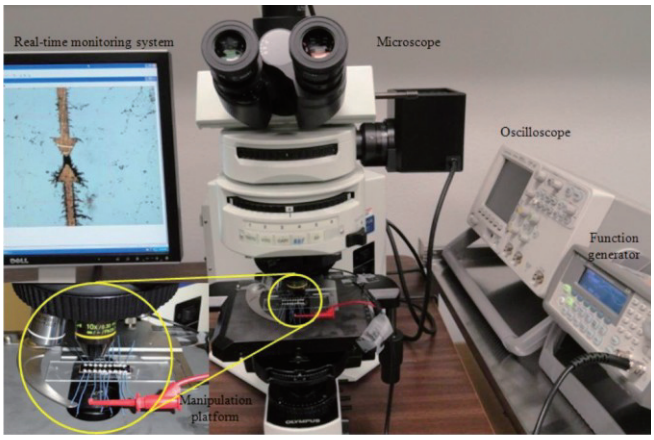

Fig. 7. Experimental setup for DEP application.

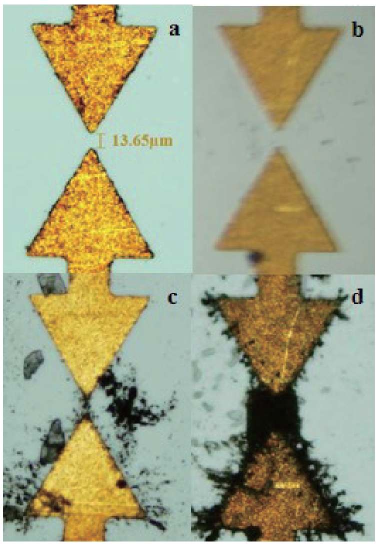

Fig. 8. Pairs of Au electrodes observed by optical microscope: a. gap measure; b. covered by tiny CNT droplet; c & d. bridged by SWCNTs and MWCNTs respectively.

D. *Electrical Property Measurement*

For testing I-V characteristics, the gap distance is about 20µm and a pipette, whose sucking range is from 0.5 to 10µl, is used to deposit a 1.5µl CNT droplet from the 10X dilutions onto the gaps. Figure 9 shows I-V curve measurement results of all the nine pairs of electrodes. As we can see, both SWNTs and MWNTs aligned between the gaps possess a linear I-V curve. This linear relationship reveals that these CNTs are metallic and possessing very excellent ion conductive properties. Once ISFET is activated and the ions are generated between the source and drain, this CNT-based enhanced inversion layer will allow a lot more ions to go through it at the same time. Therefore, the drain current should increase accordingly.

V. Conclusion

In this paper, we have proposed a novel idea for developing CNT based NANO pH sensor based on ISFET. In addition, AFM-based nanomanipulation has been used to develop an enhanced inversion layer in ISFET system. The nanochannels scratched by AFM tip connect the electrodes and are full of aligned CNTs. The dimensions of the channels are perfect to hold the tubes. Owing to CNT's unique electrical properties, the drain current is expected to improve significantly. Furthermore, the electrical properties of the aligned CNTs between the electrodes are tested through DEP application.

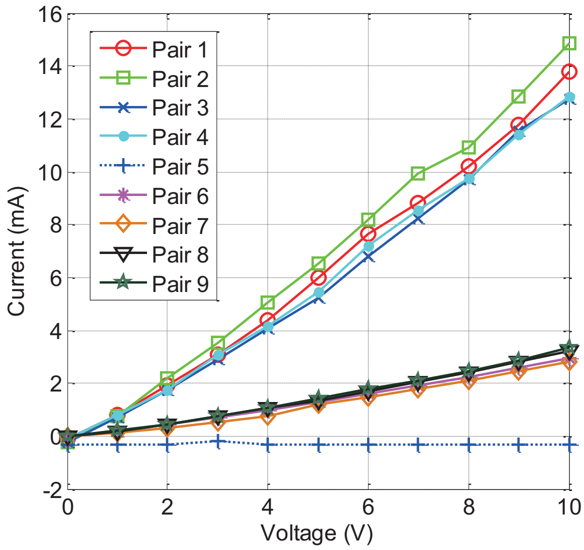

Fig. 9. I-V curve measurement with SWCNTs alignment (Pair 1-4) and MWCNTs alignment (Pair 6-9) in the scratched gaps. Pair 5 is for the bare electrode.

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