2011 11th IEEE International Conference on Nanotechnology
Portland Marriott
August 15-18, 2011, Portland, Oregon, USA

A Study of Sulfuric and Acetic Acid Effect on Vertically Aligned Carbon Nanofibers for Bio/Chemical Sensors Development

Siva Naga Sandeep Chalamalasetty[1],*Student Member, IEEE*, Uchechukwu C. Wejinya[2], *Member, IEEE,* Zhuxin Dong[2], *Student Member, IEEE,* and Meyya Meyyappan[3].
[1]Department of *Microelectronics and photonics, University of Arkansas, Fayetteville, AR 72701, USA*
[2]Department *of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701, USA*
3Center for Nanotechnology, NASA Ames Research Center, Moffett Field, CA 94035
E-mail: uwejinya@uark.edu

***Abstract*- Materials behave differently with different chemicals. Carbon Nanofibers are no exclusion for this. During the fabrication process of carbon nanofibers, the chips are treated with a lot of chemicals including a variety of acids. Thus with a better understanding about the fibers behavior in the presence of commonly used acids will give us edge in the development of the well defined fibers. In our previous papers, we have discussed about the effects of Hydrogen Fluoride (HF), Hydrogen Chloride (HCl) on the carbon nanofibers dimensions. In this paper, impact of sulfuric and Acetic acid are discussed and statistically analyzed.**

I. INTRODUCTION

Carbon nanofibers were brought into lime light with two major discoveries two decades ago. In 1985, Buckminster fullerene C_{60} was discovered by the team headed by Kroto [1] followed by the illustration of IIjima [2] that carbon nanotubes are formed during arc discharge synthesis of C_{60}. The fact that four billion dollars have already been invested on the researches involving this exciting material since their discovery shows up the importance of this material. The applications of this material in the fields of electronics, mechanics, sensing and diagnostics, photochemistry, gene delivery etc is comprehensive. In the recent trends of carbon nanofiber chip integration, vertically aligned carbon nanofibers (VACNFs) have received tremendous attention because of their attractive properties such as high electrical and thermal conductivities, superior mechanical strength, a wide electrochemical potential window, flexible surface chemistry and biocompatibility [3-4]. Advances in Microfabrication technology have provided platform for developing different electrode configurations such as microelectrode arrays [5] and interdigitated arrays (IDA) [6], but their performance can be further enhanced by nanofiber integration. Many scientists had tried integrating different nano materials like carbon nanofibers [7-9], carbon nanotube bundles [10-11], nanoscale IDA [12], silicon nanowires [13] and diamond nanowires [14], which are capable of high spatial and temporal resolutions, possibly yielding sufficient sensitivity to single molecule detection. During the fabrication, the grown carbon nanofibers interact with a variety of chemicals including a wide variety of acids. Thus a better integration would be possible if we understand how the fibers react with different acids. That's why most commonly used acids are selected and treated with carbon fibers and then the change in the dimensions of the fibers after the interaction are measured using the Atomic Force Microscopy (AFM). In our previous paper, we have put forward the results of the nanofiber interaction with two different acids i.e., Hydrogen Fluoride (HF) and Hydrogen Chloride (HCl). In this paper, we are going to present the results from two other acids namely Sulfuric (H_2SO_4) and Acetic acid (CH_3COOH). It is believed that acids will etch off the surface because of their high oxidation capability. Hence etch rate is taken and calculated to better understand the dimensional change and the formula for etch rate calculation is given in Equation 1. The results are then statistically analyzed for accuracy and error measurement.

$$Etch\ Rate = \frac{Change\ in\ Height}{Time} \quad (1)$$

II. ATOMIC FORCE MICROSCOPY

Atomic Force Microscope (AFM) is a very high resolution type of scanning probe microscope that has resolution of fractions of a nanometer. The AFM was created specifically to generate a three-dimensional view of a scanned object, unlike the Scanning Electron Microscope (SEM) that can only produce two dimensional views. With the ability to scan almost any type of surface, the AFM is used in many types of research. Surfaces include polymers, ceramics, composites, glass, and biological samples. The AFM also has a variety of operation modes including contact mode, lateral force microscopy, noncontact mode, tapping mode, and phase imaging. This feature induces the stunning capabilities of this microscope by only applying a simple set of modifications. The microscope uses a micro scale cantilever with a probe at the end that is used to scan a surface. A beam deflection system consisting of a laser and photodetector is built into the microscope to measure the position of the beam and ultimately the position of the cantilever tip. To calculate the force, Hooke's Law, F= -kz where F is the force, k is the spring constant of the cantilever, and z is the displacement of the cantilever, is used. The laser beam is placed on the cantilever tip and the beam deflection measures the displacement the

sample exerts on the cantilever. The spring constant is known based on what type of scanning probe is used. With its three dimensional capabilities and ability to operate in air/liquid rather than a vacuum sealed environment, the Atomic Force Microscope aids many studies in biological macromolecules, tribiology, optical and imaging sciences. The microscope has the capabilities of scanning living organisms through the study of measurements of protein-ligand interactions on living cells and many other research applications. The atomic force microscope has been used as the primary microscope in the direct measurement of interatomic force gradients, detection and localization of single molecular recognition events, single molecule experiments at the solid-liquid interface and fractured polymer/silica fiber surface research. Owing to the advantages stated above, AFM is capable enough to complete the size measurement of the nano fibers and cavities.

III. Fabrication of Nano Electrode Array Chips

The intensively sensitive fabrication process of vertically aligned carbon nanofibers (VACNFs) nano electrode arrays (NEAs) includes six major steps done on a four inch silicon (100) wafer that is previously coated with 500 nm of silicon dioxide.

The fabrication process is shown in Fig. 1 and the steps include A) metal deposition; (B) Nano-patterning of Ni catalyst dots; (C) directional growth of CNFs; (D) silicon dioxide deposition for electrical isolation and mechanical support; (E) chemical mechanical polishing (CMP) to expose CNF tips and (F) a wet etch with 7:1 HF.

A. Deposition of Metal

In this step metal is deposited for micro pads, contact pads and interconnects. A single 4-in Si wafer is lithographically patterned for 9 micro pads, 9 contact pads and channels for interconnects. This patterned structured is inspected microscopically and then electron beam evaporation is compression, exercised to deposit a 200 nm thick Cr film and then the wafer is immersed in acetone for one hour. Once removed from the acetone, the wafer is sprayed with methanol and isopropyl alcohol and blown dry with N_2.

B. Nanopatterning of Ni-catalyst Dots

Using e-beam lithography, Ni dots are patterned onto the substrate. Approximately ~39000 Ni catalyst dots are patterned onto each of the micro pads. A 400 nm thick Poly(methylmethacrylate) (PMMA) A7 was spun coated at 3000 rpm, baked at 180^{o}C for 90 s, and exposed at 100 K eV, 2 nA, 1950μC/cm^2. Exposures were developed in a solution of 1:1methyl isobutyl ketone (MIBK): IPA for 2min, immersed in IPA for 30 sec, and blown dry with N_2. Subsequently, the patterned catalyst dots are verified using an optical microscope and a 10 nm Cr followed by 30 nm Ni catalyst were deposited by electron beam evaporation at ~2 Å/s. The coated wafers were immersed in acetone for 1 h. The wafers were then removed from the acetone while being sprayed with IPA and then blown dry with N_2.

C. Directional Growth of VACNFs

The next step is directional growth of VACNFs on the nickel dots that were created in step B. A DC-biased PECVD is employed at a processing pressure of 6.3 mbar, plasma power of 180W and 700^o C, 125sccm C_2H_2 feedstock and 444sccm NH_3 diluents were initiated. Then a five minute thermal annealing at 600^{o}C is carried out before initiating the plasma with 250sccm NH_3. To attain the required growth temperatures and thermal anneal, a 60^{o}C/min thermal gradient was used. Each individual CNF is vertically arranged to free stand on the surface with Ni catalyst on each tip. Operating deposition for 15 minutes produced CNFs of height 1.5μm, base diameter 100nm and tip diameter 70nm on average. At this step Scanning Electron Microscopy (SEM) is used to validate the results.

D. Deposition of Silicon Dioxide

In order to passivate the side walls of nanofibers, a 3 μm ± 0.8% of SiO_2 layer is deposited onto the wafers using a pressure of 3Torr, temperature of 400^{o}C and RF power of 1000W. A mixture of ~6000 sccm of O_2 and 2-3 ml/min of tetraethlyorthosilicate (TEOS) is used in a parallel plate dual RF PECVD to obtain highly conformal coating of SiO_2 on newly created nanofibers and interconnects.

E. Chemical Mechanical Polishing

Surface polarization along with exposing the nanofiber tips is attained by removal of excess SiO_2 and partial removal of

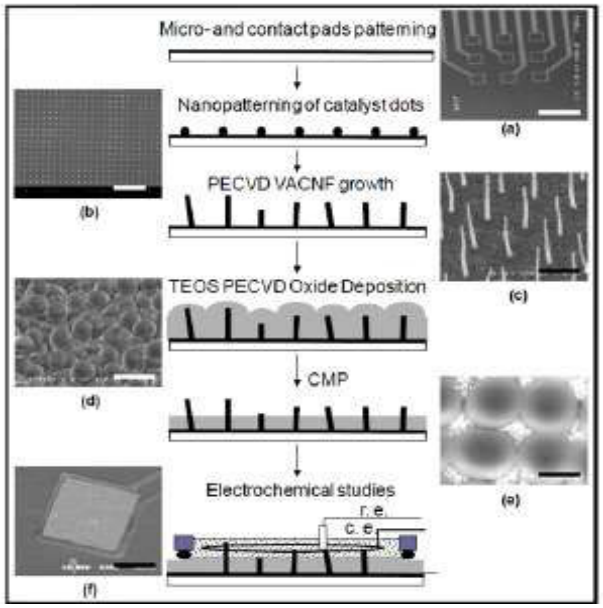

Fig 1.Schematic diagram showing Fabrication steps and the changes on the wafer can be seen in the pictures in-sight. a) Deposition of metal, b) Nanopatterning, c)Growth of CNF's, d) Deposition of Silicon Dioxide and e) Chemical Mechanical Polishing.

nanofiber tip using Chemical Mechanical Polishing (CMP). This process involves removing the existing material with 0.5 µm alumina (pH 4) at 10 ml/min, 60-rpm platen, 15-rpm carrier, and 15 psig down force at 150nm/min for irrefutable polishing. Wafer was then cleaned by immersing it into a solution composed of water, hydrogen peroxide, and ammonium hydroxide at a ratio of 80:2:1 respectively and then spin-dried.

F. Wet etch

This is the final step in the fabrication of VACNFs. In general, wet etch is used for exposure of contact pads which are covered with SiO_2. A 7:1 diluted HF solution is expended to etch oxide ~15 Å/s. Wafers are then diced for individual chips.

IV. Experimental Setup

Wet bench treatment of acids is carried out followed by cleaning with water and then drying in the dry box. All the chemicals used in the current study are bought through VWR Inc. USA. For consistency and to make an easy comparison, all acids used were of the same concentration 5N and they are treated for 5 minutes and then measured for dimensional changes using the Atomic Force Microscope.

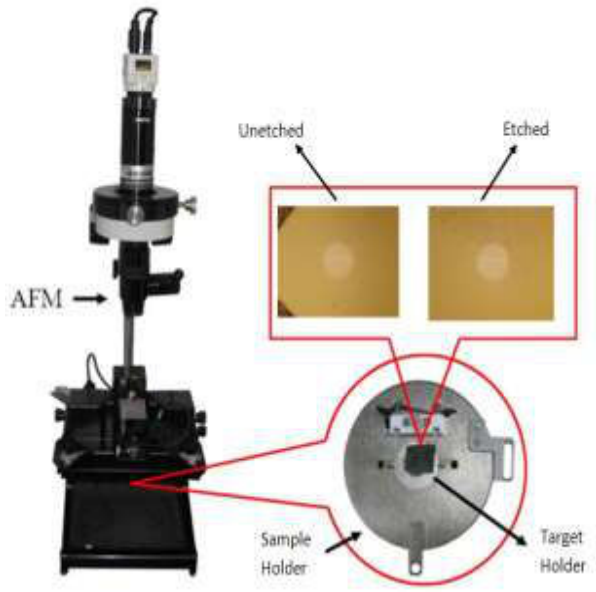

Fig. 2. AFM-based experimental setup showing the sample holder and chips for scanning and characterization

In order to accurately determine the height and diameter of the VACNFs on the etched and unetched substrates, an Atomic Force Microscope is employed. The AFM used in the experiment is the Agilent 5500-ILM highly sensitive microscope shown in Fig 2. The scanning and characterization is done under Acoustic AC (tapping) imaging mode as shown in Fig 3. The AFM probe utilized during imaging has a resonant frequency of 190 kHz and a spring constant of 48 N/m. As introduced in the AFM manual, during intermittent contact, the tip is brought close to the sample so that it lightly contacts the surface at the bottom of its travel, causing the oscillation amplitude to drop. Hence, we may completely ignore the influence of the cantilever tip during the size measurement as it cannot change anything of the target shape without contacting. It is important to note that the VACNFs are not electrochemically treated.

As shown in Fig. 2, the sample chip i.e. either the unetched or the etched is placed over the target holder and in the microscope for scanning. By using a optical microscope, we tried to see the surface over the unetched and etched substrate. The surface looks like as shown inset of Fig. 2.

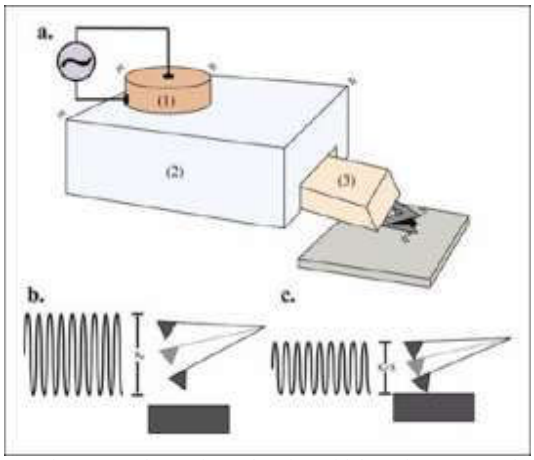

Fig. 3. Scan in AC mode: a. tip under sinusoidal motion (1) AC from nose cone, (2) the base body of cantilever, (3) cantilever with tip; b. oscillation amplitude driven by (1); c. reduction from the interaction with sample as a feedback signal to maintain constant amplitude.

V. Experimental Results

A. Scanning and Measurement

After the treatment with the acid, the chips are scanned using the AFM to find the change in dimensions. By measuring the unetched and the etched chips simultaneously, we can find out the effect of the acid on the dimensions of the nanofiber. At first, a 5µm square is scanned to find the nanofibers in the area. Then a 2 µm square area, in which we felt there are definite nanofibers, is specifically selected and zoomed in. When a fiber appears clear in a scan topography image, a straight line is drawn in any direction in the 2-Dimensinal topography image to cross the target. At the same time, we can obtain the vertical information along the line to complete a measurement. This procedure is repeated until adequate amount of data is collected before starting on another.

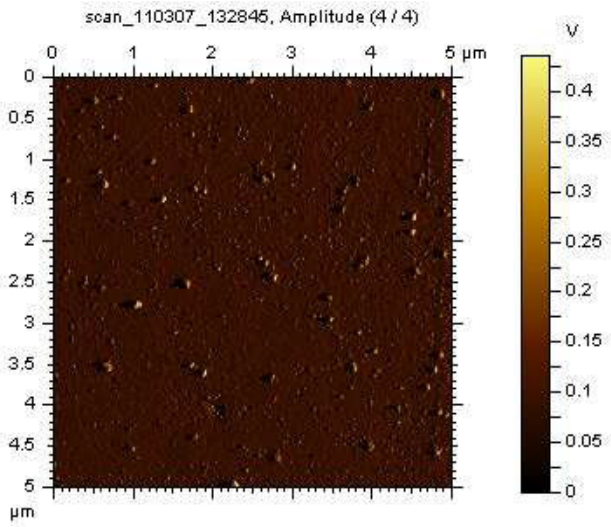

Fig. 4 A 5µm topographical scan area scanned after the treatment with acetic acid. All the patterned dots in the image are the standing Vertically Aligned Carbon Nano Fibers (VACNFs)

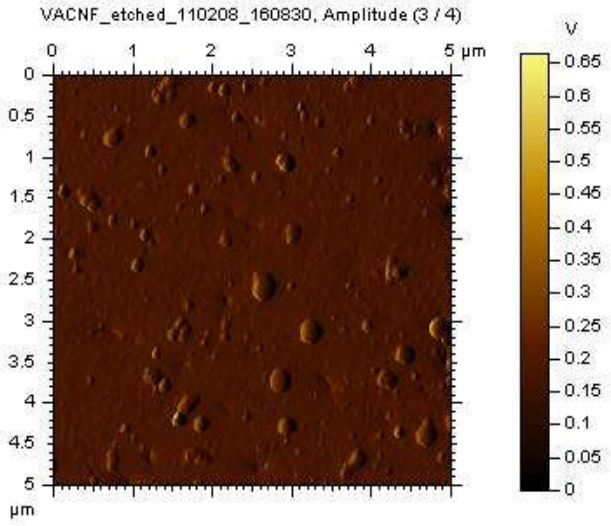

Fig. 5 A 5µm topographical scan area scanned after the treatment with sulfuric acid. All the patterned dots in the image are the standing Vertically Aligned Carbon Nano Fibers (VACNFs)

A 2-D cross section image of roughly 5 µm square area after the treatment with acetic acid (CH_3COOH) and sulfuric acid (H_2SO_4) are shown in Fig 4 and Fig 5 respectively. Patterned carbon nanofibers are clearly visible in the figures. We then go for measuring the dimensions of each fiber by drawing a linear line across the fiber to get a graphical 2-dimensional image of the nanofiber from where we can measure the fiber dimensions. The cross section line drawn for measurement of the nanofibers is shown in Fig. 6. As shown in Fig. 6, the horizontal line indicates the diameter of the nanofiber while the vertical line indicates the height of the nanofiber.

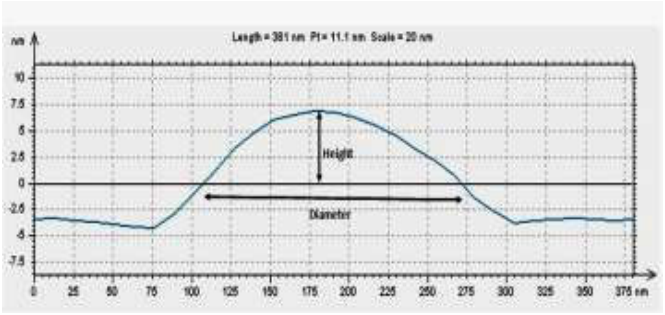

Fig. 6. Graph obtained from AFM by drawing a line across the VACNF.

For clearer view, the images are converted into real time 3-D images using the simulation software in AFM. This amazing capability of AFM gives us leverage over the scanning microscope. Fig. 7 and 8 shows a clear 3- dimensional software developed images from the 2-D image shown in Fig 4 and 5. It provides a better understanding of the material characteristics.

Fig. 7 3-D scan image of the acetic acid treated 2-D scan.

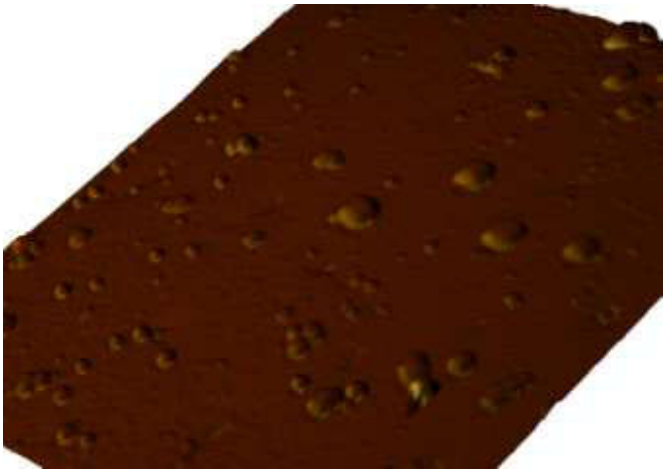

Fig. 8 3 D scan image of sulfuric acid treated 2-D scan.

B. Results and Discussion

Table I shows the average dimensional data of 75 different fibers after the treatment with the acids. From the dimensional data, it is clearly observed that while the sulfuric acid caused an increase in the diameter with simultaneous decline in the height of the fiber, the acetic acid caused an increase in the height with a decrease in the diameter of the fiber when compared to the original nanofiber. Since the side walls are passivated in the case of the VACNFs, thus the diameter is change can be left unnoticed. It is thus the height change that is of prominence in our present study. Thus acetic acid has given a height increase in the fibers and thus can be used to bring in a positive height change in the vertically aligned carbon nanofibers.

TABLE I: AVERAGE DIAMETER AND HEIGHT OF NANOFIBERS AFTER THE TREATMENT WITH ACETIC AND SULFURIC ACID

Etchant Used	Average Diameter (nm)	Average Height (nm)	Etch rate (height) nm/min
None / unetched	204.66	20.44	-
H_2SO_4	306.9	12.52	-1.584
CH_3COOH	150.61	24.75	+0.862

C. Statistical Analysis

For the experiments like these with high data acquisition, statistical analysis is of pivotal importance. In statistics, a confidence interval (CI) is an interval estimate of the overall population. It would help us define the population more accurately by defining them by a range which includes the mean of the population. This in general is calculated based on the mean and standard deviation of the population. The range varies based on the percent of the population that should be included. In general for a huge data, 95% population inclusion will be a very good estimate. Hence we calculate the confidence interval for 95% population following equation (2) for calculating the confidence intervals.

$$CI = [\bar{X} - Z \times \frac{\sigma}{\sqrt{N}}, \bar{X} + Z \times \frac{\sigma}{\sqrt{N}}] \quad (2)$$

Where, $\bar{X}$ is the mean values of the samples; Z, the critical value, is equal to 1.96 in a 95% CI; σ is the standard deviation and N is the number of the samples which is equal to 90 in this case.

Thus making use of the average dimensional data, standard deviation and the critical value for 95% confidence, confidence intervals for untreated, acetic acid treated and sulfuric acid treated fibers are calculated and is tabulated in Table II. From the confidence data, it is obvious that the data obtained is accurate as the range of the data is within 20 nm for the diameter and within 2 nm for the height of the fibers.

TABLE II: CALCULATION RESULTS OF CI FOR THE SIZES OF UNTREATED AND ACID TREATED FIBERS

		CONFIDENCE INTERVAL	MEAN	STD DEV.
UNETCHED	DIAMETER	[199.86 211.19]	205.53	25.03
	HEIGHT	[18.78 22.06]	20.42	7.23
H_2SO_4 TREATED	DIAMETER	[296.37 317.47]	306.88	46.71
	HEIGHT	[11.91 13.06]	12.51	2.39
CH_3COOH TREATED	DIAMETER	[147.45 153.77]	150.61	13.97
	HEIGHT	[22.77 24.71]	22.74	4.28

All dimensions are in nm.

CONCLUSION

From the present study, we can conclude that while sulfuric acid can be used to decrease the height of the fiber, acetic acid can be used to increase the height of the fiber. While contrarily, acetic acid caused a reduction in the diameter of the fiber while sulfuric acid caused an improvement in the height of the fiber.

ACKNOWLEDGMENT

The authors would like to express their sincere gratitude to Dr. Jessica Koehne of NASA AMES research center for providing us with the fabricated unetched chips and for her timely support. This work is partially supported by the University of Arkansas, College of Engineering External Mentoring Award Program.

REFERENCES

[1] W. Kroto, J. R. Heath, S. C. Obrien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] S. Iijima, Nature (London) **354**, 56 (1991).

[3] A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes and M. L. Simpson, 2003. "Large-Scale Synthesis of Arrays of High-Aspect-Ratio Rigid Vertically Aligned Carbon Nanofibers". *Nanotechnology* 14(2003), 1029-1035.

[4] National Research Council and Committee on Indicators forWaterborne Pathogens, 2004. Indicators for Waterborne Pathogens. National Academies Press, Washington, DC.

[5] K. Dill, D. D. Montgomery, A. L. Ghindilis, K. R. Schwarzkopf, S. R. Ragsdale and A. V. Oleinikov, "Immunoassays based on electrochemical detection using microelectrode arrays : Microarrays for Biodefense and Environmental Applications" 2004. *Biosens. Bioelectron*. 20, 736-742.

[6] O. Niwa and H. Tabei, "Voltammetric Measurements of Reversible and Quasi-Reversible Redox Species Using Carbon Film Based Interdigitated Array Microelectrode", 1994. *Anal. Chem.* 66(2), 285-289.

[7] J. Li, J. Koehne, A. M. Cassell, H. Chen, Q. Ye, H. T. Ng, J. Han and M. Meyyappan, "Miniaturized Multiplex Label-Free Electronic Chip for Rapid Nucleic Acid Analysis Based on Carbon Nanotube Nanoelectrode Arrays", 2004a. *J. Mater. Chem.* 14, 676-684.

[8] J. Li, J. Koehne, A. M. Cassell, H. Chen, Q. Ye, H. T. Ng, J. Han and M. Meyyappan, "Bio-Nano Fusion in Sensor and Device Development", 2004b. *MCB 1* (1), 69-80.

[9] M. A. Guillorn, T. E. McKnight, A. Melechko, V. I. Merkulov, P. F. Britt, D. W. Austin, D. H. Lowndes and M. L. Simpson, "Individually Addressable Vertically Aligned Carbon Nanofiber Based Electrochemical Probes", 2002. *J. Appl. Phys.* 91 (6), 3824-3828.

[10] P. He and L. Dai, "Aligned Carbon Nanotube-DNA electrochemical Sensors", 2004. *Chem. Commun.*, 348-349.

[11] Y. H. Yun, V. Shanov, M. J. Schulz, Z. Dong, A. Jazieh, W. R. Heineman, H. B. Halsall, D. K. Y. Wong, A. Bange, Y. Tuf and S. Subramaniam, "High Sensitivity Carbon Nanotube Tower Electrodes", 2006. *Sens. Actuators B 120*, 298-304.

[12] P. V. Gerwen, W. Laureyn, W. Laureys, G. Huyberechts, M. O. D. Beeck, K. Baert, J. Suls, W. Sansen, P. Jacobs, L. Hermans and R. Mertens, "Nanoscaled Interdigitated Electrode Arrays for Biochemical Sensors", 1998. *Sensors and Actuators B*, vol. 49, 73-80.

[13] F. Patolsky, G. Zheng and C. M. Lieber, 2006. "Fabrication of Silicon Nanowire Devices for Ultrasensitive, Label-Free, Real-Time Detection of Biological and Chemical Species", *Nat. Protocols 1*, 1711-1724.

[14] N. Yang, H. Uetsuka, E. Osawa and C. E. Nebel, "Vertically Aligned Diamond Nanowires for DNA Sensing", 2008. *Angew. Chem. Int. Ed. 47*, 5183-5185.