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Acid Etch Study of Vertically Aligned Carbon Nanofibers (VACNFs)

Zhuxin Dong*, Uchechukwu C. Wejinya, Siva Naga Sandeep Chalamalasetty, Mathew R. Margis and Theodore G. Duensing

Abstract— **One of the major limitations in the development of ultrasensitive electrochemical biosensors based on one dimensional nanostructures is the difficulty involved with uniform growth of the nanofibers. Fabrication of the Vertically Aligned Carbon Nano Fibers (VACNFs) involve treatment of several chemicals including a variety of etchants. In previous work, successful measurement and characterization of electron beam patterned VACNFs is demonstrated using Atomic Force Microscopy. Also the effect of most commonly used etchant i.e. HF is studied. In this paper, the effect of acid etching on VACNFs is observed and characterized using a highly sensitive and precise Atomic Force Microscopy (AFM). Furthermore, statistical analysis is performed on AFM data to demonstrate data confidence and verify experiments.**

Index Terms – Carbon Nanofiber, Acid etch, Atomic Force Microscopy, Nanomaterials

I. INTRODUCTION

IT has been known for over a century that filamentous carbon can be grown by catalytic decomposition of a carbon source onto a metal surface. In a US patent published in 1889 [1], it is narrated that carbon filaments are grown from carbon containing gases using an iron crucible. Despite of the high probability that this early material is a carbon nanofiber and due to the lack of appropriate tools to verify this observation, scientists waited until the invention of high resolution microscope to verify the observation. Research works through the 1950s have shown that filamentous carbon can be grown onto a heated metal surface using a variety of hydrocarbons, other gases and metals the most effective of which were the iron, cobalt and nickel. In 1985, Buckminster fullerene C_{60} was discovered by team headed by Kroto [2] followed by the illustration of IIjima [3] that carbon nanotubes are formed during arc discharge synthesis of C_{60}. Throughout the evolution, detection of diseases and their causing pathogens have become a big challenge for the researchers. Initially, researchers used to rely on indicator organisms for predicting the disease. But researchers have concluded that use of indicator organism is no more a safe practice for quantification [4]. Thus the need for fast, reliable, ultrasensitive, portable and automated devices has increased. Advances in microfabrication technology have provided electrode configurations such as microelectrode arrays [5] and interdigitated arrays (IDA) [6], but their performance can be further enhanced by miniaturizing to nanoscale. Recent progress in nanofabrication technologies like electron beam lithography and nanoimprinting enable fabrication of one dimensional nanostructure electrodes, 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. Among various types of one-dimensional nanoscale electrodes, 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 [15-16]. One hindrance in miniaturization of devices based on VACNFs is their inability to grow uniformly. After the first successful development of carbon nanofibers, many researchers have proposed and grown the fibers using different techniques. Of these, catalyst enhanced Plasma Enhanced Chemical Vapor Deposition (PECVD) is the most common. Yet the methods need refinement in order to grow fibers of uniform shape and size. With an increase in the number of ways that are available for the fabrication of Vertically Aligned Carbon Nanofibers (VACNFs), the need for the advanced microscopic analysis tools has increased. From a close look into the fabrication methodologies, it can be inferred that as a part of end operations, substrate chip including fibers is treated with several etchants which can either react or leach the substances that are present over the surface of the substrate or the substrate itself. Hence end operations like etching might play a predominant role in the development of fibers with uniform characteristics.

II. ATOMIC FORCE MICROSCOPY

Atomic Force Microscope (AFM) is a very high resolution type of scanning probe microscope that has

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*Corresponding Author: Zhuxin Dong is with Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (phone: 479-575-6821 fax: 479-575-6982 e-mail: dzhuxin@uark.edu).

Uchechukwu C. Wejinya is with the Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (e-mail:uwejinya@uark.edu).

Siva Naga Sandeep Chalamalasetty is with Department of Microelectronics-Photonics, university of Arkansas, Fayetteville, AR 72701 USA (e-mail: schalama@uark.edu)

Matthew R. Margis is with the Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (e-mail: mrmargis@uark.edu).

Theodore G. Duensing is with the Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (e-mail: tduensin@uark.edu).

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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, non-contact mode, tapping mode, and phase imaging. 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 rather than a vacuum sealed environment, the Atomic Force Microscope aids many studies in biological macromolecules, tribiology, optical and imaging sciences. Owing to the advantages stated above, AFM is capable enough to complete the size measurement of the nanofibers and cavities.

III. FABRICATION OF UNETCHED AND ETCHED 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 steps of the fabrication process of both Unetched and etched are shown in Fig. 1. 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

Electron beam evaporation is used to deposit a 200 nm thick Cr film and then the wafer is immersed in acetone forone hour. Once removed from the acetone, the wafer is sprayed with methanol and isopropyl alcohol and blown dry with N_2.

B. Growth of CNFs

The next step is growing the VACNFs on the nickel dots that were created in step B. The growth is DC- biased PECVD growth. At a processing pressure of 6.3 mbar, plasma power of 180W and 700 degrees Celsius, 125sccm C_2H_2 feedstock and 444sccm NH_3 diluents were initiated. Then a five minute thermal annealing at 600 degrees Celsius is carried out following with 250 sccm NH_3. To attain the growth temperatures and thermal anneal needed, a 60 degree Celsius per minute incline was used. Each individual CNF vertically arranged to freestand on the surface with Ni catalyst on each tip. To check and affirm the process was done correctly, a fifteen minute deposition was conducted. Average results included a height of 1.5 microns, 100 nanometer base diameter, and 70 nanometer tip diameter. The uniformity of the growth was then checked by SEM.

C. Deposition of Silicon Dioxide

PECVD of silicon dioxide is managed next. To passivate the sidewalls of each individual fiber, a 3 micron SiO_2 layer was deposited onto the wafers using a pressure of 3Torr, temperature of 400 degrees Celsius and RF power of 1000W. The process included a parallel plate, dual RF, PECVD using a mixture of 6000 sccm of O_2 and 2-3 ml/min of tetraethlyorthosilicate (TEOS). A highly conformal coating of SiO_2 was created on the newly created fibers and interconnects.

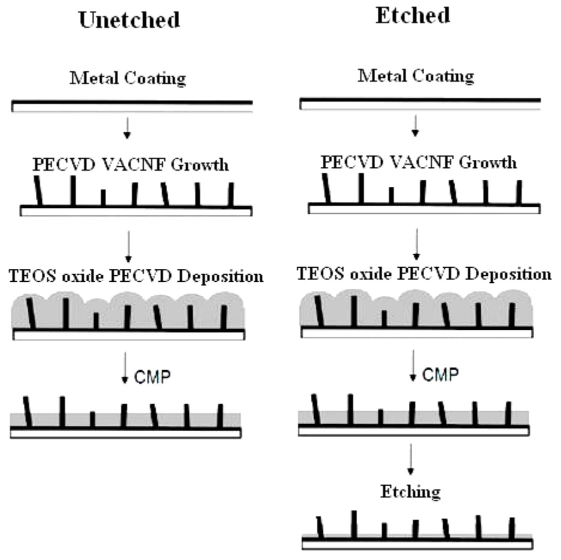

Fig. 1. Schematic showing the steps involved in unetch and etch fabrication of VACNFs.

D. Chemical Mechanical Polishing

By CMP, existing of stock removal and final polish, the overrun oxide and a portion of the VACNF's are removed. This process involved removing the existing material with 0.5 m alumina (pH 4) at 10 ml/min, 60-rpm platen, 15-rpm carrier, and 15 psig down force at 150nm/min. A 0.1 µm alumina (pH 4) at 10 ml/min, 60-rpm platen, 15-rpm carrier, and 25 psig down force was operated for final polish at 20nm/min. The wafer was 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. The aim to re-expose the VACNF tips was carried out as well as planarization of the surface.

Figure 1 shows the schematic of the fabrication steps involved in the unetched and etched substrate preparation.

From the schematic it is clear that all the fabrication steps are the same for both unetched and etched except that after fabrication, etchant is used for the etch substrate.

IV. CHEMICAL PREPARATION AND TREATMENT

A. *Chemicals Preparation*

1. HCl: Standard 5N stock solution is purchased from the VWR and is used directly for the treatment.

2. H_2SO_4: 5N solution is prepared from the 10N stock solution by adding acid to the water.

3. HF solution: 0.1N solution which is used directly from the stock solution

B. *Etching*

Standard Etching procedure is employed by wet bench etch method using the acids and then treating the sample for 5 min

C. *Etch rate Calculation*

In order to determine the effect of the etchant over the carbon nanofibers and the silicon dioxide, we calculate the etch rate using the equation (1). Higher the etch rate higher is effect of the etchant over the carbon nanofibers and it cannot be employed for etching the surface of the Si wafer.

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

V. EXPERIMENTAL SETUP

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.

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 light microscope, we tried to see the surface over the unetched and etched substrate. The surface looks like as shown inset of Fig. 2.

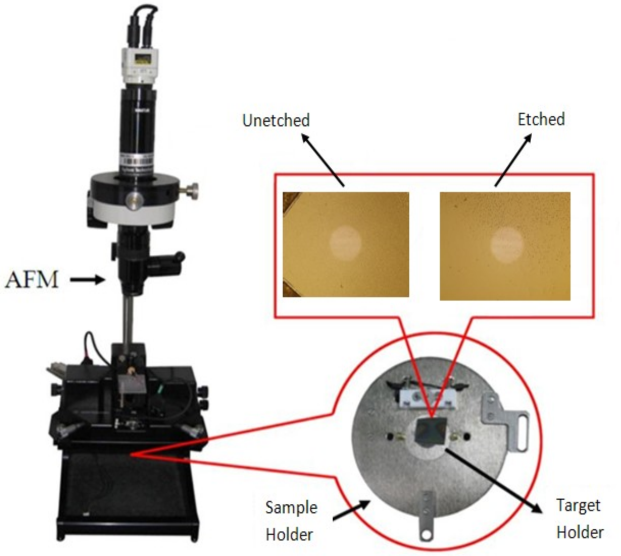

Fig. 2. AFM-based experimental setup showing the sample holder and chips for scanning and characterization.

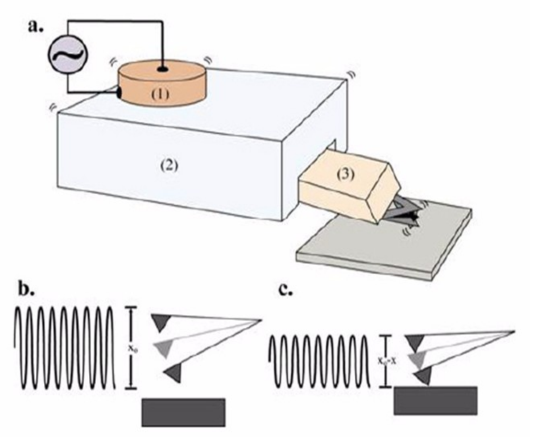

Fig. 3. Scan in AC mode: a. tip under sinusoidal motion (1) AC from nose cone, (2) the base body of cantilever, (3) cantilever with tip; b. oscillation amplitude driven by (1); c. reduction from the interaction with sample as a feedback signal to maintain constant amplitude.

VI. EXPERIMENTAL RESULTS

A. *Scanning and Measurement*

After the treatment with the etchant, 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 etchant 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 is specifically selected in which we felt there are definite nanofibers and is zoomed. 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.

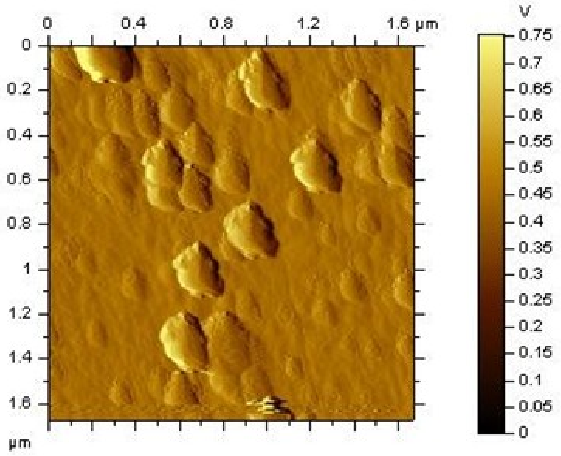

Fig. 4. 2-D image of the unetched surface showing the VACNFs.

Figure 4 is a scan 2-D image of unetched substrate from the AFM. The dots which are seen over the surface are supposedly the VACNF's. The presence of VACNFs on the image shown in Fig. 4 cannot be verified immediately until the 2-D image is converted into a 3-D image where it can be clearly seen that there are VACNFs as some hills over the surface.

Fig. 5. A 3-D view of VACNFs over unetched substrate surface.

Figure 5 is a 3-D view of the Fig. 4. Here, the hills on the surface can be clearly visualized. These hills are none other than the VACNFs. Once the VACNFs are recognize over the surface, dimensional analysis (height and diameter) is conducted on the nano fibers using the highly sensitive AFM.

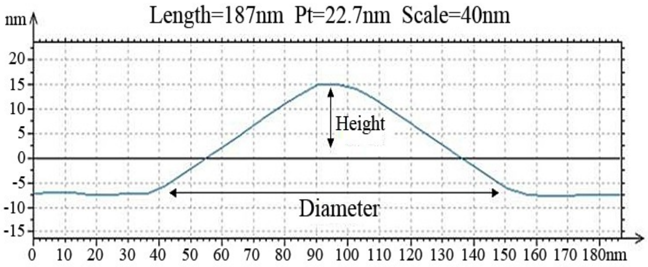

Fig. 6. Cross section information for measurement based on line crossing (unetched).

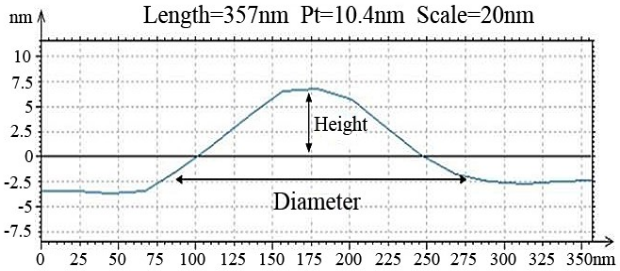

Fig. 7. Cross section information for measurement based on line crossing (HF etched).

Figures 6 and 7 shows the graphical representation of the nano fibers over the unetched and etched surface. This figure is obtained by drawing a line across the fiber in Fig. 4. This line gives a profile of the height. The peak is clearly seen in the figure. This peak corresponds to the VACNF. The distance between the base points gives the diameter while the distance from the base line to peak will be the height. Fiber dimensions are independent of the tip width.

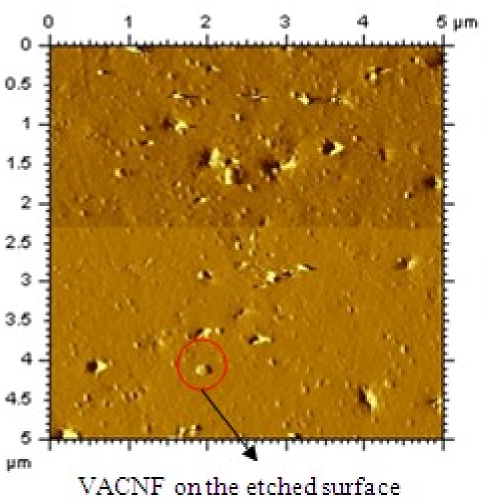

Fig. 8. 2-D view of the HF Etched surface using AFM.

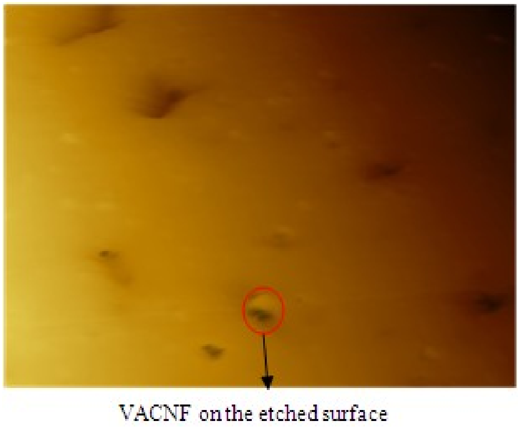

Fig 9. 3-D view of VACNF's over the HF etched surface.

Figure 8 shows 2-D scan of 5 x 5 µm^2 area of the HF etched substrate. From the figure it can be inferred that the HF not only affected the VACNF but also affected the substrate surface as well. Once the surface topology is obtained, it can be zoomed further to get a clear view of the fibers. Figure 9 shows 3-D view of HF etched substrate surface. The height of the fiber is affected by the etchant and from the figure it is clearly observed.

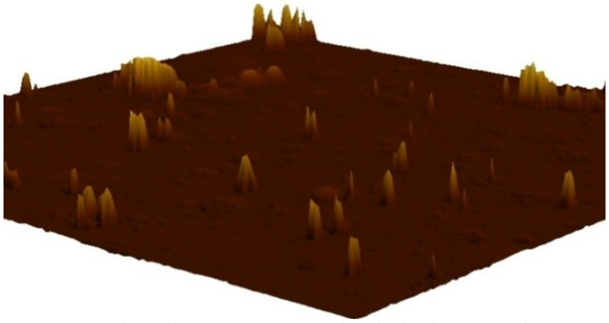

Fig. 10. A 3-D view of VACNFs over HCl etched substrate surface.

Figure 10 shows 3-D view of HCl etched substrate surface. The peaks have become sharper and there is a decrease in the height and diameter as well.

TABLE I
DIAMETER MEASUREMENTS OF UNETCHED HF ETCHED AND HCL ETCHED CHIPS

Measurement No.	Unetched Diameter	HF Etched Diameter	HCl Etched Diameter
1	126.28	140.9	147.01
2	145.85	143.7	195.95
3	150.89	155.8	192.1
4	161.21	165.08	202.31
5	162.25	168.32	158.7
6	172.77	175.56	152.56
7	173.01	176.65	205.43
8	179.25	176.87	187.42
9	179.8	177.73	158.1
10	180.4	178.3	165.71
11	181.08	178.43	177.12
12	181.86	179.07	153.8
13	183.2	179.37	208.97
14	183.47	182.41	178.4
15	184.6	187.342	196.73
16	186.26	187.87	178.13
17	188.39	188.87	213.95
18	188.51	190.5	146.91
19	188.98	191.2	178.91
20	189.36	191.38	197.21
21	189.57	193.51	215.09
22	191.33	193.74	185.36
23	192.43	194.5	170.55
24	193.51	194.5	175.45
25	194.59	194.55	192.95

All dimensions are in nm.

TABLE II
HEIGHT MEASUREMENTS OF UNETCHED HF ETCHED AND HCL ETCHED CHIPS

Measurement No.	Unetched Height	Height after HF etch	Height after HCl etch
1	10	5.1	8.3
2	10.01	5.5	7.3
3	10.3	5.5	11.5
4	11.8	5.6	7.8
5	11.9	5.6	8.7
6	12.4	5.8	6.6
7	12.4	5.9	7.4
8	12.6	5.9	7.4
9	12.7	5.9	7.1
10	12.8	5.9	6.6
11	12.8	5.9	6.4
12	13.2	6.1	6.9
13	13.7	6.2	7.1
14	13.7	6.2	7.5
15	13.8	6.3	9.5
16	14.5	6.4	6.3
17	14.5	6.4	9.3
18	15.1	6.4	5.4
19	15.3	6.5	4.3
20	15.3	6.7	5.8
21	15.4	6.7	7
22	15.5	6.7	9.9
23	15.5	6.8	16.6
24	15.6	6.8	8
25	15.8	6.9	6.6

All dimensions are in nm

TABLE III
DIMENSIONS AND ETCH RATES OF UNETCHED HF ETCHED AND HCL ETCHED CHIPS

Etchant Used	Average Diameter	Average Height	Etch rate (height) nm/min
None / unetched	204.66	20.44	-
HCl	180.62	10.86	-1.92
HF	205.51	8.40	-2.4

Average height and diameter are in nm.

Tables I and II show the summarized results from the AFM measurement of 75 nanofibers. Table III shows the average values of the total 75 measurements and the etch rate of the fibers. The results are statistically analyzed and discussed.

B. Statistical Analysis

The recorded observations from the Atomic Force Microscopy are tabulated in Tables I and II. In statistics, a confidence interval (CI) is an interval estimate of a population parameter. Instead of estimating the parameter by a single value, an interval likely to include the parameter is given. Thus, confidence intervals are used to indicate the reliability of an estimate. Therefore, we apply this statistical method to our experiment to obtain the interval to describe the size of fibers. We will consider 95% confidence for the purpose of our calculation.

The mean diameters of unetched and etched are 205.529 nm and 205.509 nm respectively while their standard deviations are 25.03 and 28.14 respectively. We can calculate the confidence interval using equation (2) [17].

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

Where, $\overline{\mathrm{X}}$ 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.

Therefore for the unetched with a mean diameter of 205.529nm and standard deviation of 25.03, confidence interval is [199.86 nm, 211.19 nm] while for the HF etched with a mean diameter of 205.529 nm and standard deviation of 28.14 is [199.16 nm, 211.86 nm]. Similarly calculating the confidence intervals for heights of unetched and HF etched, we get [18.78 nm, 22.06 nm] and [7.73 nm, 9.08 nm] respectively. A summary of the calculated confidence intervals, mean and standard deviation for all unetched and etched chips is shown in Table IV.

TABLE IV
CALCULATION RESULTS OF CI FOR THE SIZES OF UNETCHED AND ETCHED 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
HF ETCHED	DIAMETER	[199.16 211.86]	205.51	28.14
	HEIGHT	[7.73 9.08]	8.40	2.99
HCL ETCHED	DIAMETER	[176.14 185.1]	180.62	20.45
	HEIGHT	[9.92 11.8]	10.86	4.28

All dimensions are in nm.

C. *Result Discussion*

From the surface topography images of the AFM shown in Figs. 5, 9 and 10, it is clearly evident that different etchants have different effects over the surface of the substrate. From Table III it can be inferred that while HF has only effect over the nanofiber height, HCl has effect on both nanofibers height and diameter. At the same time it should be noted that the height decrease in the case of the HCl is less compared to that of HF etch.

VII. CONCLUSION

Micro fabrication enables the development of miniaturized tools for different applications. However, from the present study it can be concluded that different etchants have reduced the height and diameter of the VACNFs to different extent. Since height is of prime importance when it comes to sensor development, we should choose an etchant which has little or no effect on the nanofiber height. It can be concluded that the fiber height is less changed in HCl etch compared to HF etch. Hence we recommend an alternative etchant i.e., HCl in lieu of Hydrogen Fluoride (HF) for etching over the Carbon Nanofiber grown substrates.

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