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Design, Fabrication and Measurement of CNT Based ISFET for NANO Devices

Zhuxin Dong and Uchechukwu C. Wejinya
Department of Mechanical Engineering
University of Arkansas
Fayetteville, Arkansas, USA
Email: {dzhuxin, uwejinya}@uark.edu

***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 are involved. An Atomic Force Microscope is used to test the conductivity of Single-Walled Carbon Nanotubes with a conductive cantilever-tip. The resistance and the I-V characteristics of the carbon nanotube can be obtained to describe its electrical properties. Ultimately, this technological development will lead towards the efficient and effective manufacturing of CNT-based ISFET for pH sensor application.**

Index Terms – pH, CNT, AFM, ISFET, MEMS.

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]. CNTs have also been known to possess 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 semiconducting CNTs can be used for nano transistors [3]. In order to determine the band structure, dielectrophoresis (DEP) and Atomic Force Microscope are exploited.

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, etc. 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.

A general approach has been developed to determine the conductivity of individual nanostructures while simultaneously recording their structures. Conventional lithography has been used to contact electrically single ends of nanomaterials, and a force microscope equipped with a conducting probe tip has been used to map simultaneously the structure and resistance of the portion of the material protruding from the macroscopic contact [6]. Nowadays, with rapid development of modern technology, Atomic Force Microscope (AFM) has been playing an important role in many areas, especially for the applications in micro and nano scale. With an AFM from Agilent Technologies providing us with a Current Sensing AFM (CSAFM) function, many experiments related to particle electrical properties can be realized efficiently, including impedance measurement and testing of I-V characteristic. Hence, making use of this advantage, an approach to measure the electrical properties of CNTs based on AFM has been developed and the results are introduced in this paper.

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, 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) pH sensor [7] is one of the most well-known examples. Furthermore, with 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. However, 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 areas, including medicine, biology and industry.

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II. CNT Based 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 change accordingly. Here, the solution is used as the gate electrode instead of the traditional metal gate. 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) [8]. 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. Then, devices with this structure can be applied to pH measurement [9]. 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. Furthermore, the semiconducting CNTs are able to be fabricated as nano transistor. If that is verified, then we can make these devices compact and cheap earning to CNT's unique mechanical and electrical properties, such as high current carrying capabilities. Hence, in this paper, two means of testing conductivity properties are introduced.

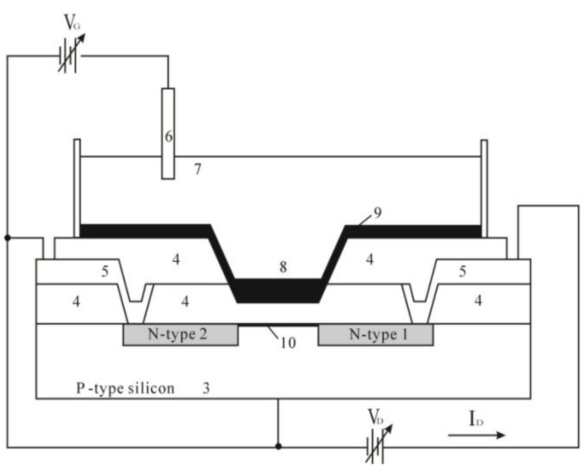


Fig.1. Schematic diagram of a composite gate, dual dielectric ISFET: 1 drain; 2 source; 3 substrate; 4 insulator; 5 metal contacts; 6 reference electrode; 7 solution; 8 electroactive membrane; 9 encapsulant; 10 inversion layer.

III. Test of MWCNT By DEP Application

A. *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 method is illustrated in Fig. 2. For the electrode fabrication, a mask is first designed for the desired chips. Triangular electrodes with 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.

For wire bonding, since the traditional method of soldering can damage micro chips easily, conductive epoxy is used to stick wires onto Gold (Au) pads. In this experiment, the two parts of conductive epoxy are mixed together, and then 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. Eventually, we have wires ready coming from the metal pads to apply DEP forces in between the electrodes.

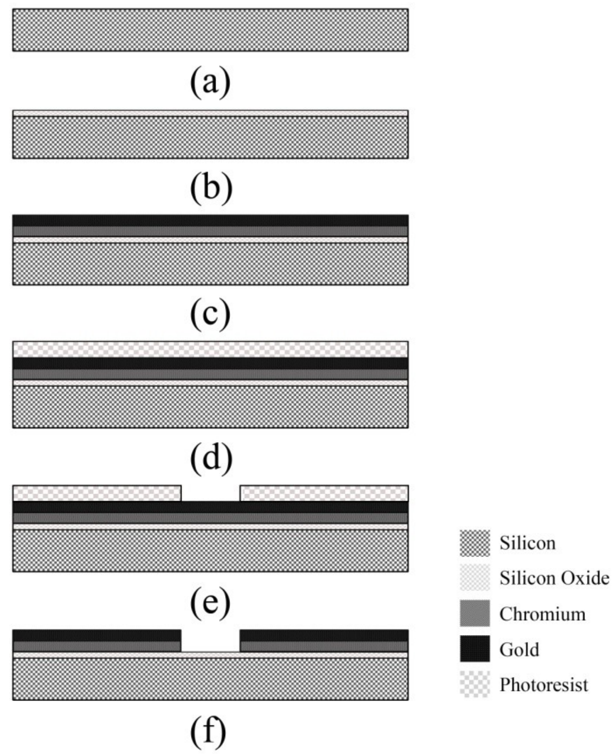


Fig.2. Fabrication process of micro electrode: (a) silicon substrate; (b) 300Å silicon-dioxide by thermal oxidation of silicon wafer; (c) both chromium and gold are deposited on the silicon dioxide surface by evaporation; (d) cover the surface by photoresist layer; (e) photoresist is patterned and exposed;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

B. *CNT Solutions*

At the beginning, the stock solution is a mixture of 0.5mg MWCNTs, 3µl surfactant (Nanospere®) and 5ml Deionized (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. Sometimes, another centrifugal process may be brought into the process to increase the dispersion if necessary. Then after the sonicator has been working for about 30-60 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.

C. *DEP Force*

As it is known, AC power supply is needed 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. 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. 3, two cables from the function generator provide the electrodes with AC power through connecting to the wires bonded on the Au pads.

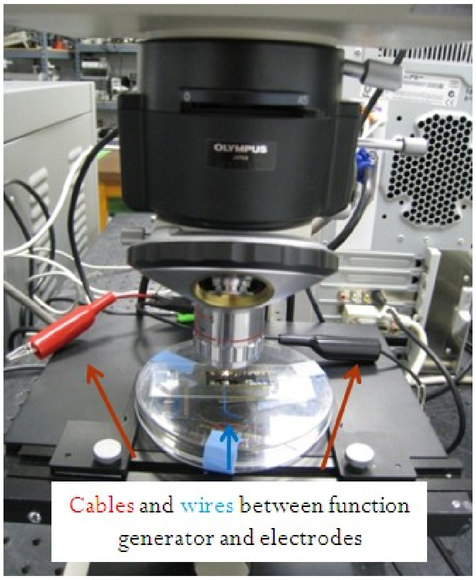
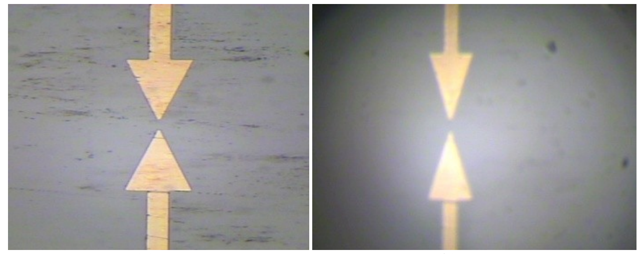


Fig. 3. Operation platform in a microscope: apply AC power to a pair of electrode through wires.

D. I-V Curve Measurement

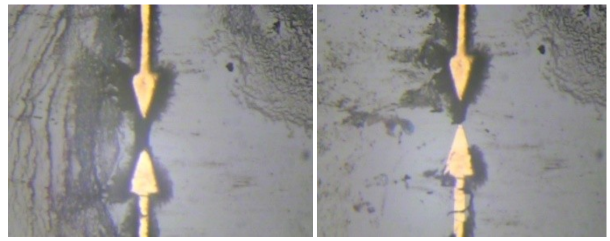
For testing I-V characteristics, the gap distance is about 30 microns, and a pipette, whose sucking range is from 0.5 to 10μl, is used to deposit a 1.5μl CNT droplet from the 10X solution onto the gap. Fig. 4 illustrates the electrode before and after the droplet is deposited observed. Next, the function 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. 5 shows the result of CNT alignment: there is a nano wire consisting of MWCNTs connecting the two electrodes. Fig.5 (b), the resistance of the nano wire is measured by a multimeter, 1.215kΩ.

Fig. 6 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 increment 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. 7, the current values in blue are not from any of the three groups but the averaged current values. The curve in red in 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.



(a) (b)

Fig.4. Electrodes observed by the camera: (a) before deposition; (b) after deposition.



(a) (b)

Fig.5. (a) Electrodes after alignment is done; (b) cleaned by acetone.

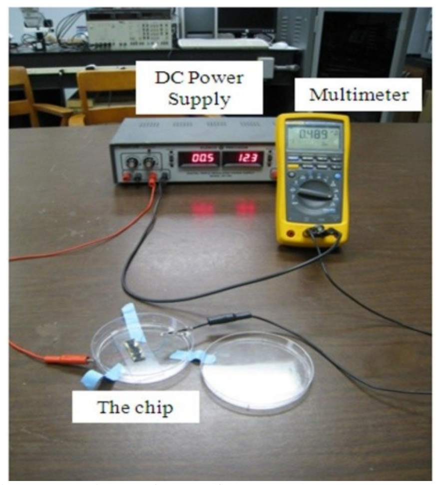


Fig.6. Experimental setup for I-V curve measurement.

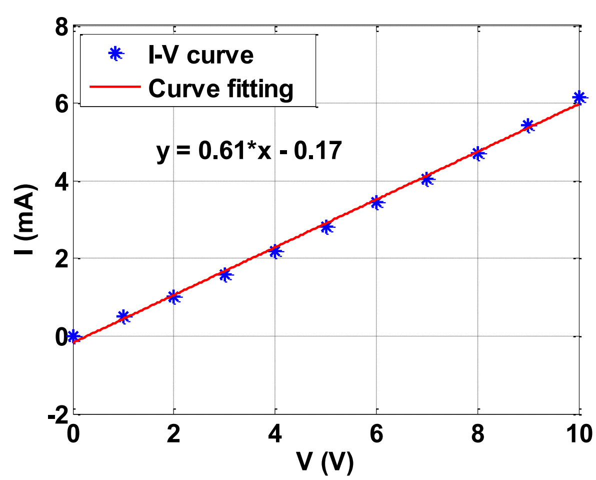


Fig.7. Experimental result of I-V curve characteristic measurement.

E. 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.8 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.9, 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.

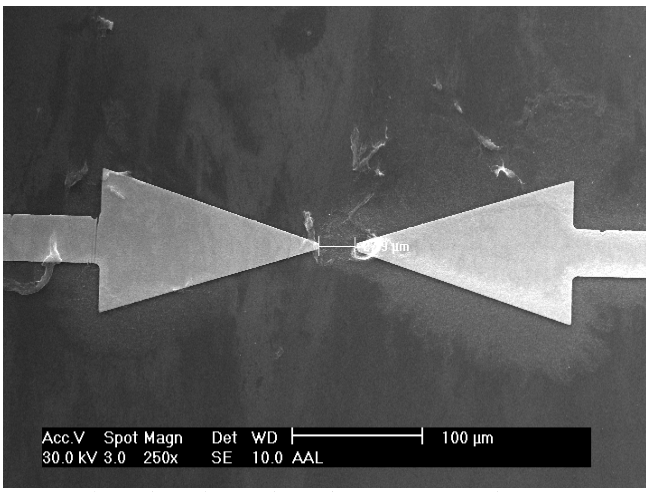


Fig.8. Electrode scanning and gap measurement by SEM.

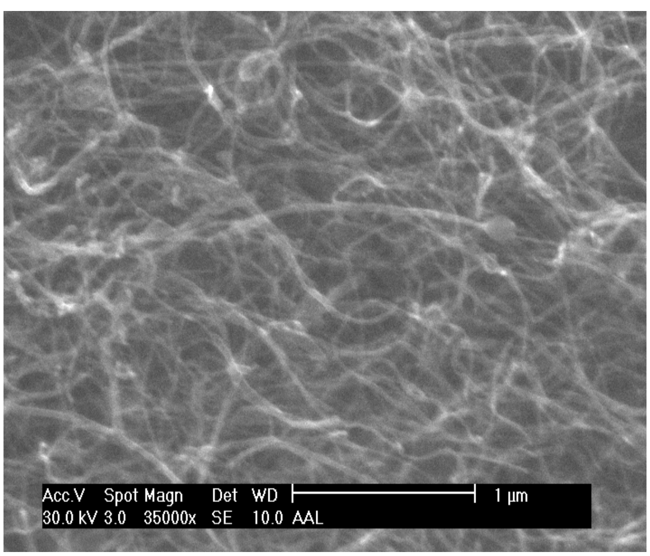


Fig.9. Observation of CNT alignment by SEM.

IV. Test Of SWCNT Based On AFM

A. Theory

To measure the electric properties of SWCNTs, we need, first of all, a conductive surface to sustain the tubes. In our experiment, a glass slide is coated by an indium tin oxide (ITO) layer on the top, which is conductive. A droplet of CNT solution is dropped on the surface and the glass wafer is dried by heating. Then the SWCNT sample is ready for scanning. Agilent 5500 supplies a Current Sensing AFM (CSAFM) function, where an ultra-sharp AFM cantilever, coated with conductive film, probes the conductivity and topography of the sample surface simultaneously. CSAFM requires a special 10˚ nose cone containing a pre-amp. A bias voltage is able to be applied to the sample while the cantilever is kept as virtual ground. During scanning, the tip force is held constant and the current is used to construct the conductivity image of the surface. It has proven useful in joint I-V spectroscopy and contact force experiments as well as contact potential studies. Fig.10 shows the schematics how the measurement is done.

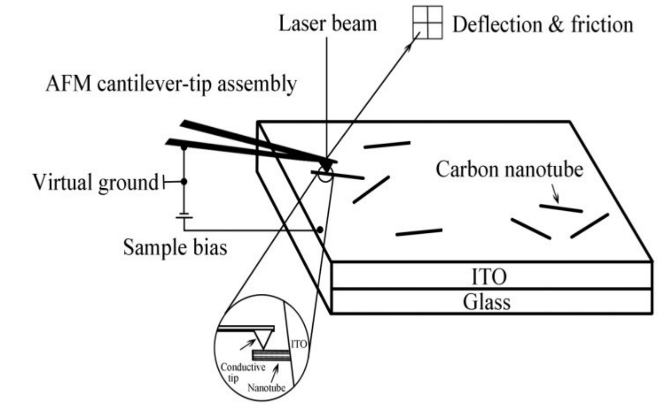


Fig.10. Schematics of electrical properties measurement of SWCNTs through AFM.

B. CNT Solution And AFM Probe

A CNT stock made up of 0.5mg SWCNTs' powder, 998µl DI water and 2µl Triton is used to provide samples. The solution is also sonicated for about 1 hour to achieve uniformly suspended CNTs. Finally, 20µl from the stock is deposited on the ITO surface to scan.

The resonant frequency and force constant of the silicon AFM probes are 13kHz and 0.2N/m respectively. And these probes are coated by Cr/Pt conductively on both sides. The special nose cone assembled has a sensitivity of 10nA/V.

C. Scan And Measurement

Fig.11 illustrates the topography image of the surface in 10µm square from scanning. In this image, it is clear to find one nanotube in the middle separating from the others. At the same time, the conductivity map of that area is also complete with a bias of 200mV as shown in Fig.12. After that, the scanning is stopped and the tip is moved to contact with the nanotube at one point of its body (see Fig.11) and the set-point, which controls the force of the probe acting on its target, is slightly increased to confirm the electric connection. Next, the sample bias is modified and input in terms of range from -3V to 3V to draw the I-V curve. In Fig.13, we can see the SWCNT has a non-linear curve of CSAFM/Aux BNC vs. Sample Bias. Eventually, a conclusion that these SWCNTs are semiconducting is established.

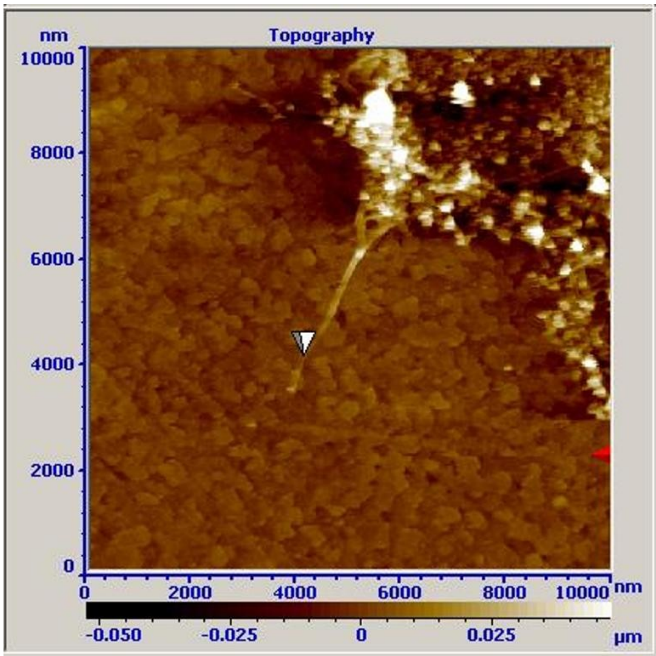


Fig.11. A topography of ITO surface with CNTs sitting on: the position of white cursor is where the probe tip is located to measure.

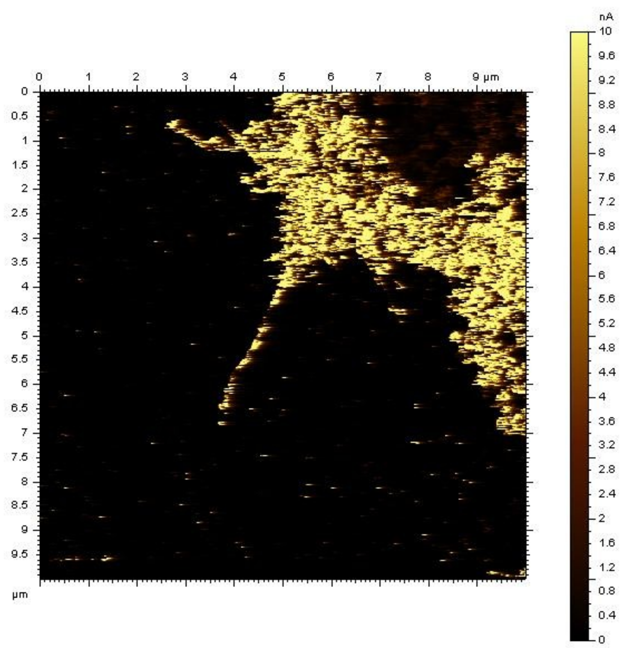


Fig.12. A conductivity map obtained simultaneously with topography at bias 200mV.

V. CONCLUSION

In this paper, we have proposed a novel idea for developing CNT based NANO pH sensor based on ISFET. Moreover, testing of CNT I-V characteristic has been done in order to verify if they are metallic or semiconducting. 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 while the other kind of CNTs with semiconducting properties is able-

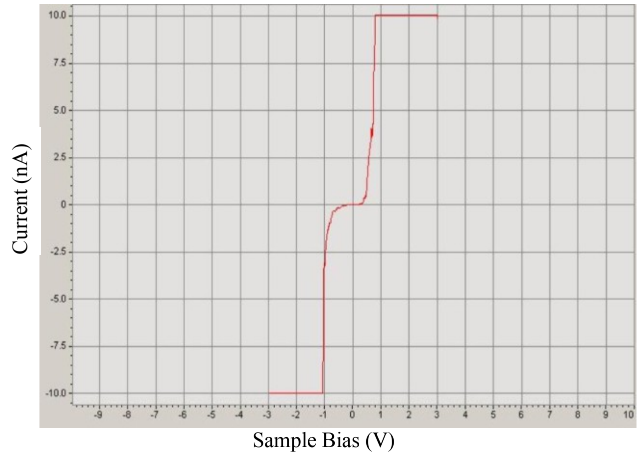


Fig.13. I-V curve measurement on CNT body with bias from -3 to 3V.

-to be applied to the manufacture of the transistor in FET. According to the experimental results, we can tell whether the CNTs have metallic or semiconducting properties by means of either DEP or CSAFM. Overall, this novel idea on development of nano pH sensor based on CNTs has great value for research and commercialization.

In the future, to improve the experimental results, CNTs need to be dispersed better in stock. A more proper collocation of CNTs, surfactant and medium will be achieved. In addition, the distance of electrode gap and parameters of AC function for CNT deposition and alignment can be adjusted towards the demanding of practical application.

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