

Magnetic Resonance Force Microscopy Using Nanotubes and Nanowires

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BOSTON COLLEGE

MAGNETIC RESONANCE FORCE MICROSCOPY
USING NANOWIRES AND NANOTUBES

A SENIOR HONORS THESIS

SUBMITTED TO

DEPARTMENT OF PHYSICS

AT

BOSTON COLLEGE

BY

KATHERINE E. KWASNIK

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Chapter 1

Introduction

This is an Honors Thesis for the academic year 2003-2004, at Boston College in the Department of Physics on research conducted in the laboratory of Dr. Michael J. Naughton.

Magnetic resonance force microscope (MRFM) is a relatively new form of microscopy, which provides very high-resolution images in three dimensions (3D). Further development of this microscope would provide a great instrument that would further many areas of research, including physics, material science, and biology. This research project aims to explore the possibilities of making a MRFM more sensitive by using carbon nanotubes or zinc oxide nanowires as cantilevers, making the resolution much higher and the scans accurate to a much smaller scale.

The Magnetic resonance force microscopy is a cross between a magnetic resonance microscope (MFM) and atomic force microscopy (AFM). It combines Magnetic Resonance Imaging (MRI) technology with scanning probe microscopy to create an apparatus that can scan a surface and obtain images somewhat like those obtained by current MRI technology but on a much smaller scale. These images can be put back together to create a 3D image of the material.

This thesis consist of the following chapters:

1. Introduction
2. Background of MRFM and Nanostructures
3. Specific Goals
4. Accomplished Goals and Procedures
5. Further Research

Chapter 2

Background on MRFM and Nanostructures

Magnetic resonance force microscopy (MRFM) is a relatively new form of microscopy, which provides very high-resolution images in 3D. Further development of this microscope would provide a great instrument that would further many areas of research, including physics, material science, and biology. This research project aims to explore the possibilities of making a MRFM more sensitive by using carbon nanotubes or zinc oxide nanowires as cantilevers, making the resolution much higher and the scans accurate to a much smaller scale.

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Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) technologies have been very successful in imaging larger objects, such as human tissue and organs. They allow for a three dimensional image to be obtained, which is often used in biology and medicine to look at tumors, for example. It is a non-invasive technique of “seeing” inside a body and understanding what is there. It is also useful in materials science and many other areas of science where a non-destructive means is desired to ‘see’ inside an object. The principles behind MRI have to do with magnetic moments of the atoms in the object. The nucleus of each atom has a magnetic moment, which is randomly aligned when the material is not in a magnetic field. When a magnetic field is applied, however, the

magnetic moments of all nuclei in a substance will align directly opposite to that magnetic field. The same principles are used in MRFM to obtain data.

Aligned atoms can be excited and detected by a time varying radio-frequency (r.f.) magnetic field. Since the energy of a wave is related to its frequency, an oscillating magnetic field can carry just enough energy to change the atoms magnetic moment to flip from the low energy position to the high-energy position. This high-energy orientation corresponds to the magnetic moment being aligned with the uniform magnetic field. Once the atom is in an excited state, which is very unstable, it can relax back to the stable position, releasing the energy it had absorbed and is ready to accept energy to flip it again. These excited atoms can be detected through the energy absorbed, and the information gained from this detection can be put together to form an image of the material.

Magnetic resonance is defined by satisfying the equationⁱ:

$$hf = 2\mu_z(B_{ext} + B_{local})$$

where z is the direction of the uniformly applied magnetic field, h is Planck's constant, f is the frequency of the imparted r.f. radiation, B_{ext} is the external static magnetic frequency, and B_{local} is what allows the aspects of a material to be identified. When placed in the magnetic field, all of the magnetic moments tend to align in the same direction. There are, however, slightly different local magnetic environments, which is the principle that allows the images to be made. Usually in experimental situations, the frequency is kept constant (in our case, the frequency will be kept at the mechanical resonance frequency of the cantilever used) and the B_{ext} will remain constant.

Because the varying magnetic field is arranged to be felt at different strengths throughout the material, only atoms receiving the exact amount of energy from the oscillating magnetic field to excite them will be able to absorb the energy and flip, allowing the MRFM

to detect them. Atoms who feel more energy or less energy from the oscillating magnetic field will not be able to absorb the energy (i.e. are not resonant), and will thus be “invisible” to the data collector. This allows for information to be gathered from below the surface and used to create an image. By varying the distance into the substance where the field is felt, images can be taken of different depths below the surface. This is what makes MRI useful for medical purposes. It allows images to be taken in slices which when put back together, allowing doctors to see exactly where problems are occurring, be they tumors, bleeding or swelling.

The way that MRFM uses these principles and techniques in combination with the AFM scanning method makes it capable of very fine resolution – on the Angstrom level eventually as technology develops. MRFM can use the AFM machine, but with a modified cantilever. The tip that is used in MRFM has at the end of it a ferromagnetic particle, which produces a spatially inhomogeneous magnetic field. The sample is immersed in a uniform magnetic field, as in the NMR and MRI technology, which aligns all the magnetic moments in the sample in the same direction. The material is then scanned with the tip, oscillating at the resonant frequency of the cantilever. This creates a variable magnetic field, which is very localized on the sample.

As the distance of the oscillating cantilever changes above the sample, the external magnetic

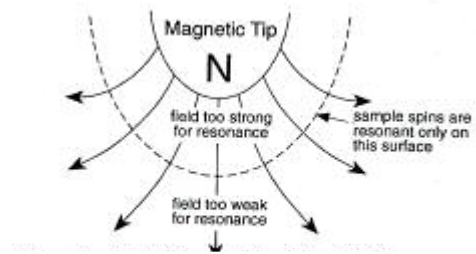


Figure 2.1: MRFM tip applying $B(\text{ext})$

field in the equation is varied. The slices, which are actually bowl shaped, become more concave as the tip becomes sharper and more accurate (Fig 2.1)ⁱⁱ. The tip is usually raised to about 100 nm above the sample, and the cantilever typically has a force constant of about 0.01 to 3.0 N/m. A sharper tip produces a more accurate image at higher magnification than a

larger tip. The smaller the area excited by the tip as it scans, the less noise will be detected from neighboring areas which can also feel some of the magnetic resonance provided by the oscillating cantilever, achieving a clearer, more localized responseⁱⁱⁱ.

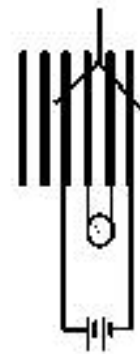
MRFM is achieved by having two simultaneous frequencies: the high frequency r.f. which puts the sample spins into magnetic resonance, and the lower frequency of the mechanical resonance of the cantilevers. The r.f. radiation is typically of the order of 100 MHz and the cantilever resonance is around 100 kHz. But by modulating the 100 MHz radio frequency at 100 kHz, a force is applied by the sample spins onto the cantilever, which then alters its resonant frequency. This is ultimately what is measured in MRFM.

Normally, AFM and MRFM use a laser reflected off the back of the cantilever to monitor the position of the cantilever. With AFM, the tip of the cantilever is scanned along the surface, and the force between the sample and the cantilever which carries the information used in imaging is on the order of 10^{-9} N. In MRFM, the magnetic force between the sample and the cantilever is much smaller, as little as 10^{-18} N.

In AFM, this force deflects the cantilever, and this deflection carries the information for the image of the surface of the material. The laser beam is bounced off the back of the cantilever with the reflection directed onto two photodiodes, positioned one right above the other. When the cantilever deflects, the beam is directed up or down on the photodiodes, creating a voltage difference between the two, which in turn creates a current that is measured and used to create the 3D topographical image of the surface. MRFM uses a similar technique. The oscillation of the cantilever is used to monitor the material being scanned, with alterations in the amplitude or frequency of the cantilever due to the excitation of the atoms in the material detected.

This project is interested in creating a nanoscale cantilever, thus creating a much sharper point. This will make the area scanned much smaller and more accurate. Since the cantilever would be so small, a new way to monitor the deflection of the cantilever without the use of the laser must be developed. This is because as the dimensions of the cantilever become smaller than the wavelength of visible light (400 – 700 nm) such light cannot be used in reflective mode. Potentially, the piezoresistive properties of the material may be used.

Piezoresistivity is a property of a material that occurs when that material's resistivity changes as the material changes shape. In this case, as the cantilever is deflected by a force from the material, it is bent. The current would change as a function of this deflection through the material, it must be conductive. For this purpose, carbon nanotubes or ZnO nanowires would be used, the third having the magnet attached to the end. This



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Piezoresistivity on such small scales has been demonstrated. Nanowires have been known to grow in tetrapod structure, which would be an optimal shape for the use as a MRFM cantilever.

Figure 2.2: Schematic for measuring piezoresistance

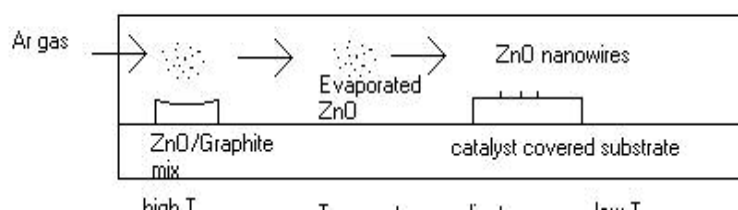
Their growth can be controlled by several methods used in growing. The most common method of growing ZnO nanowires is the VLS – vapor-liquid-solid – method. Zinc oxide powder mixed with an equal amount of graphite powder are ground together and placed in a boat made of a material with a very high melting point. Alumina boats have been used by P. Yang et al.^{iv}

A substrate is then covered with thin layer of catalyst, usually gold, which stimulates the growth of the ZnO nanowires. Other catalysts such as Sn, Cu (H) have been used in place

of gold. Common substrates are alumina, silicon, and sapphire. The thickness of the catalyst has been found to have a direct effect on the diameter of the nanowires. For example, a film thickness of 0.5, 1, or 3 nm will produce an average thickness of 88, 110, and 150 nm respectively.^{iv} When the substrate is placed in the furnace and heated, the Au will melt and bead up on the surface, forming nanoclusters of Au on the substrate, which will be the sites from which the ZnO nanowires grow.

The boat containing the ZnO/graphite mix is placed in another boat, such as quartz, and the metal-covered substrate is placed in the same boat about 5 cm from the ZnO/graphite mix. This is covered by another boat and placed in the furnace. Argon gas then flows in the direction that brings the evaporated ZnO to the substrate, which is in a cooler area of the boat. The gas will then settle on the substrate, supersaturate the Au on the surface, and will grow into nanowires. This boat is placed in a furnace that has a large temperature gradient. The shape and type of the structures formed depends on the temperature at which the substrate sits.

Instead of Au, graphite flakes can be used to instigate ZnO nanowire growth. This catalyst was used in an experiment conducted at Boston College, where it was found that in a high temperature zone (800-850°C) which corresponds to close proximity to the source material, that long thin nanowires resulted, on the order of 5-10 μm in length and about 20-50 nanometers in width. At lower temperatures (700-800°C) the structures were much shorter, 0.5 - 5 μm and thicker, measuring 60-100 nm in diameter, known as nanorods.^v The growth was found to be primarily in the [001] direction, directly perpendicular to the surface of the substrate, and there was a high level of crystallinity, with few blemishes or inconsistencies in the lattice, making strong, flexible wires. (Fig 2.3)



One way of controlling growth of the nanowires is to control the gold distribution. With no catalyst such as gold or graphite, no nanowires will form. Several experiments have been conducted of this nature, where a grid is placed over the substrate, the Au evaporated onto it. When the grid was removed, a pattern of Au and non-Au covered areas was left behind.^{vi} Nanowires were found to grow on the areas that had been covered with gold, while no nanowires were found on the areas that had been covered with the grid and thus had no gold to act as a catalyst. In another experiment conducted at the University of California, Berkeley, where a hexagonal pattern of Au was evaporated onto the surface, not only did ZnO nanowires grow only on the Au covered sections, but also many nanowires actually bridged the gap between hexagons, connecting them in a sort of network.^{vii}

This phenomenon could be used to test the piezoresistivity of the nanowires. If a nanowire can be grown to connect two conducting objects on a surface, then wires can easily be connected to these macroscopic objects, which can run current through the ZnO nanowire. Using an AFM, pressure can be applied to the nanowire, and the current can be measured as a function of pressure or deflection. If the resistivity changed as a function of deflection, the structures would be piezoresistive and a relation could be drawn.

As the nanowires grow, they first supersaturate the gold, and then grow from the substrate up, lifting the small ball of Au at the tip of the nanowire. Once all the gold is used up, the nanowire will stop growing. However, there is usually a small ball of Au at the tip of

the nanowires left over from the growing, although it may be covered with a thin layer of ZnO.^{viii} Metals can easily be attached to gold, which would allow a nanoscopic magnet to be easily be attached to the tip, which is necessary for MRFM.

There have also been several experiments done with regard to coating these nanowires with magnetic metals. Nanoscale magnetic layers have been deposited on nanowires by evaporation with success. Several magnetic materials have been tried including Fe, Co, Ni, and $\text{Ni}_{x-1}\text{Fe}_x$ ^{ix} and Au, Cu and Pt^x all deposited successfully. Metal which was evaporated onto ZnO nanorods was found to cover the tips, and because of the density of nanorods, the coating could not penetrate into the forest of nanorods, leaving most of the nanorod length uncovered except for the tips, which were coated with a thin layer of metal, in the range of 100-300 Å thick. It was also determined that if the evaporated metal was introduced at an angle, the metal would distribute itself much as snow does in on trees on a windy day. One side of the nanorods can have the deposited evaporated metal, while the other side remains untouched. Nanorods that are blocked by other nanorods in the path of the evaporated metal will not collect any of the metal.

The shape in which the nanorods grow is also conducive for use as a cantilever for MRFM. One shape that can be made is a tetrapod, another it tripod (Fig 2.4). There are four legs all equidistant from each other in the tetrapod. These could be useful, allowing a current to be run through two legs, and a magnet applied to a third. The current that is

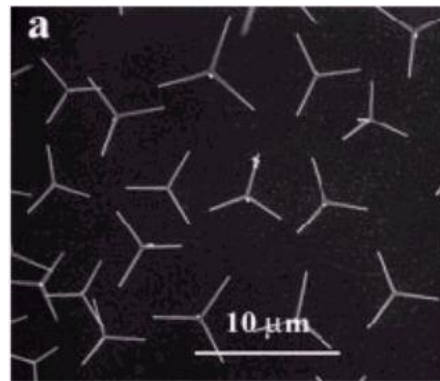


Figure 1.4: ZnO tetrapods

run through the tetrapod would change if the material is piezoresistive. One group who produced these tetrapods followed the procedure outlined above, with a temperature of 800-900°C for between 10 and 30 minutes.^{xi}

Because of the properties and qualities that other groups have found during their study of ZnO nanowires and nanorods, it is possible that they would be useful for making cantilevers to use with MRFM. The scale of the ZnO nanowires is desirable because better resolution and higher magnification depends on there being a more precise excitation, with little signal from neighboring areas which might be affected by the external magnetic field. This noise signal decreases as the areas excited become smaller and more precise. In addition, the nanowires are shaped in a way that is optimal for the piezoresistivity that we hope to use for monitoring the oscillations, as opposed to the lasers, which would be hard to detect bouncing off such a small surface as the nanowire, even if it was reflective enough. The gold that is found at the tip when synthesized as described above is also convenient for attaching the nanoscale magnets that are required by the design of the MRFM as described. If ZnO nanowires are indeed piezoresistive enough to monitor oscillations of the nanowire, it could be a novel approach to the MRFM cantilever and a more sensitive MRFM.

Determining the properties of the nanowires could lead to the development of a much more sensitive MRFM, which would be of use in many fields. It would lead to 3D imaging of atomic scale particles, including proteins, cells, nanostructures, and many other objects. Especially in biological sciences, this information would provide important information into chemical processes, which would aid in the curing of diseases and disorders.

Chapter 3

Specific Goals

This research is part of a larger research project aimed to develop nanoscale MRFM using branched nanostructures such as Y-junction carbon nanotubes and ZnO nanowire tripods and tetrapods. There are many steps leading to the development of the MRFM using nanostructures as cantilevers. First, the ZnO and carbon nanotubes must be grown in branched morphologies.

To test the electrical resistivity of these nanostructures, a manner in which to make electrical and mechanical contact to them needed to be devised and constructed. It is a non-trivial matter to be able to direct a current (I) through the nanotube and then measure the voltage (V), and therefore be able to extract the resistivity from the I-V curve. If a series of parallel nanoscale wires could be made with the capability of being able to connect them to macroscopic wires, a current

could be fed through the nanowires and the voltage read across the nanotube. Provided the nanotubes could be placed or manipulated so that only one lays across the parallel nanowires, a current can be run through the ends of the nanotube, and the voltage can be measured through separate wires,

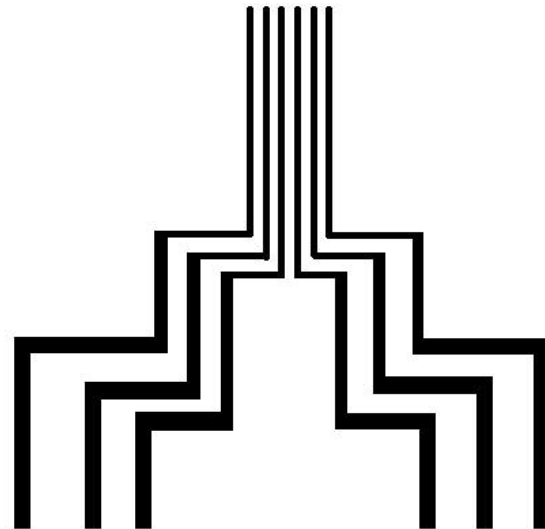


Figure 3.1: Schematic design of the electrode pattern on a wafer.

giving a clean four-probe measurement. Such a nanoscale measurement platform was designed and fabricated by Dr. Naughton, his post-doctoral fellow Dr. J.I. Oh, and graduate student Yong Sun as described later, resulting in a wiring platform as sketched in Fig. 3.1.

To test the piezoresistivity of the nanowire, the Y-junction should be aligned so that two of the legs lie across the wires, with the third leg parallel and not touching the wires, allowing a force to be applied while a constant current is running through the two legs that lie across the wires. In this way, the piezoresistivity can be found as a function of deflection or force applied. A relation between current in and voltage across the nanotube can be made as a function of this deflection. (Fig. 3.2)

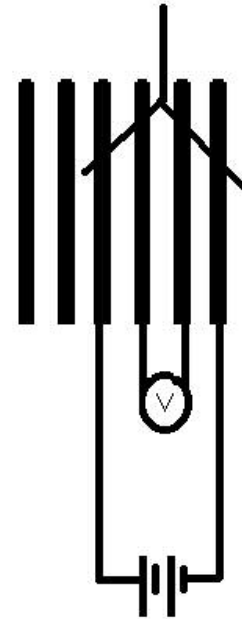


Figure 3.2: Measuring piezoresistance.

In order to do this, there are several problems that must be overcome. After the nanowires and carbon nanotubes or ZnO tetrapods are made, the nanostructures must be put on the nanowires and manipulated into the desired position. Sonication is commonly used method of cleaning a substrate or mixing a solution. The solution to be sonicated is placed in a glass container and immersed in a water bath in a sonicator. High frequency acoustic waves are passed through the water, which shake the solution or object to be cleaned without causing violent movement. The nanostructures can be deposited on the nanowires by first sonicating the substrate that the structure was grown or deposited onto, and then putting a drop of the solution on the wires. When this is done, however, if the nanostructures do not happen to land in an optimal position, they must be manipulated into place. In addition, from

previous experience, it is known that there is an adhesion from the deposition that must be overcome in order to move the nanostructures. To overcome this, the strength of this adhesion must be found, as well as how to overcome it without destroying the nanostructures. Learning to manipulate the nanostructures into the desired positions using the AFM is one of the major obstacles that must be overcome.

In addition, in some situations, it may be useful to be able to cut the nanowires precisely to within less than 100 nm, to stop a circuit from shorting, or to direct the current as desired. A method for severing wires needs to be developed using the AFM and tested for accuracy to see if this indeed is a possibility. Also, to position the nanostructures across the wires manually, the effect of moving the nanostructures on the wires should be examined. There is a good possibility that moving the nanostructures may damage the wires, and the effect of this may be to cause a short in the circuit, making the resistivity measurement impossible.

Once a circuit is made using the nanowires and the nanostructures, the resistivity can be measured using the four-probe measurement technique described earlier. In order to test the piezoresistivity of the structure, a force must be exerted on the free arm of the structure in a controlled manner. In order to find the resistivity as a function of this force, it must be monitored. The force can be applied using an AFM, and a method for accurately applying this force at a particular place must be developed. If this is accomplished, then a relation between the force and resistivity can be found, which would allow for the structure to be used as a potential cantilever for an MRFM device.

Chapter 4

Accomplished Goals and Procedures

The first step in this process was to create the carbon nanotubes (CNT) and ZnO Y-junctions that are believed to be good candidates for MRFM cantilevers. The Y-junction CNTs were fabricated in Prof. Zhifeng Ren's lab at Boston College by Dr. Wenzhi Li, now an Assistant Professor at Florida International University. To create these nanostructures, a catalyst of MgO supported Co was prepared by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ethanol alcohol, and immersing MgO powder into it, sonicating for 50 minutes. After drying, the catalyst was then calcined at 130°C for 14 hours to remove moisture. To grow CNT, the catalyst was heated to 1000°C in flowing H_2 with N_2 at 40 sccm and 100 sccm respectively at a pressure of 200 Torr. After one hour, the N_2 gas was replaced by CH_4 at 10 sccm, starting the CNT growth, which normally lasts for an hour.^{xii}

The ZnO tetrapods and tripods were made in Dr. Ren's lab by Debasish Banerjee following a recipe in the literature^v. Approximately 1 gram of zinc powder was placed at one end of a quartz boat, and a silicon wafer coated with a thin film of chromium is placed at the other end of the boat. Because the shape of the resulting ZnO nanowire depends sensitively on the temperature gradient between the powder and the substrate, it is important to find the distance between the powder and the substrate which provides the appropriate temperature difference. The boat is mostly covered with a quartz sheet leaving a small opening left over the end of the boat containing the substrate so that evaporated Zn flows towards the substrate when heated. The boat was placed in the furnace, which was pumped down to between 1-2 Torr slowly to avoid causing the zinc powder to fly around inside the boat. Ar (50 sccm) and O_2 (0.5-0.6 sccm) gas was pumped through the chamber.

The chamber was heated at 50°C per minute until it reached a high temperature that allowed the temperature the zinc to be roughly 500°C with the substrate positioned at a lower point on the temperature gradient. Once this temperature had been reached, it was kept steady for 30 minutes, to make sure that all of the zinc evaporates. If some of the zinc is left in the boat, when it condenses and cools it is very difficult to clean off. The evaporated zinc reacted with the O₂ gas and as the gas passed through the cooler end of the temperature range, 350-400° C, it condensed onto the silicon chip in nanorods.

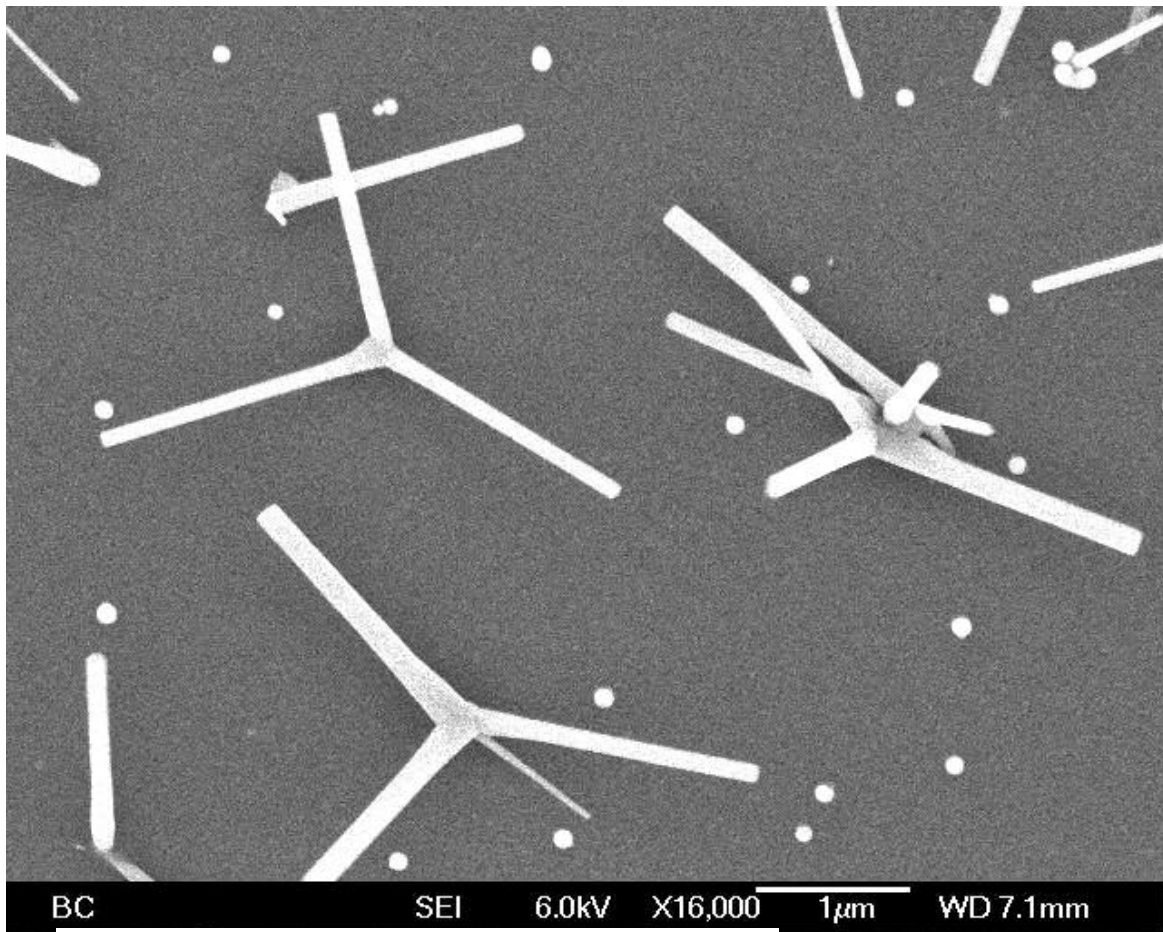


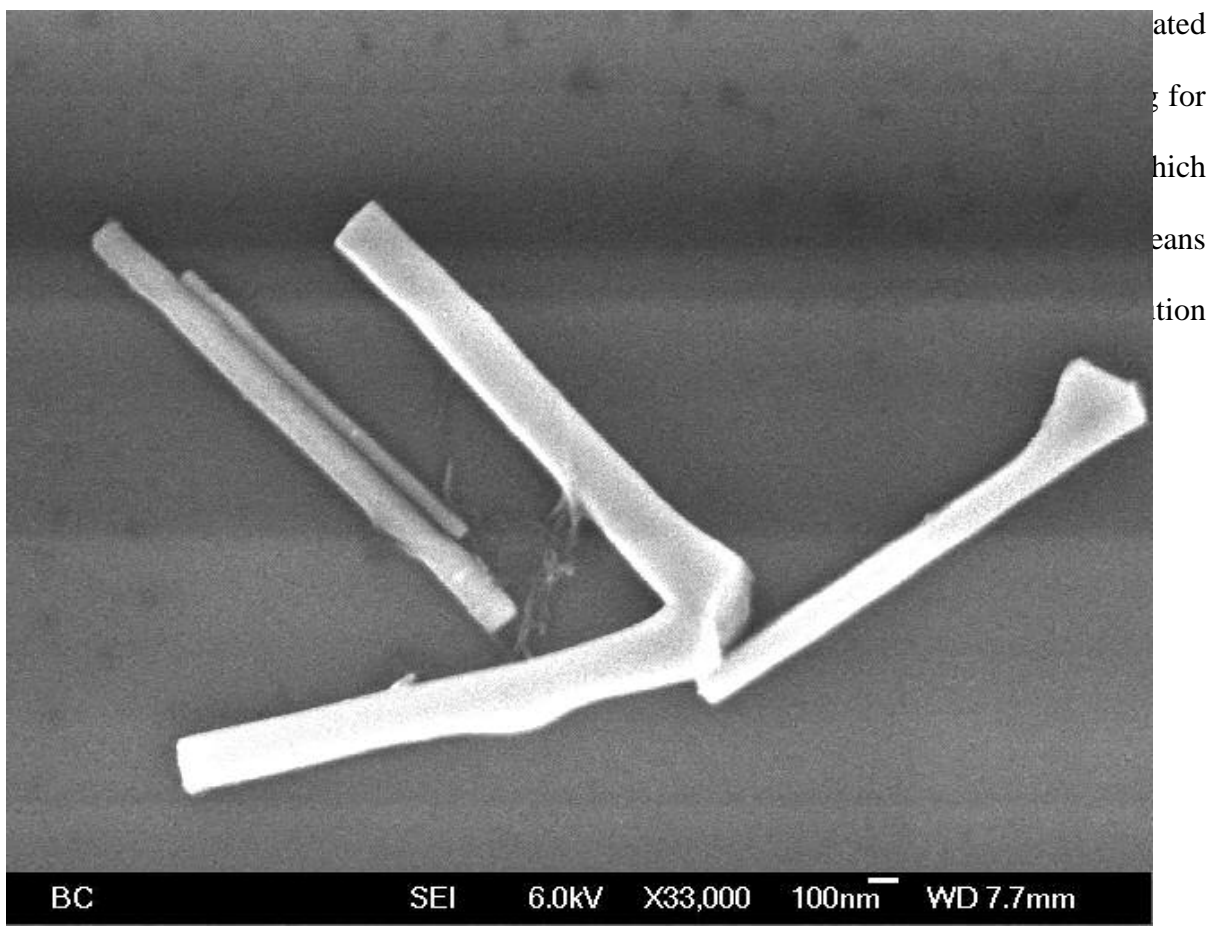
Figure 4.1: ZnO nanowires prepared in this project. Scale bar = 1μm

The temperature was then lowered again to room temperature, and the silicon chip which acted as a substrate now had on it ZnO tetrapods or tripods. Because of limitations of control over the amount of O₂

gas due to equipment in the lab, and the sensitive dependence of the concentration of O₂ gas on the shape of the ZnO nanowires that are produced, the results are difficult to reproduce.

To examine both the CNT and the ZnO nanowires, a scanning electron microscope (SEM) was used to determine if the three- or four-armed particles had been made successfully. Images of the CNT and ZnO nanostructures produced are included in Fig 4.1.

The platforms containing gold nanowires to be used in measuring the resistivity of the structures were fabricated. First the design was prepared using computer-aided design (CAD) for a series of photolithography and electron beam nanolithography masks using L-Edit © software. Then Dr. Oh and Mr. Sun went to the Cornell Nanofabrication Laboratory at Cornell University to use these masks in a series of process steps to deposit nanowires on silicon wafers. First, nanopatterns were made with e-beam lithography and a micromesh was made with photolithography, creating two parts of the circuit. Next, the nanopattern and micropattern were aligned, with contact alignment used to connect the two. Finally, gold was deposited onto the wafers.



First, the process of transferring the structures was tested to see if any damage was incurred to the structures during transfer. The solution was transferred drop wise by pipette onto a clean silicon chip, which was then examined in the SEM (Fig 4.2). It was found that many of the tetrapods were broken in one or more places. These breaks may have occurred during sonication, or they may have occurred during the transfer from being sucked into the pipette. The concentration of the nanostructures in this solution is fairly low, so that the density of the structures in one drop when placed on a set of gold wires is low enough that the structures are individual and not clumped together or tangled. It is a trial and error process to acquire a set of gold wires with only one nanostructures lying across it in the proper orientation, but it does happen. SEM images of the gold wires with the nanostructures deposited on them show the positions of the nanostructures (Fig 4.3).

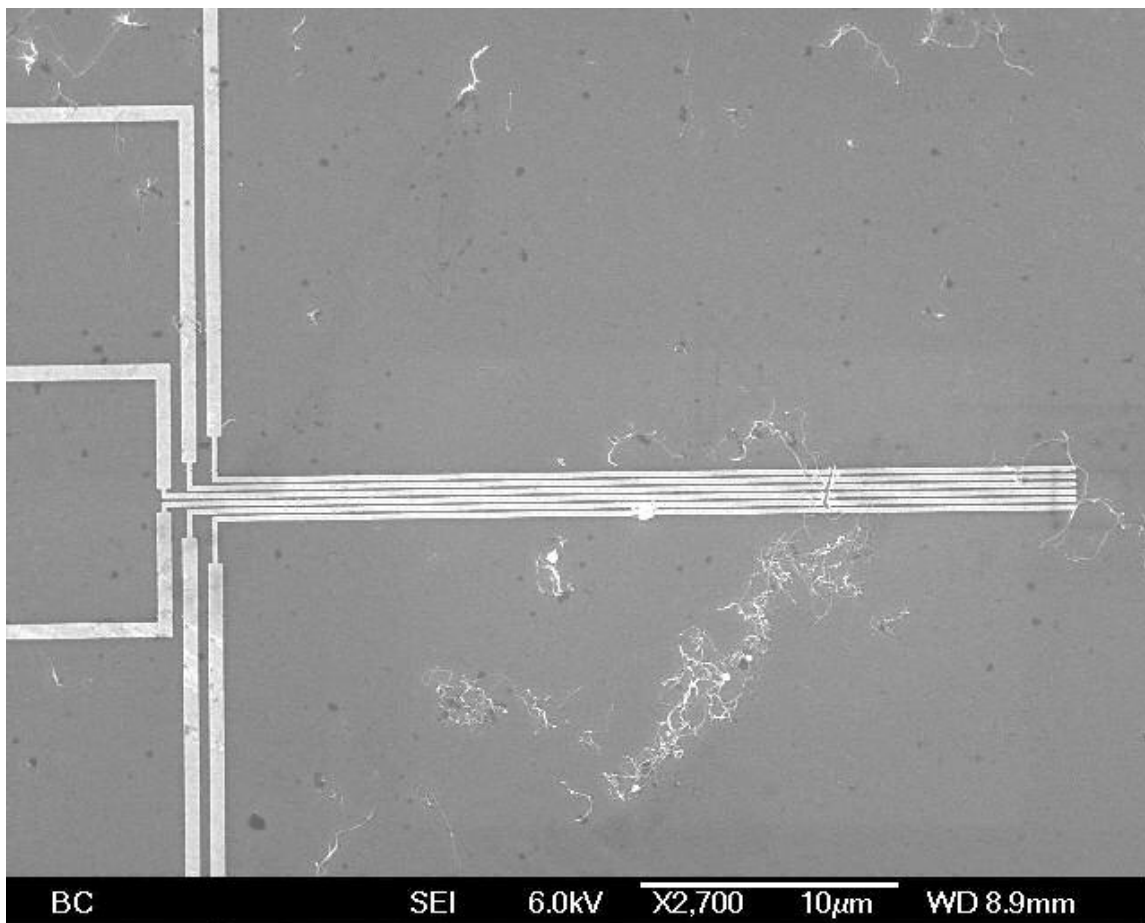


Figure 4.3: CNT on gold wires

The nanostructures sometimes fall across the gold wires in the desired position, but more often do not, or there may be more than one, which would create a more complicated circuit with nanostructures in parallel, and the resistivity of one structure would not be able to be measured. In order to be able to position the nanostructures in the desired positions and not rely on chance to acquire the proper position, the nanostructures must be manipulated, both on and off of the gold wires. In addition, the effect of manipulation to both the nanostructures and the gold wires must be known.

To do this manipulation, the AFM was used. Y-junction CNT's were sonicated in dichloride methylene (CH_2Cl_2) and one drop was placed on the gold nanowires. This was first imaged in the SEM so that a map of where the y-junction CNTs were on the gold wires was available, making navigation around the chip easier with the AFM. The chip was then placed in the AFM, and imaged using tapping mode.

Previously, it had been found by Naughton Lab that the CNT could be manipulated with the AFM by first focusing on a portion of the CNT to be moved and then switching the AFM mode from tapping to contact mode without changing position or cantilever to push the CNT. It was found to be possible to sweep the tip and push the CNT in the direction of the tip's movement, since tapping mode cantilevers are shorter and more rigid, not giving as much when pressure is applied as a contact mode cantilever. Tapping mode was used to image the surface because a light touch was required so as not to damage the structure. A contact mode scan would scratch the surface and possibly ruin the gold wires, cutting them or the nanostructures. It had also been found from experimentation that the first manipulation sweep in contact mode used to push the CNT usually cut it and broke the adhesion with the

surface, allowing subsequent sweeps of the tip move the CNT more easily with less breakage.

To practice manipulating the nanostructures, CNT's were chosen that were away from, as opposed to on, the gold wires, to avoid damaging them. Once a wire was found that was not tangled with others, a higher resolution image of the CNT in relation to its surrounding CNT's was taken to allow for comparison with the position of the CNT after the manipulation had taken place. This allowed for the effects of the manipulation to be seen easily and readily from a before and an after image. It was important to record the exact position and settings of the scan so that the same area can be imaged later.



Figure 4.4: Quesant 250 AFM

screen.

To position the CNT to be manipulated, tapping mode is used. The direction of the scan can be changed by changing the angle of the scan. This allows the direction the CNT is pushed to be specified. Once the scan had been focused on the CNT to be moved and the

The AFM that was used was a Quesant model Q-Scope 250 (Fig 4.4). Each scan of the tip begins at the upper left hand corner, and goes across to the upper right hand corner, returning to the left side for the next scan, proceeding in a left to right, top to bottom progression. To manipulate a CNT, the point where force is to be applied must be positioned in the upper left hand corner of the AFM image as it appears on the computer

nanostructure was positioned in the upper left hand corner of the screen as in Fig. 4.5, the tip was retracted a small amount, and from the ‘configure’ menu, the mode was changed from “wavemode” to “broadband” mode, which changed the mode from tapping to contact. The photodiode that records the laser deflection must be adjusted to contact mode position, as well as the computer and machine now are operating in contact mode. The cantilever was then re-engaged.

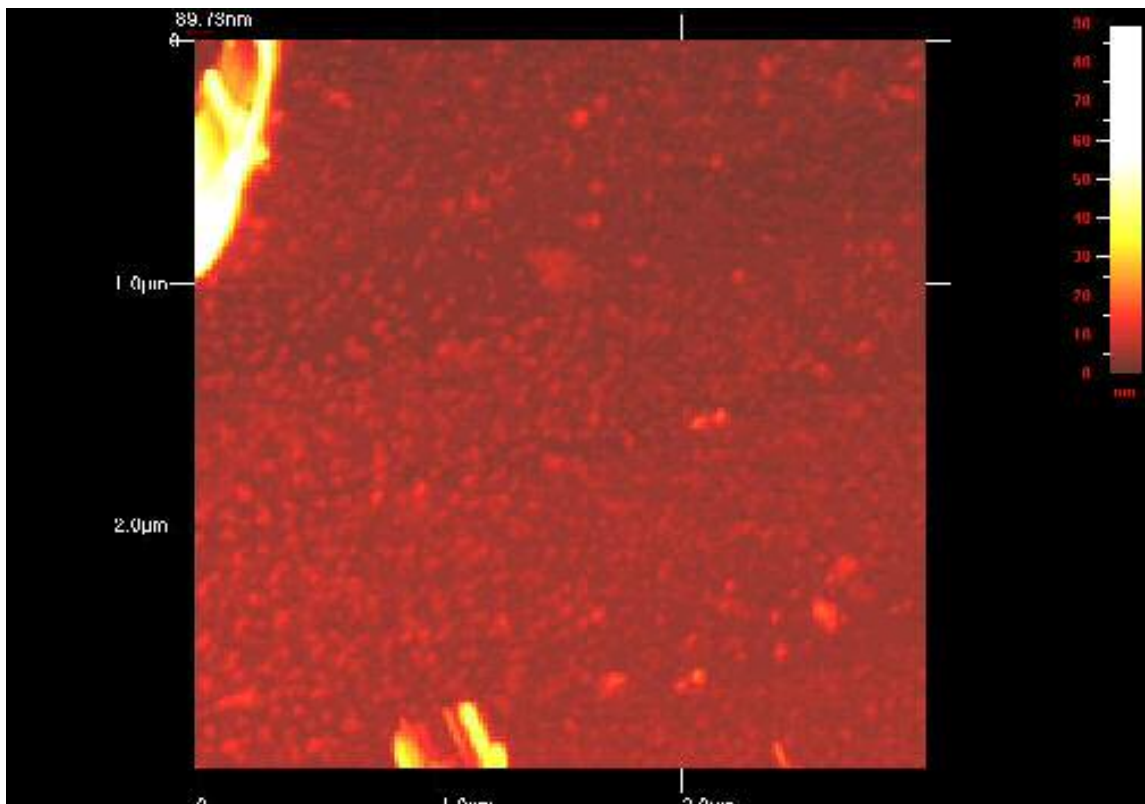


Figure 4.5: AFM image of a CNT in position to be manipulated in upper left hand corner.

To help avoid cutting the CNT, the tip should be moved slowly across the surface. The three parameters that control the speed of the tip sweep are scan size, scan rate, and

resolution. A smaller scan size, lower scan rate, and/or higher resolution will all slow down the tip so that instead of crashing into the CNT, it will approach more carefully, lowering the chance of cutting and shattering the CNT. The tip was allowed to scan only once across the surface and then the scan was stopped as soon as the first scan line's image appeared on the screen. This is so that the CNT feels only one push in one direction. The tip of the AFM is also dulled by using a tapping mode cantilever for contact mode, and as few movements in contact mode as possible are desired.

Once this one sweep was done, the tip was retracted and the configuration was changed back to tapping mode. An image is taken with the same coordinates as had previously been used in the first scan so that a comparison can be made and the movement of the CNT can be explicitly seen (Fig 4.6). This procedure of placing the

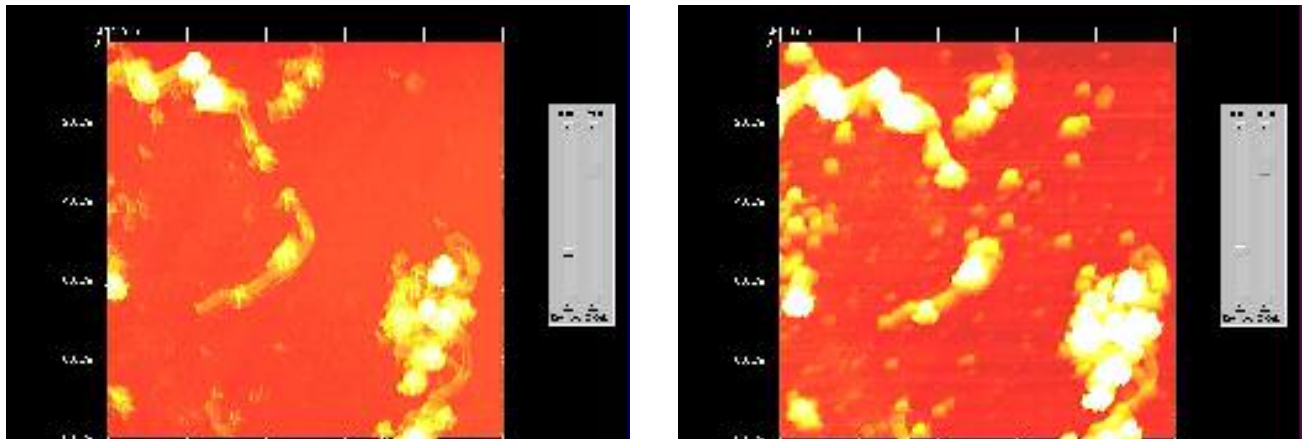


Figure 4.6: CNT before and after manipulation

segment to be manipulated in the upper left hand corner and changing the settings to contact mode can be repeated for subsequent manipulations.

The first time the manipulation was attempted, the speed was not low enough, and instead of cutting or moving the CNT, it disappeared. Presumably, the Y-junction was

shattered into small pieces, some of which stuck to the tip and were dropped onto other places on the substrate. The pieces seemed to have disappeared from the surface. When there is debris or parts of CNT stuck to the tip of the cantilever, the image can become blurry. When this happened, one way to clean off the tip is to retract the tip a small amount, and increase the amplitude of the oscillation using the 'set frequency' setting for about 30 seconds, hoping to shake the debris off the tip. This was done, and the amplitude was lowered back to the recommended range. The tip was re-engaged, and scan the of the surface was repeated. This was found to help increase the sharpness of the images collected in some cases by removing debris from the tip.

This first attempt at manipulating the CNT was not successful because the CNT was broken and scattered and could not be found. But in subsequent attempts, the manipulation was more successful. Another CNT was found and focused on, and an image was taken to serve as a reference image (Fig 4.7). The CNT was then positioned so that it was in the upper left hand corner of the scan, as before. The tip was retracted, the mode was changed once again to contact mode, the photodiodes were realigned with the laser, and the tip was re-engaged. One sweep of 5 μm at 1 Hz was allowed to scan the surface. The tip was retracted, the mode was reset to tapping mode, and a full scan of the surface was taken to compare with the image before manipulation. A section of the CNT had been cut and was moved slightly in the direction of the scan.

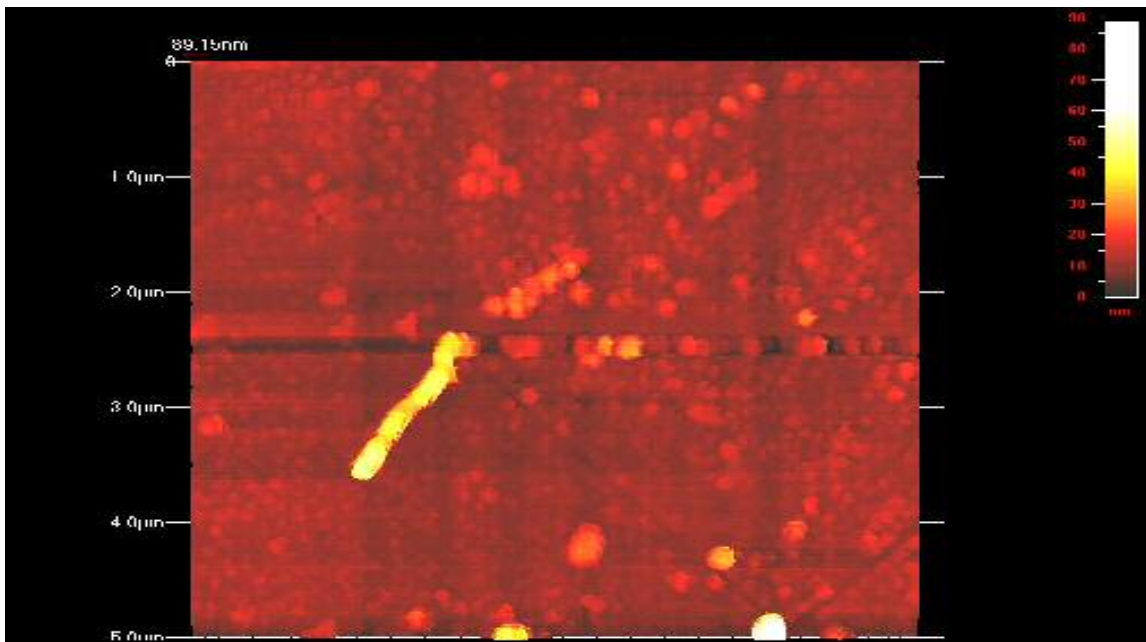
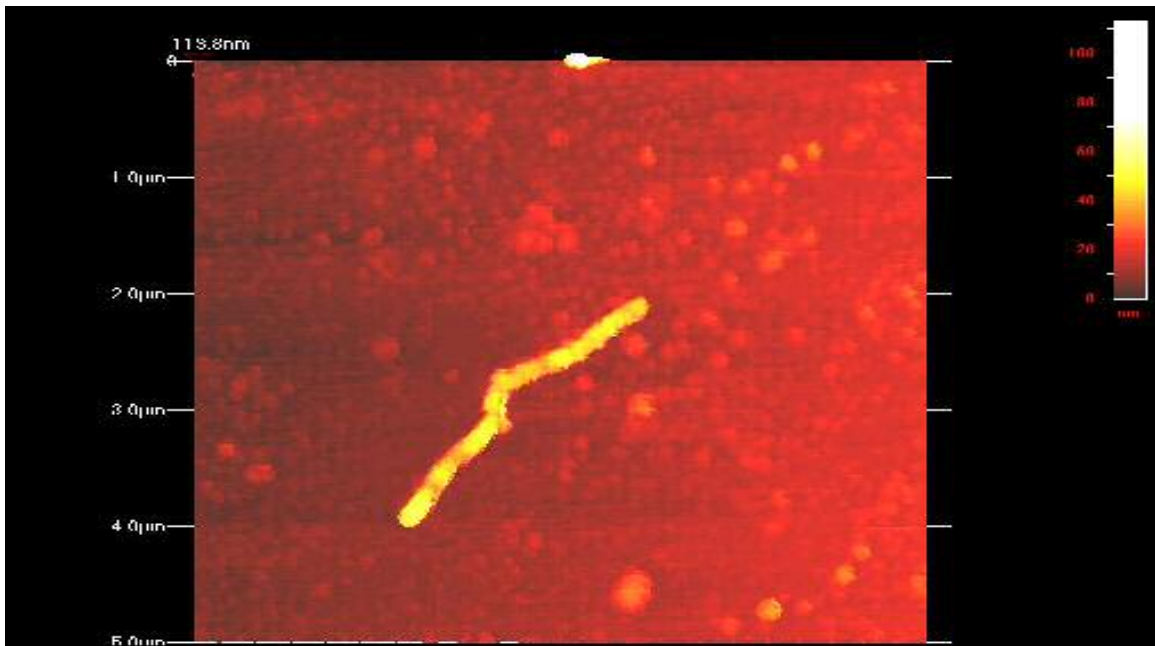


Figure 4.7: AFM image of a CNT before (above) and after (below) manipulation

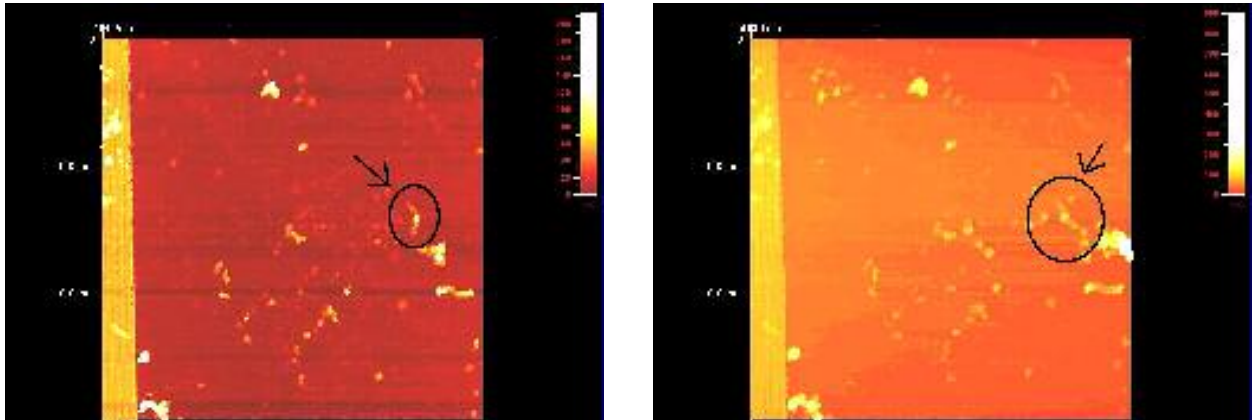


Figure 4.8: Manipulation back towards original position.

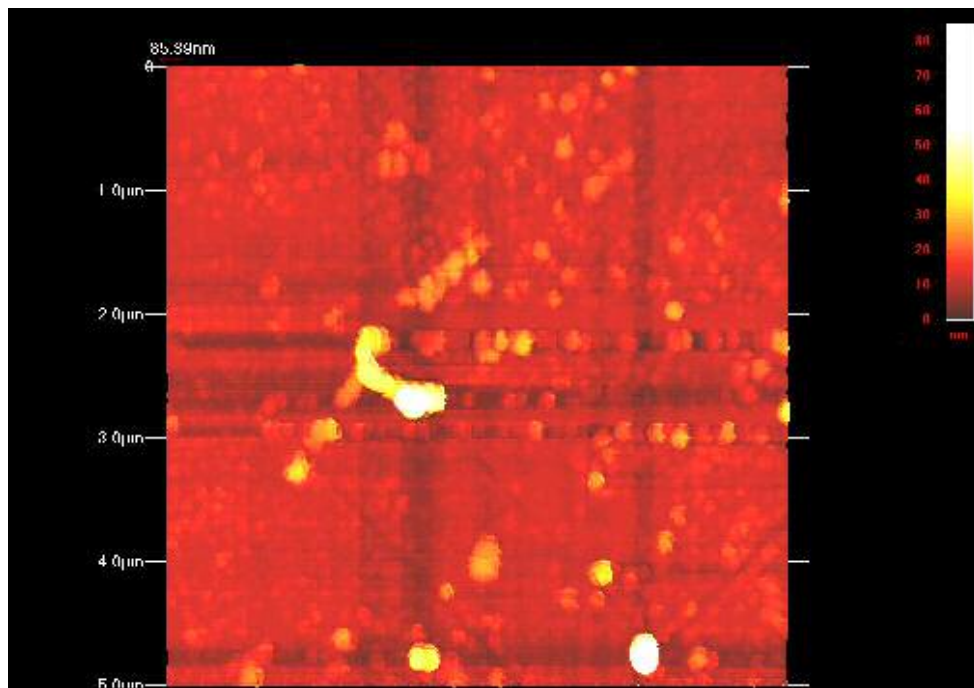


Figure 4.9: After 2nd manipulation

After the initial manipulation scan was made, a section of the cut nanotube was focused on, and successfully pushed in the direction of the scan. To avoid breaking the cut nanotube section, the speed of the manipulating scan was slowed down. The second manipulation had a scan size of 5 μm , scan rate of 0.5 Hz, at a resolution of 200. Again, an image was taken at the same coordinates and range as a previous scan to compare, and the move was confirmed (Fig 4.9). The bottom part of the CNT which had been manipulated had been pushed in the direction of the tip sweep.

A third manipulation was made on the same CNT which had just been moved, this time to move it back in the direction it had come from. Since the AFM can only scan from left to right, to move the CNT from the right to the left, the CNT to be moved was placed in the lower right hand corner of the scan, and then the scan was set to sweep, but with a 180° rotation. This essentially makes the AFM scan from the lower right to the lower left, moving upwards in subsequent scans instead of downwards, as it normally does. When the position of the CNT was as desired, the tip was retracted as before, the mode changed, and the scan was made at 0.5 Hz over 5 μm at 200 resolution as before. The CNT that was moved appeared to be spun around instead of simply pushed from right to left when compared to earlier scans (Fig 4.8).

Another variable which was examined as a feature that could improve the success of the manipulations was the z-voltage variable. As the z-voltage is changed and made more negative, the pressure of the tip on the surface increases, which may possibly help move the CNT and overcome the initial adhesion to the surface. The initial scan was made as a reference, and then a CNT was focused on and positioned in the upper left hand corner as before. The manipulation scan was made at 1 Hz over 4 μm at 200 resolution. When the image was taken of the manipulated CNT with the same scale and coordinates as previously, the CNT had been cut, and a scratch on the surface of the silicon chip could be seen.

Now a manipulation of the broken CNT was attempted, this time with the z voltage changed to -0.1 V at 0.5 Hz and 2 μm , with the resolution at 600. The resulting move can be seen in the image below (Fig 4.10).

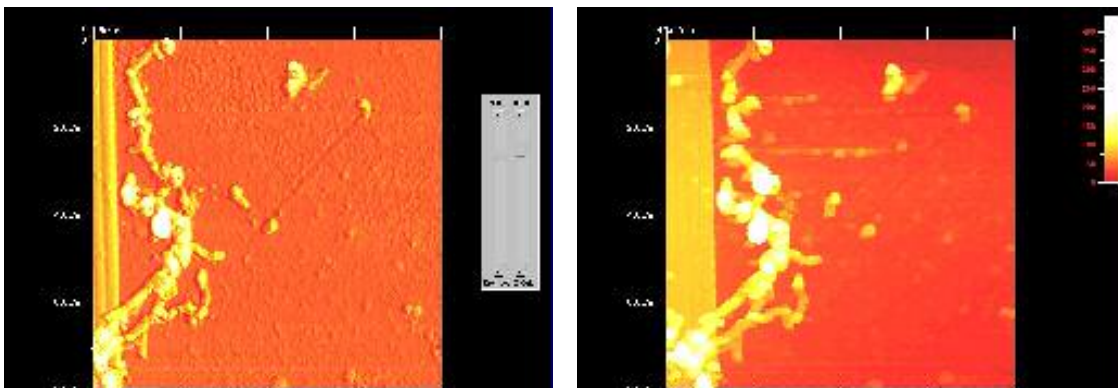


Figure 4.10: AFM image of CNT before and after manipulation

The images of the CNT after being moved become less precise and more blurry with each successive move, because the tip is dulled from being dragged across the surface. It can no longer follow the contour of the surface as precisely, as can be seen as the resolution of the space between the gold wires becomes more and more blurred. As the tip is dulled, it can no longer fit into the smaller spaces as it could when it was sharper, and so the features are enlarged as the details are not resolved and the tip cannot follow the contours as closely. One way to obtain a clearer view of the image is to choose the option of sunrise from the pull down menu on the 'view' screen. Often this makes the image clearer, and has been used to view several of the images shown in this thesis.

Another effect of the manipulation scans that can be seen from the images is the trace of the manipulation scan on the surface. The tapping mode cantilever is more rigid than the contact mode cantilever. When the AFM is set to contact mode, it assumes that a contact mode cantilever is in the machine, and so reacts accordingly. The tapping mode cantilever does not give and deflect as much as the contact mode cantilever, and so with a given force from the surface, deflects less than a contact mode cantilever does, in turn therefore scanning with more pressure, scratching the surface.

The scratches follow a triangular path, giving an indication of the path that the tip follows. The tip begins in the center of the area to be scanned, and moves from the center to the upper left hand corner, scanning across to the right. For the manipulation scans, the tip was allowed to complete only one scan before being stopped, and the trace that goes from the upper right hand corner of the window to the center shows that the tip returns to the center of the window after the scan is completed. Knowing the path of the scan is

important. To manipulate a specific CNT, it is important to make sure that there are no other CNT or features in the path of the tip as it moves from the center to the position to push that specific CNT. If there are other structures in the path, they may also be manipulated, which could result in moving a structure that should not be moved, possibly pushing it into the CNT that was meant to be manipulated, or even destroying the AFM tip if the structure is too large.



Figure 4.11: Position of nanostructure which would benefit from being able to cut the 3rd wire from the left.

It had been found by Yong Sun that the gold wires are very fragile to the contact mode AFM, and can be easily distorted and scratched by the tip. The selectivity of this scratching was another aspect to be examined. If the wires could be selectively cut, it would be useful in creating circuits with Y-junctions or tetrapods which did not lie in exactly the right position, but which could be made into the correct circuit if a wire could be selectively cut, such as if the wire happened to lie across the wires as in Fig 4.11.

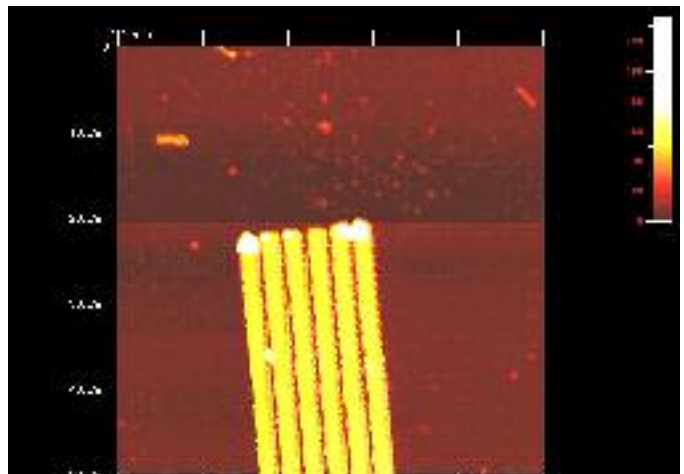
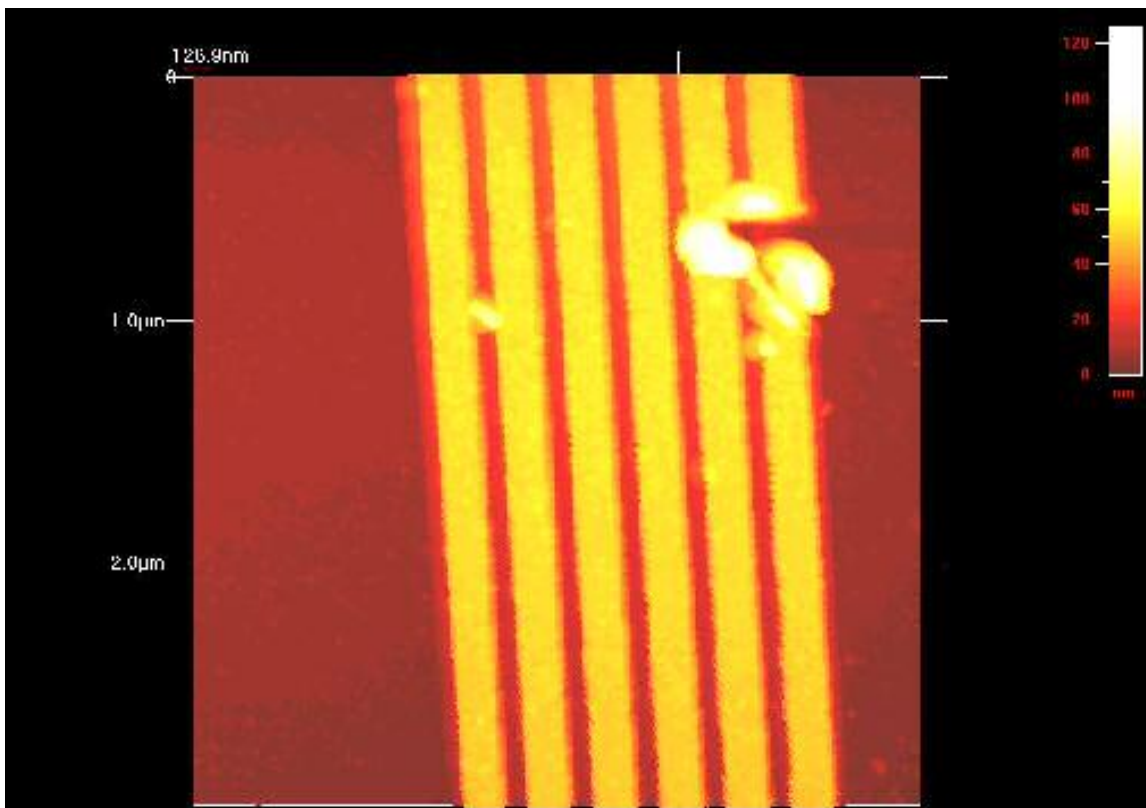


Figure 4.12: Wire before intentional severing.

An SEM image of the set of gold wires had been taken to be sure that there were no breaks in the wires before they were intentionally cut. Then the chip was placed in the AFM. An image of the end of the set of gold wires was taken using tapping mode to compare to the image after the cut had been made (Fig 4.12). To cut the gold wire, the process was to follow the same procedure as was used in manipulating the CNT, to see if the same force that could move the nanotubes could sever the gold wires. Since the tip had scratched the surface of the silicon surface, it was probable that the tip would be able to cut the gold wire.

The easiest cut to attempt first was the outer right hand wire of the six, because that would only require the starting point of the scan to be precise instead of the ending point



as well. Several scans were made,

Figure 4.13: Gold wire after first cut

making the coordinates of the center of the scan more precise until only the right end wire was visible on the scan screen.

Then, as had been done with the manipulations, the tip was retracted and the mode was changed from tapping to contact without changing position or the cantilever itself. The photodiodes were readjusted for contact mode and the cantilever was re-engaged. To try and make the cut as clean as possible, the speed of the sweep was slowed by making the scan size $2\ \mu\text{m}$, with a rate of 0.5 Hz at a resolution 500. The tip was allowed to scan the surface once and then stopped. The tip was retracted and the mode was once again changed back to tapping mode, the photodiodes reset, and the tip was re-engaged.

When the scan was made with the same coordinates as before, the image showed that the wire had indeed been cut (Fig 4.13). However, the gold was malleable and had been pushed up on the sides of the path that the tip had made. This second scan was not as clear, presumably because there was gold stuck to the tip making it much less responsive. However, it appeared that the gold that had been pushed aside had formed a short circuit between the two rightmost wires. The wire had, however not been cut as cleanly as hoped.

Now the AFM was used to attempt to cut one of the interior wires, since if the wires are to be cut selectively, it is important to be able to cut the middle wires and not only the outer wires. This is more difficult, since the precision must be sharper. Additionally, the wires are about $0.2\ \mu\text{m}$ wide, and so the scan area must be much smaller than had been used previously. This tip had been used before, and it was already duller than it had been the first time, so the image that was not as clear as it had been when focusing for the first cut. The area focused on had a scan size of 250 nm which included on the screen only the

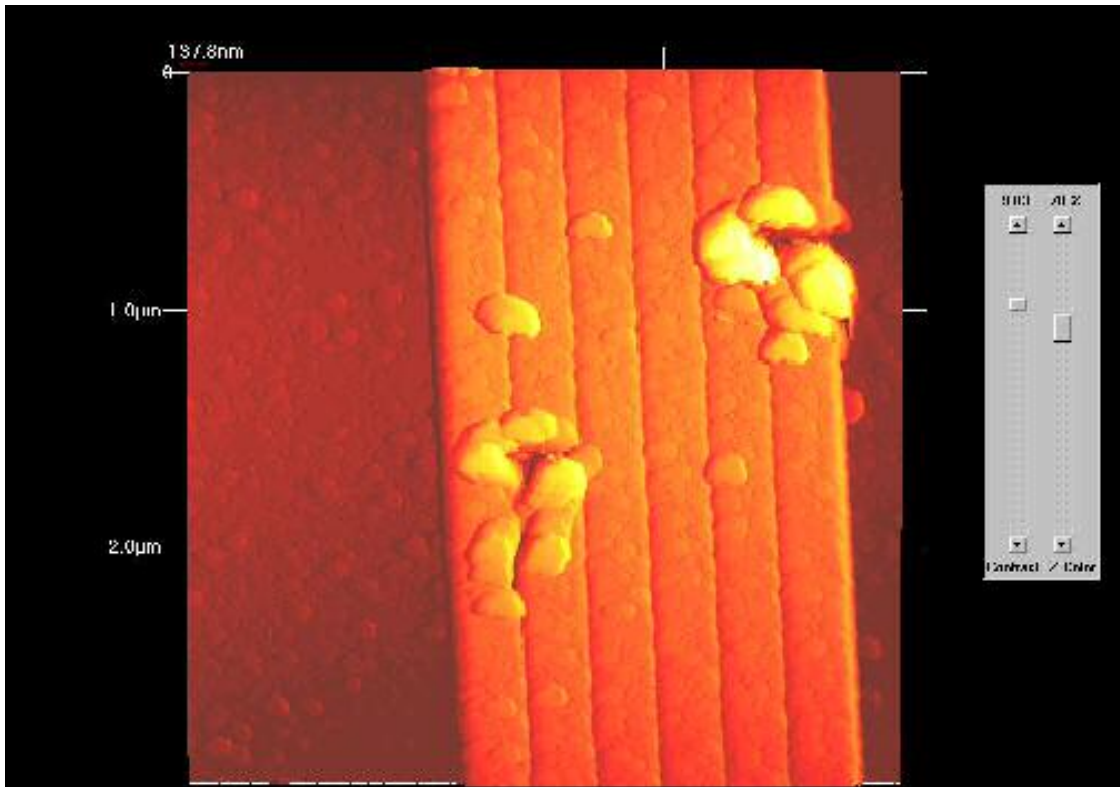


Figure 4.14: Gold wire after cut in second wire from left was made.

wire that was to be cut. The tip was retracted, the photodiodes and AFM set to contact mode, and re-engaged. To cut, the wire, the scan size was kept at 250 nm at a rate of 0.5 Hz at 500 resolution. The tip was allowed to sweep only once and then retracted, and the AFM reset to tapping mode and re-engaged. The scan that was taken to compare this second cut to the image before the cutting showed a significant further dulling of the tip

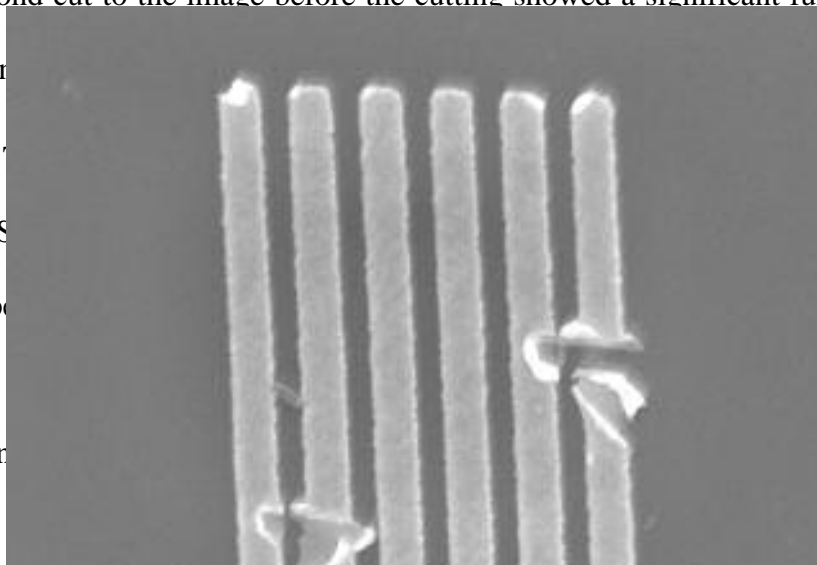
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Figure 4.15: SEM image of the severed wires

What is also made clearer in this SEM image is that the cut does not sever only the wire that is in the image screen but also scratches the wires to the sides of the wire that was intended to be cut. This is most likely due to two variables. First, when the tip is retracted and re-engaged, it may drift very slightly to one side or the other. When the precision is required to within tens of nanometers, this drifting can cause the tip to cut wires that are close to the wire that was intended



to be cut. From the SEM images, it appears that the tip may have drifted in the negative x direction (to the left on the image) since the wire that was scratched more was to the left of the intended wire. Another reason why these wires may be partially cut is the size of the tip. With a very sharp tip, these wires may not be cut, or may be cut less. However, with a duller tip, the tip size is much larger, so that simply because the tip does not appear to touch a wire on the scan screen image, does not mean it does not touch it (Fig 4.16). This can be seen in both of the intended wire cutting attempts.

When the CNT are deposited on the gold wires, at times they lie across the gold wires in the desired position without requiring any manipulation. This occurred by chance in

Figure 4.16: The effect of a dull tip (bottom) compared to a sharp tip (above)

several of the chips, allowing for a preliminary resistivity measurement to be made. The circuit used to make this measurement involves running current through the gold

nanowires and through the nanotube, and measuring the voltage as the current is changed through two probing gold wires. From this current – voltage curve, the resistivity can be extracted.

This circuit was constructed by Yong Sun, and a preliminary measurement of the resistance was taken as the current was increased slowly from 0 to 1 μA , and then back down to 0, continuing on to -1 μA . The resistance was not constant according to the I-V curve, but rather decreased and then increased again with time. This was strange and unexpected because no pressure had been applied to the nanotube, and so the resistivity should have been constant. When the chip was placed in the SEM, it was found that the gold wires had melted and created a short circuit, either as a result of a current that was too high, or electrostatics due to the wires being attached. Therefore the resistance that had been measured was not the resistance of the CNT, but the resistance of the CNT and the gold wires as they melted, and eventually ran into each other creating a short circuit.

This measurement was also carried out in the AFM before the SEM image had been taken and the melting of the gold wire was found. To apply a pressure to the CNT, the AFM was put in tapping mode with a tapping mode cantilever, and while the current and voltage was being read, the CNT had been scanned with the tapping mode cantilever to see if there was any effect was seen as the tip crossed and tapped the CNT. There was no result found because the wires had been shorted by melted gold, but another interesting effect was found. The cantilever had been left engaged, and had happened to be positioned over the CNT. It had been left there tapping for approximately half an hour before the tip had been retracted. When the SEM image was taken, it was found that the

CNT which had been only one across had been cut by the tapping tip. To avoid this, the tip should be retracted when the AFM is not being used to image a surface or apply force.

Chapter 5

Further Research

The research done in this project can be extended to determine whether the ZnO tetrapods or tripods, or Y-junction CNT can be used as cantilevers for use with MRFM. This research gives a good foundation off of which future research can be based and expanded.

The procedure for manipulating the CNT away from the gold wires has been found to be valuable. One element of this procedure that could be improved upon is the initial manipulation that breaks the adhesion of the CNT to the surface. One possible variable to experiment with may be the solvent used to deposit the CNT on the surface. It can be studied to see if a different solvent creates less adhesion making the manipulation easier. The effect of very small scans, on the order of 500 nm, and slow scan rates of about 0.5 Hz is another element to examine. Perhaps this very low tip speed would help further reduce the breakage of the CNT and promote movement of a CNT as a whole.

The possibility of using ZnO nanostructures was discussed, however, manipulation of the ZnO was not researched here. The CNT can be cut fairly easily with the AFM tip, but the effect on ZnO is not known. Nor is it known how easily these ZnO nanostructures can be moved on the surface. If they can be moved more easily with less breakage than the CNT, then they perhaps would be a better candidate for use as a cantilever.

The effect of moving a CNT or ZnO nanostructure that is already on the gold wires can be examined to see if there is any damage to the gold wires. This can be done by locating a CNT that lies across the gold wires from being deposited there, and scanning a sharp AFM tip in tapping mode along the space between the gold wires, to push the CNT without touching the gold wires. The adhesion between the gold wires and the CNT may be stronger

or weaker than between the CNT and the silicon wafer. If the adhesion is lower, the CNT may be able to be manipulated on the gold wires without damaging them. The tip of the cantilever must be sharp, however, to be sure that it will not touch the gold wires but be able to fit easily in the 150 nm space between the wires.

As was mentioned in Chapter 4, the gold wires melted when excess current was run through them. What causes this spreading of the gold wires should be examined. It could be due to the electrostatic forces between the wires, because they are in such close proximity. This phenomenon has been seen before by Yun Peng in Naughton Lab while doing research in the electrical properties of biomolecules using similar nanochips.

It is also possible that the wires merged due to melting caused by too high a current being run through them. If this is the case, then the threshold current should be found so that it will not be exceeded in the future. This can be found by running very small currents through the wires, taking SEM images of the gold wires, and if there was no melting, then increase the current by a small amount and take another SEM image. This can be repeated until the wires begins to melt, indicating the upper current limit. If the current is kept below this threshold, then the wires will remain separated, and the current will be able to run through the circuit to the nanostructure whose resistance is being measured. The measurement can then be taken using the procedure described earlier.

If nanostructures can be aligned by manipulation or chance on the gold wires, and current can be run through it and a resistivity measurement can be successfully taken, the next step is to test piezoresistivity. This can be done in one of two ways. With a constant current being fed through the circuit and the voltage being measured, the AFM tip can be positioned exactly over the free arm of the nanostructure. The pressure can then be applied from above by varying the z-voltage applied to the tip, which determines the pressure exerted

on the surface by the tip. This may prove to be difficult, however, since the tip must be exactly over the sample, and too great a force exerted on the nanostructure may cause it to snap.

The second and possibly easier method of testing the piezoresistivity is to again align the nanostructure so that current runs through two arms, with one arm free and not in contact with any of the gold wires. Then, while running a constant current through the circuit and measuring the voltage constantly, scan slowly in contact mode so that at one end of the scan, the tip just touches the nanostructure, exerting a

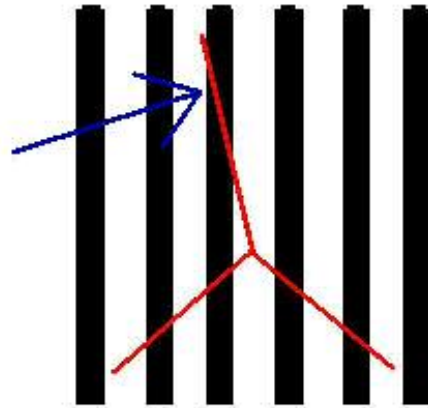


Figure 5.1: Schematic diagram with the blue arrow representing a force exerted on the nanostructure while current is run through the other two arms

force on it (Fig 5.1). If the material is piezoresistive, the voltage vs. current curve will reflect that by showing a sharp change in voltage across the structure corresponding to the periods of time when the structure is being stressed by the AFM tip. If a relation can be drawn between the force exerted on the structure, or similarly the deflection of the structure, and the resistance, this relation can be used to monitor the magnetic force due to the excited spins in an MRFM, allowing for the structure to be used for a cantilever.

To use the structure as a cantilever, further, a nanoscale ferromagnet must be attached to the tip of the structure. Also the resonant frequency of the structure must be found. This further research is left to the remaining project team members.

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