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Characterization of Etched and Unetched Vertically Aligned Carbon Nanofibers (VACNFs) Using Atomic Force Microscopy

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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. In this paper, the effect of etchant on VACNFs dimension (height and diameter) is observed and characterized using a highly sensitive and precise Atomic Force Microscopy (AFM). Furthermore, statistical analysis is performed on AFM measured data to demonstrated data confidence.**

I. Introduction

T has been known for over a century that filamentous carbon Ican 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 with the increase in awareness of the diversity exhibited by microbes, 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. Newer methods involving immunofluorescence techniques and nucleic acid analysis provide valuable opportunities for rapid and more specific analytical methods. Particularly, electrochemical (EC) biosensors are attractive for detecting a wide range of species, including proteins, nucleic acids, small molecules and viruses because of their relative simplicity, portability, low cost and low power requirement. EC biosensors consist of two primary components: a recognition layer containing a biomolecule and an electrochemical signal transducer. They make use of electrochemical reactions or the surface property changes upon target binding. 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]. Compared to other carbon materials such as glassy carbon, carbon black, carbon microfibers, and pyrolytic graphite, the open-ended VACNF arrays present well-defined edgeplane structure suitable for selective covalent functionalization of primary amine-terminated oligonucleotide probes. 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.

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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 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 photo detector 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. 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 nanofibers and cavities.

III. Fabrication of Unetched And Etched VACNFs

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 for one 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 freely stand on the surface with Ni catalyst on each tip. To check and affirm the process was done correctly, a fifteen minute deposition was conducted. The 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 SiO2 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 SiO2 was created on the newly created fibers and interconnects.

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 20 nm/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.

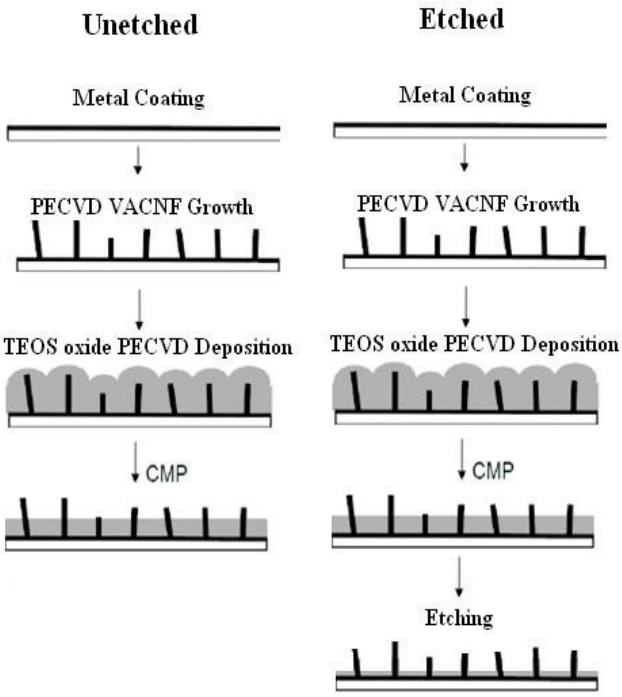

Fig. 1. Schematic showing the steps involved in unetch and etch fabrication of VACNFs

Figure 1 shows the schematic of the fabrication steps involved in the unetched and etched substrate preparation. It is clear from the schematic 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. Experimental Setup

In order to accurately determine the height and diameter of the VACNFs on the etched and unetched substrates, a highly sensitive Atomic Force Microscope (AFM) is employed. The AFM used in the experiment is the Agilent 5500-ILM microscope shown in Fig. 2. The scanning and characterization is done under Acoustic AC (tapping) 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. 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 will be placed over the target holder and is placed in the microscope for scanning. By using a light microscope, we tried to see the surface over the unetched and etched substrate as illustrated in the inset of Fig. 2.

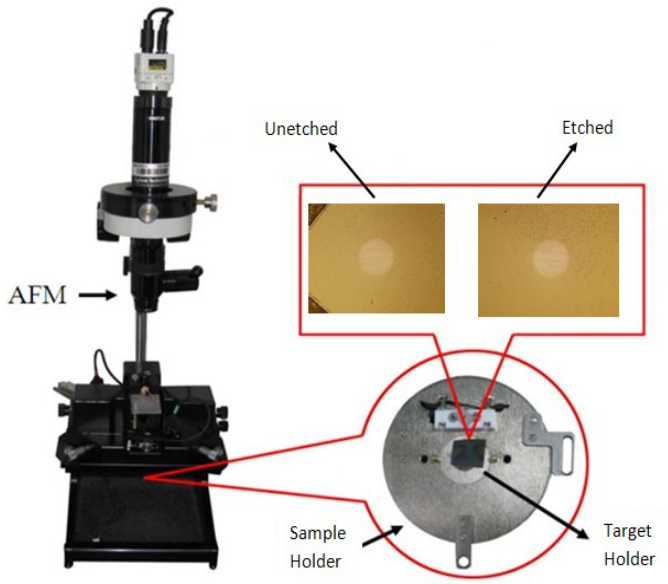

Fig. 2. AFM-based experimental setup showing the sample holder and chips for scanning and characterization

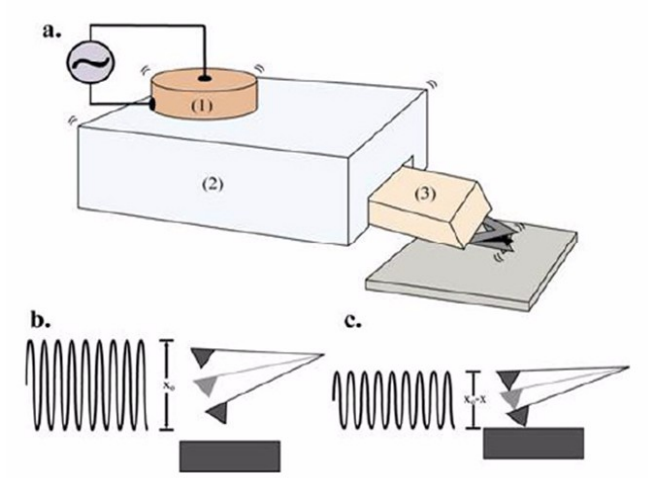

Fig. 3. AFM probe motion under Acoustic AC Mode: a. (1) AC applied to the nose cone; (2) the base body of the cantilever beam; (3) the cantilever bean with its tip; b. & c. the cantilever driven to oscillate in sinusoidal motion.

As shown in the Fig. 3, as the tip approaches the surface, there will be a change in the frequency of wave. Computer software is used to record the changes in wavelength and convert it to real time surface topography.

V. Experimental Results

A. Scanning and Measurement

Before measuring the size (height and diameter) of the etched and unetched VACNFs, their location should be determined. Thus, we scan a 5 µm x 5µm square area in the middle of the chip. After locating the fibers in the scanned area, we zoom into a 2µm square area, which encloses the identified fiber tips to obtain clear scan image and guarantee a better and more accurate measurement. When a fiber appears clear in a scan topography image, a straight line is drawn in any direction in the 2-D 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 array of fibers.

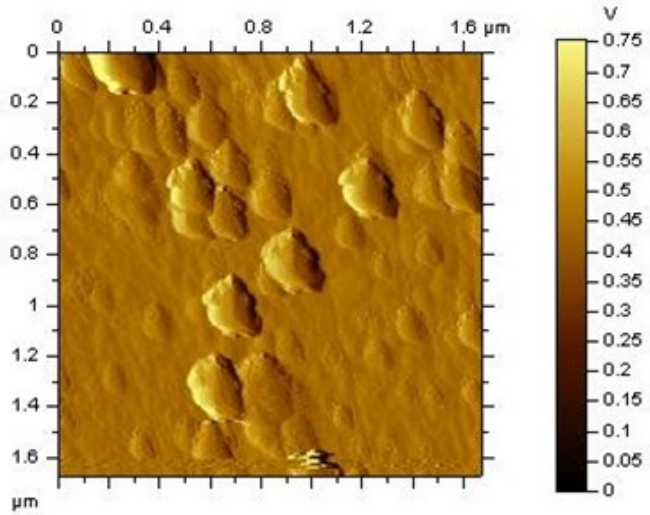

Fig. 4. 2-D image of the unetched surface showing the VACNFs

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 VACNFs. 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.

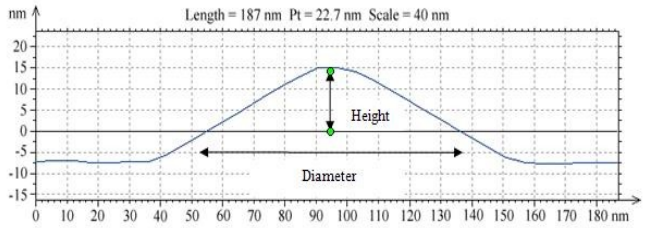

Fig. 6. Cross section information for measurement based on line crossing (unetched)

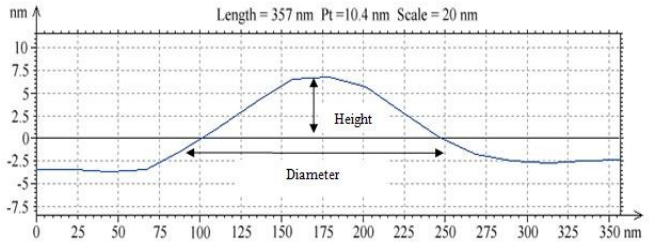

Fig. 7. Cross section information for measurement based on line crossing (etched)

Figures 6 and 7 shows the graphical representation of the nanofibers over the unetched and etched surfaces respectively. These figures are 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 and it corresponds to the VACNF. The distance between the base points gives the diameter while the distance from the base line to peak is the height. The fiber dimensions are independent of the tip width.

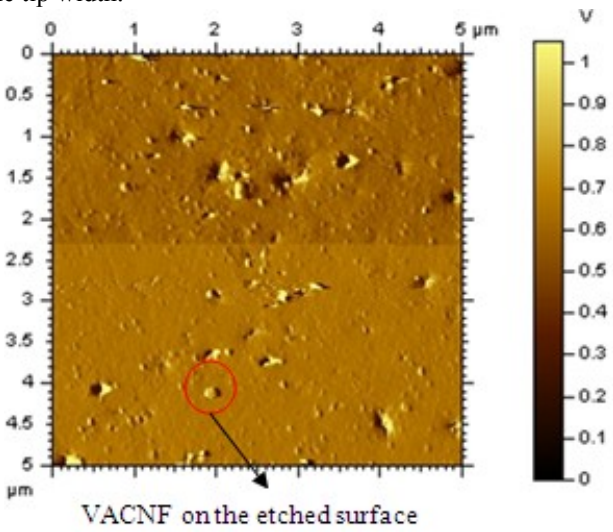

Fig. 8. 2-D view of the Etched surface using AFM

Figure 8 shows 2-D scan of 5 x 5 μm^2 area of the etched substrate. From the figure it can be inferred that the etchant 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.

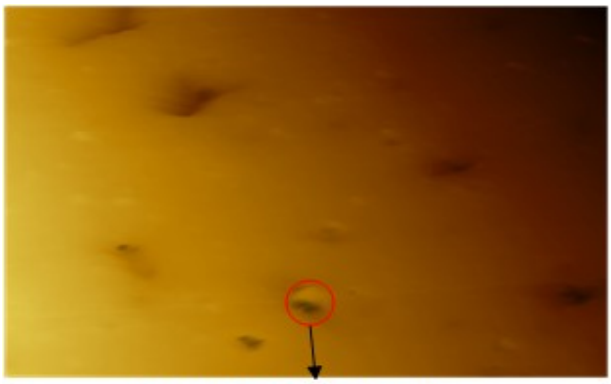

Fig. 9. 3-D view of VACNF's over the etched surface

Figure 9 shows 3-D view of etched substrate surface. The height of the fiber is affected by the etchant and from the figure it is clearly observed.

TABLE I
DIAMETER AND HEIGHT MEASUREMENTS OF UNETCHED AND ETCHED CHIPS

Measure #	Unetched Diameter	Etched Diameter	Unetched Height	Etched Height
1	126.28	140.9	10	5.1
2	145.85	143.7	10.01	5.5
3	150.89	155.8	10.3	5.5
4	161.21	165.08	11.8	5.6
5	162.25	168.32	11.9	5.6
6	172.77	175.56	12.4	5.8
7	173.01	176.65	12.4	5.9
8	179.25	176.87	12.6	5.9
9	179.8	177.73	12.7	5.9
10	180.4	178.3	12.8	5.9
11	181.08	178.43	12.8	5.9
12	181.86	179.07	13.2	6.1
13	183.2	179.37	13.7	6.2
14	183.47	182.41	13.7	6.2
15	184.6	187.342	13.8	6.3
16	186.26	187.87	14.5	6.4
17	188.39	188.87	14.5	6.4
18	188.51	190.5	15.1	6.4
19	188.98	191.2	15.3	6.5
20	189.36	191.38	15.3	6.7
21	189.57	193.51	15.4	6.7
22	191.33	193.74	15.5	6.7
23	192.43	194.5	15.5	6.8
24	193.51	194.5	15.6	6.8
25	194.59	194.55	15.8	6.9

All dimensions are in nm.

Furthermore, the above procedures are used to characterize the height and diameter of fiber of the etched substrate by crossing a line over the nanofiber. Figure 7 shows the graphical representation of a VACNF over the etched substrate. The diameter and height can be measured as was the case for the unetched fiber.

Table I shows the results from the AFM measurement of 75 nanofibers. The results are statistically analyzed as discussed below.

B. Statistical Analysis

The recorded observations from the Atomic Force Microscopy are tabulated in Table I. 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. How likely the interval is to contain the parameter is determined by the confidence level or confidence coefficient. 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 the following equation [17].

$$CI = [X - Z \times \frac{\sigma}{\sqrt{N}}, X + Z \times \frac{\sigma}{\sqrt{N}}] \quad (1)$$

Where, 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 etched with a mean diameter of 205.529nm and standard deviation of 28.14 is [199.16 nm, 211.86 nm]. Similarly calculating the confidence intervals for heights of unetched and 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 both unetched and etched chips is shown in Table II.

TABLE II
RESULTS OF CI FOR THE SIZES OF UNETCHED AND ETCHED FIBERS

		CONFIDENCE INTERVAL	MEAN	STANDARD DEVIATION.
UNETCHED	DIAMETER	[199.86 211.19]	205.529	25.03
	HEIGHT	[18.78 22.06]	20.42	7.23
ETCHED	DIAMETER	[199.16 211.86]	205.509	28.14
	HEIGHT	[7.73 9.08]	8.40	2.99

All dimensions are in nm.

C. Result Discussion

Based on the surface topography in Figs 4 and 8, we can clearly see that there is a large decrease in the number of fibers for unetched and etched samples. Also cavities appeared in the etched substrates while there aren't any in the unetched confirming that the etchant has effect on the surface of the substrate. If we observe the data collected from the AFM, the average height of the unetched to etched changed from 20.422 nm to 7.23 nm while the diameters of unetched to etched are at 205.53nm and 205.51nm respectively indicating that height is largely effected by the etchant.

VI. Conclusion

Micro fabrication enables us to develop miniaturized tools for different applications. However, from the present study we can conclude that etchant has reduced the height of the VACNFs though the diameter almost remains the same indicating that it has impact on the fiber. Hence we recommend an alternative etchant in lieu of Hydrogen Fluoride (HF) for etching over the Carbon Nanofiber grown substrates.

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