

# **FABRICATION AND PROPERTIES OF RAPID THERMALLY PROCESSED CARBON NANOFIBERS**

NSF Summer Undergraduate Fellowship in Sensor Technologies  
Santiago Serrano (Electrical Engineering) - Drexel University  
Advisors: Dr. Jorge J. Santiago-Aviles, Yu Wang

## **ABSTRACT**

The fabrication and properties of carbon nanofibers are interesting because of the fiber's expected conductivity properties. If we can successfully control the fabrication and manipulation of carbon nanofibers we should be able to build nanoscale electronics. In this attempt, we have been able to successfully control some of the properties for the fabrication of nanofibers. Carbon nanofibers were obtained by electrospinning a polymer solution, polyacrylonitrile, and then heating it on a vacuum furnace. Thermal analysis helped us determine the minimum heating temperature that the fibers must be exposed to obtain carbon fibers. The relationship between voltage, and the amount of solvent, with the thickness of the fibers was studied using a scanning electron microscope. A strongly non-linear relationship between the voltage and the thickness suggests a sinusoidal relationship. On the other hand, a linear relationship between the amount of solvent and the inverse of the thickness was observed. The resistivity of a single carbon fiber was studied; its total resistance agreed with the sum of the resistances of smaller sections. This implies that the resistance along the carbon fiber is linear. Raman microscopy established the chemical bonding of the carbon nanofibers as a function of the heating temperature.

## **1. INTRODUCTION**

The fabrication and properties of carbon nanofibers are interesting because of the fibers' expected conductivity properties. Carbon nanotubes and thin films are extremely good conductors [1,2]. The problem with nanotubes is that they are not easily obtainable, their structure cannot be controlled, and results cannot be repeated. Thin films have problems too: they are not thin enough, a circuit cannot be built with them, among others. In contrast, carbon nanofibers are very thin, the results can be reproduced, and they are easier to manipulate than nanotubes.

Polyacrylonitrile (PAN) has been widely used as a precursor for carbon fibers. Because PAN can be turned into a polymer solution by being dissolved in dimethylformamide (DMF), it can be used for electrospinning. By electrospinning the polymer solution we can obtain fibers at the sub-micron level. These fibers can then be heat-treated on a vacuum furnace to obtain carbon nanofibers.

Recent theoretical and experimental investigations of carbon nanotubes indicate properties suitable for applications in the areas of nanoscale electronics, mechanics, and

composites, among others [2]. There have been some attempts to manipulate nanotubes to actually build nanoscale electronics, but these have not yielded much improvement. If we can successfully control the fabrication and manipulation of carbon nanofibers we should be able to build nanoscale electronics. In this attempt, we have been able to successfully control some of the properties for the fabrication of nanofibers. By varying the voltage and viscosity we have controlled the thickness of the fibers. In addition, by changing the heating temperature we have controlled the carbon contents. Other factors such as distance, shape of the collection plate, angle of the syringe, etc. can also alter some of the properties.

## 2. BACKGROUND

### 2.1 Electrospinning

Electrospinning (Figure 1) is a well-known technique for the electrostatic fabrication of polymer fibers on the sub-micron level [3,4,5]. Although the technique has been known since the 1930s, until recently it has not been exploited. Its applications include scaffoldings for tissue growth, protective clothing, light sails, and filters. Electrospinning is an attractive method for obtaining fibers because it is easy to use, it produces non-woven mats, and the volume/area ratio is outstanding. When an electric field is applied to a polymer solution that is being held at the tip of a syringe, and this field exceeds the polymers' surface tension, a continuous jet stream is obtained. Because polymer particles coming out from the jet are positively charged they repel each other, creating the fibers. In the process, the solvent evaporates, yielding a dry sample. An appropriate substrate is then placed over the metal screen, which needs to be grounded, to collect the fibers.

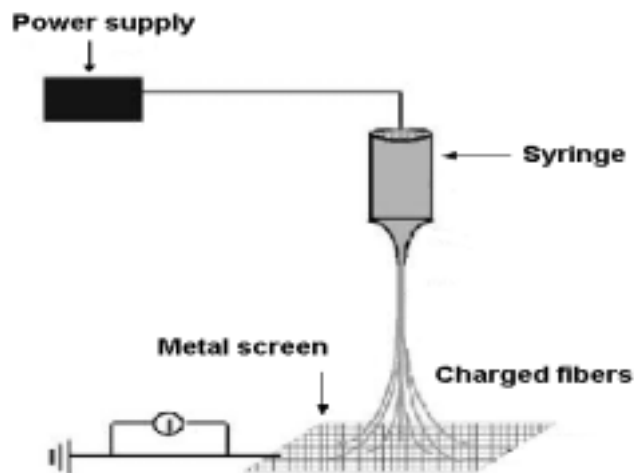


Figure 1: Schematic drawing of the electrospinning process. Positively charged particles repel each other creating the fibers, which are then collected on a grounded metal screen.

## 2.2 Scanning electron microscope

The scanning electron microscope, or SEM, is an excellent tool to see what conventional light microscopes cannot. Light microscopes use a series of glass lenses to bend light waves and create a magnified image. The SEM creates magnified images by using electrons instead of light waves. The SEM displays very detailed 3-dimensional images; they are black and white because light waves are not present.

Because the SEM illuminates the sample with electrons, the substrate and the sample have to be made to conduct electricity. Making a nonconductive sample conductive requires coating the sample with an extremely thin layer of gold or carbon, using a machine called a sputter coater (Figure 2).



Figure 2: Samples are coated with a very thin layer of either gold or carbon using a Sputter coater. This is done to make a sample conductive so that it could be seen on the SEM.

Then the sample is placed inside the microscope's vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun, located at the top of the microscope, emits a beam of high-energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons on to a very fine spot (see Figure 3). Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is then built up from the number of electrons emitted from each spot on the sample [6].

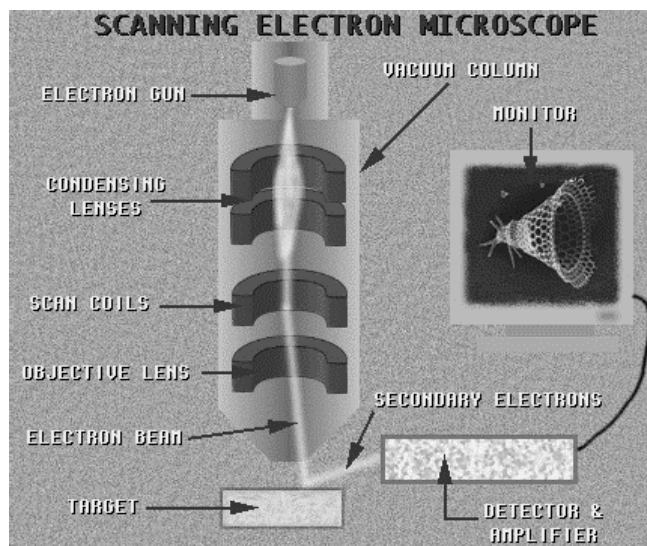


Figure 3: On a scanning electron microscope an electron beam passes through a series of coils to be focused, then it hits the sample, and after the information has been processed an image is obtained.

### 2.3 Raman microscopy

A Raman microscope is a very specialized optical microscope. As in any optical microscope its spatial resolution is on the micron level. In Raman microscopy the sample is illuminated with monochromatic light (a laser), and a conventional optical microscope coupled to a Raman spectrometer or a very sophisticated filter, analyzes the light scattered by the material (Figure 4a). This scattering of light is called the Raman effect after Chandrasekhara Venkata Raman, who discovered it.

The Raman scattered light has a shifted wavelength because of a subtle change in energy (Figure 4b). The Raman microscope collects all the light scattered by the sample and filters out any photons that are at the original frequency, leaving only those with shifted frequencies. These shifted frequency photons are then sent to the spectrometer and the exact frequency shift is determined. These values are directly related to the induced vibrational and rotational motions of the molecules. Most of the scattered light has the same frequency or color as the laser, but a very tiny amount experiences a frequency shift, which is characteristic of the chemical bonds or molecules present in the material. The analysis of the scattered frequencies gives information on the material's chemical composition, state, aggregation, and even factors such as stress, orientation, and temperature [7].

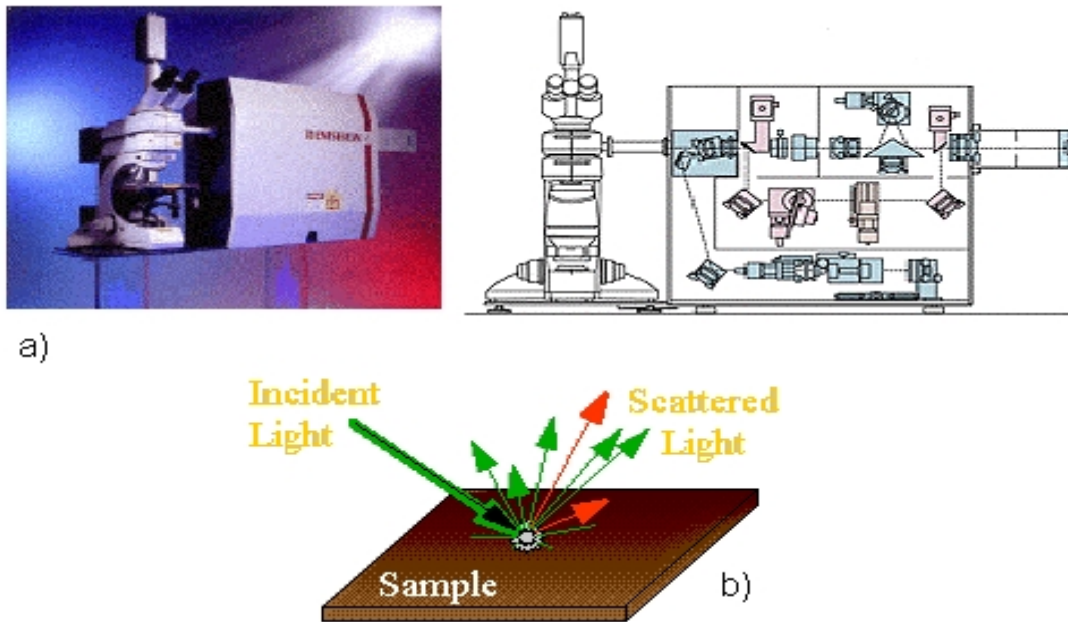


Figure 4: a) An outside and inside look of the equipment used for Raman microscopy. b) Scattered light has a different wavelength that is recognized by the spectrometer.

### 3. EXPERIMENTAL RESULTS

#### 3.1 Carbon composition at different temperatures

Carbon nanofibers were heated at different temperatures and then were examined using Raman microscopy. A green laser with a wavelength of 412 nm was used in the experiment. Figure 5 shows a peak at  $1590\text{ cm}^{-1}$  that is due to the C=N group, and it is called the G band. The peak at  $1371.5\text{ cm}^{-1}$  is called the D band. The G band is due to the graphitic structure, whereas the D band is due to a disordered structure in carbon. Ko and Chen established that the G band increases with an increase in the degree of stabilization [8]. In addition, “its shifts and line-width variations are indications of the defects of the lattice” [8, p. 2222]. Shi et al. point out that the width of the G band increases with increasing compressive stress [9]. The ratio of the G band to the D band represents the amount of  $\text{SP}^2$  (graphite) clusters on the sample. In addition, the higher the G/D ratio, the higher the graphite crystal quality. We can see that the intensity of the D band decreases as the temperature increases, which indicates that the graphitic structure (G band) increases. Therefore, the temperature is responsible for an increase in the fiber’s carbon contents. A wide peak between  $938$  and  $980\text{ cm}^{-1}$  is due to the second-order Raman peak of the silicon substrate. The appearance of this peak is a measure of the transparency of the sample [9].

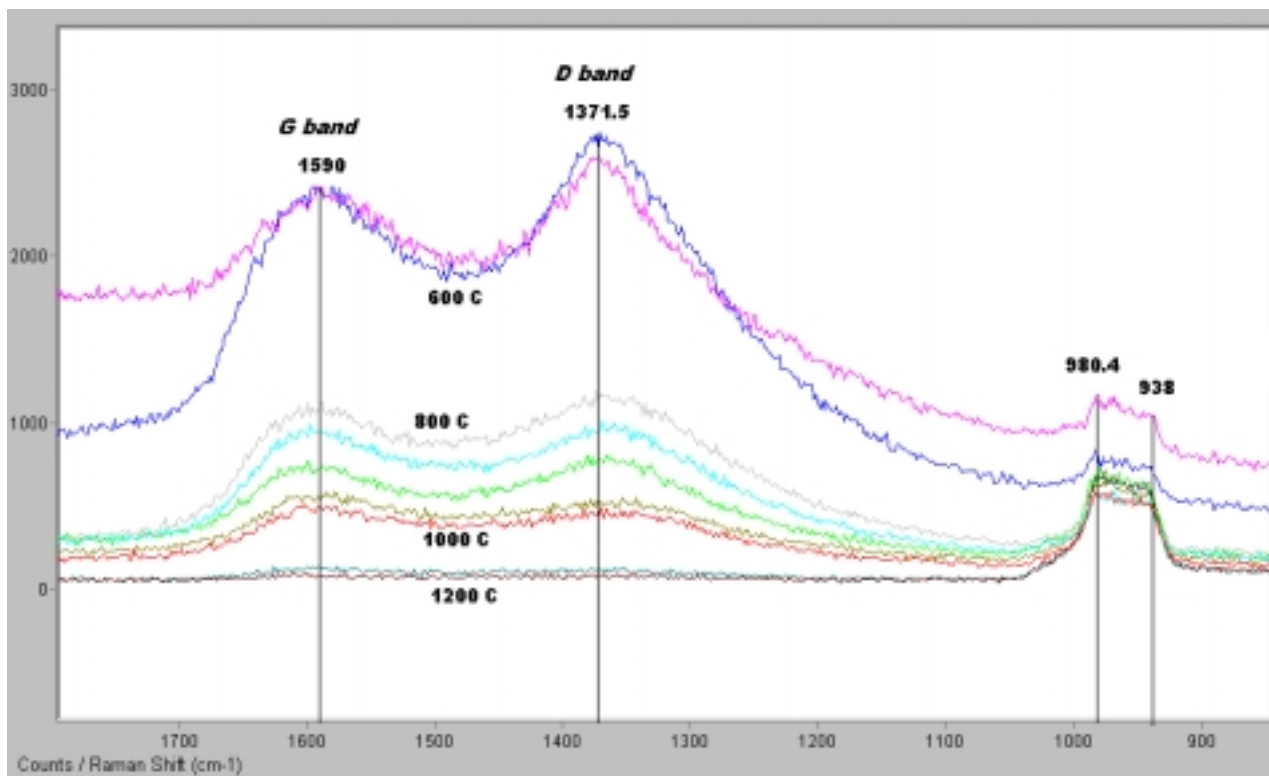


Figure 5: Carbon contents of nanofibers using Raman microscopy. As D band decreases G band does the opposite. Therefore, there is an increase in the graphitic structure.

### 3.2 Voltage vs. thickness of fibers

The effect of the force that the electric field exerts on the fibers is important in the fabrication of nanofibers because it changes the rate at which the fibers are being formed. Therefore, we tried to establish the relationship between the applied voltage and the thickness of the fibers. By keeping a constant distance between the tip of the syringe and the collection screen, and varying the voltage, we obtained PAN fibers. A strongly non-linear relationship between the voltage and the thickness of the fibers suggests a sinusoidal relationship (Figure 6). Dietzel et al. [10,11] explain how the electric field affects the trajectory and behavior of the fibers; this might explain the observed behavior. Then we used an SEM to measure the diameter of an average fiber in each sample. The information gathered is represented in Figure 6. We can see that the behavior of the thickness as a function of voltage is sinusoidal, and it might vary with the viscosity of the polymer.

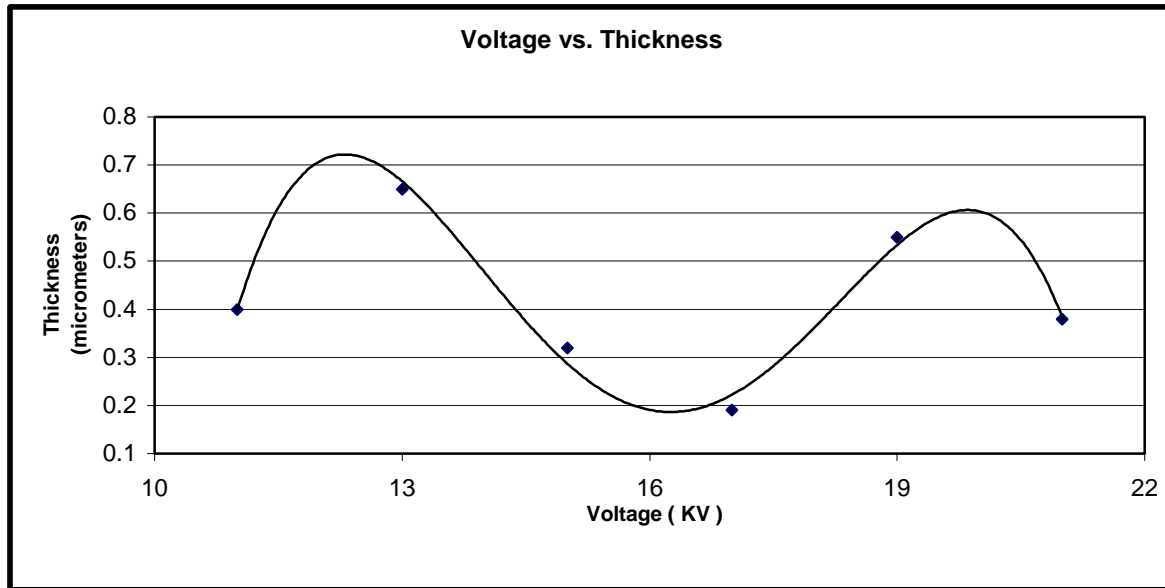


Figure 6: Effect of voltage on the thickness of the fibers. A strongly non-linear relationship suggests a sinusoidal one.

### 3.3 Viscosity vs. thickness of fibers

The most important factor in the fabrication of polymer nanofibers is the effect of the polymer's viscosity [12,13]. In fact, when the viscosity of the solution is too low fibers cannot be obtained; instead little dots are obtained. The same problem arises when the viscosity of the polymer is too high because the surface tension is too high. In the second case a jet will not form, and nothing will be collected on the substrate - not even dots, as in the previous case. Viscosity has also been linked to the formation of beads on the fibers [13]. The polymer solutions were obtained by adding different amounts of DMF to 1.4 grams of PAN. Figure 7 demonstrates these changes. As the amount of solvent is increased the thickness of the fibers does the opposite. We would like to measure the viscosity of the samples, but unfortunately we don't have access to the necessary equipment (a rheometer).

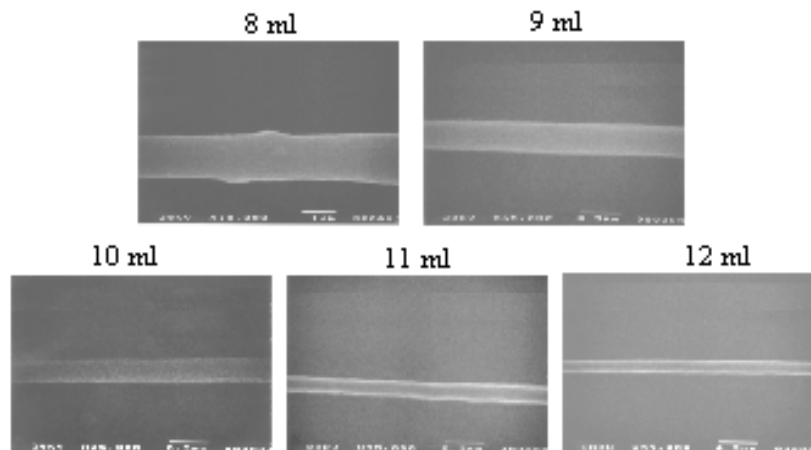


Figure 7: SEM images of the fiber’s thickness as a function of solvent added. As the solvent is increased, the thickness of the fibers decreases.

After gathering the results obtained from the SEM (Figure 8), we were able to determine the linear relationship between the amount of solvent and the inverse of the thickness. This implies that there is a constant  $C$  such that  $C$  divided by the amount of solvent is equal to the thickness of the fibers. But we have to keep in mind that there exists a limiting factor.

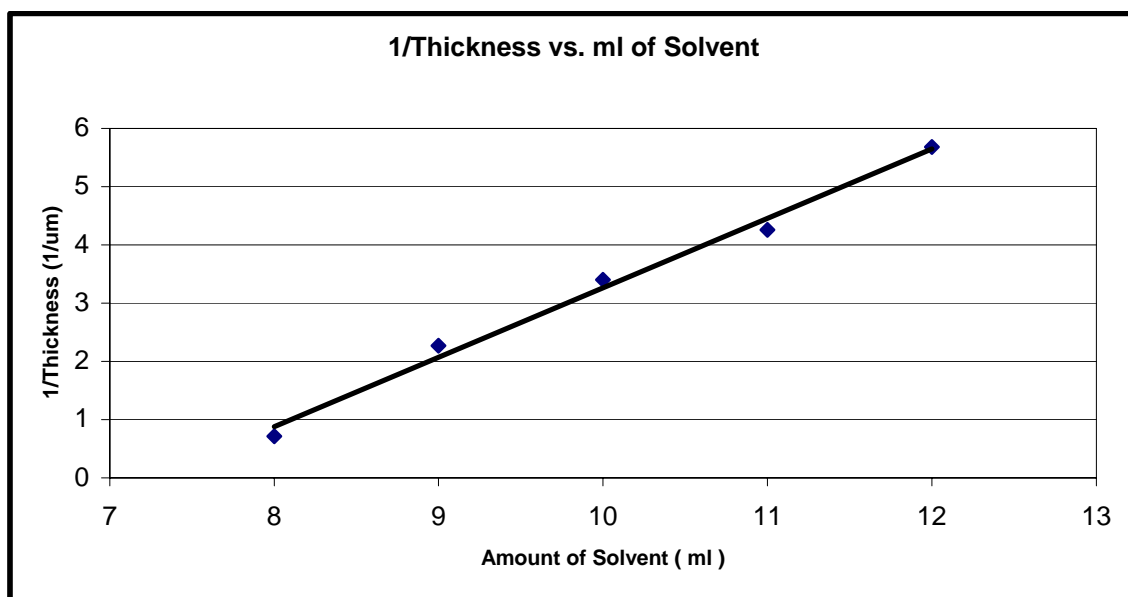


Figure 8: Effect of solvent on the thickness of the fibers.

### 3.4 Thermal analysis and heating process

Thermal analysis (TA) helped us to determine the minimum temperature at which PAN needs to be heated to change into carbon. This test was carried out on argon because any organic material like PAN, when heated at high temperatures in air, disappears. We found



that when heated to a temperature above 200° C, PAN changes its electrical conductivity as a result of conjugation and cyclization [1]. TA results (Figure 9) showed that the sample needed to be heat-treated to at least 500° C. We therefore proceeded to use a vacuum furnace to treat our samples at different temperatures, ranging from 600° C to 1200° C. We are currently working on our own ultra high vacuum system (UHV) to heat-treat our samples. Components of the system have been designed, built, and tested; we hope to have the system running by the end of our Penn program.

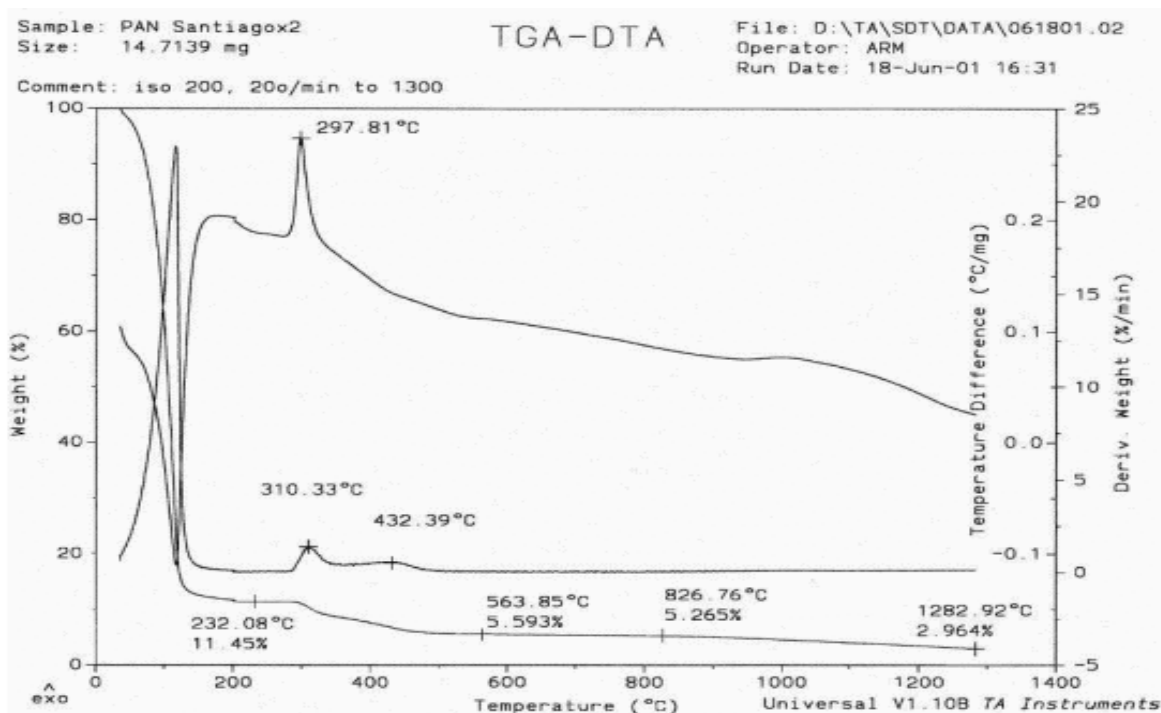


Figure 9: Thermal analysis of PAN determined the minimum temperature that the samples must be submitted to turn into carbon. Starting at the bottom we have the weight loss, followed by its derivative, and the inverse of its derivative.

### 3.5 Electrical properties

Recent theoretical and experimental investigations of carbon nanotubes indicate properties suitable for applications in the areas of nanoscale electronics, mechanics, and composites, among others [2]. We are interested in finding similar applications for carbon nanofibers and how we can achieve them. First, we wanted to measure some of the electrical properties of carbon nanofibers and determine how good they are as conductors. As mentioned before, if PAN is heated to a temperature above 200° C its electrical conductivity increases as a result of conjugation and cyclization [1]. With the help of an electrometer we measured the conductivity of the fibers before and after the heating process. An enormous increase was noticed. The resistivity of the unheated samples was in the order of  $10^{12}$  m $\Omega$ /cm, and after they were heat-treated the resistivity was in the order of  $10^7$  m $\Omega$ /cm. The resistivity of a single carbon fiber was studied; its

total resistance agreed with the sum of the resistances of smaller sections. This implies that the resistance along the carbon fiber is linear. We hope to explore this property further, by observing how the resistance changes with both the initial heating temperature. After the carbon fibers have been obtained we want to observe the changes in its resistance when the temperature is increased.

#### **4. DISCUSSION AND CONCLUSION**

Using PAN as a carbon precursor and electrospinning, we were able to obtain fibers on the sub-micron level. After heating them in a vacuum furnace, we successfully obtained carbon fibers.

We were able to control the thickness of the fibers by altering two parameters in the fabrication process: the viscosity and the force of the electric field (applied voltage). The relationship between the amount of solvent and the inverse of the thickness was found to be linear. On the other hand, a strongly non-linear relationship between the voltage and the thickness of the fibers suggests a sinusoidal relationship. Both relationships were studied using an SEM.

Thermal analysis helped us determine the minimum heating temperature to which the fibers must be exposed to yield carbon fibers. We also used Raman microscopy to investigate how the heating temperature affects the graphite contents in the fibers. It was found that as the temperature increases, so do the carbon contents.

The resistivity of a single carbon nanofiber was studied; its total resistance agreed with the sum of the resistances of smaller sections. This implies that the resistance along the carbon nanofiber is linear.

As part of my work I designed and built some of the components of a new ultra high vacuum system (UHV) that will be used to rapidly thermally process the polymer fibers. We were not able to use the system for our experiments because of some problems with leaks. Our goal was to at least go to  $10^{-8}$  Torr, but because of the leaks we were only able to go up to  $10^{-6}$  Torr. I am currently working on fixing the leak problem.

#### **5. RECOMMENDATIONS**

Once carbon nanofibers have been successfully obtained and their internal behavior understood, it would be interesting to manipulate the fibers to build a circuit. This might be possible with the help of an atomic force microscope (AFM).

Studies on the resistivity of carbon nanofibers were not completed because specially prepared silicon wafers were unavailable. These wafers must have several gold contacts, very close to each other, on which to deposit the fibers and measure their conductivity. The resistance of fibers deposited on a silicon wafer, with the pattern shown in Figure 10, could be easily measured with an electrometer; then an AFM could measure the fiber's area and we could find the resistivity.

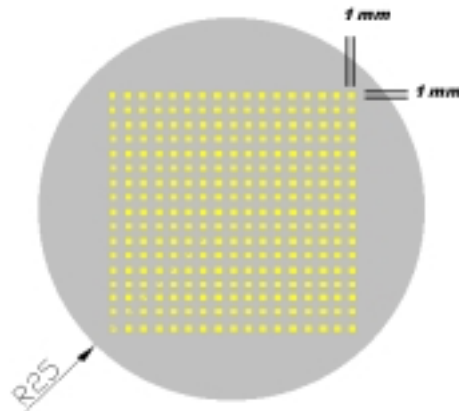


Figure 10: Silicon wafer with gold contacts to measure the resistance of the carbon nanofibers.

While working with PAN, we were able to use electrospinning to generate fibers using alkoxydes such as  $\text{Pb}(\text{ZrTi})\text{O}_3$  (lead zirconium titanate) and  $\text{BaTiO}_3$  (barium titanate). The study of this alkoxydes is important because of its ferroelectric properties.

## 6. ACKNOWLEDGMENTS

I'm very thankful with the NSF for giving me such a wonderful experience through their joint program with University of Pennsylvania (SUNFEST). I would like to thank my advisor, Dr. Jorge Santiago, and his graduate student, Wang Yu, for all their help and encouragement. I would also like to thank Gerald Harrison for his help with the SEM, William Romanow for the experiments carried out in his laboratory, Nevin Naguib for her help with Raman microscopy, Vladimir Dominko for providing us with tools needed for the experiments, Janice Fisher for checking my final report, Andrew R. McGhie for his help with thermal analysis, and Lois Clearfield for those great biweekly lunches and the coffee every morning.

## 7. REFERENCES

1. A.M. Summan, Electrical conductivity of heat treated polyacrylonitrile and its copper halide complexes, *J. Appl. Pol. Sci.*, 37 (1999) 3057-3062.
2. Ph. Avouris, T. Hertel, R. Martel, T. Schmidts, H.R. Shea, and R.E. Walkup, Carbon nanotubes: nanomechanics, manipulation, and electronic devices, *Appl. Surface Sci.*, 144 (1999) 201-209.
3. J. Doshi and D.H. Reneker, Electrospinning process and applications of electrospun fibers, *J. Electrostatics*, 35 (1995) 151-160.

4. M. Bognitzki, W. Czado, T. Frese, A. Schaper, M. Hellwig, M. Steinhart, A. Greiner, and J. Wendorff, Nanostructured fibers via electrospinning, *Adv. Mater.*, 13 (2001) 70-72.
5. I.D. Norris, M.M. Shaker, F.K Ko, and A.G. MacDiarmid, Electrostatic fabrication of ultrafine conducting fibers: polyaniline/polyethylene oxide blends, *Synth. Met.*, 114 (2000) 109-114.
6. Museum of Science [Boston], Scanning electron microscope (SEM), July 20, 2001, <<http://www.mos.org/sln/sem/intro.html>>.
7. F. Agulló-Rueda, Raman microscopy, July 20, 2001, <[http://www.icmm.csic.es/Fagullo/ramicr\\_e.htm](http://www.icmm.csic.es/Fagullo/ramicr_e.htm)>.
8. T.-H. Ko and C.-Y. Chen, Raman spectroscopic study of the microstructure of carbon films developed from cobalt chloride-modified polyacrylonitrile, *J. Appl. Pol. Sci.*, 71 (1999) 2219-2225.
9. J.R. Shi, X. Shi, Z. Sun, S.P. Lau, B.K. Tay, and H.S. Tan, Resonant Raman studies of tetrahedral amorphous carbon films, *Diamond & Related Materials*, 10 (2001) 76-81.
10. D.H. Reneker, A.L. Yarin, H. Fong, and S. Koombhongse, Bending instability of electrically charged liquids jets of polymer solutions in electrospinning, *J. Appl. Phys.*, 87 (2000) 4531-4541.
11. J.M. Dietzel, J. Kleinmejer, D. Harris, and N.C. Beck Tan, Controlled deposition of electrospun po(ethylene oxide) fibers, *Polymer*, 42 (2001) 8163-8170.
12. J.M. Dietzel, J. Kleinmejer, D. Harris, and N.C. Beck Tan, The effect of processing variables on the morphology of electrospun nanofibers and textiles, *Polymer*, 42 (2001) 261-272.
13. H. Fong, I. Chun, and D.H. Reneker, Beaded nanofibers formed during electrospinning, *Polymer*, 40 (1999) 4585-4592.