Selective Isolation of Single-Walled Carbon Nanotubes using AFM Lithography

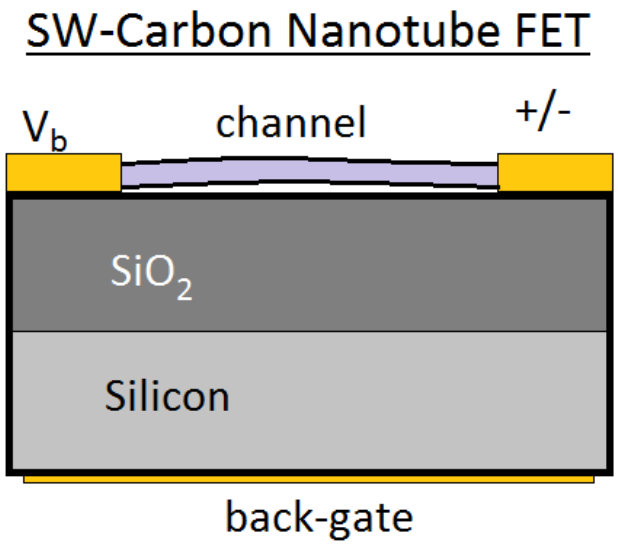
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Abstract

In nanotechnology, the single-walled carbon nanotube field effect transistor is a hot topic of research due to carbon nanotubes' unique and malleable electronic properties. In this study, an Atomic Force Microscope (AFM) is employed to manipulate small single-walled (SW) tubes. The goal of this project is to determine a general set of parameters for moving, manipulating, and cutting SW CNTs with and without a charged tip. The parameters developed may be valuable for FET fabrication and isolation of single tubes for research. While exploring parameters for such a task, several postulates about nanotubes were confirmed. Results show that SW CNTs can almost never be moved around, though they can be cut rather easily. The AFM tip, charged or not, provides enough electrostatic force to repel CNT electrons and cause a rupture in the tube, or a cut. The study provides general parameters for cutting nanotubes with a regular tip, a charged voltage tip, and compares the differences between the two.

Introduction

Carbon nanotubes are seamlessly wrapped graphene structures that exhibit unique electrical properties, making them useful in physics and nanotechnology. Carbon nanotubes, an allotropes of carbon, are unique in that they have semiconducting and super-conducting properties not common to other carbon materials. The complex nature of the hybridization in these cylindrical graphene structures constitutes a certain electron pathway that enables the 'tubes" to conduct (or not conduct) in accordance with their precise atomic arrangements. Because carbon nanotubes, commonly referred to as CNTs, have modulating conductance, they have become the basis of nano-scale Field Effect Transistors (FETs). Single-walled CNTs in particular are becoming widely popular because their small diameter (roughly 1 nm) enhances these unique electronic properties.



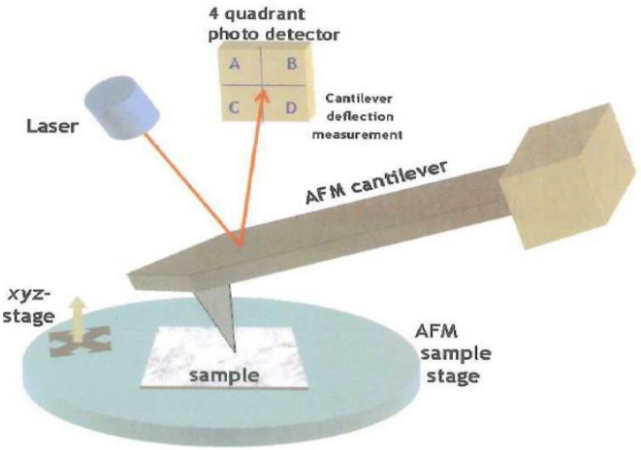
However, not all CNTs are semi-conducting. Only about 66% of every growth sample of carbon nanotubes is semi-conducting, while 33% is characteristically metallic. The two types of CNTs cannot be distinguished by their size or shape, and the difference in their electronic properties is the only thing that really sets them apart. The problem then arises of determining which nanotubes are metallic and which are semi-conducting through non-destructive methods. Several methods are being developed for purifying CNTs chemically to leave only the semi-conducting CNTs behind, but these are both painstaking and potentially harmful for the nanotubes. Alternately, FETs and other nano-devices can be made using a combination of both types of CNTs in parallel, but then the undesired type of CNT must be removed. Since the two types of CNTs have different electronic properties, it is necessary to isolate any given tube in order to produce consistent and functional FETs, or other nano-devices.

The Atomic Force Microscope

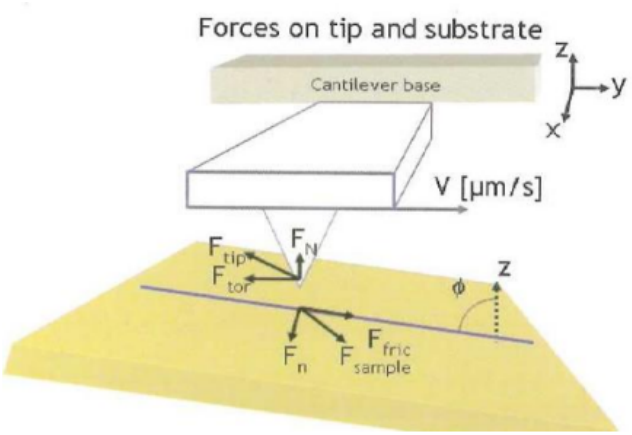
An Atomic Force Microscope (AFM) is an instrument which rasters a fine tip across a surface to measure topography at the nano-scale. Using an

AFM, single CNTs can ideally be located and even pushed around on a surface. Even though the semi-conducting CNTs look the same as metallic CNTs, they have different electronic behavior and thus may need to be isolated to a particular device. In this project, we will try to develop efficient parameters to cut, or even push, single walled carbon nanotubes using a metallic AFM tip
with a given voltage so that in the event that a tube is unwanted, we can "scratch" it aside using the AFM tip, allowing for clean and consistent devices with only one long, single walled CNT of the desired type to remain.

We would expect that a charged tip will make cutting SW CNTs far easier with respect to the threshold scan speed (how fast the tip rasters) and set point voltage (how low the tip goes). The charge repulsion between the charged tip and the nanotubes, we expect, will greatly affect how well, or efficient, cutting or rolling will be. The charge interactions should theoretically repel the two objects enough to either move the tube (small parameters), or destroy the connection and cut the tube (anything past the threshold limit). This experiment will fluctuate the scan speed, the set point, and tip voltage (voltage running through the tip) to develop these parameters and threshold limits.



[Ref. 5]

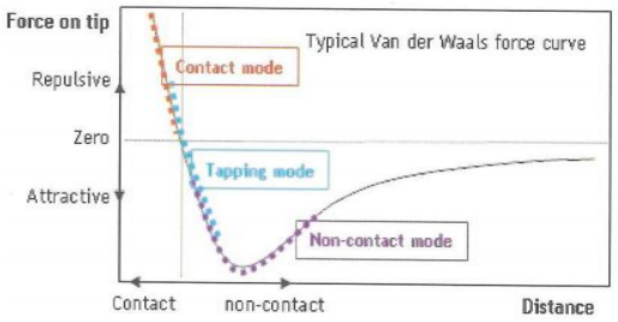


[Ref. 5]

A motivation for this is not only to increase the efficiency of the process, but also to explore the differences from using an uncharged tip. This electrical method would be less intrusive than any of the chemical methods developed, and provides a safe method of selectively isolating single-walled CNTs, whatever their type.

Lithography with the AFM (LPM capabilities)

Before investigating these parameters, it is important to first understand the forces acting on both the AFM cantilever tip as well as the nanotube itself. The standard force of this experiment is the electron repulsion between the nanotube and the tip. The force of repulsion between the two is inverse squares of their distances, though this cannot be calculated accurately due to the complex interactions of several atoms and molecules in the substrate as well as the force being a mixture of Van der Waal's mass forces and electron repulsion (Coulomb's Law). However, the AFM tip can be calibrated using its measured oscillation frequency. In other words, the laser of the AFM can measure how many times the cantilever tip is oscillating, calculate how much force is acting on the tip, and provide us with a numerical calibration of the electron repulsion or distance to the surface. The numerical value used is known as the "set point", and is generally measured in milli-volts (mV). Because we aim to move or cut the substrate, a single walled carbon nanotube, we want a repulsive force on the tip and thus use the AFM in "contact mode".

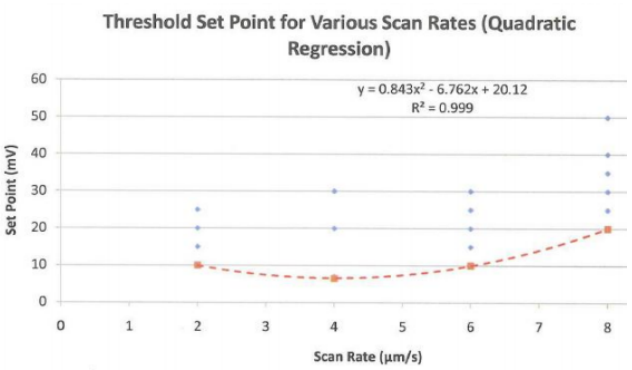


[Ref. 5]

In addition to the natural forces present, a significant electrical potential is introduced by running a wire through the conducting tip. This electrical potential results in additional electron repulsion. The potential is measured in milli-volts (mV) and is controlled using a
DAC board connected to the AFM. In addition to these two "force controllers," it is necessary to also consider the rate of scanning, or the speed of the restoring cantilever. The speed of the tip is calibrated in micrometers per second (µm/s). It should be expected that a high velocity tip will "miss the substrate" and do little work on the tube, while a low velocity tip will interact strongly with the tube. These three variables, the set point, tip voltage, and scan rate will help to create usable parameters to effectively manipulate single walled carbon nanotubes.

Manipulation without Tip Voltage

A general setting for cutting nanotubes is 8µm/s at a set point of +20 mV and tip voltage of 0 mV. Because tips with charged capabilities require more work to produce, most laboratories use regular AFM tips for lithography. Starting at these values, we worked our way down to find the threshold set points for different scan rates for cutting, and lowered the scan rate even further in attempt to find appropriate parameters to move them around. After heavy testing, it was determined that the movable parameter is far too small to accurately establish, though theoretically possible. The inability to effectively move tubes around can be explained by the static friction (Fs) between nanotubes and the surface, and nanotubes' well documented "sticky" nature. We were, however, able to determine the threshold set points for various scan rates quite easily. By performing quadratic regression on the data, the relationship V=.843(r2) – 6.762(r) + 20.12 was determined, where R is the scan rate and V is the threshold set point. The correlation coefficient, R2
(not to be confused with "r" that represents the scan rate), was .999, confirming the parabolic regression line.



The parabolic shape of the threshold scan rate--set point curve can be explained by the time of "contact" between the tip and the substrate. Very large scan rates, we can expect, require very large set points to make up for the tip's quick jerky motion that seems to "miss" the nanotube. However, this only accounts for the direct correlation between the threshold set point for a given scan rate. The portion left of the vertex can be explained by the small parameter for moving the tube around. We would expect that the slower the tip moves, the larger electrostatic force is required to cut the tube, rather than brushing over it or moving it around. It should be noted that a set point lower than +4 mV will have negligible effect on the nanotube, and thus cannot be accurately charted though it may still be possible to manipulate a tube inconsistently at extremely low scan rates.

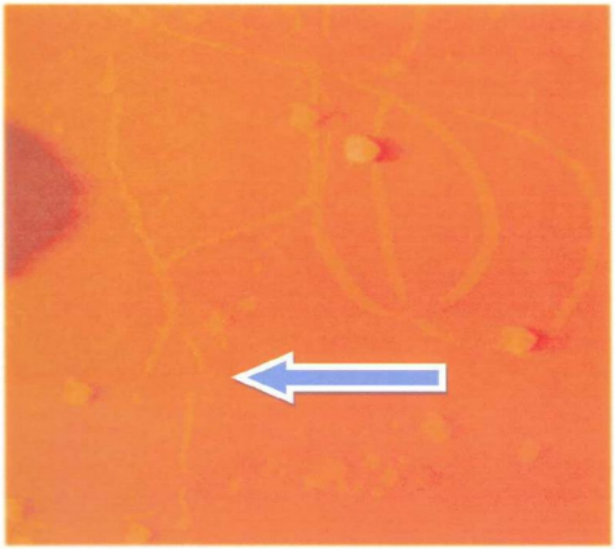


Figure 1 Scan #11 - Standard Lithography, 5 micron scan area

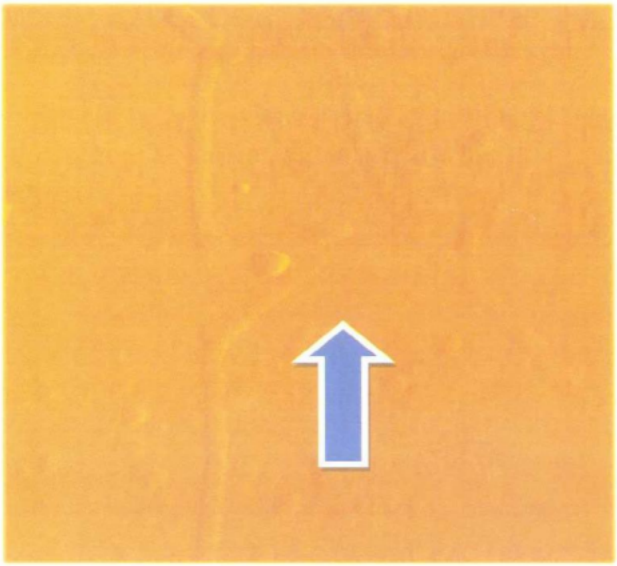


Figure 2 Scan #6 - Charged Lithography, 5 micron scan area

Manipulation with Tip Voltage

A charged tip, as we would expect, cuts nanotubes more efficiently than an uncharged tip due to the increased electrostatic interactions induced by the potential difference. Other factors such as cantilever length and tip shape, it would seem, may deem the comparison between the two inconsistent. The charged tip used in this experiment had a much longer length and wider base. Though this may seem like a significant issue, these factors are negligible because the tip does not usually come in physical contact with the tube. In other words, only the electrostatic forces present affect manipulation, regardless of the dimensions of the tip. After a couple general tests, a standard setting of 10 µm/s, +10 mV set point, and +10 mV tip voltage was determined to produce a clean cut. Starting from these values, we varied the set point and tip voltage to establish threshold cutting parameters. At this point, it is accepted that it is virtually impossible to move around nanotubes, especially with a potential difference on the tip, so we have ceased to pursue the small parameter.

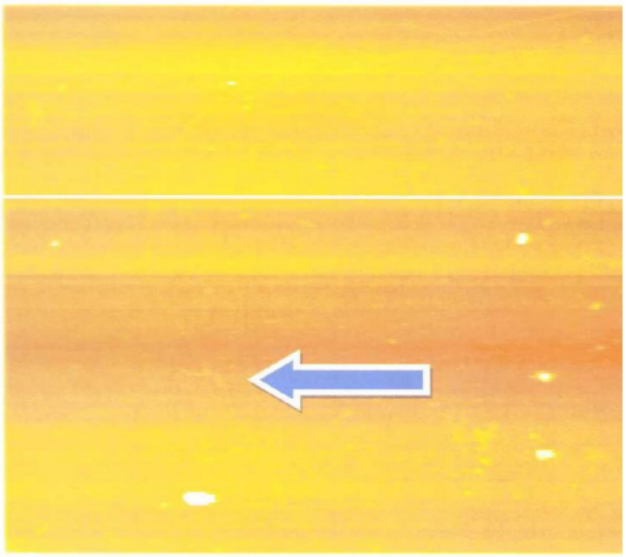
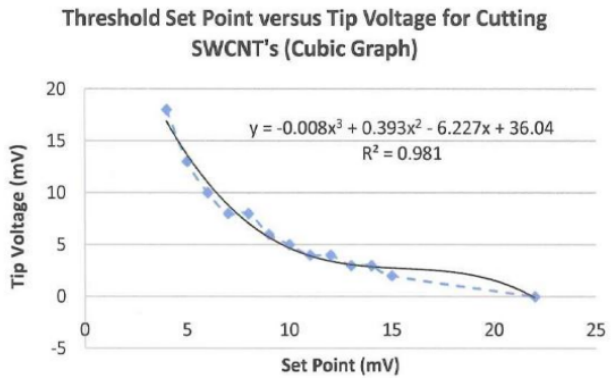


Figure 3 Scan #11 - Charged Lithography, 10 micron scan area

By measuring and plotting the threshold values for cutting nanotubes at a constant scan rate of 10 µm/s, an inverse relation between the set point and the required tip voltage was established. The graph of this data, while it reveals the relationship between the two parameters and perhaps insight into what sort of values to use, presents more questions as to what type of interactions are occurring on the substrate. The inverse relation was expected, but modeling the curve is far more difficult. Several different function regressions were performed on the threshold data points with varying results. The correlation coefficient for linear regression is .7706, which tells us that the two values are probably not

related linearly. The coefficients for the quadratic and cubic regressions are .9403 and .9816 respectively. Regressions of high power polynomial functions resulted in larger coefficients (closer to 1), but it is highly unlikely that these types of functions model the electrostatic interactions between an AFM tip and a carbon nanotube substrate. The most reasonable model for this experiment is a cubic relation, though in reality the interaction is probably an augmentation of two quadratic functions.



Results

It was observed that single walled carbon nanotubes were cut by an uncharged AFM tip at a lower set point voltage when the scan rate was small, around 4 µm/s. As the scan rate increases, the required set point also increases to account for the moving tip and the time interval over which the tip would do work on the tube. However, an interesting outcome that was overlooked in the hypothesis was discovered; as the scan rate becomes very small, below 4 µm/s, the required set point voltage to cut the tube increases. This can be explained by the fact that very slow scan rates will tend to “push” the tube rather than cut it due to the friction between the nanotube and the surface. The electrostatic force is provided is not enough to overcome the static friction (Ks) of the nanotube surface interface. The resulting curve of the data is almost a perfect parabola, which agrees with the above explanation.

In addition, it was established that when nanotubes are cut by a charged AFM tip, at a constant scan rate, the threshold tip voltage varies inversely with the given set point. Note that a higher set point means a larger repulsive force, and therefore a smaller distance to the substrate. The relation makes sense, because a larger repulsive force provided by the tip itself varying the distance (set point) can make up for a very small tip voltage. No adequate curve was determined to fit the data, but a cubic function most reasonably models this experiment.

Further Research

This paper only studied the relationship between the three variables set point, scan rate, and tip voltage. There are several possible extensions of this project, such as a study that develops a standard equation modeling ideal AFM cutting. In addition, only integer values were used as variables, while it may be the case that the threshold occurs at a defined decimal value; further research can encompass this possibility and test for threshold parameters more accurately. The model for the variation between tip voltage and set point is also yet to be determined based on concrete evidence.

Lithography is not the extent of nanotube research involving AFM technology, however. One possible research topic would be the electronic characterization of single walled carbon nanotubes as metallic or semi-conducting. While cutting nanotubes is useful, it is somewhat meaningless unless a chip fabricator knows already which tube he or she needs to cut. Identifying the conducting character of carbon nanotubes is extremely useful because it allows a device fabricator to select which nanotubes to keep or remove using AFM lithography.

Acknowledgments

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