I, Anshuman A. Sowani, hereby submit this original work as part of the requirements for the degree of Master of Science in Mechanical Engineering.

It is entitled:  
Exploration of Electromagnetic Assisted Spinning and Electrical Annealing of Carbon Nanotubes

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Exploration of Electromagnetic Assisted Spinning and Electrical Annealing of Carbon Nanotubes

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ABSTRACT

This thesis summarizes the work done in the Nanoworld Laboratories at University of Cincinnati towards making of a stronger carbon nanotube (CNT) material by use of new techniques during the post processing phase, specifically during 'spinning' and 'annealing'.

The first part of the thesis describes various methods attempted to spin thread from non-spinnable or partially spinnable CNT arrays. Different approaches were used to try spinning of yarn, electromagnetic assisted spinning of yarn (EASY) being one of them. Two parallel conductors carrying like currents generate a magnetic field that attracts the two conductors together. This simple principle was applied to CNTs in an array and spinning experiments were set up for pulling a CNT ribbon while passing current through the CNTs. It was predicted that the CNTs carrying current will attract each other and the electromagnetic force will assist the van der Waals’ forces while drawing a yarn. Experiments were carried out under vacuum and in air, and with different types of arrays, varying in CNT length, properties, and using different tools e.g. an edge of a blade, a pointed electrode etc. Both AC and DC were used, with a range of voltages and frequencies. Finally, arrays were coated with nickel by electro-deposition, and using a magnetic probe drawing of yarn was tried out.

In the second part of the thesis, improvement of CNT material by a high temperature treatment is discussed. The method used is resistive annealing, i.e. heat is generated by passing an electric current through the sample to be annealed. The experiments were set up from scratch, and gradually evolved by improvements in processes, equipment, raw-materials used and handling expertise gained with experience. Different types of CNT materials were annealed, viz. tall arrays,
spun thread and thin tiles. Different temperatures and different current densities were studied. Effect of experimental environment was observed by carrying out annealing in vacuum, argon etc. After annealing, samples were characterized to see the effect of annealing. Electrical properties (resistivity), mechanical properties (tensile strength) were tested. Samples were also imaged under the Scanning Electron Microscope (SEM). Finally, Raman spectroscopy was performed to compare Raman signature of the annealed vs. non-annealed samples and their $I_G / I_D$ ratios.

The annealing process used is a relatively low temperature annealing. The work done is a step towards study of thermal annealing, which is a high temperature, high volume, and probably more uniform type of annealing. On the other hand, ease of experimentation, quick setup, better control over experimental parameters, absence of cool down time needed, huge savings on energy as compared to a thermal furnace are advantages of electrical type of annealing. This method provided valuable information regarding effects of various annealing parameters on CNT properties, characterization techniques to be used, and handling of different types of CNT material. It helped to project estimation about outcome from the thermal annealing.
I would like to take this opportunity to express my gratitude and appreciation to all those who are directly or indirectly involved in completion of this project.

I would like to thank my research advisor Dr. Schulz. Without his guidance, motivation and support this thesis would not have come true. Equally valuable is the contribution of Dr. Shanov, who advised me time to time in my experimental setups, procedures and direction of the research.

I would like to thank my fellow researchers involved in this work. Aaron Johnson helped me in Raman characterization of CNT thread and tiles, as well as tensile testing of thread. Bolaji Suberu and Yi Song helped in tensile testing of CNT tiles. Weifeng Li assisted me in imaging of CNT material with the Environmental Scanning Electron Microscope.

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1 Introduction

It was in 1991 when Sumio Iijima published his breakthrough paper about “microtubules of graphitic carbon” [1]. Even after two decades, researchers find these carbon nanotubes (CNTs) a remarkable, extraordinary and enigmatic material. With the highest aspect ratio (height to diameter ratio) than any other known material, CNTs boast as the strongest and stiffest substance ever been discovered. They are not only strong, but also good conductors of electricity and heat. Adding to their asset is their feather-light density, which when combined with the above make their specific properties soar so high that they easily surpass those of conventional top-notch materials like Kevlar (toughness) or copper (conductivity). It is no surprise that many laboratories worldwide are striving towards improving CNTs, understanding their mechanisms better and finding diverse and innovative applications for them. This is a dynamic and highly motivated field of research and new inventions are disclosed every day.

What exactly is this peculiar material that has grabbed attention of not only the scientific community but also various industries like aerospace, sports equipment and special fabric? And what makes them so special?

1.1 What are carbon nanotubes?

Simply put, CNTs are allotropes of carbon. They are rolled-up thin cylinders of graphene, joined seamlessly end to end with hemispherical caps on the ends. Graphene is a one atom thick sheet of graphite. It has carbon atoms arranged in a regular hexagonal pattern connected by covalent sp2 bonds, and so do CNTs. Typically, the length to diameter ratio of this roll of graphene is tremendously high, and can be in hundreds of millions.
CNTs can be classified in different ways. If only one cylinder is present, the CNT is called single-walled CNT (SWNT). If there are two or more cylinders stacked co-axially, like rings of a tree trunk, the nanotube is called a double-walled CNT (DWNT) or multi-walled CNT (MWNT) respectively. Diameters of SWNTs range from 0.3-2 nm, while those of MWNTs are 10 nm and larger [2,3].

The hexagonal sheet which is rolled up can be done so in infinite number of ways, by rolling it up in different directions. This introduces another property to CNTs, viz. ‘chirality’. CNTs can thus be classified by chiral angle. The chiral angle is the angle formed between the long axis of the CNT and the line created by the carbon atoms on the wall. This is shown in Figure 1.

![Chiral angle for a CNT and chiral vectors](image)

Figure 1: Chiral angle for a CNT and chiral vectors [4]

The chiral angle is always between 0-30° due to limited number of arrangements possible with hexagonal structure. Two special types are zigzag CNTs and armchair CNTs, with corresponding chiral angles 0° and 30° respectively. Chiral angle decides whether a CNT is metallic or semi-conducting.
Figure 2: (A) Schematic illustration of armchair, zigzag and chiral CNTs L-R respectively [5]; (B) An atomically resolved image of a chiral nanotube as observed in STM experiments [6]; Schematic of a multi-walled carbon nanotube [7].

1.2 Properties of CNTs

CNTs possess outstanding material properties, and their physical and chemical properties have been pretty much established in the past decade.

Table 1 gives a good summary of physical, electrical and thermal properties of CNT material on molecular level as well as macroscopic level, and their comparison with conventional materials.
1.3 Vision and objective

Looking at the properties of CNTs, it is obviously a super-material. Why don’t we see CNTs in our daily lives then? CNTs themselves on molecular level are one of the strongest materials on this globe, but the macro-scaled product can reach nowhere near that. Only a few percentage of reported CNT strength is shown by a CNT yarn [9–12]. In fact, CNT yarns produced by dry spinning methods can still not match the tensile strength of commercially available high strength fibers like Kevlar or Dyneema.
Thus, in theory CNTs surpass most of the known materials, but their true potential, unfortunately, has hardly been utilized in practical use. According to Jiang et al. [13] there are three major hurdles to overcome. i) How to scale up the synthesis to meet industrial demand? ii) How to control diameter, number of walls and synthesize super-aligned SWNTs? iii) How to achieve real applications?

There are numerous defects present in actually manufactured CNTs, and this brings a huge limitation on their real-life applications. Defects are introduced during their growth phase, during their assembly into a macro-scale material, and even during the post-processing. There can be amorphous carbon, non-hexagonal rings (5-7 pair), kinks and different crystallographic defects present. To realize true potential of individual CNTs, defect reduction is the key. High temperature annealing is one of the approaches used to heal defects. We sought to improve material properties of available CNTs by this process, which is explained in the second part of the thesis.

The reason behind low strength of CNT yarns lies in the fact that although the building blocks (CNTs themselves) of the yarns are super-strong, during assembly they do not form a monolithic uniform structure but just a collection of discrete CNTs [14]. In order to achieve the best of the properties into the macro-scale materials, plus meet the ever-growing demand for industrial use, synthesis and use of long CNTs is inevitable. At the same time, long CNTs can very rarely be dry-spun into fibers. How to overcome this catch-22? First part of this thesis describes attempts made to achieve this target. Section 2.1 explains this need of an improved spinning process in detail.

1.4 An overview of yarn spinning
To enable practical use of CNTs, they need to be transformed into a usable, macroscopic form. One of these macroscopic forms is a CNT yarn. A CNT yarn is in general produced by three different approaches, viz. ‘Solution spinning’, ‘Gas phase spinning’ and ‘Forest dry-spinning’. While the first approach can only be used to produce composite yarns made of CNTs and polymers, the latter two produce pure CNT yarns [14].

1.4.1 Solution spinning

In 2000, Vigolo et al.[15] invented a method to assemble SWNTs into long ribbons or fibers. The ‘solution spinning’ or ‘wet spinning’ approach works by dispersing CNTs in a fluid medium (e.g. a surfactant solution) and then forming a thread or sheet, by coagulation of the medium or by filtration of CNTs from the medium [16] as shown in Figure 3. Productivity and properties of threads produced by this approach are strongly dependent on how well the CNTs are dispersed and how the drawing and post-processing is performed [17].
The other two approaches, viz. forest spinning and direct spinning eliminate the necessity of this intermediate liquid medium and directly utilize CNTs to make threads.

1.4.2 Gas phase spinning

In the gas-phase spinning technique, CNTs are synthesized in vapor phase in a vertical reactor. They form an aerogel inside the reactor, in the shape of a sock or stocking. CNT ribbon is drawn at the bottom of the reactor. It is a continuous method, and the longest reported thread drawn by this method is longer than a kilometer [18]. Apart from high productivity, another major advantage of this method is the strength of the yarns produced. These CNT yarns have easily surpassed the specific strength of other commercially available high-strength fibers [19].
1.4.3 Solid state (forest) spinning

The 'forest spinning' technique was discovered ten years ago in 2002 by Jiang et al [22]. They drew a 30 cm long yarn from a super-aligned CNT array for the first time. In such kind of an array, CNTs are vertically aligned and almost perpendicular to the substrate [23]. It closely resembles a densely packed forest of bamboo trees (hence the name). An SEM image comparison of ordinary and super-aligned arrays is shown in Figure 5(L). It is a highly pure, high quality array with minimal metal catalyst contamination present only at the tips and roots of straight CNTs. Unlike solution spinning, there is no contamination from fluid residue in the final assembly [16]. Hence forest spinning is advantageous when a very high purity CNTs product is desired. A drawing of ribbon from an array is shown in Figure 5(R).

Figure 4: Schematic of direct gas phase spinning: (a) drawing of a CNT fiber [20], (b) drawing of CNT ribbon outside the furnace hot zone [20], (c) important reactions taking place in the process [14][21]
Figure 5: Left: Comparison of super-aligned (a) and ordinary (b) arrays. CNTs in array (a) have a much better alignment than those in array (b) [24]. Right: Close-up SEM image showing drawing of a ribbon from a super-aligned array in progress [16]

However, it is a fairly complex process dictated by the ‘drawability’ of a CNT array. Drawability can be defined as the ability of a pulled row of CNTs at the edge of an array to pull along with them the adjacent row of CNTs, forming a continuous ribbon of CNT material [9,25]. This drawing-capability is attributed to the strong van der Waals forces between neighboring CNTs. For maximum van der Waals attractive force, (a) the CNT surface should be extremely clean, (b) the CNTs should be closely spaced to each other and (c) there should be minimal amorphous carbon present [13]. According to a more recent approach proposed by Kuznetsov et al [26], the ‘drawability’ not only depends on the good alignment of CNT bundles in an array[24,27], but it more importantly depends upon the structural interconnections between larger MWNT bundles in an array. They explain the mechanism of dry-drawing of yarn from a super-aligned MWNT array through a structural model, as shown in Figure 6. Individual CNTs or smaller CNT bundles connect larger CNT bundles in such arrays. There are two processes that take place during dry-drawing. When attempted to draw, these interconnections are peeled off preferentially and CNTs are
unzipped. Further, densification at the top and bottom of the forest takes place when bundles are being re-oriented, which further strengthens the interconnections.

Figure 6: Interconnect approach of drawing: (L) Schematic of CNT forest consisting of bigger and smaller bundles. (R) Unzipping – zipping process causes the interconnects to move along the forest tree lengths, so as to concentrate these connects at forest tree ends. In the detail, angles of peeling at both adjacent bundles and the respective forces $F_1$ and $F_2$ are indicated. Red arrow represents the external force used for the draw. [26]

In 2004, Zhang et al.[9] introduced a twist during drawing ribbon of CNTs, and achieved yarn strengths greater than 460 MPa. An example of such a twisting process is shown in Figure 7.
Figure 7: CNT forest in the process of spinning. Overall process and detailed imaging of different parts during spinning: (A) Overview; (B) Self-assembly of CNTs while being pulled; (C) details of twist insertion; (D) Details of yarn structure [16].
2 Electrically Assisted Spinning of Yarn

2.1 The need of an improved spinning technique

Synthesis of spinnable CNT arrays is a difficult process which needs very special and precise growth conditions [28][26]. Present methods of dry-spinning are limited to short arrays, with extremely clean surfaces and close CNT spacing. Many arrays are rendered useless for dry-spinning by slightest deviation from the synthesis recipe. Today we are facing an ever-increasing demand for high-quality, uniform and high-purity CNT thread for research, potential applications and commercial use. Long-array CNT twisting has become a hot topic for many industrial applications, like high-strength fibers with excellent conductivity, especially for high-frequency use[29]. Forest spinning has its own advantages, but at present, it lacks the commercial viability of producing yarn at the competitive production rates. The demands for faster production of CNT yarn are high, and ultra-tall CNTs can satisfy that need [30].

Further, taller CNT forests can produce a much thicker thread than short CNT forests for same array width (60-80 µm thread diameter for an array height of 5 mm vs. 5-10 µm diameter for array height 300-600 µm) [29]. This property can be important in certain applications.

The number of defects dictates the quality of CNT thread. A CNT yarn is nothing but a structure built from discrete CNTs held together, and each gap or junction between two CNTs can be termed as a defect. Longer nanotubes not only lessen the number of gaps in a given length of thread, but also provide a longer length for mechanical interlocking of each nanotube with its neighbors [31]. It has been shown that in order to achieve better physical properties, a better contact between adjacent CNTs must be attained. e.g. higher specific and dynamic moduli of CNT yarns achieved by a novel technology have been attributed to a high CNT-CNT contact length in denser packing [32].

Thus yarn strength can be improved by increasing (a) CNT quality (b) CNT length and (c)
CNT aspect ratio [16]. Liu et al. have also reported the similar finding for sheets, that longer drawable arrays give denser sheets with lower resistivity [24]. Naturally, longer and longer CNTs will be used to spin thread when we are able to grow high quality long CNTs [31].

Unfortunately, presently manufactured longer CNT arrays are rarely spinnable. Many research groups have recently focused on producing longer CNTs, but only a few have synthesized high-quality long CNT arrays [33–38]. Further, even fewer have achieved drawing of yarn from longer arrays. Zhang X. et al. [39] have reported nanotube fibers spun from 0.65 mm long CNTs, while Zhang S. et al. [40] succeeded in drawing yarns by dry spinning a 1 mm long MWNT array. Our group was the is the only group (Jayasinghe et al.) which has reported direct dry-spinning from ultra-long arrays of lengths 4-6 mm [29].

Except above notable exceptions, drawability is generally limited to short super-aligned arrays of height less than 300 µm, which limits not only the production potential but also the strength of the thread produced to a few hundreds MPa [9,25]. Thus, from the point of view of productivity and superior material property, it is important to use longer arrays.

If a method could be developed to improve spinnability of long, strong but conventionally non-spinnable arrays, it will be a breakthrough idea. We now explain the attempts made towards achieving this goal through use of simple principles of physics, such as electricity and magnetism. Different approaches are used, including electromagnetic drawing, electrostatic drawing, use of permanent magnets with deposition of a ferromagnetic metal on arrays etc.

2.2 Basic Principles

Electromagnetic assisted drawing is an improved drawing method making use of electrical energy. In this method, magnetic attractive forces induced by electrical current are used to assist the drawing of yarn.
2.2.1 Generation of magnetic field

A moving charge produces a magnetic field around it. Thus, whenever a wire is carrying current, there is a magnetic field generated around it. This is shown in Figure 8.

![Figure 8: Schematic showing magnetic field generated by flow of current around a carrier](image)

The direction of the field is given by the right hand thumb rule. When you curl your fingers around the conductor in such a way that your outstretched thumb indicates the direction of the conventional flow of current, the curled fingers indicate the direction of the magnetic field around the conductor. The magnitude of the magnetic field is given by following equation (Eq. 1):

\[ B = \frac{\mu . I}{2 \pi r} \]

where \( I \) is the current flowing through the wire, \( r \) is the radial distance between then wire and the point at which field is measured and \( \mu \) is a constant called magnetic permeability and is specific to the medium in which the whole setup lies. For vacuum, \( \mu \) becomes \( \mu_0 \), and is called 'permeability of free space'. \( \mu_0 \) equals \( 1.2566 \times 10^{-6} \) T.m/A.

Further, whenever a charge is moving in a magnetic field, a force is exerted on the charge, according to Lorentz force law, which states \( \vec{F} = q (\vec{E} + \vec{V} \times \vec{B}) \). Because no electrostatic field (E) is present, it reduces to \( \vec{F} = q \cdot \vec{V} \times \vec{B} \), where \( q \) is the charge on the particle, \( \vec{V} \) is the direction vector ...
for the moving charge and $\vec{B}$ is the magnetic field in which the charge is moving. Again, it is a vector cross product and direction of $\vec{F}$ is given by right hand rule.

Finally, consider a segment of a wire of length $\Delta L$ carrying a current $\vec{I}$, and $q$ is the amount of total moving charges in the wire segment. Thus $\vec{I} = q \cdot \vec{v}$ and hence (Eq. 2)

$$\vec{F} = (\vec{I} \times \vec{B}) \cdot \Delta L$$

where $\vec{F}$ is the force on wire segment.

These two concepts (Equations 1 and 2) are the fundamentals used in modeling the electromagnetic assisted spinning.

2.2.2 Attraction between two parallel conductors

As seen earlier, whenever a conductor carries a current, it generates a magnetic field around it. When two conductors are placed side by side, parallel to each other, and both of them are carrying electrical current, they both generate their own magnetic fields around themselves. Further, magnetic field generated from each conductor applies a force on the moving charges in the other conductor.
As shown in Figure 9, consider two parallel wires carrying currents $I_1$ and $I_2$ respectively, placed at a distance $r$ from each other. Magnetic field at wire 2 because of wire 1 is $B_{21}$, and field at wire 1 due to wire 2 is $B_{12}$. Hence, $B_{12} = \frac{\mu I_2}{2 \pi r}$, and $B_{21} = \frac{\mu I_1}{2 \pi r}$. Force exerted on a segment of wire 2 of length $\Delta L$, from earlier equations will be

$$F_2 = \left( I_2 \times B_{21} \right) \Delta L$$

Because the angle between $I_2$ and $B_{21}$ is 90°, magnitude of $F_2$ is

$$F_2 = I_2 \cdot B_{21} \cdot \Delta L \cdot \sin 90° = I_2 \cdot B_{21} \cdot \Delta L$$

Substituting value of $B_{21}$,

$$F_2 = I_2 \cdot \frac{\mu I_1}{2 \pi r} \cdot \Delta L$$

Hence, force per unit length of conductor is given by

$$\frac{F_2}{\Delta L} = \frac{\mu I_1 I_2}{2 \pi r}$$
Similarly, force per unit length exerted on wire 1 will be

\[
\frac{F_1}{\Delta L} = \frac{\mu \cdot l_1 l_2}{2 \cdot \pi \cdot r}
\]

2.3 Theory and modeling

Carbon nanotubes are good conductors of electricity[41]. In a CNT array, nanotubes are standing parallel to each other with a small spacing, depending upon their synthesis. Also, during drawing of yarn, CNTs maintain their alignment. A web is nothing but many CNTs sticking end to end to one another held in place by van der Waals force of attraction. This means that if a current is passed through CNTs in an array or a drawn web, they will act just like parallel conductors placed next to each other. Using above equations on a densely packed CNT arrays, we can estimate the force with which two CNTs will be attracted to each other while being pulled out of the array. If this force exceeds the force holding back the next row of CNTs, there might be a continuous drawing possible.

In prior experiments in Nanoworld Labs[42], a CNT thread was suspended between two electrodes in vacuum. When an alternating current was passed through the thread, it started to whirl due to the interaction of magnetic field generated in the thread with the earth’s magnetic field, as shown in Figure 10. This showed that even small force can move the CNTs by magnetic interaction, especially owing to their ultra-low density.
2.4 Experiments

2.4.1 Macro-scale experiments with CNT threads

We sought to test the electromagnetic attraction on a macro scale first, using pre-spun CNT threads. These results would later be used in drawing CNT yarn from the arrays while conducting current.

2.4.1.1 Thread experiment #1

The very first setup consisted of 4 bare copper wires mounted on a PCB. CNT thread was mounted at the top ends of the copper wires using silver epoxy paste, as shown in Figure 11.

Figure 10: A glowing thread, whirling due to magnetic field [42]
Figure 11: Attraction of CNT Thread – Initial experiment

Bottom ends of the pair of copper wires on the same side were tied together for simplicity of connections. A piece of paper was put in the background for visual contrast. Resistance measured between the two terminals after making all the connections was 566 Ω. Even after passing sufficient current, there was no movement observed in the two CNT threads. This might have been because the threads were not very close to each other and had a fair tension in them. After re-adjusting and bending the copper wire supports towards each other and hence making the threads slightly slack, the experiment was repeated.

This time, resistance between the external contacts changed to 674 Ω. This variation is normal, due to the role played by the contact resistance at every connection. Also, the paper piece in the background was replaced by aluminum foil, because paper is not good in vacuum chamber for the turbo-pump health.

The experiment was successful. The two CNT threads were clearly apart before passing the current. Although the movement was difficult to observe due to thin wires and bad contrast, after passing current the wires glowed red, and a reasonable portion of the two wires was seen touching each other. After reducing the voltage threads, now back to black, were again separated. This was repeated one more time with the same observations. Although values of current and voltages were
not noted, this experiment validated the principal of attraction of two parallel conductors carrying like currents.

It was a rather crude setup, with many practical difficulties. Mounting of thread on the wires was troublesome. Also because there were 4 leads to manage, it was difficult to get the two threads straight, with low sag, and exactly parallel to each other.

2.4.1.2 Thread experiment #2

The second setup consisted of only two copper wires, instead of four, mounted at about 1.5” apart on a PCB. Again, CNT thread was mounted using silver epoxy at the ends of the wires, but this time a loop of CNT thread was made around the two copper wires. This ensured that the two CNT threads are fairly parallel to each other. It was also easier to manage.

![Image](image1.png)

**Figure 12: Attraction between CNT threads: (L) PCB with threads mounted on copper wires. Black arrows point to the threads. (R) Tripod setup with camera to record video of the experiment**

The trial was conducted inside the vacuum chamber. A tripod stand was set up outside the vacuum chamber to record a video of the experiment. Voltage and current values, along with the distance between threads observed are reported in Table 2 and then the curves are plotted.

- Resistance between two terminals = 670 Ω
- Power-supply used: Up to 50 V DC
Table 2: Current and voltage relation for magnetic attraction of CNT treads, experiment #1

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current-Up (mA)</th>
<th>Current - Down (mA)</th>
<th>Distance (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>26</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.65</td>
<td>25</td>
</tr>
<tr>
<td>1.5</td>
<td>2.37</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>3.57</td>
<td>3.38</td>
<td>20</td>
</tr>
<tr>
<td>2.5</td>
<td>4.32</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>5.35</td>
<td>5.42</td>
<td>16</td>
</tr>
<tr>
<td>3.5</td>
<td>6.28</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>7.46</td>
<td>7.51</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>9.9</td>
<td>9.88</td>
<td>5</td>
</tr>
<tr>
<td>5.5</td>
<td>11.07</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

The distance is measured from the video-recording of the experiment. It was not possible to measure actual distance between the thread due to unknown scaling factor, so on screen distance is measured in arbitrary units.

![Current - Voltage - Distance Chart](chart_image)
It is seen that the current-voltage curve is very linear and also repeatable. The experiment definitely showed that there is electromagnetic attraction between two CNT threads carrying like-currents. However, some improvements in the setup were discussed over. In the current setups, the CNTs are freely hanging from the two wires and are free to move in a 3-D space. It was suggested the movement of the CNT thread could have been affected by the earth’s magnetic field, as in case of the whirling thread. Hence, another setup was proposed with the CNTs lying on a flat surface, constricting their motion to a single plane, i.e. 2-D freedom of movement.

2.4.1.3 Thread experiment #3

In order to achieve a 2-D movement of the CNT threads, two CNT threads were laid out flat on a glass slide, parallel to each other with very small distance between them, and held in place with small drops of conductive epoxy at the two ends.
Figure 14: Attraction between threads experiment – preparation of the glass slide

A bare copper wire was placed on the epoxy joint and held in place using clamps. More conductive epoxy was applied on the joint, and allowed to set. The same procedure was followed for the other end.

This arrangement was neater than mounting the CNT threads on two poles of copper wire directly. The CNT threads were much more parallel to each other and very closely spaced. This was nearly impossible to achieve practically in both the previous setups. The slide, spacing between the thread and the overall thread length is shown in Figure 14. Again, the experiment was conducted inside the vacuum chamber and recorded using a Sony camcorder.

Narrowest Spacing = 0.2 mm
Overall Length = 15 mm

Additional safety measures as compared to the PCB experiment were taken as follows:

1. The work-table was grounded using a thick grounding wire.
2. All the connections made using alligator clips were taped using insulating tape, making sure there is no exposure to bare metal.

Figure 15: Safety measures taken: (L) grounding of the work-table using the green wire, (R) coating exposed wires with masking tape
The experiment was conducted in vacuum. The current and voltage was observed. The experiment was conducted in three parts,

Part 1. I-up (1st run)
Part 2. I-down (1st run)
Part 3. I-up (2nd run)
Part 4. I-down (2nd run) could not be plotted because the thread broke at the end of Part 3 when the thread was glowing brightly.

Table 3: Current and voltage relation for magnetic attraction of CNT threads, experiment #2

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Part 1 I-up (mA)</th>
<th>Part 2 I-down (mA)</th>
<th>Part 3 I-up 2nd run (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.8</td>
<td></td>
<td>1.08</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.73</td>
<td>2.17</td>
<td>2.07</td>
</tr>
<tr>
<td>1.1</td>
<td>2.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>2.1</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>2.27</td>
<td>2.89</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>2.66</td>
<td></td>
<td>3.45</td>
</tr>
<tr>
<td>1.6</td>
<td>2.94</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>3.21</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>1.9</td>
<td>3.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.76</td>
<td></td>
<td>4.49</td>
</tr>
<tr>
<td>2.1</td>
<td>4.04</td>
<td>4.82</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td></td>
<td>4.03</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>4.44</td>
<td>5.48</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>4.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>4.89</td>
<td></td>
<td>5.84</td>
</tr>
<tr>
<td>2.6</td>
<td></td>
<td>5.08</td>
<td>6.12</td>
</tr>
<tr>
<td>2.7</td>
<td>5.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td></td>
<td>6.78</td>
<td></td>
</tr>
</tbody>
</table>
Figure 16: Curves showing Current-voltage relation for magnetic attraction of CNT threads on glass slide

A video was captured showing clearly how the two CNT threads got attracted towards each other.

Some observations made are below:

Table 4: Observations for attraction of threads on glass-slide

<table>
<thead>
<tr>
<th>Part</th>
<th>Voltage range (V)</th>
<th>Current range (mA)</th>
<th>Behavior of threads</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 to 2.1</td>
<td>3.76 to 4.04</td>
<td>Threads stick together</td>
</tr>
<tr>
<td></td>
<td>2.6 to 3.0</td>
<td>5.08 to 6.21</td>
<td>Thread start going apart, even when the current is steadily increased</td>
</tr>
<tr>
<td></td>
<td>3.1 to 4.0</td>
<td>6.6 to 9.73</td>
<td>Threads stay apart</td>
</tr>
<tr>
<td>2</td>
<td>4.0 to 0</td>
<td>9.73 to 0</td>
<td>Threads stayed apart throughout the range as the voltage is</td>
</tr>
<tr>
<td></td>
<td>0 to 5.9</td>
<td>0 to 19.36</td>
<td>Threads did not get together, even though the current was much higher than the first run, where the threads were pulled together at only 6 mA</td>
</tr>
<tr>
<td>---</td>
<td>---------</td>
<td>-----------</td>
<td>--------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>6.2</td>
<td>22.8</td>
<td>Threads started getting closer. This current is way higher than the one in first run.</td>
<td></td>
</tr>
<tr>
<td>6.7</td>
<td>34</td>
<td>Threads started to glow when they were together. Most probably, this is when one of the threads broke.</td>
<td></td>
</tr>
</tbody>
</table>

As seen from the table above, there was some unexplained behavior of the thread regarding getting pulled together by current. A possible explanation could be localized melting of the glass slide due to red hot thread. Marks were observed on the glass slide after the experiment.

In this experiment both the wires were laid perfectly flat against the glass slide, eliminating the possibility of 3D movement in space. As the wires were clearly attracted towards each other, this experiment showed that the principal of attraction between two parallel conductors carrying like currents is applicable for CNT threads and the movement in the earlier experiments was not due to gravity or earth’s magnetic field.

2.4.2 Micro-scale Experiments with CNT arrays

After the experiment of electromagnetic attraction of two parallel CNT threads, the same principal was applied to a CNT array on a microscopic scale. Given that the CNTs are very closely spaced, even very small currents can generate a strong attractive force between adjacent CNTs. It was proposed that this will be useful when trying to spin non-spinnable arrays.

Figure 17 shows the proposed setup.
2.4.3 Razor edge drawing in vacuum

The experiment was conducted inside the vacuum chamber and in vacuum in the range of about $10^{-4}$ mbar. A Teflon base was machined and fitted on the bottom manipulator screw rod. Another longer rod of Teflon was fitted on the rear manipulator screw rod, and a razor blade was attached at its end by making a slot in the end. An insulated electric wire was attached to the blade using alligator clamp. A non-spinnable CNT array was prepared to be mounted on the pedestal. On one side of the array a short bare copper wire was attached using conductive epoxy, so that the epoxy covered the entire edge of the array. After curing it overnight and then in the oven at 80 °C for 10 min, the array was placed inside the vacuum chamber on top of the Teflon pedestal using double sided tape. Another insulated electric wire was attached to the array through the copper wire. The rod and the base pedestal were adjusted in such a way that the blade just touched the top of the inside edge of the array. With movement of the manipulators, the razor edge could be touched to the array or moved away from the array at a slight angle and in a smooth movement.

Figure 17: Schematic of suggested setup: (1) is the spinning machine Teflon spool. We can adjust the height of pulley (2) which also acts as an electrode to vary the angle of pull. Electrode plate (3) would be at the end of the array close to the drawing spool.
Figure 18 shows the setup. The Teflon pedestal, Teflon rod, razor blade, alligator clamps, double sided tape, array with conductive epoxy and the copper wire can be seen. DC supply with constant voltage used.

![Figure 18: Drawing of thread with help of current using razor blade in vacuum. (L) Setup: Double sided tape, array, razor etc. can be seen (R) A spark while drawing](image)

Observations are noted in Table 5 below.

**Table 5: Observations of razor edge electrical drawing in vacuum**

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Peak current (mA)</th>
<th>Comments / Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>0.7</td>
<td>No drawing of the ribbon / thread.</td>
</tr>
<tr>
<td>2.0</td>
<td>2.1</td>
<td>No drawing of the ribbon / thread.</td>
</tr>
<tr>
<td>3.0</td>
<td>4.5</td>
<td>No drawing of the ribbon / thread.</td>
</tr>
</tbody>
</table>
| 4.0         | 7.0              | 1. Residual current of 0.65 mA when the blade was far from the array and it later dropped to almost zero as the blade was moved still farther away.  
2. First sign of arcing. A glow at the point of contact (POC) when I = 0.6 mA  
3. Occasional momentary arcing at 2 POCs  
4. Arcing repeated while retracting the blade                                                                                                                                                                                                                     |
| 5.0         | 9.6              | 1. Arcing at first POC with I = 0.7 mA,  
2. A *steady* arcing at two points repeated while retraction.                                                                                                                                                                                                                                                                                             |
<table>
<thead>
<tr>
<th>Voltage</th>
<th>Time</th>
<th>Observations</th>
</tr>
</thead>
</table>
| 6.0     | 12.0  | 1. 0.3 mA residual current, brighter arcing, arcing seen at 3 or more points.  
2. A small thread appeared to be sticking to the blade as it is retracted, with a visible arc, even when the blade was away. It was repeated, when the blade was advanced and then retracted. |
| 7.0     | 14.4  | Arcing at multiple points. |
| 8.0     | 17.2  | 1. Brighter sparks.  
2. A 1 mA residual current observed, even when the blade is away. It dropped down to 0.3 mA as the blade was advanced towards the array but not touching yet. |
| 9.0     | 19.9  | - |
| 10.0    | 24.0  | Still Brighter sparks at multiple points. No drawing of the ribbon visible.  
Slow retraction showed the same results. |
| 11.0    | 26.6  | 1. Much brighter sparks. Multiple sites of arcing.  
2. While retracting the blade, sparks observed when the blade was slightly away from the array.  
3. In the 2nd run at 11.0 V, a small thread looks like being pulled, which breaks after a short distance. |
| 12.0    | 30.0  | 1. As the blade is advanced towards the array, a small lump of CNTs sticking to the blade is pulled towards the array.  
2. Signs of sparks between blade and the wafer (when the blade is away from the CNT array) while changing the height of the pedestal. |

Discussion:

At 8 V, a residual current was observed even when blade wasn’t touching the array. Could this be because of tiny threads sticking to the blade invisible to the naked eye?

At 11 V, sparks were observed when blade was slightly away from the array. This is something similar to the previous comment.
At 12 V, a CNT lump jumped towards the array from the blade. This probably means there was some attraction due to applied potential difference.

A plot of current vs. voltage is shown below.

![Graph showing peak current vs. voltage](image)

*Figure 19: Curve showing peak current with voltage during razor edge electric drawing*

2.4.4 Experiments in air

Some yarn-drawing experiments were carried out outside of the vacuum chamber, with and without current, using a manual probe, either a flat edge or a pointed electrode. These experiments are explained below.

2.4.4.1 Using needle / probe

Drawing of yarn was attempted in air, using a conductive tip with DC voltage applied. A non-spinnable CNT array on Si substrate (1.5 mm tall) was fixed on a piece of paper and mounted on a plastic box using tape. The array was connected to a bare copper wire from one side using conductive epoxy. The box then was placed under the optical microscope. Figure 20 shows the setup. A probe with steel tip and wooden grip was used to try drawing a ribbon. A DC power supply (50V, 3A) was used to supply voltage. A multimeter was used to measure current. The experiment
was observed under the microscope, when the drawing was attempted. Also, the whole experiment was recorded using a Sony camcorder mounted on a table-top tripod stand.

![Figure 20: Setup of drawing of yarn in air using a needle probe with direct current](image)

Precautions:

Gloves were worn to avoid CNT contact. Mask to avoid particle inhalation was used. All the electrical connections were taped to make sure there are no exposed parts except for the tip of the probe.

Procedure:

Continuity of electrical connections was tested. Drawing of CNT ribbon or a thin yarn was attempted with no voltage first, by probing the array with the tip. Voltage was gradually increased in steps of 1 V and the experiment was repeated. Values of current at different points were noted. Observations were recorded for each voltage step. A picture of array as seen under the microscope is shown in Figure 21.
Figure 21: An optical microscope image showing (L) Array to be drawn; (R) Needle probe seen next to the array

Observations:

No significant drawing observed, other than occasional thread of a few mm length. Sparking started to occur at 5V DC, after which the experiment was stopped. Values of currents observed at different points at different voltages are listed below.

Table 6: Observations: Electrical drawing of yarn in air using a probe

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Current at arbitrary points (mA)</th>
<th>Comments / Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10, current is highly contact dependent.</td>
<td>When seen through the microscope, there did not seem to be any difference due to applied voltage, as compared to 0 voltage.</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Some part of CNTs started coming out with the probe, but no major drawing effect seen.</td>
</tr>
<tr>
<td>3</td>
<td>59, 43, 67</td>
<td>No significant drawing observed. A chunk of CNTs got attached to the probe at the point of 67mA current. But no drawing of ribbon seen.</td>
</tr>
<tr>
<td>4</td>
<td>40, 81, 104, 74</td>
<td>No significant difference</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Slight arcing was seen when the probe touched the array. Arcs were also seen when the CNT lump on the probe touched the main CNT array. Experiment was stopped</td>
</tr>
</tbody>
</table>
because a fume-hood or vacuum chamber should be used if there is arcing.

Finally, a picture of a spark while spinning is shown in Figure 22.

![Figure 22: Sparks observed during drawing in air](image)

2.4.4.2 Using Blade edge

Similar experiments were carried out using a straight sharp edge of a razor blade. Arrays were connected to copper wire using conductive epoxy, and voltage was applied while attempting to draw a ribbon. Observations were very similar to those listed in the previous observation table. Similar safety precautions were taken for this experiment also.

2.4.4.3 Use of conductive substrate

Instead of applying voltage only through the drawn portion of the ribbon, another setup was proposed which might provide a stronger magnetic field. In this setup, both top and bottom of the nanotubes are connected to two electrodes having a voltage between them. This setup requires that the substrate is conductive (so that it can act as an electrode at the bottom).

Trial on some arrays on conductive substrates (provided by Wondong Cho) was carried out. Observations are as below.
The array had a very brittle and hard top layer, almost ‘crunchy’. It cracked when pressure was applied and was attempted to draw. Even particles could be seen flowing out of the layer, looked almost like locally breaking a glass.

The substrates on which the arrays were never grown were tested. They were perfectly conductive. The substrate on which array was grown showed a small resistance (30 – 35 Ω) between opposite corners of the array. (CNTs from corners were scraped off to expose the substrate.)

![Figure 23: Schematics of (L) Array with conductive substrate – corners cleared for testing; (R) Partially spinnable array during drawing](image)

As seen sideways under the microscope and probed, the array was soft to touch. Looked quite straight grown. Except for the hard top, rest of the array looked good. However, no drawing was seen when attempted with a razor blade, a probe (with or without voltage) or a tape end.

2.4.4.4 Partially spinnable array

Partially spinnable arrays were tested for the above methods. Yarn started to get pulled but then broke after a short distance. The array itself was uneven at the spinning side due to partial spinning at places time to time.

An exhaust fan was used with a filter to grab loose particles. The suction fan was efficient in that it not just sucked in broken array particles, its powerful draft could be sensed on the partly drawn ribbon also.
2.4.4.5 Soft sticky amorphous array

An array was mounted on top of the Teflon base using double sided tape. Again, the array was connected to a copper wire using conductive epoxy on the opposite edge.

No voltage - It looked like a sticky mass of carbon nanotubes getting pulled apart. The array was soft and got squeezed easily. Unlike the other arrays, it stuck to the probe quickly but still there was no drawing or yarn.

Voltage was turned up at 1V. Current values kept fluctuating: 15 mA, 17.2 mA, 14.1 mA etc. It still felt like a soft and sticky mass, almost like it was wet. Probably there was too much Carbon in the recipe. Higher voltage was tried: 2.5V, Current: 57mA, 48 mA

No attraction between the lump of CNTs stuck to the tip and the rest of the array. The array seemed to crumble under pressure. No yarn was drawn.

Voltage: 5V - There was some sticking seen, but that might have been due to the fact that the array itself was sticky. Under closer inspection, if array was attempted to displace or move, it broke apart. There were small cracks seen while trying the drawing. Also, when pushed inside, the array got squeezed easily. Some small sparks were seen.

Voltage: 7.5 V- Current: 168mA, 181mA - Definite arcing and sparks were observed. While trying the drawing, the sparks seemed just to burn off the nanotubes. No drawing was observed. Some burning smell was noticed, and the experiment was stopped.

Usual safety measures including gloves, goggles, insulation tape, and exhaust fan were in place for the experiment.

After using the probe tip, drawing was also attempted with tweezers to see how the array behaves when grabbed into tweezers and pulled. Some CNTs indeed got attached and started getting pulled away. But then they broke apart in a very short distance. Drawing in different directions and angles was also attempted.
A video-recording of the whole experiment was made for reference and to closely watch the mechanism of drawing.

2.4.4.6 Annealed arrays on tape – with and without current

Tall CNT arrays (centimeter long) were high-temperature annealed at the Air Force Research Laboratory (AFRL). Drawing a yarn from these arrays was attempted. The arrays were taken off the substrate before annealing, because the substrates cannot withstand the high temperatures. Hence to provide a base to the arrays, they were put on a double sided tape and then drawing of ribbon was attempted.

![Figure 24: Drawing of a tall annealed array on double sided tape](image)

The process was watched under optical microscope for closer observation. It was noticed that the array even after heat treatment, was still not spinnable. It did not form a continuous yarn when tried to pull, instead, smaller chunks of array broke off from the tape. Also, it was noticed that the tape was too sticky, and the CNTs could not separate from the tape with ease. This could have been a reason for non-spinnability of the array.

Hence, another type of tape was used. We chose Painter’s tape because of its low adhesive properties. The tape was stuck to the base using a double sided tape with painter’s tape’s sticky side up. Then the array was placed gingerly on the tape making sure it was not pressed too firmly into
the glue. Drawing of yarn was attempted, as shown in Figure 25. It was noticed that even though the array was still non-spinnable, it could come off more easily than last time, and it did not break-off into pieces much. Some bundles were pulled while drawing yarn (unlike the previous case), but they broke off fairly easily and no ribbon was formed.

![Image](image.jpg)

**Figure 25: Drawing of a tall annealed array on painter’s tape**

2.4.5 Ni coating of CNT arrays

Arrays were coated with Ni to improve their conductivity and spinnability. Also, coated arrays were tested for drawing of ribbon using a permanent magnet. Two trials were conducted. Setup consisted of a Nickel electrolyte solution, a Ni wire coiled on a plastic strip to be used as an anode, DI water and a power-supply.
Preparation of arrays:

A razor blade was used to cut up an array at one of its edges and clear-up a small area on the Si substrate. Then an insulated copper wire with a stripped end was placed at the cleared-up edge and connected to the array using conductive silver epoxy. It was made sure that the whole cross-section of the cut edge was in contact with the epoxy. The epoxy was allowed to cure at room temperature overnight before conducting the experiment.

Procedure:

Prepared arrays were electroplated with Ni, by immersing into the electrolyte and applying voltage. The array was connected to the negative terminal of the power supply making it a cathode, while bare Ni wire was connected to the positive terminal via copper wire making it an anode.
Arrays were coated for different times and at different voltages. Then arrays were washed with DI water to remove excess electrolyte.

2.4.5.1 Trial # 1

Four arrays were coated. This trial was only to check possibility of electro-deposition of Ni on CNT arrays, so the experimental conditions were not observed very stringently.

Time and voltage was kept constant, viz. 60 seconds and 2 V. Current varied with each array.

Table 7: Observations: Ni coating on CNT arrays, Expt. #1

<table>
<thead>
<tr>
<th>Array</th>
<th>Description</th>
<th>Current (mA)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Array 1</td>
<td>Narrow, short array</td>
<td>20</td>
<td>Ni was visibly coated</td>
</tr>
<tr>
<td>Array 2</td>
<td>Short array, wider</td>
<td>7</td>
<td>Ni was visibly coated</td>
</tr>
<tr>
<td>Array 3</td>
<td>Long array, but the array had come off the substrate partially</td>
<td>37</td>
<td>Ni was visibly coated on the array. A lot of Ni was coated on the exposed</td>
</tr>
</tbody>
</table>
and Si substrate was exposed surface too.

| Array 4 | Long array. The array was dislodged from the Si substrate | 48 | Ni was coated visibly on the array. It was also seen visibly on the side of the array, but not so much on top. |

This trial showed that Ni can be coated on CNT arrays. Hence another trial with varied type of arrays, and different time and voltage was conducted as below.

2.4.5.2 Trial # 2

Five arrays of different sizes and shapes were used. Arrays were again connected using silver epoxy and a copper wire. Before electro-deposition, the type of the array, its observable physical properties were noted. Each array was attempted for drawing of yarn, and also its strength was roughly judged using tweezers. Arrays were given a relative strength rating on a scale of five. Afterwards the arrays were coated using the procedure as before. A constant voltage of 1V was applied and each array was immersed in the electrolyte for 30 s. Currents varied for each array depending on its area of exposure, resistance and other factors. Also, current varied during the coating. Initial and final currents were noted.

<p>| Table 8: Observations: Ni coating on CNT arrays, Expt. #2 |
|---|---|---|---|
| Array | Dimensions HxBxW (mm) | Current Start, end (mA) | Description / Notes | Strength Rating |
| Array 1 | 5x7x7 | 7, 4.5 | Had some springy curls at the top surface. Had a very aligned parallel smooth look from side. Easily cut with blade. When taken a lump of CNTs into tweezers and tried to pull, it broke fairly easily. | 2.5 / 5 |</p>
<table>
<thead>
<tr>
<th>Array 2</th>
<th>2.5 x 12 x 6</th>
<th>4, 8.5</th>
<th>Did not crumble to powder, however.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A more brittle top, but still could be cut with the blade fairly easily, as compared with the shorter array (array 4). No springy curls on the top surface. Did not crumble. Top crust was thicker, more prominent. The array was non-uniform in height, a bigger valley at center.</td>
</tr>
<tr>
<td>Array 3</td>
<td>7 x 6 x 6</td>
<td>3, 10</td>
<td>Squarish array. Crunchy brittle top crust. Hardly any coils / springs. Smooth and aligned from side. While cutting through the top, an audible 'crunch' was heard. Most brittle top crust among all the five arrays.</td>
</tr>
<tr>
<td>Array 4</td>
<td>&lt;1 x 10 x 13</td>
<td>2, 3</td>
<td>It was a very short, flat array. Crumbled when tried to pull a bundle apart. Definitely non-spinnable: when tried to draw, bundles just came off the array in chunks. Top looked smooth, not crunchy or brittle: easily penetrated. But very easily crumbled to powder, very difficult to handle. Could not get a strength rating.</td>
</tr>
<tr>
<td>Array 5</td>
<td>4 x 8 x 6</td>
<td>3, 7</td>
<td>Height was uneven. But average height reported. Smooth top, with crust. Crunchy. Broke fairly easily. When tried pulling with tweezers, broke quite easily.</td>
</tr>
</tbody>
</table>
SEM images of the coated samples are shown in Figure 28. As seen from the SEM images, Ni was successfully deposited on the CNT arrays. Especially, top surface of the arrays was densely coated with Nickel for cases of high currents. The array, however seems to be broken into smaller lumps of CNT bundles grouped together with Ni deposited on top of each lump.

![Figure 28: SEM images of Ni coated arrays](image)

Drawing of ribbon was attempted for these arrays with the help of a strong permanent magnet. Even though ferromagnetic Ni was deposited on the arrays, it showed no significant attraction towards the magnet, and the array could not be drawn into a ribbon.

2.5 Results and discussion

Various methods were attempted for spinning of yarn from non-spinnable arrays. Even though a method to make non-spinnable arrays spinnable was not found, valuable information was obtained through the experiments. Behavior of CNTs was better understood under certain
situations, e.g. when coated with Ni, or while conducting current in vacuum. The whole endeavor was a steep learning curve in regards with the safety measures to be taken, material handling, electroplating etc. Experience with the use of equipment like SEM, vacuum chamber etc. was gained, which was useful for the various experiments carried out later.
3 Electrical Annealing of CNT Material

3.1 An overview of annealing methods

As mentioned in Chapter 1, CNTs show a high potential for use as a novel material in varied applications. Research has proved that they are a promising material for electrical interconnects [43–45], thermal interfaces [46–48] and high performance fibers [15,19,49], and many more state-of-the-art applications. However, their true potential has hardly been utilized in practical use. This is because of numerous defects present in actually manufactured CNTs, which brings a huge limitation on their real-life applications. To realize true potential of individual CNTs, defect reduction is the key [50]. High temperature annealing is one of the proven methods which helps heal defects in CNTs.

3.1.1 What is annealing?

Annealing is nothing but a high temperature, vacuum or inert environment treatment on CNT arrays. Lambert et al. [51] first used annealing (at 1600 °C, 10⁻⁶ mbar) to remove metal impurities from CNTs, and while doing so observed formation of some new graphitic structures. Since then, a lot of research has been performed to understand, control and benefit from this phenomenon for practical use.

Typically, 1200 °C is temperature needed to anneal SWNTs [52], while a higher temperature (above 1900 °C) is needed for annealing of MWNTs [53–55]. Another study [56] indicates that 1700 °C was optimal temperature for annealing of DWNTs.

3.1.2 Types of annealing

There are different types of annealing methods used today. Thermal annealing is the conventional method, and has been studied in depth [57–59]. Other recent methods include microwave annealing [50], vacuum arc annealing [60,61] and use of laser pulses for heating [62].
Electrical heating (Joule heating) of CNTs and their interconnects has also been studied till breakdown of CNTs, and highest current densities have been determined [63,64].

3.1.3 Effects of annealing

In an annealing study (ranging 900 – 2800 °C), Chen et al. [65] confirmed that temperature and time both play a role in defect healing, but temperature is a more important parameter. There are 3 temperature zones of structural changes: the first zone in which no significant changes occur, the 2nd zone in which there are radical enhancements and the 3rd zone in which structural development saturates. Several effects of annealing on CNTs have been studied, as discussed below.

3.1.3.1 Healing of structural defects and removal of amorphous carbon

A study concluded that Raman was a more effective way to measure kinetic studies of annealing of CNTs (for their experiments)[65]. Generally, the I_G/I_D ratio can be used as an indicator of the extent of defect or disorder within CNTs [57]. With degree of disorder, D and D' bands' intensities increase and that of G band reduces. Also, D band’s width is a better parameter to indicate degree of disorder, while its position doesn’t much vary with it [66]. A sample Raman signature of annealed versus non-annealed CNTs is shown in Figure 29: Raman signatures of annealed and non-annealed CNT samples [67]. The I_G/I_D ratio shows the extent of disorder within the CNTs.
3.1.3.2 Purification and removal of catalyst

Metal catalyst particles are often trapped in the nanotubes. There can be metal inclusions inside the tubes or at the tips. These metal particles cause toxicity [68], and hence their removal is critical for biomedical applications of CNTs. Methods exist to remove metal impurities, e.g. acid washing, but they are not very effective for removal of metal particles enwrapped by carbon layers [69]. A long time ago, Lambert et al. [51] confirmed that catalytic metal particles can be successfully removed by annealing at temperatures higher than evaporation temperatures of the metal catalyst. A sample graph of catalyst residue with temperature is shown in Figure 30 (R).
3.1.3.3 Improvement in electrical properties

Electrical properties of CNTs are dependent on the annealing treatment given to the nanotubes [71]. In a research conducted by Bulmer et al. [72], it was discovered that annealing temperature plays a vital role in this process. At an optimal temperature of 2500 °C, specific conductance of the CNT yarn tested was increased by 70%. Above this temperature, though, effect of annealing again starts to fade. This result is shown in Figure 31.
3.1.3.4 Improvement in mechanical properties

Because of removal of structural defects, kinks and dislocations, and possible formation of extra walls in a MWNT, mechanical strength of CNTs goes up after annealing, as shown in Figure 32. This is seen for both individual tubes as well as composites.

Figure 32: The curve shows improvement in Young's modulus of CNTs after graphitization [67]
3.1.3.5 Stability at higher temperatures

Heat treated nanotubes show higher thermal stability, as shown in numerous studies [56,73–75]. Thermo-gravimetric analysis curves of a study are shown in Figure 33 as an example.

![Figure 33: TGA curves of three types of nanotube samples: AC are as received CNTs, C-12 are heat treated at 1200 °C and C-18 at 1800 °C. [76]](image)

3.2 Electrical annealing

We sought to develop a quick set-up, convenient to use and easy to monitor annealing method for CNTs in different shapes and forms, like CNT thread, tile or tall arrays. CNTs are conductive, but just like any other material, they still offer some internal resistance to the flow of electrons. We used this property to heat up carbon nanotubes up to annealing temperatures by forcing an electric current through them.
3.3 Annealing of Arrays

3.3.1 Using copper foil electrodes

Annealing was attempted using thin copper foil as conduction electrodes. The proposed experiment is shown in Table 9.

Table 9: Proposed experimentation of annealing of arrays: Axial and transverse

<table>
<thead>
<tr>
<th>Part (A)</th>
<th>Part (B)</th>
<th>Part (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing with axial current</td>
<td>Annealing with transverse current</td>
<td>Untouched, for comparison</td>
</tr>
</tbody>
</table>

3.3.1.1 Experiment #1

Vacuum annealing of CNT arrays by passing direct current was attempted. A long CNT array (height = 6 mm) was sliced in half, and taken off the substrate. The other half was kept untouched for comparison later. Setup was as below.

The array was held between two copper foil pieces. The copper plates were attached to electric insulated wires using flat-headed copper clamps. The top of the array was not flat, as is the case with most of the long arrays. The top copper plate was bent to achieve a better contact surface. This whole setup was placed inside a thick-glass Petri dish. The insulated wires were secured to the Petri dish using electric masking tape to restrict any movement. The wire was bent and taped in such a way that the arrangement ensured some constant pressure on top of the array. The Petri
dish was then placed inside the vacuum chamber and electrical connections were made. Picture of the setup is shown in Figure 34.

![Figure 34: (L) schematic of curved top of the array and a conforming electrode; (R) Actual setup of array annealing.](image)

Direct current was passed after maximum vacuum, and values of voltage and corresponding current were noted. At about 4 V the array started getting red hot. The array was getting heated non-uniformly due to uneven contact with the electrode. The experiment was continued until the current reached a maximum value of 1 A which was the limit of the power supply. It was maintained there for 10 min, and then the voltage was dropped to zero in steps of 1 V. To test repeatability, it was repeated in steps of 0.5 V and values of current were noted.

**Before Annealing**

Array resistance (between copper clamps only) = 235 Ω

Array resistance (across terminals out of the vacuum chamber) = 274 Ω

**After Annealing**

Array resistance was 11.6 Ω immediately after annealing, but the multi-meter showed an unstable value. Resistance increased rapidly with time and reached a steady value of 105 Ω finally.
Figure 35: Picture sequence showing stages of glowing of array due to current

Table 10: Current and voltage relation for annealing of tall array

<table>
<thead>
<tr>
<th></th>
<th>Increasing Voltage</th>
<th>Decreasing Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Voltage (V)</td>
<td>Current (mA)</td>
</tr>
<tr>
<td>1st Run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
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<td>0</td>
<td>5.1</td>
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<td>1</td>
<td>40</td>
<td>4.9</td>
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<tr>
<td>2</td>
<td>92</td>
<td>4.4</td>
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<tr>
<td>3</td>
<td>156</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>3.4</td>
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<tr>
<td>5</td>
<td>700</td>
<td>3</td>
</tr>
<tr>
<td>5.15</td>
<td>840</td>
<td>2</td>
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<td>5.4</td>
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<td>0</td>
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<td>1</td>
<td>105</td>
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<td>4</td>
</tr>
<tr>
<td>2</td>
<td>228</td>
<td>3.5</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>Current (mA)</td>
<td>Resistance (Ω)</td>
</tr>
<tr>
<td>------------</td>
<td>--------------</td>
<td>----------------</td>
</tr>
<tr>
<td>2.5</td>
<td>301</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>396</td>
<td>2.4</td>
</tr>
<tr>
<td>3.5</td>
<td>481</td>
<td>1.9</td>
</tr>
<tr>
<td>4</td>
<td>604</td>
<td>1.5</td>
</tr>
<tr>
<td>4.5</td>
<td>722</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>880</td>
<td>0.5</td>
</tr>
<tr>
<td>5.4</td>
<td>1012</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 36: Curves showing current-voltage relation for annealing of array using copper foil electrodes**

It can be noted that after the initial annealing (Run 1 – Up: Red Curve), the resistance of the array decreased permanently. This can be seen from the repeatable V-I curve for further runs.

Conclusions:
Better contact area between copper and array is critical for uniform heating. A thinner foil which will deform easily and conform to the array shape might prove more beneficial. To ensure constant and uniform pressure on the array, a small deadweight can be used. Measuring resistance of a CNT array is tricky. A higher configuration multi-meter is required for accurate measurement. More experimentation with varying annealing times (e.g. 15 min, 30 min, 60 min, 120 min) and comparison is needed to test the method. Current was limited to 1 A due to the power supply limitation. A larger capacity power supply should be used.

3.3.1.2 Experiment #2

Vacuum annealing of a CNT array loaded with a deadweight, by axially passing direct current. A long CNT array (length = 7 mm) was sliced in 3 parts. Apparatus used was the vacuum chamber, two power supplies (120 V, 1 A and 18 V, 5 A), multi-meter (Fluke 87), flat copper clamps, insulated wire, glass Petri dish, masking tape etc.

This time also, the array was held between two copper foil electrodes, which were connected to the power supply through flat-headed clamps and insulated wire. The array and electrodes were set up in a glass Petri dish, which in turn was placed in the vacuum chamber. A small deadweight (20.2 g) was placed on the top copper foil to exert a uniform pressure on the array. A blind quick flange was used as a handy dead weight. This step ensured a good electrical contact between the array and the electrodes. A picture of the setup is shown in

Figure 37.
Please note that the deadweight and the clamp were not touching each other as appears in the picture. An air gap could be clearly seen from the front view of the setup.

Procedure and observations is as follows.

Resistance:

- Before annealing, without deadweight: 476 Ω
- Before annealing, with deadweight, in air: 78.9 Ω
- Before annealing, with deadweight, in vacuum: 63.4 Ω
- After annealing with the 1st power-supply: 3.9 Ω

As seen from resistance values, the weight greatly improved contact between the array and copper foil, decreasing the overall resistance from 476 Ω to 79 Ω.

Cross-sectional area of the array was 20 mm² (5 mm x 4 mm). Two power-supplies with current ratings of 1A and 5A were successively used. Using the first power-supply, voltage was increased in steps of 0.1 V. At 2.8 V, current reached the peak value of 1.013 A. The array did not get
red hot at this point. The current was passed for approx. 10 min, before turning the voltage down. It has been observed that as time passes, smaller and smaller voltage is required at a constant current. As expected, the resistance of the array kept decreasing, and after 10 min, only 2.3 V were sufficient to pass the maximum current of 1.013 A. After this, the voltage was dropped back to zero in steps of 0.1 V. Readings are shown in Table 11. Resistance was recorded at this point, which was 3.8 – 4.0 Ω. Another power-supply with 5 A range was then connected in place of the 1 A supply, and experiment repeated up to the highest current limit. The readings are recorded in Table 12.

It was observed that the array started to buckle (or to get compressed) under load as it started to glow. At higher current (and consequently higher temperatures) this buckling increased. At the peak current value of 5A, when the array was glowing very brightly white, it suddenly stopped glowing for a few seconds, and then restarted to glow suddenly. Pictures of the annealing of the array (2nd run, using 5A power supply) are shown below.

![Figure 38: A filmstrip showing successive pictures of annealing of array under deadweight. The numbers indicate voltage and current respectively.](image)

After the experiment, the copper electrodes were inspected. Burning marks were observed on the electrodes. No visible difference was seen in the physical appearance of the array. The post-annealing picture of electrodes and the array is shown in Figure 39. The flange used as
deadweight was not in direct contact with the array and was not exposed to very high temperatures. No changes were observed on the flange.

Figure 39: Burn marks on Cu foil electrodes after annealing

Table 11: Current and voltage relation for annealing array under a deadweight, with 1 A

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Increasing Voltage</th>
<th>Decreasing Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Voltage (V)</td>
<td>Current (mA)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>0.7</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
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<td>7</td>
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<td>1.2</td>
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</tr>
<tr>
<td>10</td>
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</tr>
<tr>
<td>11</td>
<td>1.4</td>
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</tr>
<tr>
<td>12</td>
<td>1.5</td>
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</tr>
<tr>
<td>20</td>
<td>2.3</td>
<td>239</td>
</tr>
</tbody>
</table>
### Table 12: Current and voltage relation for annealing array under a deadweight, with 5 A

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Increasing Voltage</th>
<th>Current (mA)</th>
<th>Decreasing Voltage</th>
<th>Current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>5.0</td>
<td>5000</td>
</tr>
<tr>
<td>2</td>
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<td>3840</td>
</tr>
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<td>3</td>
<td>0.7</td>
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<td>2190</td>
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<td>4</td>
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<td>3.0</td>
<td>1640</td>
</tr>
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<td>5</td>
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<td>330</td>
<td>2.5</td>
<td>1340</td>
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<tr>
<td>6</td>
<td>1.0</td>
<td>370</td>
<td>2.0</td>
<td>970</td>
</tr>
<tr>
<td>7</td>
<td>1.1</td>
<td>410</td>
<td>1.5</td>
<td>690</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>430</td>
<td>1.0</td>
<td>390</td>
</tr>
<tr>
<td>9</td>
<td>1.3</td>
<td>470</td>
<td>0.5</td>
<td>220</td>
</tr>
<tr>
<td>10</td>
<td>1.4</td>
<td>510</td>
<td>0.1</td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>1.6</td>
<td>640</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>1.7</td>
<td>730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.8</td>
<td>750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2.0</td>
<td>850</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2.2</td>
<td>960</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2.4</td>
<td>1070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2.6</td>
<td>1240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>3.0</td>
<td>1440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>3.3</td>
<td>1750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3.6</td>
<td>2560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>3.7</td>
<td>3550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>3.8</td>
<td>4100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>3.9</td>
<td>4300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>4.1</td>
<td>4700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4.2</td>
<td>4900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>4.3</td>
<td>4950</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Change in resistivity:

Average resistance was calculated for values of all the four runs in the range 0-2 V. Higher voltage was discarded assuming it was an unreliable zone, given the non-linear nature of the curve.

The values are reported in Table 13.

Table 13: Average resistance and resistivity of the array in successive annealing runs

<table>
<thead>
<tr>
<th>For 0-2 V range</th>
<th>RUN#1</th>
<th>RUN#2</th>
<th>RUN#3</th>
<th>RUN#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PS-1 Up)</td>
<td>(PS-1 Down)</td>
<td>(PS-2 Up)</td>
<td>(PS-2 Down)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>Average Resistance (Ω)</td>
<td>31.41</td>
<td>2.39</td>
<td>2.67</td>
<td>2.31</td>
</tr>
<tr>
<td>Resistivity - ρ (Ω-mm)</td>
<td>9.42</td>
<td>0.72</td>
<td>0.80</td>
<td>0.69</td>
</tr>
</tbody>
</table>

It can be noted from the plots that after the first run (blue curve: PS1- Up), for any given voltage current flowing through the tile is much higher for all the successive trials. This implied that the electric resistance significantly dropped. This is also evident from the values in Table 13. Given the short annealing time of the run, this drop could be either due to improved contact (more probable), or change in material properties of CNTs (less probable) or a combination of both. Also it is to be noted that the peak values (after 4 V) of the last run (purple curve and green curve) are not very reliable due to errors like buckling of the array, possible shunting of the array etc.

A few points were noted before setting up the next experiment. Good contact is important between CNTs and the electrodes, and contact resistance can vary significantly by applying mechanical force. The array did not get red hot with the 1 A current. But still it was maintained there for 10 min, and a definite improvement over the electrical resistance can be seen from the plots. Such a comparatively ‘cold resistivity enhancement’ can be investigated in future. ‘Fluke 87’ multi-meter was used, which was better than the ‘Mastertech’ multi-meter used in the previous experiment and gave steadier values. The array stopped glowing briefly at peak current. The reason, probably, is unstable contacts and/or shunting of the array due to direct contact. No harm was done as all the components were rated for 5 A, and the power-supply was regulated, ensuring that currents higher than 5 A will never flow through the circuit. Talking about burn-marks on the copper foil, a fixture to hold the array between thicker electrodes should be used to avoid such instances of electrode damage.
3.3.2 Using copper plate fixture / setup

A holding device for arrays was machined using copper discs (2” dia., 0.5” thickness). Thick discs eliminated the possibility of overheating of electrodes (unlike the foil electrodes). Four symmetrical holes were drilled in the top disc, and one diametrically opposite pair of holes was threaded. Two threaded holes were machined (diametrically opposite) in the bottom disc, and the discs were oriented in such a way that the threaded holes were staggered. Four ceramic screws were used, two of which went through the top disc holes into threads of the bottom disc. Tightening these screws brought the two discs together. The other two screws went only through the top disc threaded holes, and rested on the bottom disc surface, pushing the two discs apart when the screws were turned. Two more holes were drilled on the side of the discs, and insulated copper wires were connected through standard ring terminals.

![Figure 41: Copper discs used as electrodes, with ceramic screws](image)

Tall arrays were annealed using the copper electrodes. Arrays could be oriented in different ways, so that current would pass through the array in the direction of nanotubes or in a transverse direction. It was an easy to assemble setup, and applying pressure with the plates improved contact between the CNT array and the electrodes. Similar results were obtained as mentioned in section 3.3.1.2. It was a robust setup as compared to the earlier setups, and had ability to withstand higher temperatures and currents safely.
3.4  Annealing of thread

Another CNT form was tested for annealing. CNT thread was chosen assuming ease of characterization; viz. 4 probe resistivity testing, tensile testing etc as compared to arrays. It was also assumed that a thread would be a better material from handling point-of-view.

3.4.1  Proposed scope of the experiments

Different annealing time and different current densities were attempted for annealing thread from the same spool. To ensure repeatability, it was proposed that 2 or 3 samples should be annealed for each combination of time and current density. All annealed and non-annealed thread samples should be tested for mechanical strength, electrical conductivity and determination of $I_G/I_D$ using Raman spectroscopy. Curves will be plotted for the measured material property (strength, resistivity) against annealing time for different current densities. Sample curves plotted in Figure 42 show the initially projected scope of experiment and expected outcome.

![Graph showing expected thread annealing results](image)

**Figure 42:** A projected graph of expected thread annealing results
In the above figure, CD₁, CD₂ and CD₃ are current densities in an increasing order. Suppose CD₁ is too high for annealing, and hence damages the thread due to overheating or burning off carbon nanotubes. On the other hand, say, CD₃ is too low and does not produce enough heat to anneal CNTs at the optimum temperature. CD₂ is the in-between current density, which yields best results. Further, different annealing times will yield different mechanical or electrical properties. This way, an optimum current density and annealing time was expected to be found out using extrapolation.

3.4.2 Experimental Setup

Thread was clamped in steel clamps (McMaster part # 6076A17). An epoxy board was used to mount the clamps. Copper wires with shellac coating as insulation were used. Different types of threads were tested, viz. a 5-ply thread, a densified thread, non-densified good quality thread etc. Usual safety measures were taken. The work-bench was grounded, safety glasses, gloves and mask were used while handling the thread, and a piece of Si wafer was used below the thread being annealed to avoid burning of the epoxy due to radiation, as found during annealing of tiles which is explained in the next section. Figure 43 shows a thread being annealed.

Figure 43: Glowing thread during annealing
To ensure pure environment, Argon flushing technique was used. The chamber was first evacuated to the maximum vacuum achieved by running the vacuum pump for about 20 minutes, which was typically $3.4 \cdot 4.6 \times 10^{-3}$ mbar. Heating tape was used to elevate temperature of the chamber walls to allow faster release of embedded gases. Then the chamber was shut-off from the vacuum pump using the connecting valve and the pump was turned off. The chamber was filled with Argon (UHP quality) to a pressure slightly above atmospheric, about 1 bar. It was observed that the strong gush of Argon into the chamber caused the thread to break. Hence, aluminum foil was used as baffles to protect the clamped thread in the subsequent runs. This arrangement is shown in Figure 44. The exhaust valve was opened until the pressure was nearly back to the atmospheric pressure and then closed back again while inside-pressure was still above atmospheric. The pump was turned back on, and the valve between the pump and the chamber was opened slowly. Again, the chamber was vacuumed to $10^{-5}$ mbar range.

![Figure 44: Use of baffles (a) and (b).](image)

On Right: Gulton optical pyrometer used to measure annealing temperature

Thus by argon flushing, possibility of damage to the CNT thread due to trace moisture and oxygen present was attempted to be minimized. Temperatures were measured using gulton optical pyrometer with 0.9 emissivity settings. Resistance was measured using Fluke-87 multimeter. After annealing the thread, it was characterized by Raman spectroscopy and tensile testing.
3.4.3 Development of the experiment

Development of annealing experiments was a slow and a continuous process. The experiments kept improving with every step because of experience and better setup. Table 14 shows the sequential development and refinement of the above experimental procedure.

**Table 14: Development of annealing experiments**

<table>
<thead>
<tr>
<th>Expt #</th>
<th>Description</th>
<th>Observations</th>
<th>Conclusion / Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>First trial of annealing. Densified thread was used. Thread length = 4&quot;. The power supply used was limited to 30 V maximum. The experiment was conducted in Argon environment with Ar being purged at 100 std. mL/min, as measured by a Cole-Parmer 150 mm flow meter.</td>
<td>R = 12.52k (steady), I = 3mA at V\text{max} = 30 V</td>
<td>Current was too low to try annealing. Thicker thread or shorter piece of thread (i.e. lower resistance, meaning higher current) should be used, or a power supply with a higher voltage limit is needed.</td>
</tr>
<tr>
<td>2</td>
<td>A 5-ply thread was used in order to try a thicker thread. Length = 4&quot;. The experiment was conducted in Argon environment with Ar being purged at 100 std. mL/min. A power-supply with higher voltage was used.</td>
<td>R = 2.776k, I = 20 mA at V\text{max} = 51.5 V</td>
<td>There was no sign of thread getting red hot. Smaller length of thread must be used.</td>
</tr>
<tr>
<td></td>
<td>A shorter length of thread was used. Length = 2”. Same 5-ply thread was used as above, again, in the Argon environment with Ar being purged at 100 std. mL/min. Annealing was done for 15 min.</td>
<td>At ( V_{\text{max}} = 51.5 \text{ V}, I = 50 \text{ mA} ), and the thread started to glow dull red. The thread did not glow uniformly. Temperature fluctuated on parts of thread with time and rate of flow of Argon. Further, even after purging of Argon was stopped, the glow was still non-uniform and dull red.</td>
<td>Argon in the chamber must be drawing away the heat from the thread by convection. Hence the thread cannot get as hot as necessary for annealing.</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>Annealing was attempted in partial vacuum. 2” thread length of the 5-ply thread was used. The chamber was flushed with Argon twice. Vacuum = -22 in Hg. The experiment was conducted for 47 min.</td>
<td>In partial vacuum, due to lower convective losses, the thread glowed uniformly. The color was somewhat bright orange. ( V_{\text{max}} = 51.5 \text{ V}, I = 40 \text{ mA} ).</td>
<td>The non-uniform glowing of thread was definitely due to the convection by argon. The experiments must be carried out in complete vacuum for best results. The chamber can be flushed to minimize trace oxygen / moisture.</td>
</tr>
<tr>
<td>5</td>
<td>Annealing was attempted in vacuum. 2” thread length of the 5-ply thread was used. The experiment was conducted again for 47 min. The chamber was flushed with Argon twice to minimize traces of oxygen / moisture by dilution.</td>
<td>( R = 1.431 \text{ k}\Omega ) at start, ( R = 1.507 \text{ k}\Omega ), after 1st flushing with Argon, ( R = 1.487 \text{ k}\Omega ), after 2nd flushing with Argon, ( R = 1.486 \text{ k}\Omega ), just before annealing. Thread started glowing (dull red) at 22 V and 20 mA. At ( V_{\text{max}} = 51.5 \text{ V}, I = 60 \text{ mA} ), and thread was glowing really bright yellow-orange. Temperature noted using</td>
<td>It is possible to achieve temperatures high enough for annealing if conducted in vacuum. However, even larger voltages can be applied in order to push more current through the thread to get higher temperatures.</td>
</tr>
<tr>
<td>6</td>
<td>A densified 2” thread sample was tried for annealing under vacuum. 5-ply thread used previously was used-up and insufficient for further experiments.</td>
<td>R = 7.54k. The resistance being much higher than 5-ply thread, the annealing was not as effective because of low temperatures due to low currents possible.</td>
<td>An even higher voltage power supply was a must.</td>
</tr>
<tr>
<td>7</td>
<td>Densified thread was used. Thread length = 2”. Annealing was conducted in vacuum. A larger power supply with higher voltage range up to 120 V was used. Annealing was done for 1 hour and 3 hours. Three 2” samples were annealed for each duration. The chamber was flushed with Ar once for all the samples, and then maximum vacuum was drawn before annealing.</td>
<td>Resistance at different stages was noted. Temperatures were recorded using gulton optical pyrometer. A constant current (I = 0.031 A) was used for all 6 samples, and voltage was adjusted for each run initially and during the annealing to keep current constant.</td>
<td>After annealing, the thread samples were tested for mechanical strength. Also the ratio (Ig/Id) was found out using Raman spectroscopy. Non-annealed thread samples were also characterized for comparison. It was found that for longer annealing runs, the ratio was improved. The strength testing was not conclusive due to many factors come into play while trying to find tensile strength, which are beyond experimental control. These results are</td>
</tr>
</tbody>
</table>
The seventh experiment is actually a series of experiments and discussed in detail below.

3.4.4 Observations

According to the above plan, 9 CNT thread samples were tested. 3 samples were annealed for 1 hour, 3 samples were annealed for 3 hours and 3 samples were used with no annealing.

Table 15: Observations for annealing thread (9-sample experiment)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Annealing time (h:mm)</th>
<th>R1 (kΩ)</th>
<th>R2 (kΩ)</th>
<th>R3 (kΩ)</th>
<th>Constant Current (mA)</th>
<th>Voltage (V) measured at time (h:mm) *</th>
<th>Temperature (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1:00</td>
<td>8.7</td>
<td>8.17</td>
<td>8.53</td>
<td>31</td>
<td>110 (0:00)</td>
<td>937</td>
<td>-</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1:00</td>
<td>6.89</td>
<td>7.82</td>
<td>8.11</td>
<td>31</td>
<td>100.4 (0:00) 99.5 (0:55)</td>
<td>942</td>
<td>The voltage needed to be decreased.</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1:00</td>
<td>6.77</td>
<td>-</td>
<td>7.64</td>
<td>31</td>
<td>101.6 (0:00) 99.4 (0:09) 98.3 (0:42)</td>
<td>948</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>3:00</td>
<td>7.35</td>
<td>6.89</td>
<td>6.66</td>
<td>31</td>
<td>94.0 (0:00) 108.3 (1:10) 118.6 (2:12) 124.9 (2:45)</td>
<td>982</td>
<td>The voltage needed to be increased a lot.</td>
</tr>
<tr>
<td>Sample 5</td>
<td>3:00</td>
<td>7.77</td>
<td>10.5</td>
<td>10.68</td>
<td>31</td>
<td>100.6 (0:00) 104.6 (0:07) 113.9 (2:05) 115.8 (3:00)</td>
<td>983</td>
<td>The voltage needed to be increased a lot.</td>
</tr>
<tr>
<td>Sample 6</td>
<td>3:00</td>
<td>9.48</td>
<td>9.37</td>
<td>9.01</td>
<td>31</td>
<td>105.3 (0:00)</td>
<td>928</td>
<td>Resistance did not change much.</td>
</tr>
</tbody>
</table>

*It was observed that resistance of the array changes during annealing. To maintain a constant current, the voltage needed to be adjusted intermittently. The adjusted voltage and the time of adjusted is reported.
3.4.5 Results and discussion

In the table below are the Raman spectroscopy results for the 9 samples tested.

Table 16: Raman spectroscopy results for 9-sample thread annealing experiment

<table>
<thead>
<tr>
<th></th>
<th>G/D</th>
<th>D</th>
<th>G</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>2.01</td>
<td>964.58</td>
<td>1940.1</td>
<td>1477.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.8</td>
<td>649.18</td>
<td>1169.74</td>
<td>1014.51</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1.68</td>
<td>555.08</td>
<td>933.855</td>
<td>772.052</td>
</tr>
<tr>
<td>Sample 4</td>
<td>2.27</td>
<td>972.659</td>
<td>2207.31</td>
<td>1458.23</td>
</tr>
<tr>
<td>Sample 5</td>
<td>2.01</td>
<td>1685.84</td>
<td>3392.23</td>
<td>1730.11</td>
</tr>
<tr>
<td>Sample 6</td>
<td>2.23</td>
<td>685.57</td>
<td>1533.19</td>
<td>1248.19</td>
</tr>
<tr>
<td>Sample 7</td>
<td>2.44</td>
<td>641.18</td>
<td>1564.39</td>
<td>1375.71</td>
</tr>
<tr>
<td>Sample 8</td>
<td>2.13</td>
<td>1742.47</td>
<td>3718.66</td>
<td>2745.17</td>
</tr>
<tr>
<td>Sample 9</td>
<td>2.08</td>
<td>482.828</td>
<td>1004.54</td>
<td>776.68</td>
</tr>
</tbody>
</table>

The above Raman characterization shows a small but definite change in the G/D ratio. The ratio improved with annealing time. Figure 45 is a sample Raman characterization curve of one of the above samples.
Samples were also tested for strength using Instron testing machine.

The procedure for testing was as below:

1. Mount CNT threads on sand-paper with ends anchored between two sticky-sides of tape, or use super-glue.
2. Measure diameter at six points along the thread and calculate average diameter. Also, check for points of necking and make a note of it.
3. Test in Instron.
Figure 46: Tensile testing procedure. (A) Superglue used to stick the CNT array ends to the sandpaper (B) Micrometer is used to measure dimensions of rectangular cross-section of array (C) Sandpaper tabs and array are glued together; (D) Instron machine overall setup (E) Tabs held between pneumatically actuated clamps/holders (F) Interface pad of Instron

The plot in Figure 47 shows the tensile testing results.
Discussion regarding Figure 47:

1. Sample 1 hour - 2 had a dramatic increase in strength, but this could possibly be attributed to a significantly smaller measured diameter than that of the other samples. The diameter term is squared while calculating strength; hence the measurement errors can be blown up significantly.

2. Other than this sample, all the other samples lie in approximately same region of strength. Annealing did not have significant impact on strength directly.

3. Extensibility and modulus of elasticity: The un-annealed sample had the highest extensibility, which decreased with increased annealing time. The modulus of the materials was undoubtedly improved by annealing with a greater measured modulus in the 1 hr samples as compared to the 3-hr samples.
4. 3 hour - 1 slipped in the grips due to lack of CNT contact with tape, hence the extensibility cannot be assumed accurate.

3.5 Annealing of tiles

While annealing of tall arrays it was observed that due to non-uniformity of the array dimensions, it was difficult to test the mechanical properties in a consistent manner. Around the same time, new array tiles were being produced in the Nanoworld Labs using Nano-imprint Lithography technique. These tiles were of uniform thickness of 1 mm and contained tall nanotubes (7-9 mm). Figure 48 shows a picture of a Si wafer with array tiles grown on it. Annealing of these thin and uniform tiles was carried out. Changes in electrical and mechanical properties were studied.

![Figure 48: Thin, uniform tiles grown on Si substrate: Raw material for tile annealing](image)

3.5.1 Setup and Observations

Different experiments were carried out, as reported below.

3.5.1.1 Experiment on Si substrate

A rectangular tile was separated at its base from the wafer using a razor blade. Care was taken to remove the tile as uniformly and cleanly as possible. The dimensions of the tile were (1 x 7 x 20) mm. The tile then was placed on another silicon wafer. Two shorter edges of the tile were secured on the wafer by applying conductive silver epoxy paste (Circuitworks CW2400), and curing it in the oven at 100 °C for 10 min. Two thick bare copper wires were also inserted into the epoxy drops, as
leads for connections. The arrangement was put in a glass Petri dish and placed inside the vacuum chamber. Resistance measured across the external terminals of the vacuum chamber was 86 $\Omega$.

The power supply was adjusted to supply a fixed constant current of value 0.633 A. The current was also measured using a digital multimeter (Mastertech 480A). The voltage was constantly recorded using a data acquisition device, viz. NI USB 4065 [77], and Labview Signal Express software.

The array glowed red-hot with this current as shown in Figure 49 (B).

![Figure 49: A schematic (L) and a photograph (R) of annealing of tile on Si substrate](image)

Temperature of the array was recorded using a hand held optical pyrometer (gulton 800-1600).

Temperatures were recorded at three different points on the tile.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temperature (°C)</th>
<th>Average temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>860</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>880</td>
<td>886.67</td>
</tr>
<tr>
<td>3</td>
<td>920</td>
<td></td>
</tr>
</tbody>
</table>
A picture of the setup is shown in Figure 50. The experiment was carried on for 3 hours 30 min. However, due to unfamiliarity of the software, only last 512 seconds of voltage data were recorded.

![Experimental setup showing annealing of tile](image)

**Figure 50: Experimental setup showing annealing of tile**

Discussion

1. The experiment was conducted in vacuum. Due to no convective heat transfer, the heat generated in the tile was radiated out through the tile and other heated parts of the setup. It also was conducted through the copper wires, copper being an excellent heat conductor. This resulted in very hot wires and connectors. This extended exposure to heat of about 3 hours was detrimental to the connector pins. The rubber coating on the alligator clamps was deformed, partially molten and became sticky due to the heat.

2. The shorter sides of the array were embedded inside the silver epoxy. The epoxy was deformed by heat too. A moment was created at the array ends due to this change in shape of epoxy. This bent the array in the middle, which led to its breakage. This is shown in Figure 51.
Figure 51: Silver epoxy deformation due to heat causing the CNT tile to break

3. In future, steel clamps with direct contact with the array (no conductive epoxy) and thicker copper wires with no rubber insulation would be used.

4. Silver epoxy, even after complete curing, still contained some water, which got evaporated during annealing and was seen as moisture on the glass window.

Results

A plot of voltage vs. current for last 5 minutes is shown in Figure 52. Although it shows only partial data, the steady fall of voltage is evident. The previous part of the curve was observed while conducting the experiment and that also showed a similar trend. The steady resistance fall pattern is a promising result for further annealing experiments, although experimental setup needs to be modified.
3.5.1.2 Experiments using steel clamps

New setup was designed. A steel clamp fixture was made, using two steel clamps (McMaster part # 6076A17) just like the thread earlier. Thicker copper wires with no rubber coating were used. The wires were pre-coated with shellac and hence were insulated. The clamps were mounted on an epoxy board. The tiles were clamped between two steel clamps and current was passed through the tile. Figure 53 shows pictures of the board setup and a close-up of clamped tile.

Figure 53: New setup of tile annealing using steel clamps
Temperature readings were taken using the gulton optical pyrometer. Tiles were annealed for different durations, such as 1 hour, 3 hours, 6 hours, 12 hours. The longest annealing run was 28 hours.

There was a point of concern of long runs of the experiment, due to continuous generation of heat and its effect on the steel clamps. It should be noted that even for such long runs, temperature equilibrium is soon reached. At the equilibrium the steel clamps always stay at a much lower temperature that the tile, and hence are safe from melting or getting damaged. The tile being a bad thermal conductor as compared to the clamps, the clamps draw the heat out of the tile in a quicker fashion than the glowing tile can dissipate the heat to its ends. The temperature of the tile is very low at the edges where it is clamped, and it rises very quickly and reaches a nearly constant value away from the edge. This is shown in Figure 54.

![Figure 54: Schematic of temperature distribution across the tile; Picture of a glowing red-hot tile held between steel clamps during annealing](image)

For an annealing run, voltage was recorded against time. Current was kept constant using 'constant current' setting on the power supply. Thus, any change in resistivity can be directly associated with the change in voltage required to drive the preset constant current through the tile. A typical voltage - current curve is shown in Figure 55.
Following observations can be made looking at the curve:

1. Voltage falls very steadily throughout the annealing run.

2. At the beginning of the curve, there are fluctuations because voltage was being adjusted to achieve the decided current flow.

3. There is no drastic drop in resistivity.

Another tile sample that was annealed for 28 hours has voltage vs. time plot is shown in Figure 56.
3.5.2 Results and discussion

Two types of improvements are observed due to electrical annealing, and discussed below. One is electrical conductivity and the other is tensile strength.

3.5.2.1 Drop in resistivity

Because the current was kept constant, the change in voltage can be directly associated with the change in resistance of the tile.

\[ V = I \cdot R \]

But \( I = \text{constant} = 1.5 \, \text{A} \),

\[ \therefore V \propto R \]

Now, assuming the contact resistance is negligible, \( R = \rho \frac{\ell}{A} \)

Given that dimensions of the tile are not changing, \( \ell \) and \( A \) are constant.

\[ \therefore R \propto \rho \]
For the 8 hour run,
Voltage at start = 19.02 V
Voltage at end = 15.26 V
Percent change in voltage indicates percent change in resistivity.
Hence,
\[ \Delta \rho = \frac{15.26 - 19.02}{15.26} \times 100 \% \]
\[ \Delta \rho = -19.74 \% \]
The negative sign indicates decrease in resistivity.

For the 28-hour run,
Voltage at start = 22.91 V
Voltage at end = 11.39 V
Percent change in voltage indicates percent change in resistivity.
Hence,
\[ \Delta \rho = \frac{(11.39 - 22.91)}{11.39} \times 100 \% \]
\[ \Delta \rho = -50.30 \% \]
The negative sign indicates decrease in resistivity.

It should be noted that the power dissipated through the tile also varied in direct proportion with the voltage. Hence due to the fall in voltage, the power dissipation and hence the annealing temperature was not maintained constant.
3.5.2.2 Improvement in tensile strength

Along with electrical annealing, same tile samples were sent to UDRI for thermal annealing. The thermal annealing conditions were around 2000 °C. The annealed tiles were tested for tensile strength using Instron testing machine, in the same fashion as explained earlier. Curves in Figure 57 show tensile strengths of different samples of tiles. The electrically annealed tile shows promising results because strength is increased three times that of non-annealed tile.

![Figure 57: Tensile testing results of CNT tiles.](image)

Legend for Figure 57 is as below:

1- Blue- Annealed at UDRI, non-densified
2- Red- Annealed electrically at UC, densified for 1 hr
3- Green- Annealed at UDRI, densified for 1 hr
4- Violet- Annealed electrically at UC, non-densified
5- Cyan- Non annealed CNT sample #1, raw
The table below shows a comparison of ultimate strengths of different samples.

### Table 18: Strength testing results of tile annealing

<table>
<thead>
<tr>
<th>#</th>
<th>Line Color</th>
<th>Annealing</th>
<th>Densification</th>
<th>Average Loading rate (micron/s)</th>
<th>Max. Slope (Automatic Young's modulus) (N/mm/mm)</th>
<th>Ultimate Stress (MPa)</th>
<th>Improvement in Ultimate Stress (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blue</td>
<td>UDRI, Thermal</td>
<td>No</td>
<td>6.64</td>
<td>246.14</td>
<td>1582.20</td>
<td>346%</td>
</tr>
<tr>
<td>2</td>
<td>Red</td>
<td>UC, Electrical</td>
<td>Yes</td>
<td>6.59</td>
<td>152.76</td>
<td>1418.67</td>
<td>300%</td>
</tr>
<tr>
<td>3</td>
<td>Green</td>
<td>UDRI, Thermal</td>
<td>Yes</td>
<td>6.63</td>
<td>208.46</td>
<td>1113.34</td>
<td>214%</td>
</tr>
<tr>
<td>4</td>
<td>Violet</td>
<td>UC, Electrical</td>
<td>No</td>
<td>6.57</td>
<td>268.86</td>
<td>1126.48</td>
<td>217%</td>
</tr>
<tr>
<td>5</td>
<td>Cyan</td>
<td>Not annealed</td>
<td>No</td>
<td>6.65</td>
<td>126.18</td>
<td>316.09</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Orange</td>
<td>Not annealed</td>
<td>No</td>
<td>6.64</td>
<td>179.78</td>
<td>393.73</td>
<td></td>
</tr>
</tbody>
</table>

Average value of Tensile Stress for non-annealed tiles is:

\[
\sigma_{\text{non-annealed}} = \frac{(316.09 + 393.73)}{2} = 354.91 \text{ MPa}
\]

Improvement in Strength can be calculated as:

\[
\%\text{Improvement} = \frac{\sigma_{\text{final}} - \sigma_{\text{initial}}}{\sigma_{\text{initial}}} \times 100;
\]

\(\sigma_{\text{final}}\) is the ultimate stress for each sample,
\( \sigma_{\text{initial}} \) is average of ultimate stresses of two raw samples.

E.g. for tile sample #1,

\[
\% \text{ Improvement} = \left( \frac{1582.20 - 354.91}{354.91} \right) \times 100 = 345.80 \% 
\]

It is observed that tensile strength of the electrically annealed tiles increased by 3 and 2.17 times as compared with raw tiles. For thermal annealing, these figures are 3.46 and 2.14 times respectively. Densification did not have a consistent effect on tensile strength. This could be attributed to (a) possibility of only a small change in area due to densification, (b) manual error during measurement, or (c) application of good pressure using micrometer while measuring cross-section dimensions which automatically led to mechanical densification. SEM imaging of the tiles was done.

![Figure 58: SEM images of annealed (1-4) and non-annealed (5-8) tiles from above experiments.](image)

Referring to Figure 58, no significant change in structure was seen under SEM. However, this does not necessarily indicate whether CNTs have improved structurally, electrically or
thermally. Thus, SEM imaging might not be the ideal characterization method, because it might not reflect defect healing to intra-molecular level. This was seen in a study by Jung et al. [57], when SEM images showed no difference in surface morphologies between the annealed and non-annealed samples, but other techniques like TGA and Raman.

3.5.3 Issues encountered

Burning of epoxy board

During electrical annealing, it was observed that due to the radiation heat from the brightly glowing tile, the epoxy board started to burn and showed dark marks right below the glowing tile. This can be seen in the picture below.

![Figure 59: Burning of epoxy board due to radiation heat from tile](image)

This led to two possible risks:

1. Melting of the epoxy material at elevated temperatures, and release of gases (out-gassing) which would be detrimental to the vacuum environment.

2. Physical failure of the epoxy board, leading to high risks of electric short circuit.

To avoid this, a simple yet effective solution was found. A silicon wafer was cut in rectangular shape in a size which would fit comfortably between the two posts holding the clamps.
Being polished and highly reflective, the wafer would reflect off a considerable amount of radiation. Any absorbed radiation will increase the temperature of wafer. However, melting point of Silicon is 1410°C, while temperature of the array being annealed was in the range of 1500 °C. Considering there was no direct contact of wafer with the bright-hot tile, and that a considerable amount of incident radiation was being reflected, temperature of the Si wafer was very unlikely to go beyond its deformation point let alone its melting point. The experiment was repeated with the Si wafer in place, and the wafer was inspected for damage after being exposed to the radiation. It was found that there were no visible signs of any damage. A picture of the modified setup is in Figure 60.

![Image of modified setup](image)

**Figure 60: Use of Si substrate to protect the board from heat**

**Non-uniform heating of the tile**

While measuring temperature using gulton optical pyrometer, it was observed that the tile was not getting heated uniformly. The edges of the tiles were at a higher temperature than the center of the tile. This was more prominent at lower temperatures, at which the contrast between the colors of the edge and center of the tiles was very easily seen. The image below shows the non-uniformity of annealing.
Figure 61: Tile glowing non-uniformly – Edges brighter than center

The reason behind this phenomenon was not clearly understood, however it could be attributed to the following factors:

a) Non-uniform clamping of tile

b) Residual amorphous carbon at the top or bottom of the tile, or some other chemical anomaly in the tile composition at the edges

However, this non-uniform heating did not make much difference in tensile strength testing, because for tensile testing, only central portion of the tile is used. The brightly glowing edges get clamped into the Instron machine’s mechanical clamps anyway.

Finally, there is a requirement of a correction factor for the measured temperatures. The use of optical pyrometer is tricky while measuring temperatures of small surface areas as in the present case. The pyrometer was set to measure and hold the highest measured temperature for each measurement. It is quite likely that it measured and recorded the edge temperature and not the center temperature, which in turn would be the true annealing temperature, because center of the tile that was tested for tensile strength and not the edge.
3.6 Comparison of conventional annealing with electric annealing

3.6.1 Advantages

Electric annealing offers several advantages over conventional (thermal) annealing.

**Faster process**

Electrical annealing eliminates the long start-up and cool-down time required by the conventional giant thermal furnaces.

**Easier setup**

Once a fixture to hold CNT material in place is installed, the setup is quite simple.

**Low running and equipment costs**

It is a direct intrinsic heating method, which means the only material getting heated during is CNTs, unlike the thermal furnace heating. This saves a lot on electricity, and hence in running costs. Further, the simple setup with small equipment implies lower investment in equipment and lower startup cost.

**Better and direct control**

Control over annealing parameters, e.g. highest temperature, the rate of increase of the temperature is directly monitored. Resistivity and change in resistivity can be directly obtained from the voltage applied and current passed, and its values for every instance are available.

3.6.2 Limitations

Resistive annealing is still a developing process, and intrinsically has certain limitations. In particular, limitations of our setup are discussed.

**Lower Temperatures**

In the present setup, the highest temperatures measured were in the range of 1600 °C, this being the limitation of the pyrometer used. The temperatures higher than 1600 °C have been estimated from current density, but they still cannot match the highest temperatures in thermal annealing of
the order of 2600 °C [78,79]. The temperature limitation is due to various factors, such as limitation of the power source, limiting temperature of the clamping device which includes clamps, board, wires etc.

**Accuracy of temperature measurement**

In electrical annealing, a much localized heating takes place, which makes the use of conventional thermocouples nearly impossible. An alternative but reliable temperature measuring device would be a latest technology IR camera. However, the vacuum chamber viewing port is made of Kodial glass [80]. This glass blocks most of the IR radiations, and hence the port appears completely opaque to the IR camera. Hence, an IR camera cannot be used, which leads to the use of an optical pyrometer. As mentioned previously, its use is tricky and not very reliable for small area measurement. Further, the tile is being heated non-uniformly. All these factors contribute to an erroneous temperature measurement. In contrast, temperature in a conventional furnace is measured with thermocouples which measure the surrounding temperature, and where heating of the tile is supposedly uniform.

**Purity of environment**

Trace oxygen analyzers (specifically the sensor) are not designed for operation under vacuum. The only accurate way to tell purity was QMS, which was not feasible due to unavailability of equipment. The TMP worked fine and could go to pressures as low as $10^{-6}$ mbar range, i.e. *high vacuum* range. The chamber is flushed twice with argon. All the measures that could practically be taken to achieve the perfect environment were taken, the only problem being no direct measure of purity.

It should be noted that the setup and the equipment is continually being updated to overcome these limitations.
4 Conclusion

4.1 Electric Assisted Yarn Drawing

Despite various attempts made, a fool-proof method for drawing of yarn from a non-spinnable array could not be established.

However, this attempt helped in understanding behavior of CNTs under different conditions, such as after electroplating with Ni or while being manually pulled under an applied potential difference.

4.2 Annealing of CNT material

The defects in CNTs were healed due to annealing, as shown by the improvement in $I_G/I_D$ ratio of thread, e.g. 1.68 for a non-annealed sample and 2.44 for an annealed sample. It should be noted that the $I_G/I_D$ ratio of the initial samples was not high to start with, which shows a very low crystallinity of the raw sample. The improvement, though only marginal, is consistent throughout the samples. It is a definite indication in improvement in the structure of CNTs.

The annealing process also showed a drop in the resistivity of tiles. Even though direct resistance measurement was not feasible due to very small dimensions of the sample and availability of annealed sample, the overall resistance can be used as a measure of resistivity. For an 8-hour annealing, the overall resistance was decreased by 20% while for 28-hour annealing, this change was 50%.

Most importantly, the strength testing of tiles shows promising results for further study. Tensile strength improvement of electrically annealed tiles can compare to the improvement by thermal annealing. This, we feel, is an important result, because it proves that electrical annealing is just as effective as the conventional annealing under correct experimental conditions, yet a much
simpler and faster technique. Strength of the tiles improved 3 times and 2.17 times by electrical annealing, as compared with 3.46 and 2.14 times improvement by thermal annealing.

Figure 62 shows a schematic of flow of current through a thread and a tile. In the thread, there is a discontinuity at every junction of two nanotubes. Thus electrons have to jump across this high-resistance joint. Similarly, the orientation of the CNTs in the annealed tiles was perpendicular to the direction of current. This means that the current did not primarily flow axially through the CNTs but through the interconnects that are present in the mostly aligned structure of CNTs. It is possible that temperature is much higher on microscopic level at these high resistance junctions. Further work needs to be performed in order to understand these propositions in depth.

![Figure 62: Schematic of flow of current through thread (L) and tile (R)](image)

Finally, referring to Figure 55 and Figure 56 (8-hour and 28-hour annealing V-I curve), it can be seen that voltage drop is much sharp in case of 28-hour annealing. This is probably because the higher annealing temperatures in that case. This confirms the fact pre-established by other researches that annealing temperature plays a vital role in the rate of healing of defects.
5 Future work

5.1 Further modifications in Argon chamber

The rate of leakage-air seeping into the chamber under full vacuum was recorded and curves were plotted as shown in Figure 66. The curves indicate that additional measures need to be taken in order to eliminate the possibility of oxygen seepage.

5.1.1 Remove unnecessary components from the chamber

The extra feed-through, unused valve, screw manipulator etc. should be removed from the chamber and replaced by blind flanges.

5.1.2 Bigger port for turbo-pump

The pump can be connected to the chamber via bigger diameter port which will help removal of air molecules form the chamber faster, and higher vacuum level can be achieved. The 1.33” CF port can be switched to a 2.75 CF port which will be available after removal of the displacement manipulator.

5.1.3 Use of QMS for residual gas analysis

A quadrupole mass analyzer should be used if accurate measurement of residual gases is to be performed. If this is installed, there will be a very definite method to ensure purity of environment inside the vacuum chamber.

5.2 Uneven heating of tiles

To check effect of non-uniform heating of tiles, Raman spectroscopy can be used. While characterizing, check at the edge of the tile and the center to see if there is difference in g/d. If there
is a repeatable and significant difference in center and edge values, the non-uniform g/d can be attributed to non-uniform heating, and then further measures will need to be taken to ensure even heating.
6 References


“Kurt J. Lesker - CF Flanged Zero Length Kodial Glass Viewports.”

7 Appendices

7.1 Recording of experiment videos

Record-keeping is an important part of any experiment. To make sure no observations are lost, it is important to record them in a permanent fashion. This helps in keeping a better track of the experiment.

7.1.1 Advantages of video recording of experiments

Video recording is a great way of storing information digitally. Advantages are listed below:

- It can capture minute details human eye can often overlook.
- In a dynamic experiment it can sometimes be difficult to keep track of all the changes need to be observed at the same time, and record them later from memory.
- Recording experiments by a video camera allows the researcher to continue the experiment in an interruption-free manner, by avoiding the need of manual intermittent entries. You can record the observations verbally as you experiment.
- Finally, an image or a video can convey information in a very effective way, especially in presentations or talks where a lot of information needs to be delivered in a short time. Videos in a presentation make it interesting and lively.

7.1.2 Camera and settings

A Sony handy-cam (an HD camcorder) was used to record the experiments. The camera featured different recording modes – auto focus, manual focus, optical and digital zoom, snapshot capability. They were used as and when required.
7.1.3 Tripods

Correct mounting of camera for recordings is important for stability of the setup, and good quality images and recording.

Two types of tripods were used. A tall 57” collapsible lightweight tripod was used for overall recording of experiments where close-up recording was not necessary. A 9” table-top tripod (Vanguard VS-82) was used whenever the camera needed to be setup very close to the experiment.

7.2 Vacuum chamber modifications for Argon environment

It was observed that the Turbo Molecular pump could only go to pressures as low as 3.4 x 10^-3 mbar. This pressure is not low enough for annealing of CNTs, as there could be some trace oxygen in the environment which might cause oxidation damage of CNTs. In an attempt to get an inert environment, it was decided to use argon instead of vacuum.

Even other than the argon modification, during the course of experimentation many changes were made to the vacuum chamber.

7.2.1 Argon experimental setup

Figure 63 shows a schematic drawing of the vacuum chamber with that can create an inert Argon environment.
The adaptations in the vacuum chamber for argon setup were as below:

The screw manipulator fitted through a 1.33” CF flange at the rear of the chamber was removed and replaced by a Swagelok gas shut-off valve. The valve was a custom-made part with a 1.33” CF flange welded to it on one end and a Swagelok tube welded to the other end. This was to be used as Argon exhaust from the chamber. Its 3D projection is shown in Figure 64.

An electrical feed-through was removed from the bottom of the chamber and was replaced by another custom-made gas shut-off as above. This outlet was to be used for QMS to test purity and composition of the gases inside. It would also work as a venting valve in emergency when QMS
was not connected. A third custom-made gas shut-off valve was previously attached at the bottom of the chamber, which would be used as an inlet for argon. This valve, however, had the opposite gas flow direction, i.e. into the chamber.

An HTS Amptek Heavy Insulated heater tape was wrapped around the Argon chamber, as shown in Figure 65. The tape length was 8ft and width 0.5”. The power rating was a 416 W, 120 V. It was used for bake out of the chamber to ease the release of air molecules embedded in the chamber wall from inside.

The tape was connected through a 120 V variable autotransformer to adjust the input voltage to the tape in order to control temperature. The chamber temperature could be measured using an IR camera. Figure 65 shows temperature measurement while the chamber was being heated up.

![Figure 65: Measuring temperature of chamber with heating tape on. Pictures taken with FLIR Infrared light camera](image)

A standard Ultra High Purity Argon cylinder from Wright Brothers Co. was used as the argon source (pressurized to 2640 psig at 70 F). The cylinder was secured to the work-table using standard clamping straps.
The exhaust from the cylinder as well as the vacuum pump was vented through 0.25” PFA tubing to the suction vent across the room, using two separate lines. Similar PFA tubing was used for inlet lines as well.

A Cole-Parmer 150 mm, correlated, variable area flow-meter tube with a glass float was installed in the inlet-line between the cylinder and the vacuum chamber. The flow-meter was disassembled, rinsed with water, then rinsed with alcohol, dried and then reassembled to remove impurities and avoid contamination. Inlet flow of Argon was maintained at 100 std. mL/min.

The Pfeiffer digital pressure transducer connected to the chamber was removed, because it was not suitable for pressures above atmospheric. It was sent back to Pfeiffer for recalibration because contamination and dust was suspected on the gauge. A dial gauge (McMaster part # 38545K33) was installed in its place, with range -30 in Hg to 60 psi. It was connected through a converter (CF to QF flange) for easy assembly and disassembly in future.

7.3 Troubleshooting

Several obstacles needed to be overcome during the course of the experiments. A few of those are reported here.

7.3.1 Burning of the epoxy board

When tiles were annealed, huge amount of heat was radiated given that this happened in vacuum, heated up the board just below the red-hot tile. The board got a burnt mark on it. As a solution, a silicon wafer was inserted below the material to be annealed on top of the epoxy board. Melting point of Si is fairly high viz. 1480 °C. Also the Si wafer is a much better reflector. This eliminated the issue.
7.3.2 Convection in Argon

When the same current was passed as compared to vacuum environment, the thread did not get red hot in argon atmosphere. The current had to be increased to about twice the value to become noticeably red. Even further, the heating was not uniform. Some parts of the thread were getting red hot and some were cold, and it kept fluctuating quite fast. The reason behind this was the convective currents formed inside the chamber due to the hot filament. Even when the flow of argon was stopped, the internal currents prevented uniform heating.

7.3.3 Outgassing of various components

In a well-designed, well-constructed vacuum system, in the absence of deliberately injected gas, the major contributor to the gas load is the desorption of gases/ vapors from the vacuum surfaces. This is called outgassing [81]. The metallic chamber walls require a significant amount of time to discharge absorbed gases, especially when higher vacuum levels are to be achieved. Furthermore, the epoxy board used to mount the clamps on outgassed a lot and for a long time. This was verified from testing the vacuum chamber pressure with and without the epoxy board inside, and plot pressure as a function of time. As a solution a vacuum compatible ceramic tile was used in place of the original board. The heating tape as mentioned previously wrapped around the chamber raised the temperature of chamber to help the walls outgas faster.

7.3.4 Pressure gauge recalibration

The whole purpose of using argon to create purely inert environment was based on the assumption that turbopump was ineffective in generating ultra-high vacuum (UHV). The original pressure gauge mounted on the chamber was a Pfeiffer PKR 261. While troubleshooting the vacuum chamber, turbopump and attached equipment, an MKS cold cathode pressure gauge was
mounted on the chamber. It was brought into light that the Pfeiffer gauge was faulty and reading an abnormally higher pressure than actual pressure inside the vacuum, and the turbo-pump was functioning properly. The lowest pressure noted was in the range of $10^{-7}$ mbar with MKS pressure gauge. Thus it was concluded that the use of argon is redundant, and flushing / rinsing the chamber with argon and then generating a high vacuum was sufficient to ensure inert environment.

7.3.5 Leakage testing

The vacuum chamber was tested for leakage of air into the chamber. This information was required in order to get the correct specifications of the “O$_2$ getter” pill to absorb residual oxygen in the chamber. Two runs were performed. The vacuum pump was run for different times in each case, so the starting vacuum in the two cases was different. After this, the valve separating the pump and the chamber was shut off and timer was started. Pressure in the chamber was noted at different times. The 2$^{nd}$ run was a more thorough run with higher vacuum in the beginning and longer duration for pressure measurement. Below are the observation tables and the curves plotted.
Figure 66: Curve showing leakage air seeping into the vacuum chamber

The air seepage rate is considered to be rather high, and to minimize this seepage, further vacuum chamber modifications need to be done as mentioned in the future work section.