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SUNFEST REU Program

MAGNETORESISTANCE OF ELECTROSPUN CARBON NANOFIBERS PYROLYZED AT LOW TEMPERATURES

NSF Summer Undergraduate Fellowship in Sensor Technologies
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ABSTRACT

Carbon fibers with diameters of approximately 100 nm can be produced by heating electrospun polyacrylonitrile (PAN) nanofibers in a reduced-pressure chamber. These nanofibers' outstanding properties, especially their high specific surface area, make them promising materials for scaffolds in tissue engineering and also for high-performance filtration and sensor applications. However before any of these potential uses can be explored, the nature of these nanofibers must first be better understood.

One important quantum effect phenomenon that occurs in carbon nanofibers is magnetoresistance (MR).This is a measure of how the electrical resistance of the carbon nanofiber changes in the presence of a transverse magnetic field. To make this measurement, the PAN nanofibers were placed in the right orientation on a patterned silicon wafer by electrospinning. The PAN nanofiber samples were then pyrolyzed in a vacuum chamber at a temperature of 1173K to produce carbon nanofiber samples. The four-point probe method was used to measure their conductivity. Initially, the temperature dependence of the nanofiber was observed, with no applied magnetic field, within a temperature range of 0K to 300K. The resistance decreased exponentially as the temperature was increased. Then measurements were taken at temperatures of 1.9K, 3K, 5K, and 10K within a magnetic field range of –9T to 9T each. These current and voltage measurements were then manipulated to calculate MR. In general, MR was negative, and its magnitude increased with an increase in magnetic field and a decrease in temperature. This result was attributed to the weak localization effect model.

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1. INTRODUCTION

Conventional fiber spinning methods usually use mechanical forces to drive fiber formation. These conventional methods are strong enough to produce fibers with micron-meter-range diameters. The significance of these carbon fibers lies in their chemical inertness, strength, and electrical and thermal conductivity. These materials can thus be conveniently used for batteries, plastic, and asphalt applications. However, when mechanical forces are combined with electrostatic forces, the diameter of the carbon fibers produced reduces significantly to the nanometer range (see Figure 1). This more effective spinning technique is known as electrospinning.

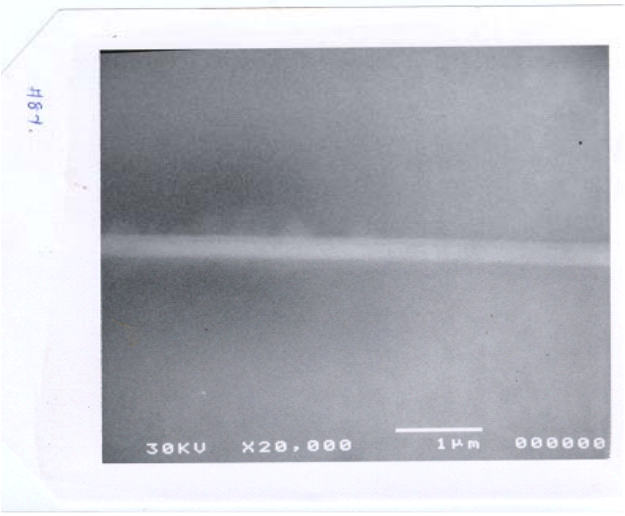

Figure 1: Image of carbon nanofiber obtained from scanning electron microscope.

The ultrafine nanofibers produced by electrospinning are more outstanding than ordinary carbon fibers because they have unusually large specific surface areas [1]. There has been much recent research on carbon nanofibers because of their promising potential uses in the field of nanotechnology. These nanofibers also have high porosity and very small pore size, making them likely candidates for use in highly selective filtration applications. They are also absorbent. This quality, combined with their chemical inertness and high conductivity properties, makes them prospective materials for sensors. Their electrical resistance and thus conductivity is highly dependent on the physical conditions of their surroundings. Consequently, the practical application of this project is to use these carbon nanofibers as sensors for physical measurements such as temperature, pressure, and levels of certain atmospheric gases. Nevertheless, the feasibility of this application depends on the scope and accuracy of knowledge of the nature of the carbon nanofiber. Unfortunately, the nanoscopic size of these fibers makes them hard to manipulate; thus, not enough research has been done in this field.

This project helps to further characterize carbon nanofibers by measuring magnetoresistance (MR) — the change in electrical resistance when an electric field is

applied perpendicularly to the carbon nanofiber. MR reflects the electron transport properties of the nanofiber. In accordance to classical electron theory [2], electrical resistance should increase when a perpendicular magnetic field is applied to the carbon nanofiber. Thus, MR should be positive. However, it has been observed that in carbon fibers resistance tends to increase as the magnetic field increases. When temperature is lowered, the degree of disorderliness increases, also increasing MR. The fibers thus exhibit negative MR properties that are attributable to their structure and quantum mechanic effects. The Bright Model [3] explained this negative MR in terms of an increase in the density of carrier electrons when a magnetic field is applied at low temperatures. Although the Bright Model represented a significant breakthrough in understanding the negative MR of carbon nanofibers, it could not efficiently explain all observed data. Another model [4] explained negative magnetoresistance in terms of weak localization effects. This phenomenon is an inherent interference effect based on the scattering of carriers at low temperatures.

This project will further investigate if the same phenomenon of negative magnetoresistance that exists in carbon fibers also exists in nanofibers. Previous research has examined nanofibers pyrolyzed at high temperatures of 2273K and above [5,6]. However, not much work has been done on nanofibers pyrolyzed at low temperatures. Thus this project aims to measure MR at a low temperature of 1173K to observe the trends at different low temperatures.

2. BACKGROUND

2.1 The Potential Sensor Application

The effects of certain physical parameters on electrical resistivities of carbon nanofibers demonstrate that they can be used in sensor applications. Resistivity (ρ), an intrinsic property of a material, is a measure of its longitudinal electrical resistance. Resistivity is related to electrical resistance (R) by the equation $R = \rho L / S$ (1), where L is the length of the fiber and S is the surface area. According to Ohms Law, for certain materials such as carbon nanofibers, voltage (V) across and the current (I) flowing through the material are related by V=IR (2). A combination of these two equations yields $\mathbf{I = V/R = VS/ \rho L}$. Hence in making a sensor, some of these properties of the nanofiber can be fixed and only one left varying. In the sensor circuit shown in Figure 2, the length, surface area, and voltage across the nanofiber remain fixed.

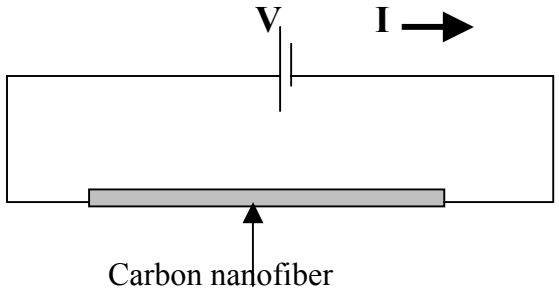

Figure 2 Circuit of potential carbon nanofiber sensor

Hence, the only property affecting the current flowing through the circuit is the resistivity. If a physical parameter that affects resistivity, such as temperature, changes, resistivity will change, thus affecting the current through the circuit. Thus if this parameter is being monitored, this change in current output can be interpreted by a program that will trigger a desirable response (see Figure 3).

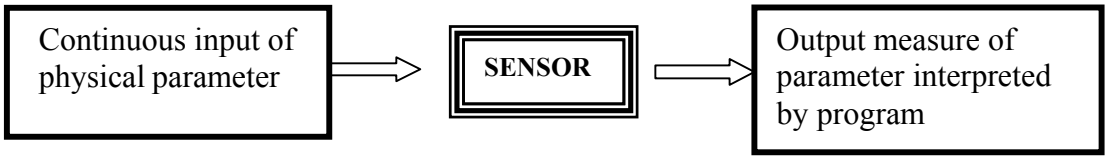

Figure 3: Diagrammatic representation of sensor application.

2.2 Substrate Preparation

The substrate is a silicon wafer that undergoes certain processes before it is ready to be used for the MR measurements.

2.2.1 Photolithography

Photolithography [7] is the process of transferring geometric shapes on a mask to the surface of a silicon wafer. The first step is to prepare a mask with the desired pattern on a glass plate. The wafer then has to be thoroughly cleaned chemically and dried, making it ready to be coated with a layer of silicon dioxide. The next step is to add another thin layer of an ultraviolet sensitive polymer known as a photoresist (see Figure 4). Photoresists can be either positive or negative. For our experiment a positive photoresist was used.

The mask is then aligned with the silicon wafer. The parts of the photoresist that need to be removed to form the pattern are exposed to ultraviolet light through the mask. This process modifies the chemical structure of the photoresist, making it soluble in the developer. The wafer is then developed, thus transferring the pattern on the mask onto the wafer. The solvents are then removed from the photoresist to make the coating photosensitive

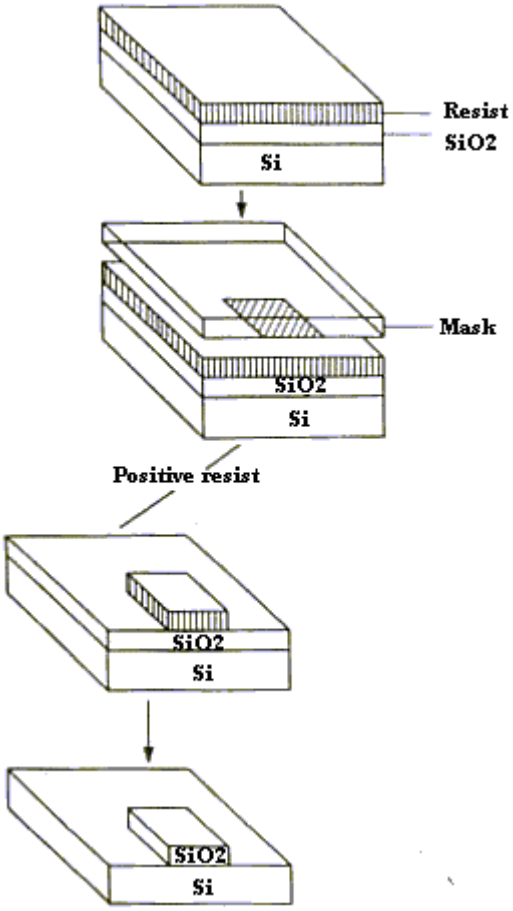

Figure 4: The photolithography process.

2.2.2 Liftoff etching

The next step is an etching process known as "liftoff": a stenciling technique used to pattern noble metals such as gold. To ensure better adhesion, a layer of nickel is deposited on the wafer before depositing the thin layer of gold. The pattern is then stenciled through the gaps in the resist and the unwanted metal is lifted off (see Figures 5 and 6).

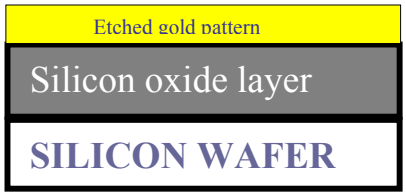

Figure 5 Cross-section of sample

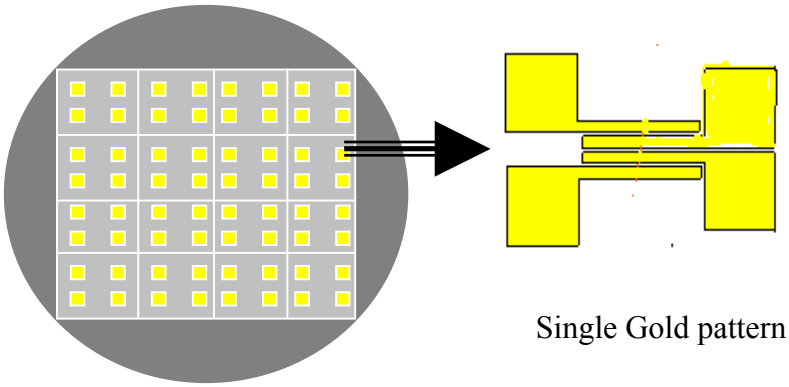

Figure 6 Top view of sample with several etched gold patterns

2.3 Electrospinning

Conventional fiber spinning techniques, such as melt spinning, dry spinning, and wet spinning, use mechanical forces in fiber production. With these processes, a polymer solution is forced out of a spinnerette to produce non-woven fibers as the drawn solution solidifies. Electrospinning combines these mechanical forces with electrostatic forces. The process was discovered in the early 1930s but not significantly exploited because of limited comprehension, but recent years have seen increased research on electrospinning [1]

Electrospun fibers usually have diameters in the nanometer range, in the order of 100 nm. These ultrafine fibers are obtained by spinning polymer solutions in a high-voltage electric field. A simple setup involves a plastic syringe with a metal tip, a clamp, a high-voltage source, and a grounded static screen. These objects are connected as shown in Figure 7, with the clamp slightly inclining the syringe at an angle and the voltage source connected to the metal tip. The polymer is put in the syringe, and a drop of solution is held at the metal tip by the surface tension force of the particles. Simultaneously, the high-voltage source positively charges the particles of the polymer solution, and the repulsion between them increases. At a certain critical point, the electrostatic force due to repulsion overcomes the opposing surface tension force, thus forcing out a jet of the charged polymer solution. While in the electric field, the solvent from this jet solution evaporates, leaving nanofibers targeted at the grounded screen.

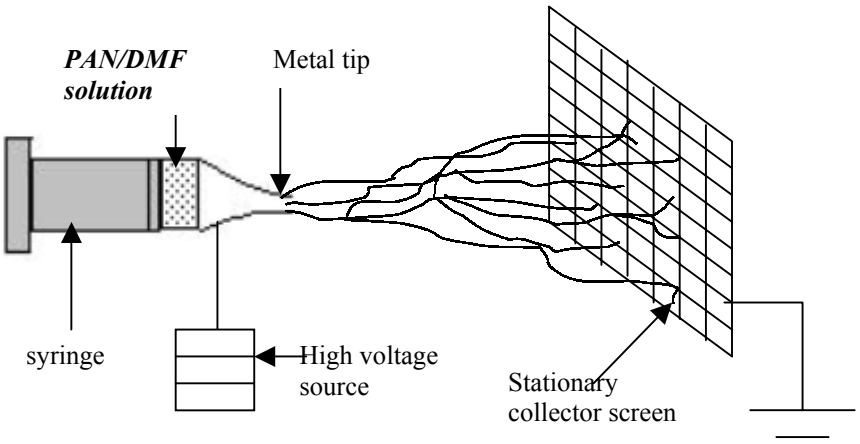

Figure 7: Electrospinning setup.

2.4 Four-Probe Method

The-four probe configuration can be used for electrical resistance measurements. The setup (see Figure 8) has four equally spaced collinear probes. The two outer probes are current-carrying probes, while the two inner ones are for voltage measurements. Since very little current flows through the voltage probes, the voltage measured is about the same as the voltage across the nanofiber. This method thus decreases the contact resistance and makes the voltage measurements more accurate.

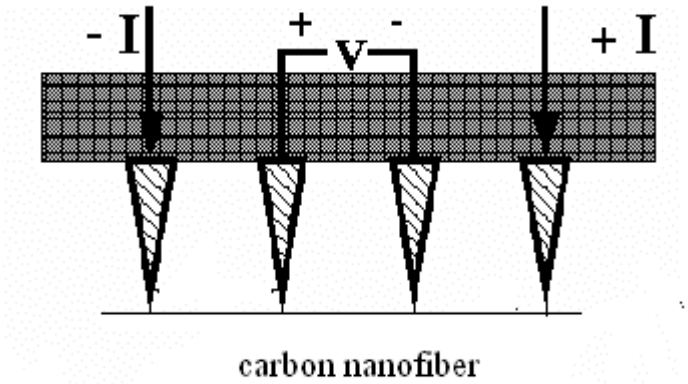

Figure 8: The four-probe method [8].

3. The Experimental Procedure and Results

The first step was to pattern the silicon wafer substrate by the process of photolithography and "liftoff" etching. The next arduous task was to obtain a carbon nanofiber placed in the right orientation across one gold pattern. To achieve this we prepared a polymer solution using 8 mg of polyacrylonitrile (PAN) and 10 ml of N, N-dimethyl formamide (DMF) solvent. This solution was then electrospun and the silicon wafer was momentarily placed in the electric field to collect some PAN nanofibers. It was important to ensure that a high density of PAN nanofibers was not deposited on the wafer, as this would decrease the probability of having a desirable sample. The wafer was then viewed under a microscope to observe whether a nanofiber had been placed in the right orientation. If not, the wafer was cleaned with DMF solution and dried to prepare it for another trial. This experiment was repeated until a single PAN nanofiber was stretched across the central part of one of the gold patterns, as shown in Figure 9. This nanofiber had to not touch any of the four contact pads nor be crossed by another nanofiber since that would affect the resistance measurements of the nanofiber.

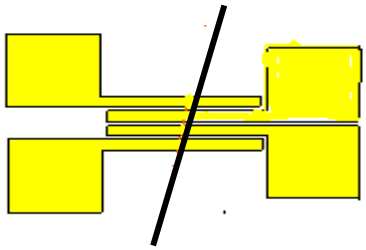

Figure 9: Pattern after successful electrospinning.

After successful electrolysis, the PAN nanofiber was chemically changed to a carbon nanofiber. This was done by heating it in a vacuum chamber at 1173K in a process known as pyrolysis: high-temperature decomposition under reduced pressure. For pyrolysis, a Brew Model 466-S with a mesh element was used. The sample was heated for 30 minutes in a vacuum of 106 Torr. The complications of pyrolysis were the high probability of either moving or breaking the nanofiber. After successful carbonization, the sample was then ready for MR measurements by the four probe method.

To enhance these measurements, silver epoxy was used to attach thin gold wires to each of the four contact pads. These gold wires were connected to the appropriate current and voltage probes. The purpose of the first set of measurements was to investigate how the resistance of the carbon nanofiber varied with temperature. Thus without applying any magnetic field, with a temperature range from 0K to 300K, the electrical resistance of the sample was calculated using the recorded current and voltage measurements. These measurements were made using the four-probe method with a Model 6000 Physical Properties Measurements System by Quantum Inc., equipped with a Keithley 237 high-voltage source measurement unit. As Figure 10 shows, as the temperature increases, electrical resistance also decreases.

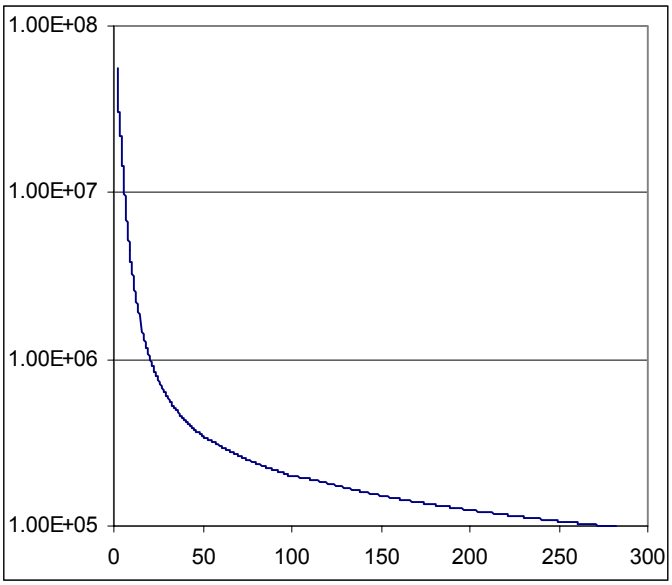

Figure 10: Relationship between electrical resistance and temperature.

Then, with the perpendicular magnetic field ranging from – 9T to 9T, voltage and current measurements were taken on the sample at temperatures of 1.9K, 3.0K, 5.0K, and 10K. MR and magnetoconductance (MC), which is the inverse of MR, were calculated using the formulae on the next page.

$$MR = \{R(B) - R(0)\} / R(0)$$

$$= \{ R(B) / R(0) \} - 1$$

$$MC = \{G(B) - G(0) \} / R(0)$$

$$= \{ G(B) / G(0) \} - 1$$

R(B) is the resistance of the carbon nanofiber in a perpendicular magnetic field of strength B. R(0) is the resistance of the carbon nanofiber when no magnetic field is applied.

G(B) is the conductance of the carbon nanofiber in a perpendicular magnetic field of strength B. G(0) is the conductance of the carbon nanofiber when no magnetic field is applied.

The figures below show the data collected for MR/MC against the magnetic field strength.

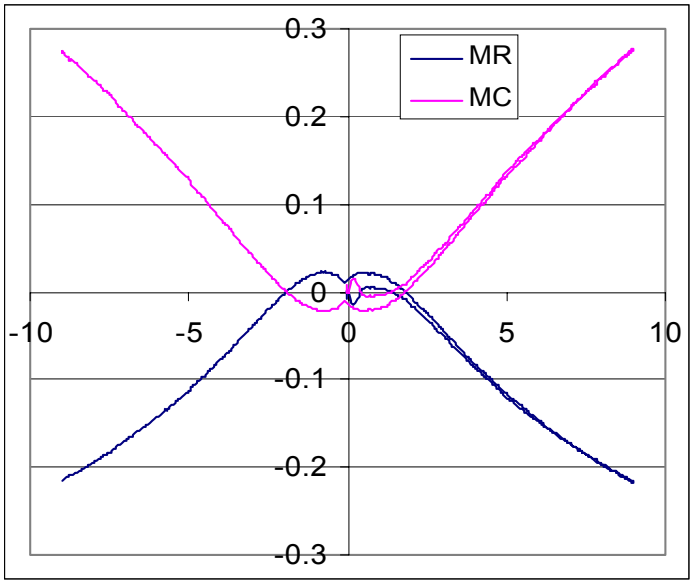

Figure 11: MR/MC measurements taken at 1.9K.

As can be seen from Figure 11, as the magnitude of the magnetic field increases, the magnitude of MR increases. However, a greater part of the curve is below the x-axis, showing that MR is negative, while a greater part of the MC curve is above the x-axis, showing that MC is positive. But an interesting result was observed between about –1.8 T to 1.8T, where on the contrary MR is positive and MC is negative. This could mean that there is a change in the scattering of the carriers in this region which affects the effect of the magnetic field. This speculation could be investigated further in future

experiments. In general, for the sample at 1.9K, the maximum MR obtained in the range was about -21.8 % when magnetic field was 9T.

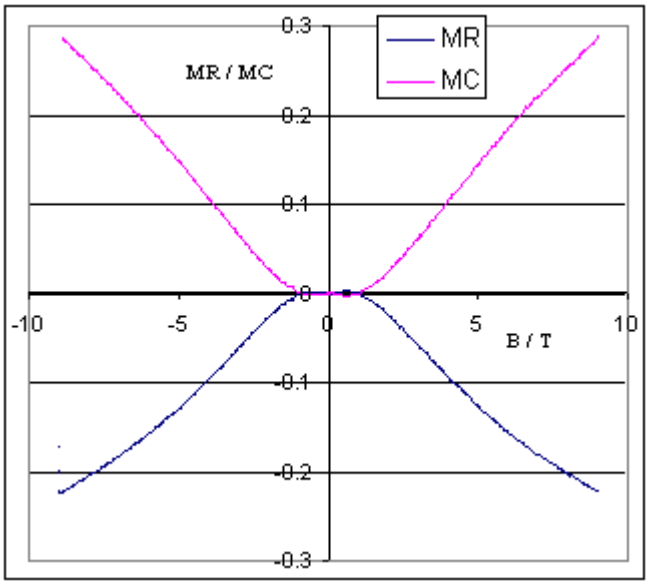

Figure 12: Measurements taken at 3K.

Just as in the previous graph, in Figure 12 MR was generally negative while MC was generally positive. Unlike the measurements taken at 1.9K, here the MR curve is fully negative, while the MC curve is totally positive. In general, for the sample at 3K, the maximum MR obtained in the range was almost -22.3%.

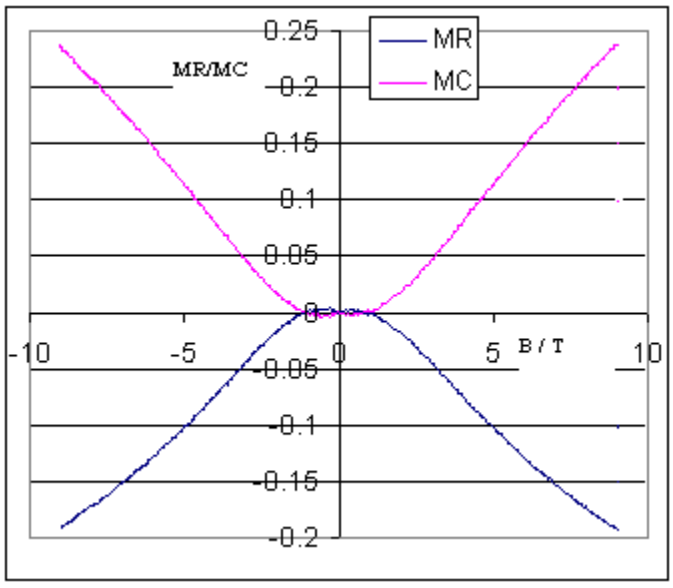

Figure 13: Measurements taken at 5K.

In Figure 13, once again MR is totally negative, while MC is totally positive. The maximum value is about -19.2%.

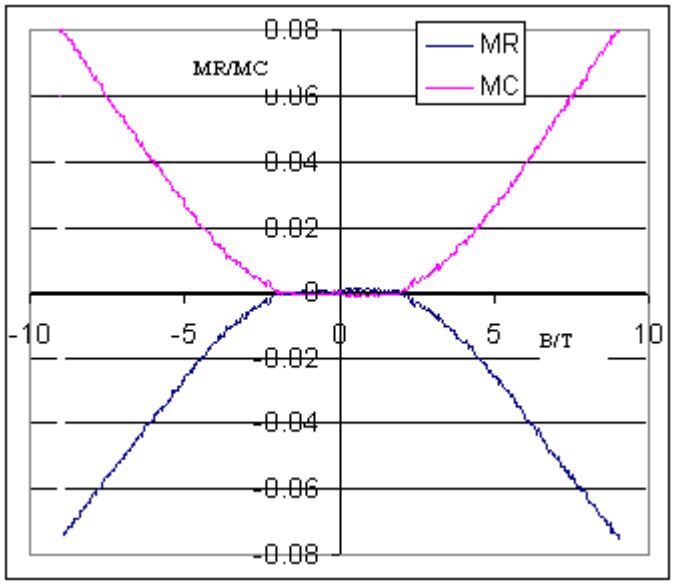

Figure 14: Measurements taken at 10K.

As expected, in Figure 14 MR is negative while MC is positive. The maximum measurement is about -7.4 %

A combination of all the results shows the relationship between MR and temperature more clearly. In general, as the temperature increases, MR decreases. It was expected that the measurements taken at 1.9K would have the highest results while those taken at 10K would have the lowest values. However, the measurements taken at 3K generally show the highest MR results.

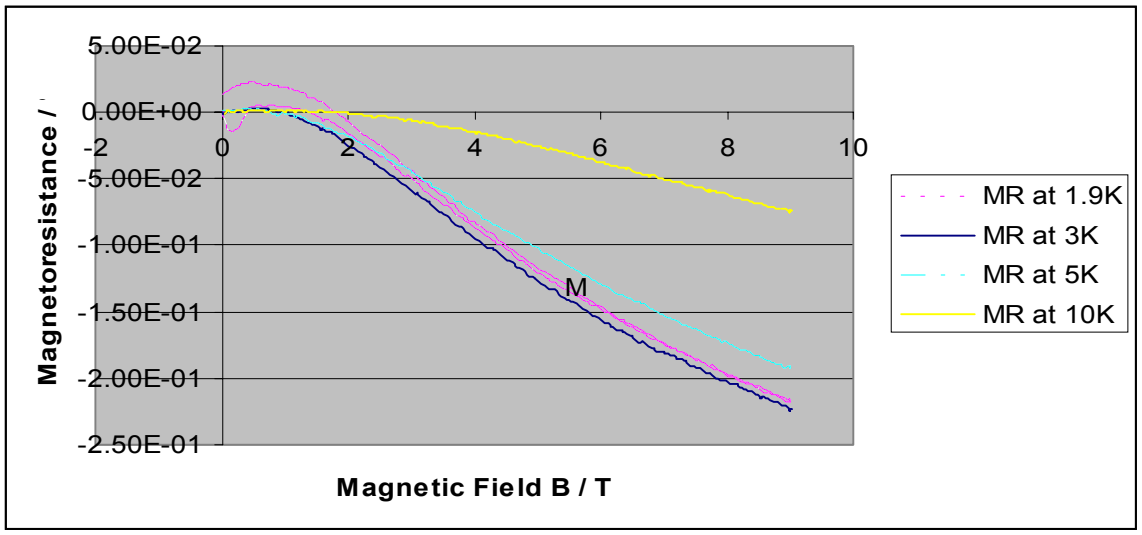

Figure 15: Graph showing combined MR measurements at 1.9K, 3K, 5K and 10K

4. DISCUSSION AND CONCLUSIONS

For most conductive materials, as temperature increases, there is an increase in the vibration amplitudes of the atoms thus increasing the frequency of collision of carriers. As a result, their electrical resistance decreases with temperature increase. However, semiconductors behave differently because of their atomic structure and the nature of their charge carriers. When temperature increases, semiconductors' electrical resistance decreases because the increased amplitudes of vibration may break some bonds between the valence electrons and the lattice atoms, hence releasing more charge carriers. The relationship between resistance and temperature is represented by

$R = R_0 e^{(1/T - 1/T_0)\Delta E/2K}$

R_0 is the resistance of the semiconductor at a reference temperature T_0 (K), usually 273K.

Thus since the shape of Figure 10 shows this relation, it confirms that carbon nanofibers have semiconductor tendencies. This observation is explained by the weak localization phenomenon discussed below.

Figures 11, 12, and 13 showed that, in general, MR is negative. The Bright Model [3] explained this in terms of free carriers. Bright argued that the density of free carriers is increased with magnetic field, causing negative MR. However, this model failed to explain certain observed phenomena. Other authors [4,5,6] turned to weak localization effects which occur in weakly disordered electronic systems like that of the carbon nanofiber because of its turbostratic structure. This weak localization is an inherent interference effect common to a wave-propagated system in a disordered medium. It occurs when the probability of elastic scattering is greater than inelastic scattering of carriers, causing the interference of the electron wave to move in the backward direction. Magnetic fields suppress the phase coherence of backscattered wave. Thus the change in electrical resistance when a magnetic field is applied tends to be negative.

It was also observed that as temperature was increased, MR decreased. The maximum for 10K was -7.4%; for 5K, -19.2%; for 3K, -22.3%; and for 1.9K, 21.8%. MR is more prominent at low temperatures because there is increase in the disorderliness of the system. Contrary to expected results, the values at 1.9K were lower than those at 3K. However, the values for these two measurements were very close. This is most likely because there is not a great change in temperature to affect the carriers immensely. The experiment can be repeated at these temperatures to verify the results and confirm that this observation was not due to experimental limitations. Since the nanofiber also displayed some positive MR at 1.9K, it will be interesting to investigate if the nanofiber undergoes some significant changes at that very low temperature.

In conclusion, the MR of carbon nanofibers pyrolyzed at 1173K is generally negative and increases while temperature decreases.

5. RECOMMENDATIONS

Resistivity, which is a measure of the longitudinal resistance, is usually a better measurement than resistance because it is an intrinsic property. However, resistivity is dependent on the surface area and length of the carbon nanofiber. Time constraints made it impossible to investigate the cross-section of the nanofiber. This should be done as a next step, and its surface area measured. The cross-section can be viewed with a scanning probe microscope operated in tapping mode. Since it is suspected that the cross-section is elliptical [9], the surface area can be calculated by measuring the vertical diameter and the full width at half maxima horizontal diameter. The length of the nanofiber can be measured using an optical microscope.

The nanofiber can also be characterized further using Raman scattering. This will show different peaks and thus the presence and levels of disorder in the nanofiber. These steps would allow us to better understand the MR results.

Finally the results can be compared to MR measurements of carbon nanofibers pyrolzed at other temperatures to observe any trends.

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