ENHANCED FUNCTIONALITY OF CARBON NANOTUBE MODIFIED ATOMIC FORCE PROBES AND APPLICATIONS

By

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Dedicated to my parents, Virendra Hari Patil and Jayashree Virendra Patil.
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ENHANCED FUNCTIONALITY OF CARBON NANOTUBE MODIFIED ATOMIC
FORCE PROBES AND APPLICATIONS

By

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To stabilize nanotube modified atomic force microscopy probes and extend their functionality, methods for conformal polymer coating of the entire probe and removal of the polymer from just the probing end are described. Expressions quantifying stabilization of the tips against buckling and bending due to stresses encountered while imaging are developed. Electrical conductivity of the probes is demonstrated by their use in scanned conductance microscopy, where a substantial advantage over standard probes is realized and explained. New applications of nanotube modified atomic force probes to as probes for Magnetic Force microscopy, with two types of probe structures, sputter coated nanotube probe and polymer stabilized cobalt nanowire probes are discussed along with preparation and characterization. Enhanced sensitivity, in the case of sputter deposited nanotube MFM probes as compared to standard probes, is clearly demonstrated by imaging of identical area; under identical conditions. Further proposed direction of
research and applications of polymer coated nanotube probes, nanotube modified magnetic probes are also discussed.
CHAPTER 1
INTRODUCTION

Scanning Probe Microscopy (SPM), for the invention of which Binnig and Rohrer won the Nobel Prize for Physics (1986), is a simple concept in which a probe is rastered across a sample surface at very small probe sample surface separation distance. By monitoring various interaction forces between the sample and probe, local information (with atomic resolution) can be obtained in real time. The evolving SPM field encompasses a collection of scanning techniques like Magnetic Force Microscopy, Atomic Force Microscopy, Scanning Thermal Microscopy, which differ from one another by the type of interaction force monitored between the probe and the sample. In all of the SPM techniques a critical factor in resolution of the local information obtained is the probe radius.

The shrinking of electronic devices brings a need to understand the physical processes occurring on the nanometer scale. Preparation of such small devices requires nanometric control of positioning, precision and machining; and reproducible creation of nanoscale features. Scanning Probe Microscopy is suited to give an understanding of the physical process and meets the requirements of preparation.

Carbon nanotubes are interesting nanostructures with remarkable electronic and mechanical properties. Earliest demonstrated applications of carbon nanotubes was as probes in SPM, the focus of our study.

Chapter 2 gives the working of SPM (set up, modes of measurements) strengths and limitations. It also explains the background of carbon nanotubes, structure,
properties, methods of production and application of carbon nanotubes as probes for SPM. Chapter 3 deals with polymer-coated Multiwalled Carbon Nanotube (MWNT) modified AFM probes; the advantages gained over standard carbon nanotube modified AFM probes; and method of preparation.

Chapter 4 demonstrates an application of the polymer-coated MWNT modified AFM probe to Scanning Conductance Microscopy (SCoM), a non-contact mode of measurement, in which enhanced contrast in the phase image is shown (as compared to standard SCoM probes). Chapter 5 explains the application of MWNT modified probes to Magnetic Force Microscopy (MFM). After explaining the basics of MFM, (and previous work done by other investigators), the chapter deals two new types of magnetic probes, (sputter-coated CNT modified MFM probes, and polymer-encapsulated cobalt nanowire MFM probes), along with their preparation and demonstration of enhanced contrast (in the case of sputter-coated CNT modified MFM probes). Chapter 6 outlines future work and directions.
CHAPTER 2
LITERATURE SURVEY

Scanning Probe Microscopy

Scanning Tunneling Microscopy (STM), invented by Binnig et al.,\textsuperscript{1} is simple concept that involves a sharp tungsten tip and an electrically conductive surface. The ability to scan the tip across the surface (at a constant tip sample separation of few angstroms), while monitoring the vacuum tunneling of electrons (using the tunneling current feedback), allows imaging of atomic structures directly in real space. This type of microscopy has enabled a broader understanding of structures and process at an atomic scale. Thus the sharp tip can be regarded as a powerful local probe, which is measuring physical properties of materials on small scale. However, vacuum tunneling of electrons is not the only means by which local properties of the surface can be measured. The development of STM technique has lead to the invention of a wide range of scanning probe microscopies (SPM), which make use of various types of forces of interaction between the tip and the sample, leading to information about nanometer scale properties (often difficult to obtain by other experimental techniques). Among the members of the family of SPM are Atomic Force Microscopy (AFM), Electric Force Microscopy (EFM), Magnetic Force Microscopy (MFM), and Scanning Conductance Microscopy (SCoM), Scanning Thermal Microscopy (SThM).

Atomic Force Microscopy

Atomic Force Microscopy, also known as the Scanning Force Microscopy (SFM), uses the tip-sample interaction force to probe the surface. Because the force of interaction
doesn’t depend upon electrical conductive properties of the sample (and tip), AFM can probe insulating samples (which cannot be investigated by electron microscopy techniques due to charging problems). The measurement of surface forces and surface profilometry, which was previously investigated by Surface-Force Apparatus (SFA) and surface profilometers, is now done with AFM.

**Invention of the AFM**

Surface Force Apparatus has high force sensitivity but it cannot obtain spatially resolved information about the force interaction. On other hand surface profilometry allows mapping of the surface topography, but the large stylus tip radius and the relatively large loading force typically about $10^{-4}$ N limits the lateral resolution.

The AFM, invented by Binnig et al., can be looked as a hybrid between SFA and a surface profilometer. As shown in the Figure 2-1, a probe tip is mounted on a flexible cantilever, and is slowly moved closer to the surface. The forces of interaction that are of importance in AFM are van der Waals forces, ionic repulsion, frictional force, adhesive force and electrostatic force. The force of interaction between the sample and the tip at a small separation distance causes the cantilever to deflect according to Hooke’s law. The deflection of the cantilever can be measured with high accuracy (by using optical method). A topographic map of the sample surface can be obtained, by keeping the force constant (using a feedback loop) while scanning the sample surface relative to the tip. The AFM can be operated in contact regime, similar to a stylus profilometer, or in non-contact regime. One of the critical components of AFM is the cantilever. To achieve high sensitivity, a reasonably large deflection for a given force is desired. Hence the spring constant of the cantilever should be as small as possible and the resonant frequency of the
cantilever should be high to minimize sensitivity to mechanical vibrations while scanning.

Figure 2-1. Layout of Atomic Force Microscope

Resonant frequency of the spring system is given by

\[ \omega = \sqrt{\frac{c}{m}} \]  

(2.1)

where \( c \) is the spring constant and \( m \) the effective mass loading the spring. For a large value of \( \omega \) and a small force constant, the mass \( m \) and the geometrical dimension of the cantilever must be kept as small as possible. Thus the idea of using microfabricated cantilever beams is obvious and helps in mass fabrication. The AFM has been used in probing of a variety of attractive as well as repulsive forces, including VDW forces, ion-ion repulsion forces, electrostatic, magnetic forces, capillary forces, adhesion and
frictional forces. The aim of probing particular forces has led to specialized force microscopes, which can operate in ambient, liquid and vacuum environments.

**AFM Design and Instrumentation**

**Probes**

The probe in AFM is a cantilever with a sharp tip (directly fabricated) at one end.

The main requirements for an AFM probe are

- The spring constant should be small enough to allow detection of forces of interaction (with a small magnitude).
- For atomic resolution the probe radius should be as small as possible. The probe cannot detect features smaller than the tip radius.
- The cone angle should be as small as possible to allow imaging of sharp trenches.

Most AFM cantilevers are microfabricated from silicon oxide, silicon nitride or pure silicon using photolithographic techniques. The advantage of batch fabrication is that large numbers of almost identical cantilevers with similar force constants are made available. Currently a large variety of probes are available depending on the application and the force of interaction being measured. For example there are ultra soft contact-mode tips (spring constant of 0.2N/m) for surface topography, soft tapping-mode tips (spring constant of 4 N/m) with magnetic coating for magnetic force microscopy.

**Cantilever deflection measurement techniques**

There are different methods to measure the deflection of the cantilever. The main requirements of any measurement technique are

- High sensitivity (sub angstrom level).
- The act of measurement of the cantilever deflection should not induce any imaging artifacts.
- The deflection measurement system should be easy to implement, in all types of environments.
A variety of techniques have been used to measure the cantilever deflection. An early method was tunneling detection. A STM tip was used to measure electron tunneling from the rear side of a gold-coated cantilever. The exponential dependence of the tunneling current on the separation between the gold and the tip offered a high sensitivity for detecting cantilever deflection. However this method has drawbacks such as thermal drifts, presence of contamination layers on the gold.

Cantilever deflections can also be measured capacitively by a counter electrode opposite the rear side of the cantilever. Since the rate of change of capacitance increases with reducing distances, the sensitivity of this method increases with decreasing separation of the electrodes. However the electrostatic forces increase with decreasing separation. Thus the geometry must be chosen with care such that maximum sensitivity to change in capacitance is obtained; yet the spring constant is larger than the attractive electrostatic forces.

By far the most common technique of measurement of the cantilever deflections is the optical lever method. A laser beam, from a diode, is reflected off the gold-coated surface of the cantilever, and is directed by a mirror to a split photodiode. The cantilever motions are magnified by the long optical arm. The change in differential signal from the split photo detector is proportional to the cantilever deflection. Sub-angstrom sensitivity can be achieved with this method.

**Imaging Modes in AFM**

AFM can be operated in three modes, contact-mode, non-contact mode and tapping- mode. In contact-mode, the cantilever is brought in contact with the surface. The short-range inter-atomic forces cause the cantilever to deflect quasistatically and this deflection is measured typically by the optical method. The photodiode signal is used as
feedback control for the z motion of the peizoscanner and by varying the pre-set values of the detector signal cause engagement with different forces. The cantilevers used for contact mode, usually, have a low force constant (~0.2 N) and have a silicon nitride tip (which has more resistance to wear by frictional forces).

Figure 2-2. Contact-mode imaging with AFM.

In non-contact mode long range forces of interaction such as magnetic dipole and electrostatic forces can be measured, by holding the tip at 10 to 100 nm from the sample surface. Dynamic mode of detection is used in non-contact mode, in which a piezo driver is used to vibrate the cantilever.

Figure 2-3. Other imaging modes of AFM. A) Non-contact mode. B) Tapping-mode
The vertical gradient of the long-range (attractive or repulsive) forces causes a shift in the resonance frequency (of the probe), change in amplitude and a phase shift; all of which can be detected and used to “map” the sample surfaces.

**Carbon Nanotube**

Multiwalled Carbon nanotubes (MWNT) are tubular structures that are several nanometers in diameter and typically microns in length. They were first discovered by Iijima in the soot of arc discharge synthesis of fullerenes. Single wall carbon nanotubes (SWNT), a more fundamental unit, were discovered by Iijima at NEC laboratory and Bethune at IBM Almaden laboratory.

A single-wall carbon nanotube can be thought of as a single graphene sheet seamless joined to form a tube; while a multiwalled carbon nanotube (MWNT) contains several coaxial cylinders, each cylinder being a SWNT. Carbon nanotubes are unusual electrical conductors, (metallic or semiconductor depending on the structure); are excellent thermal conductors; and are strongest known fibers. Many potentially important applications have been explored including the use of CNT as scanning probes, field emitters and nanoscale electronic devices.

**Growth Methods for Carbon Nanotubes**

All of the promised applications of CNT require a well-controlled and optimized method of growth. Some of the real-world applications (like composites) would require large quantities (in kilograms) of high-quality CNT grown by a simple, cost efficient method. At the present time CNT are produced by Arc-discharge, Laser Ablation and Chemical Vapor Deposition (CVD).

Arc-discharge, also known as carbon arc, is a method in which carbon atoms are evaporated by a plasma of helium gas ignited by high currents (70 to 100 Amps) passed...
through opposing carbon cathode and anode. In the process rod-shaped deposits are formed (which have a hard grayish outer shell containing a soft black material) on the cathode.

![Diagram of arc-discharge method of growth of carbon nanotubes.](image)

Figure 2-4. Arc-discharge method of growth of carbon nanotubes.

This soft black material consists of fine fibers, which under High Resolution Transmission Electron Microscopy (HRTEM) are found to be dense bundles of MWNTs. These bundles of MWNTs have a large dispersion in the size of inner and outer diameters, with typical lengths (of the MWNTs) of several microns. The by-product of the process is a large quantity of multi-layered graphitic particles. The purity and quality of the MWNTs depends on the inert gas pressure in the discharge chamber and the arcing current. The MWNTs produced are very straight (indicative of their high purity), with few defects such as pentagons or heptagons existing in the sidewalls. Purification is achieved by heating the as-grown material in oxygen environment to oxidize away the graphitic particles. The graphitic particles exhibit a higher oxidation rate than MWNTs;
nevertheless an appreciable number of nanotubes are oxidized. One effect of thermal purification is that the end caps of the MWNTs are burnt off, exposing the inner channel. The yield of purification is sensitive to various factors (such as temperature, oxidation time, metal content and environment).

To grow Single Walled carbon Nanotubes (SWNTs), by Arc-discharge, presence of metal catalyst in the carbon anode is required. Bethune et al.\textsuperscript{7} were first to demonstrate the growth of substantial amounts of SWNTs, by using a carbon anode containing small percentage of cobalt.

Another method of growing of CNT is laser ablation, first demonstrated by Smalley et al.\textsuperscript{8} to produce high quality of SWNTs. The method uses laser pulses to ablate a carbon target (containing 0.5 atomic % of nickel and cobalt). The target is placed in a tube furnace heated to 1200$^{\circ}$C. During laser ablation, a flow of inert gases was passed through the growth chamber to carry grown nanotubes downstream to be collected on a cold finger. The produced SWNTs are mostly in the form of ropes consisting of individual nanotubes.

Figure 2-5. Laser ablation method of growth of carbon nanotubes
In Arc-discharge and Laser ablation method the by-products are fullerenes, (graphitic polyhedrons with enclosed metal particles) and amorphous carbon (in the form of particles or over-coating on the sidewalls of nanotubes). Another purification method, developed by Smalley and coworkers,\(^9\) involves refluxing the as-grown material in nitric acid for long periods of time, oxidizing away the amorphous carbon species.

Chemical vapor deposition (CVD) is currently the most popular way of growing nanotubes. The method involves heating the catalyst material to high temperatures in a tube furnace and flowing a hydrocarbon gas through the tube reactor for a period of time. The nanotubes, grown over the catalyst, are collected on cooling the system to room temperature. Key parameters that affect the nanotube growth are growth temperature, catalysts and hydrocarbon feed stock.

![Figure 2-6. Chemical vapor deposition method for growing carbon nanotubes](image)

The active catalysts are typically transition metal nanoparticles. The general growth mechanism involves the dissociation of hydrocarbon molecules catalyzed by transition metal, dissolution and saturation of the carbon atoms in the metal nanoparticle. The precipitation of carbon from the saturated metal particle leads to the formation of nanotubes, an energetically favored structure than a graphitic sheet with open edges and dangling bonds. It is speculated that there are two type of growth mechanism: base
growth and tip growth. In base growth the catalyst particle is firmly fixed on the substrate, while the nanotube lengthens with the closed end. In the tip-growth model the nanotube lengthening involves the catalyst particle being lifted off the substrate and carried along at the tube end.

For MWNT growth, ethylene or acetylene is usually used for carbon feedstock (temperature is typically 550 to 750°C and catalyst nanoparticles are of nickel, iron or cobalt). A major problem with CVD-grown MWNTs is high defect densities in the structures (as compared to the low defect densities in the MWNTs grown by carbon arc discharge).

Figure 2-7. General growth modes of nanotubes by CVD. Left: base growth mode. Right: tip growth mode

Kong et al.\textsuperscript{10} published a method for growing high-quality SWNTs by CVD method using methane as carbon feedstock with a reaction temperature in the range of 850 to 1000°C. It is thought that the high temperature is required for formation of SWNTs, which have a small diameter and thus larger strain energy, with a nearly defect-free crystalline nanotube structure. The quality of the CNTs grown seems to critically
depend on the carbon feedstock used, and the catalyst particle properties (chemical and
textural properties). The size of the SWNT depends on the size of the catalyst particle

Among later breakthroughs is the growth of aligned MWNT structures. By carrying
out CVD growth on a catalytically patterned substrate, aligned MWNT and SWNT
structures have been achieved. It is thought that the driving force for self-alignment is the
van der Waals interactions between the tubes.¹¹

Structure

High Resolution Transmission Electron Microscopy (HRTEM) and Scanning
Tunneling Microscopy (STM) have been used to explore the structure of CNTs,
confirming that the CNTs are seamless cylinders made of a single layer of graphene (one
atomic layer of crystalline graphite)(Figure 2-8).

The structure of a SWNT is expressed in terms of its 1D unit cell (defined by the
vectors $C_h$ and $T$ in Figure 2-8.) The circumference of any carbon nanotube is expressed
in terms of the chiral vector $C_h = n\hat{a}_1 + m\hat{a}_2$ that connects two crystallographically
equivalent sites on the 2 D graphene sheet. The construction in Figure 2-8 depends
uniquely on the pair of integers $(n, m)$ that specify the chiral vector. Figure 2-8 shows the
chiral angle $\theta$ between the chiral vector $C_h$ and the “zigzag” direction $(\theta = 0)$ and the
unit vectors $\hat{a}_1$ and $\hat{a}_2$ of the hexagonal honeycomb lattice of graphene sheet. Three
distinct types of nanotubes structures can be generated by rolling up the graphene sheet
into a cylinder. The zigzag and armchair tubes correspond to $0 < \theta < 30^\circ$. The
intersection of the vector $\overline{OB}$ (which is normal to $C_h$) with the first lattice point
determines the fundamental one-dimensional (1D) translation vector $T$. The unit cell of
the 1D lattice is the rectangle defined by the vectors $C_h$ and $T$.

The nanotube is formed by superimposing the two ends of the vector $C_h$ and the
cylinder joint is made along the two lines $\overline{OB}$ and $\overline{AB}$ in Figure 2-8. The lines $\overline{OB}$ and $\overline{AB}'$ are both perpendicular to the vector $C_h$. In the notation $(n, m)$ for $C_h = n\hat{a} + m\hat{a}_2$, the vectors $(n, 0)$ or $(0, m)$ denote zigzag nanotubes and the vectors $(n, n)$ denote
armchair nanotubes. All other vectors \((n,m)\) correspond to chiral nanotubes. The nanotube diameter \(d_t\) is given by

\[
d_t = \sqrt{3}a_{\text{c-c}}(m^2 + mn + n^2)^{1/3}/\Pi = C_h/\Pi,
\]

where \(C_h\) is the length of the \(C_h, a_{\text{c-c}}\) is the length of C-C bond length (1.42 angstroms).

The chiral angle \(\theta\) is given by

\[
\theta = \tan^{-1}[\sqrt{3n}/(2m + n)]
\]

From above equation it follows for \(\theta = 30^0\) for the \((n,n)\) armchair nanotube and that the \((n,0)\) zigzag nanotube would be \(\theta = 60^0\). Differences in the nanotube diameter \(d_t\) and the chiral angle \(\theta\) give rise to differences in the properties for various carbon nanotubes. The symmetry vector \(R = (\psi/\tau)\) of the symmetry group for the nanotubes is indicated in the Figure2-8, where bother the translation unit or pitch \(\tau\) and the rotation angle \(\psi\) are shown. The number of hexagons, \(N\), per unit cell of a chiral nanotube, specified by integers \((n,m)\), is given by

\[
N = 2(m^2 + n^2 + nm)/d_R,
\]

where \(d_R = d\) if \(n - m\) is not multiple of \(3d\) or \(d_R = 3d\), if \(n - m\) is a multiple of \(3d\) and \(d\) is defined as the largest common divisor of \((n,m)\). Each hexagon in lattice contains two carbon atoms. The unit cell area of carbon nanotube is \(N\) times larger than that for a graphene layer and consequently the unit cell area for the nanotube in reciprocal space is \(1/N\) times smaller.

Among the early basic questions concerning the layer structure of multiwalled tubes was whether they have scroll like structure or a “Russian doll” arrangement of
discrete tubes. The HRTEM images of MWNTs have shown that the interlayer spacing is close to that of turbostratic graphite. And since each of the MWNTs are composed of nearly coaxial cylindrical layers, each with different helicities, the adjacent layers are generally non-commensurate, i.e. the stacking cannot be classified as AA or AB as in graphite. As a consequence of this stacking disorder there is a decrease in the electronic coupling between layers as compared to graphite. MWNTs also have structural features apart from well-ordered graphitic sidewalls, the tip, internal closures, and the internal tips within the central part of the tube, sometimes labeled as the bamboo structure.

![Figure 2-9. TEM image of Multiwalled Carbon Nanotube showing bamboo structure.](image)

It has been found that MWNTs are invariably closed with a cap, whose curvature is brought about by pentagons (and higher order polygons), while maintaining the $sp^2$ electronic structure at each carbon atom site. A variety of cap structures have been seen, depending on the growth method.
Properties

The uniqueness of the nanotube arises from its structures and inherent subtlety in the structure, which is the helicity in the arrangement of the carbon atoms in hexagonal arrays. The helicity along with diameter (which determines the size of the repeating structural unit) introduces significant changes in the electronic density of states, and hence provide unique electronic character for nanotubes.

Applications of Carbon Nanotubes

The combination of size, structure and topology give the nanotubes important mechanical properties such as high stability, strength, and stiffness combined with low density and elastic deformability, along with special surface properties like selectivity and surface chemistry. Since their discovery, several demonstrations have suggested potential applications for nanotubes. These include use of nanotubes as electron field emitters for vacuum microelectronic devices, individual MWNTs and SWNTs attached to the end of an AFM tip for use as nanoprobe, MWNTs as efficient supports in heterogeneous catalysis and as microelectrodes in electrochemical reactions and SWNTs as medium of storage for certain chemicals. Some of the above applications could become marketable, while most still require further modification and optimization. Areas with most promising applications, such as electronic device applications, where the applications are most promising, suffer from the lack of availability of bulk amount of well-defined samples and lack of knowledge about organizing and manipulating objects such nanoscale structures.

In the following section application of carbon nanotubes as novel probes in SPM and sensors is discussed.
Nanotube probe microscopy tips. As stated earlier, the resolution of AFM depends upon the physical structure of probe. Integrated tips, which are typically made of silicon or silicon nitride, have a cone angle of 20 to 30 nm and a radius of curvature of 5 to 10 nm. The resultant image is convolution of the tip structure and surface topography in which the sample features are either broadened by the tip or narrowed in the case of trenches. Thus a well-characterized tip is essential for accurately interpreting an image. To overcome the limitations of a standard conical tip several techniques have been explored, including FIB etching, electron beam deposition, diamond like film deposition and use of small naturally occurring asperities. These approaches represent improvements for specific samples and imaging conditions; however, none provide tip structure with both high aspect ratio and sub-nanometer radius of curvature, while being chemical stable and mechanically robust.

Among the first demonstrated applications of CNTs has been as probes for AFM, as CNTs have the properties required for an ideal probe such as a high aspect ratio, well-defined reproducible chemically inert stable structure. CNTs can bend and recover many times, due to the ability of elastic buckling, without any observable damage and hence make highly robust AFM probes.

Assembly of Nanotube tips: In the first demonstration of carbon nanotube modified AFM tips, Dai et al. manually attached MWNTs to pyramidal tips of standard AFM probes. In this process micromanipulators were used to control the positions of the MWNTs and the AFM probe under an optical microscope. MWNTs were mounted such that they were parallel to AFM tips axis and therefore perpendicular to the sample surface. Atomic force microscope, for stable imaging, requires a feedback force of at
least few nano Newtons. The normal load (along the length of the CNT) at which a CNT buckles is given by

$$F_e \propto \frac{r^4}{l^2}$$  \hspace{1cm} (2.5)

where \( l \) is the length and \( r \) is the radius.

The attached MWNTs (few microns in length) were then electrically etched back, to shorter lengths (till the buckling force becomes few nano-Newton), so as to allow stable high-resolution imaging. Mechanically assembled MWNT tips have demonstrated several important features, such as the high aspect ratio that allowed more accurate image of structures with steep sidewalls like trenches. Among the other features that were revealed were greatly reduced tip sample adhesion that allowed imaging with lower cantilever energy and the robustness of CNTs as probes (due to the elastic buckling properties). Higher resolution can be obtained by using SWNTs, which has typically radius of 0.5 to 2 nm radii. Wong et al. attached bundles of SWNTs to silicon AFM tips and electrically etched the nanotube bundles occasionally producing very high-resolution tips that were likely a result of exposure of a small number of SWNTs at the very apex. Mechanical assembly of CNTs on AFM tips has also been done in a Scanning Electron Microscope (SEM). The assembly of CNTs using SEM allows for nanotube bundles or nanotubes that are 5 to 10 nm in diameter, however the time required to make a tip greatly increases.

The problems of very low production a rate has been address by direct growth of nanotubes onto AFM probes by catalytic Chemical Vapor Deposition (CVD). CVD allows control over the nanotube size and structure including SWNTs with radii as low as 4 angstroms. Hafner et al. grew nanotube tips by CVD from pores created in silicon
tips. The “pore-growth” CVD nanotube tips were shown to exhibit the favorable mechanical and adhesion properties found earlier with manually assembled tips. In addition, the ability to produce thin individual nanotube tips has enabled improved resolution imaging \(^{20}\) of isolated proteins. More studies of pore growth by Cheung et al.\(^ {21}\) have focused on well-defined iron oxide nanocrystals as catalysts. That work resulted in the controlled growth of thin SWNT bundles 1-3 nm in diameter from pores made in silicon tip ends. The pore growth method has demonstrated the potential of CVD to produce controlled diameter nanotube tips. However the preparation of porous layer has been found to be time consuming and may not place individual SWNTs at the optimal location on the flattened apex.

In another approach, Hafner et al.\(^ {22}\) grew CVD SWNTs directly from the pyramids of silicon cantilever-tip assemblies. The “surface-growth” approach has exploited the trade off between the energy gain of the nanotube surface interaction energy and the energy cost to bend nanotubes to grow SWNTs from the silicon pyramid apex in the ideal orientation for high resolution imaging. Specifically, when a growing nanotube reaches the edge of the pyramid, it can either bend to align with the edge or protrude from the surface. The pathway followed by the nanotube is determined by a trade-off in the energetic terms introduced above: If the energy required to bend the tube and follow the edge is less than the attractive nanotube-surface energy, then the nanotube will follow the pyramid edge to the apex, that is, nanotubes are steered towards the tip apex by the pyramidal edges. At the apex, the nanotube must protrude along the tip axis since the energetic cost of bending is too high. This steering of nanotubes to the pyramidal apex has been demonstrated experimentally.\(^ {22}\) SEM investigations of the nanotube tips
produced by the surface growth method show that a very high yield of tips contain protruding nanotubes only at the apex, with very few protruding elsewhere from the pyramid. TEM analysis has demonstrated that the above tips consist of individual SWNTs and small SWNT bundles. In the case of SWNT bundles, the TEM images show that the bundles are formed by nanotubes coming together from different edges of the pyramid to join at the apex, thus confirming the surface growth model described above. By lowering the catalyst density on the surface, it may be possible to arrange growth such that only one nanotube reaches the apex.

Another method, first reported by Hafner et al., termed as hybrid CVD/assembly method, was a facile method for production with essentially 100% yield. In the method SWNTs were grown on oxidized silicon surface by CVD method. Upon scanning of such samples, AFM tip “picked up” SWNTs that were protruding from the substrate surface in a near vertical orientation. Definitive proof that the observed z position jumps corresponded to attachment of individual SWNTs to AFM apexes was obtained by TEM investigations.

**Applications of carbon nanotube modified AFM probes:** The CNT modified tips have shown potential in structural biology in which DNA and several well-characterized proteins have been imaged. DNA was imaged by manually assembled MWNT tips in air and in a fluid. The fluid imaging experiments produced height of 2 nm, the expected value based on the intrinsic DNA diameter, and the resolution in these studies was on the order of 3.5 to 5 nm. These values for resolution are consistent with that expected for multiwalled nanotubes materials, but are also similar to the best values observed with microfabricated tips. Studies of isolated proteins provided a more
stringent test of the capabilities of probe tips, and demonstrated clearly the advantages of nanotube tips. Pore growth MWNT CVD tips have been used to image isolated immunoglobulin-M (IgM) antibody proteins. The resolution of smaller diameter CVD SWNT tips has been further tested in studies of a smaller protein, GroES, which is a hollow dome shaped heptamer that is approximately 8 nm in outer diameter. CVD grown SWNT tip images of individual, well-separated GroES molecules on mica revealed that it was possible to resolve the seven-fold symmetry.

In Chemical Force Microscopy (CFM), the AFM tip is modified with specific chemical functional groups, enabling the tip to generate contrast dependent on the chemical properties of the sample from frictional signal in contact mode or phase lag signal in tapping mode simultaneously with topography. Functionalized tips have also been employed in force spectroscopy. In this mode of operation the tip is brought in contact with a surface and retracted. The forces applied to the tip during retraction are due to interactions of the tip and sample molecules. Force spectroscopy has been used to measure a variety of interactions including the intermolecular adhesion between fundamental chemical groups, the unfolding of protein molecules and DNA stretching and unbinding. The problem of using standard AFM probes is the limitation in lateral resolution (due to large radius of curvature). Also the orientation and spatial location of the attached molecules cannot be controlled, leading to uncertainty in the reaction coordinates for force spectroscopy. Carbon nanotube tips have been used to overcome these limitations. The smaller radii of curvature helps in better resolution and CNTs have been specifically modified only at their very ends, thus creating fewer active molecular sites localized in a relatively controlled orientation.
Nanotubes tips etched in air were expected to have carboxyl groups at their ends based on bulk studies of oxidized nanotubes, though conventional analytical techniques have insufficiently sensitivity to observe this for isolated tubes. Wong et al. demonstrated the presence of carboxyl groups at open ends of manually assembled MWNT and SWNT tips by measuring the force titrations, in which the adhesion force between the nanotube tip and a self assembled monolayers (SAM) surface terminating in hydroxyl groups was recorded as a function of solution pH, thus effectively titrating ionizable groups on the tip.

Covalent reactions localized at the nanotube tip ends represent a powerful strategy for modifying the functionality of the probe. Wong et al. explored the modification of the tips during electrical etching of the nanotube in presence of molecular oxygen, nitrogen and hydrogen. Subsequent force titrations carried out on tips modified in molecular oxygen, nitrogen and hydrogen exhibited behavior consistent with incorporations of acidic, basic and hydrophobic functionality, respectively, at the tip ends. Wong et al. used functionalized nanotube probes to obtain chemically sensitive images of patterned monolayer and bilayer samples. The “chemical resolution” of functionalized SWNT tip was found to be around 3 nm, which is the same as the best structural resolution obtained with this type of tip.

Nanostructures have been fabricated on hydrogen passivated Si (100) by metalized AFM probes. By applying potential to the tip while scanning across the sample surface, selective oxidation of regions was carried out. Such “written” features were typically 30 nm is width. However, as lithography approach, it was limited by a high rate of tip wear problem. Later attempts in nanolithography using carbon nanotubes tips showed the
inherent advantage of the tips such as smaller features, resistance to tip wear. The use of carbon nanotube tips for direct nanolithography of organic polysilane films was investigated by Okazaki et al. The lithography was carried out by means of low energetic electrons from the carbon nanotube tip, as an alternative to conventional high voltage electron beam, operated in the tapping mode. It was concluded that by shortening the contact time between the tip and sample surface effectively reduced the width of the patterned line which were smaller than those produced by standard tips in contact mode. Among other novel attempts was the fabrication of nanotube tweezers. Nanotube tweezers were constructed of two parallel nanotubes, mounted on a tip, with independent electrical contacts. With the application of voltages of opposite polarity the tubes were attracted to one another, thereby decreasing the gap between them. While the tweezers could pick up “nano objects”, release of objects was problematic due to van der Waals forces.

Thus while carbon nanotube tips have been shown to be superior to conventional AFM tips (in terms of resolution, resistance to tip wear) there are important limitations. Nanotubes, either manually assembled or CVD grown, have to be shortened to allow high-resolution imaging, because inspite of remarkable rigidity of the nanotube sidewall, an object so long and slender is subject to bending and buckling resulting in imaging artifacts at step edges from lateral displacement by various proximal forces. Well-defined and reproducible nanotube tip etching procedures designed to expose a desired tip radius don’t exist. Secondly though nanotubes can elastically buckle and can survive a “crash”, the alignment that ensures perpendicular orientation of the tip to the sample surface is usually lost, making the tip useless. The adhesion of the carbon nanotube to the surface of
the pyramidal tip is another source of instability. Nanotubes bonded to the surface by van der Waals are stable enough for imaging, but are liable to “fly off” incase of electrostatic charging. Thus in spite of remarkable resistance of the nanotube to “wear and tear” and the ability to elastically buckle the useful lifetime of a carbon nanotube tip, if not used with great care, is nearly equal to a standard probe.
CHAPTER 3
POLYMER-COATED CARBON NANOTUBE MODIFIED AFM PROBES

As already stated the CNT modified AFM probe is a superior AFM probe because of properties such as a high aspect ratio with near 0° cone angle, small probe radius (a couple of nanometers), structure that is chemically and mechanically stable in liquid or air environments. Thus if the problems of delamination, change in relative orientation of the nanotube (with respect to sample surface) and low buckling force are addressed there would be a substantial improvement in CNT modified AFM probes.

**Advantages of Polymer Coating.**

The method, which we came up with, that addresses all of the above shortcomings is to lay down a conformal coating of a polymer followed by controlled removal of polymer coating from the very end.

Figure 3-1. Polymer coated MWNT modified AFM probe.
Such a step makes delamination of the nanotube nearly impossible. It also reduces the chances of change in the relative orientation of the nanotube (with respect to the sample surface,) upon a crash. The main advantage is the ability to use CNTs of arbitrary lengths as probes.

An AFM requires a feedback force signal of at least few nano newtons for stable imaging. A nanotube, which is being used as an SPM probe; can modeled as a long slender homogenous column subjected to compressive buckling. The expression that characterizes such buckling is the Euler buckling

$$F_{e} = \frac{\pi^2 EI}{0.67 L^2}$$

where $F_{e}$ is the buckling force, $E$ is the young’s modulus, $I$ is the area moment of inertia and $L$ is the length. The numerical factor is derived from the fixed free boundary condition (one end is fixed by attachment to the tip, while the other end is free to pivot on the sample surface). The expression characterizing the bending displacement $W$, of a homogenous slender rod, due to lateral load force $P$, applied at the free end is given by

$$W = \frac{PL^3}{3EI}$$

These equations apply only to homogenous columns, possessing uniform modulus throughout. For a layered composite beam consisting of material A and B having moduli $E_A, E_B$ and moments $I_A, I_B$ respectively, the general approach to derive for one of the materials say B, its equivalent flexural stiffness product, $E_B'I_B'$ in terms of $E_A'I_A'$ and form an equivalent homogenous body, $B'$, permitting the application of the above homogenous body expressions.
Thus the nanotube can be treated as a solid cylindrical tube with modulus $E_N$, inner radius $R_o$ and outer radius $R_N$ and the area moment

$$I_N = \frac{\pi}{4} (R_N^4 - R_o^4)$$  \hspace{1cm} (3.3)

To arrive at an equivalent homogenous body, we construct a nanotube shell over the original nanotube, having an inner radius of $R_N$ and a variable outer radius $R$ (to be determined) and area of moment

$$I = \frac{\pi}{4} (R^4 - R_N^4)$$  \hspace{1cm} (3.4)

To impart the same flexural strength as the original polymer coating we form the equality

$$E_N I_N (R_N R) = E_C I_C (R_N R_C)$$  \hspace{1cm} (3.5)

and solving for $R$ we obtain

$$R^4 = \frac{E_C}{E_N} (R_C^4 - R_N^4) - R_N^4$$  \hspace{1cm} (3.6)

The homogenous nanotube, having equivalent flexural strength to the original polymer coated nanotube has

$$E_N I_N' = E_N \frac{\pi}{4} \left[ \frac{E_C}{E_N} (R_C^4 - R_N^4) + R_C^4 - R_N^4 \right]$$

which can be now directly used in the expression for Euler’s buckling force $F_E$ and the lateral displacement $W$.

The lateral displacement in beam bending $W$, depends on the additional applied lateral force, $P$. It is convenient to instead consider the ratio of tip displacements for a nanotube with and without coating for equal applied lateral force. Because of the inverse
relation between \( W \) and \( I \), and by cancellation of the constants, this becomes \( W_R = \frac{I_N}{I_N} \).

Both \( F_E \) and \( W_R \) are plotted in Figure 3-2 as function of Parylene C coating thickness (modulus \( E_c = 3.2 \) GPa) for a typical nanotube (inner diameter 2 nm, outer diameter 8 nm) for two distinct lengths of 1 and 2 \( \mu \text{m} \).

Despite the low young’s modulus of the polymer (3 Giga Pascal) as compared to the nanotube (1 Terra Pascal) the fourth power dependence of the flexural stiffness on the coating thickness quickly dominates, so by 40 nm of polymer (88 nm total diameter) the buckling force has increased by more than a factor of 20. Similarly, the relative lateral displacement for coated nanotube for equal lateral load has decreased by over a factor of 20. For stable imaging the nanotube needs to have \( F_E \) greater than \( \sim 3 \) nN. It can be noted from the plot that prior to the coating a 2 \( \mu \text{m} \) length nanotube would be incapable of imaging, while after 40 nm of coating imaging becomes possible. These calculations are consistent with unstable imaging observed with long, as-mounted (uncoated) nanotubes, followed by stable imaging upon coating with a thin layer of Parylene.

![Figure 3-2. Calculated Euler buckling force (left axis) and ratio of lateral displacement for a coated to uncoated nanotube (right axis) as function of coating thickness.](image)
Other advantages of using CNT as probes for SPM is that nanotubes have a high resistance to “wear and tear” as compared to silicon tips, due to the strength of carbon-carbon covalent bond, however prolonged use does result in erosion of nanotube probe end. As the CNT has a nearly constant diameter over its length (few microns), on exposing more nanotube (by removing more polymer), the probe is “resharpened and reusable”. Such resharpening is not available for the standard AFM probes.

By choosing an electrically insulating and chemical inert polymer, further advantages can be derived from the structure. The chemically inert polymer would act as a barrier layer, allowing imaging in environments which otherwise would have interacted chemically with the cantilever. With selective removal of the polymer just from the very end of the nanotube, the resulting structure is a “nanoelectrode” with an electrical footprint of few nanometers. Such a nanoelectrode, combined with the scanning probe microscope would give an unprecedented control over spatial location and application of the electrical charge and potential. Scanning nanoelectrode would have interesting applications in electrical, electrochemical, and biological investigations.

**Polymer Coating**

The polymer(to be coated on the CNT) needs to be chemically inert, electrically insulating with a facile method of deposition of a conformal layer with nanoscale control over deposition thickness. There are several polymers such as epoxies, acrylics, silicones and urethanes that have some of the requisite properties such as ability to form conformal layers, chemical inertness.

The polymer chosen by us is poly-para-xylene (trade name Parylene C), which satisfies all of the requirements. Parylene C is a vapor deposited polymer first discovered by Szwarc. A more efficient route of vapor deposition of parylene through vacuum
pyrolysis of di-para-xylene was found by Gorham. A solid at room temperatures, di-
paraxylene (DPX), sublimes with appreciable vapor pressure at temperatures above 80ºC. When this vapor is passed through a high temperature zone (> 680ºC) the DPX dimer decomposes to monomer. Upon landing on a surface at temperature below 95ºC the monomer spontaneously polymerizes forming a uniform conformal coating over all exposed surfaces. As the polymer is deposited one molecule at a time in a sublimation chamber, at low pressures (< 60 mTorr), resulting in truly conformal pin-hole free coating that can be used for exclusion of solvents and oxygen. This has lead to the use of the material for moisture barrier layers, corrosion resistant coatings in archival preservations and bio-passivation coatings in medical implants. Other potential applications for parylenes include wave-guides and coating for optical systems, acoustic matching layers for transducers, components of microelectrical mechanical systems (MEMS), such as membranes and channel walls.

Physical Properties

Parylene C is an electrical insulator with a dielectric strength (for 1 mil film, for short time) is 5600 dc volts/mil. The volume resistive at 23ºC is \(8.8 \times 10^{16}\) ohm-cm. while the dielectric constant of 3.15.

Parylene has a Young’s modulus of 3.2 GPa, density of 1.289 g/cm³ (ASTM D 1505), Rockwell hardness of R80 (ASTM D 570). Since it has water absorption of less than 0.1% (after soaking for 24 hours), parylene is used as a moisture barrier layer. The melting of parylene is 290º C (taken from secant modulus temperature curve), and has specific heat of 0.17 cal/g ºC at 20ºC. The thermal conductivity of the polymer film at 25ºC is 2 cal/cm s ºC.
Parylene is a chemically inert compound with no organic or inorganic solvents at room temperature.

**Method of Coating**

A Chemical Vapor Deposition (CVD) system was designed and assembled by us for carrying out controlled conformal deposition of parylene C is shown in Figure 3-3. It consists of a one inch diameter clear fused quartz tube running through tube furnace, which is at 650ºC, terminating in a condensation chamber. The sample (to be coated) is placed on a water chilled copper plate (~20ºC), while the walls of the condensation chamber is held at temperature greater than 90ºC. The unreacted dimer charge, dichloro-di-poly-xylene, is placed in copper plug which makes vacuum seal with the quartz tube at the open end.

![Figure 3-3. Parylene deposition system.](image)

The quartz tube and the condensation chamber are connected to a mechanical pump through a liquid nitrogen trap. The trap prevents oil from back streaming into the condensation chamber and prevents any of the unreacted monomer from getting into the mechanical pump. An argon gas line is used to flush the system and to bring it to
atmospheric pressure. A thermocouple gauge is used to monitor the pressure in sample chamber. The coating process is started by loading charge of dimer (dimer mass determines the thickness of the polymer film) and evacuating the entire chamber to a pressure less than 30 mTorr. Failure to reduce the atmospheric pressure inside to less than 60 mTorr results in poor, non-conformal film with pinholes. This is attributed to shorter mean free path in higher pressures causing polymer formation in atmosphere rather than on the sample surface resulting a clumpy and non-conformal film. A hot copper pipe (90° C) is slide over the charge end of the quartz tube causing local heating. The white crystalline dimer sublimes and the molecules move down the tube by virtue of reduced pressure at the opposite end. Inside the hot zone the dimer undergo pyrolysis to form monomers, p-xylylene reactive intermediates, which are feed down to the condensation chamber. The monomer is absorbed on surfaces with temperatures less than 90° C, and thus deposition occurs on the sample and not on the hot walls of the condensation chamber. The typical run time is 40 minutes with about 30 minutes of preparation time for set up.

Preparation of Parylene Coated CNT Modified AFM Probes

The nanotubes are mounted on to blunt tapping mode AFM tips (nominal resonant frequency of 300 kHz) with help of the nano workbench. Nano-workbench consists of an inverted optical microscope, Axiovert 100 A from Zeiss, with mechanical and piezo-transducer actuators. A fifty milliwatt green Nd-YAG laser is also coupled into the optical path of the microscope with suitable safeguards. As a first step a knife-edge of a double-sided carbon tape is gently pressed on to the surface of a boule of thermally purified MWNT stock material. The retraction of the carbon tape results in clumps of
MWNTs aligned perpendicular to the length of the knife-edge of the carbon tape (Figure 3-4).

The clumps consist of individual and bundles of MWNTs that are few microns in length. By suitable manipulation of the actuators a tapping mode AFM tip is brought close to an individual nanotube, which is oriented in the appropriate direction. Tapping mode probes manufactured by Olympus are preferred, as the probing tip is a right angle pyramidal structure, with one of the walls perpendicular to the cantilever. Individual MWNTs or bundles with constant radius (small) over a large length are suitable for use as SPM probes. Structures with very small values of radius usually are collapsed MWNTs, termed as ribbons, and don’t have the structural stability to function as probes. The silicon probe is brought in close proximity of the tube and the tube is attached on to the silicon cone surface such that the nanotube is perpendicular to the cantilever. The nanotubes can be bonded on to the surface of the silicon probe by van Der Waals force.

Figure 3-4. Manual assembly of MWNT on AFM probe.
However such bonding is not strong enough to prevent removal of tube in case of electrostatic charging. Thus before attaching CNT, the very end of the silicon probe is dipped in the acrylic glue of the double-sided carbon tape. This step increases the adhesion of the nanotube onto the silicon surface and usually prevents delamination of the nanotube upon electrostatic charging. The attached nanotubes are typically too long, even for polymer coating, with lengths up to 12 microns. The nanotubes are shortened by passing them through the focal spot of the fifty-milliwatt Nd-YAG laser. Such a step slices off the nanotube due to the very high energy densities, in the focal spot, that cause oxidation due induced high temperatures. It is our hypothesis that laser shortening leaves behind a sharp end, as compared to the electrical shortening. While preliminary TEM imaging of laser shortened nanotubes has confirmed the hypothesis, definitive proof has not been obtained as of yet.

Figure 3-5. MWNT mounted on a tapping mode cantilever.

By knowing the length of the nanotube, it is easy to calculate the amount of parylene that has to be put down to obtain higher buckling force value, (typically few nano-Newton). The MWNT modified AFM tips are placed on the water chilled copper
plate, secured in place by a piece of double-sided carbon tape and deposition of parylene is carried out by the method described earlier.

**Controlled Removal of Polymer**

Since the parylene layer is conformal, the probing end of the composite column has a large radius of curvature, typical few hundred nanometers with a concomitant poor resolution as an SPM probe.

Controlled removal of polymer from the probing end of the CNT would recover the high spatial resolution offered by the nanotube while retaining the higher buckling force of the composite column.

![Figure 3-6. SEM image of polymer-coated MWNT, left corner inset: Higher magnification.](image)

Currently we have developed two methods for controlled removal of parylene from the nanotube. The first method involves use of the laser, which is coupled to the nano workbench. The fifty-milliwatt laser had been used to slice nanotubes, by passing the nanotube through the focal spot of the beam; further investigation by us indicated the
existence of polarization dependence of energy coupling between the optical energy and nanotube. Large coupling of the optical energy to the nanotube occurs when the laser is plane polarized along the length of the nanotube generating enough temperature to oxidize the nanotube in air, while much smaller coupling occurs if the laser is plane polarized in a direction perpendicular to the length of the nanotube. Under the latter arrangement the amount of energy dumped in the nanotube is not sufficient to “burn” the tube but sufficient to vaporize and melt a small section of the polymer.

A parylene-coated nanotube is slowly inserted in the focal spot of plane polarized (perpendicular to length of nanotube) laser beam, during which the scattered light profile from the nanotube is observed via a CCD camera (coupled to the inverted optical microscope). The brightness of this scattered light is used to indicate when the nanotube is best lined up with the beam center, after which the nanotube is translated in incremental steps (60 nm) steps towards the center of the beam.

Figure 3-7. SEM image of selective removal of polymer using optical method.

It is impossible to resolve optically the amount of polymer we typically remove (< 200 nm). Rather we rely on the scattered light to discern when the polymer has been modified. That is with each incremental translation towards the beam the brightness of
the scattered light increases. In last of such translation there is an abrupt decrease (within \sim 1 \text{second}) in the scattered light profile, indicating removal of the polymer from the very end. By this method, polymer can be removed over length scales as small as 100 nm. This method of removal, which doesn’t affect the polymer film anywhere else, is repeatable and can be used to expose more length of nanotube as required.

Figure 3-8. Examples of laser-exposed polymer-coated MWNT probes.

Our other developed method (termied as “abrasion”) exploits the difference between the rate of abrasion of the nanotube and the soft polymer. As stated earlier nanotubes have ability to buckle elastically and are an extremely mechanically stable structure. If polymer-coated nanotube modified AFM probes are taken and are used to image the
surface of a hard nanocrystalline surface like diamond like carbon (DLC) at high scanning frequency, abrasion of the hemispherical tip would occur, however the resultant structure would be planar resulting in poorer resolution. A better route is the use of “Nanolithography” software package, which comes with DI Multimode Nanoscope 3A, which allows user defined spatial movement of the AFM probes via the piezoelectric scanner. In first step the program does a standard topographical scan of 400 $\mu^2$ by which average plane height (of the sample surface) is determined.

![AFM tip](image)

Figure 3-9. Abrasion removal of the polymer from the MWNT.
The composite column (nanotube and polymer) is then intentionally buckled by driving the probe some 100 nanometers past the average plane height. Then as the probe, in buckled state, driven around in spiral path, the sharp facets cut into the polymer, giving a conical probe end. The advantage of spiral path is that it ensures new facets, with different orientations, abrade away the polymer ensuring a conical abrasion profile. The first abrasion is carried out on DLC films, which has feature size of 500 nm, while successive polishing steps are carried out with films with finer feature size, typically Alumina Nitride films, feature size 200 nm, finished with Alumina oxide film, feature size 50 nm. The resolution obtained with such probes is at best equivalent to bare CNT AFM probes or slightly poor.

![SEM images of abrasion-exposed polymer-coated MWNT modified AFM probe.](image)

**Figure 3-10.** SEM images of abrasion-exposed polymer-coated MWNT modified AFM probe.

**Conclusions**

Putting down a thin conformal polymer coating results in a qualitative improvement over carbon nanotube modified AFM probes and standard AFM probes. The main drawbacks, that have plagued CNT modified AFM probes, such as delamination of the nanotube, change in orientation of nanotube, time exhaustive
methods of etching back the nanotube have been eliminated. The other benefits that have been derived as a result of the polymer coating are the ability to use nanotubes of arbitrary lengths, the ability to resharpen a tip and survive most of crashes making a polymer-coated nanotube modified AFM probes a superior AFM probe. While all of the carbon nanotube modified tips have been used in tapping mode, polymer-coated carbon nanotube modified tips can be used in contact mode, opening up investigation in lateral force microscopy such as study of adhesion.

The inert nature of the polymer coating, which stops any chemical interaction between the silicon of the cantilever and any reactive environment, also has opened up various new applications in the field of study of biological and other chemical investigations. The electrically insulating property has various applications in the field of electric force microscopy (EFM), magnetic force microscopy (MFM) and Scanning conductance microscopy (SCoM).
CHAPTER 4
APPLICATION OF POLYMER COATED CARBON NANOTUBE MODIFIED AFM PROBES TO SCANNING CONDUCTANCE MICROSCOPY

**Scanning Conductance Microscopy**

In the polymer coated carbon nanotube modified AFM probes the polymer (Parylene C) provides an insulating coating over all but the tip of the nanotube. Since nanotubes are electrically conducting, if the AFM cantilever to which it is mounted is also conducting, we obtain a nanoscale “carbon fiber” electrode (with an electrical footprint of ~80 nm$^2$ and electrically active length of ~100 nm). Such a probe would have potential applications in the area of nanoscale bio and/or electrochemical probing. As a first demonstration of application of polymer coated carbon nanotube probe, we have take advantage of their electrical conductivity to perform Scanning Conduction Microscopy, a variation of Electric Force Microscopy (a non contact mode of atomic force microscopy in which electrical dipole interaction forces are mapped).

**Non Contact Mode Atomic Force Microscopy**

As stated earlier AFM can operate in three modes, contact-mode, tapping-mode and non-contact mode. In contact-mode the AFM probe is in contact with the sample surface, and hence mapping out short-range interatomic forces by quasistatic deflections of the cantilever beam (with known effective spring constant). Though long-range interaction forces such as electrostatic, magnetic dipole forces might be present in contact mode of AFM operation, they don’t contribute to the image contrast on an atomic scale.
By increasing the tip-surface separation to 10-100 nm, only the long-range interaction forces remain and can be mapped by non-contact force microscopy. Since the magnitude of the long range forces at relatively large tip surface separation may be considerably smaller than that of the short range interatomic forces, the method of interaction force detection in non-contact mode is usually different from contact force microscopy. Instead of measuring the quasistatic cantilever deflections, the cantilever is driven to vibrate near its resonant frequency by means of a piezoelectric element, and the changes in oscillation amplitude or the resonant frequency or phase shift in oscillation of the cantilever (with respect to driving piezoelectric element) as a result of tip-surface interactions are measured. These methods of detection is sensitive to force gradients, instead of the interaction forces themselves.

An important requirement in non-contact mode microscopy is maintaining constant tip sample surface separation. Digital Instruments has introduced “lift mode”, a two pass technique in which, the topographical information is gathered in tapping mode, upon which the tip is lifted an user defined distance from the sample surface and retraces the topographical scan line, utilizing the information gained earlier, to maintain a constant user defined distance from the sample surface, thus eliminating any contribution to the non-contact image from topography. During the “lift mode” the cantilever is driven by means of a piezoelectric element with a typical amplitude at the tip on the order of 1 to 10 nm and at a fixed frequency $\omega_d$, which close to the resonant frequency. The amplitude change or phase shift of the vibrations as a result of the tip-surface force interaction is measured with the deflection sensor and appropriate electronics module. In this mode of detection there is no feedback during non-contact mode measurement. The three
dimensional images are generated by plotting the cantilever’s phase shift versus in-plane co-ordinates.

For cantilevers with a small spring constant $c$, the minimum detectable force gradient is determined by the thermal vibration of the cantilever. The rms amplitude can be derived from the equipartition theorem

$$\frac{1}{2} c \langle (\Delta z)^2 \rangle = \frac{1}{2} k_B T \quad (4.1)$$

$$\left[ \langle (\Delta z)^2 \rangle \right]^{\frac{1}{2}} = \left( \frac{k_B T}{c} \right)^{\frac{1}{2}} \quad (4.2)$$

where $T$ is the temperature and $k_B$ is Boltzmann’s constant. For a spring constant of 1 N/m, the thermal vibration amplitude at room temperature is about 0.6 angstroms.

**Electric Force Microscopy**

Thus in non-contact mode, if the measured interaction between a conductive tip and sample surface is due to long range Coulomb force, then the measurement is termed as Electric force Microscopy (EFM).

EFM is used to map the vertical $(z)$ and near vertical gradient of the electrical field between the tip and the sample versus the in plane coordinates $x$ and $y$. The field due to trapped charges, on or below the sample surface, is often sufficiently large to generate contrast in an EFM image (phase detection). Otherwise, a field can be induced by applying a voltage between the tip and sample surface. The voltage can be applied directly under AFM software controls, or from an external power supply with appropriate current limiting elements in place.

The preferred method of EFM is phase detection because the cantilever’s phase response is faster than its amplitude response to changes in the tip sample interactions.
The other advantage of using phase detection is that this method is less susceptible to height variations on the sample surface.

When voltage is applied to the tip, a force appears which is due to the separation dependant capacitance between the tip and the sample and is of the form

\[ F = \frac{1}{2} V^2 \frac{\partial C}{\partial z} \]  

where \( F \) is the force, \( V \) the voltage between the tip and the sample and \( C \) the capacitance of the tip sample “capacitor”. The phase shift (the difference between the phase of the driving oscillator and the cantilever) is of the form

\[ \Delta \phi \cong \frac{Q}{2c} \frac{\partial^2 C}{\partial z^2} V^2 \]  

Martin et al.\textsuperscript{51} measured the electrostatic force as function of tip to sample distance, and found that modeling the capacitance as that of a parallel plane capacitor was in good agreement between the theory and experiment for distances ranging from several nanometers to 170 nm and forces ranging up to 12 nN. It was determined that electrostatic forces as small as \( 10^{-10} \) N could be measured. Terris et al.\textsuperscript{52} measured the force gradient up to a distance of 1 \( \mu \) m and obtained an agreement with the theory that models the tip as a conducting sphere. Other researchers have measured forces in range of \( 14 \times 10^{-9} \) N as function of tip to sample distance in the range of 200 nm, for potentials on the order of several volts. Other researches have demonstrated the ability of EFM to measure the amount of charge. Stern et al.\textsuperscript{53} measured deposited localized charges on an insulator placed between the tip and sample. The images were proven to result from charges by varying the tip-sample dc voltage and observing the effect on image. Ferroelectric domains have been imaged by Saurenbach et al.\textsuperscript{54} EFM has been used
extensively to investigate electrical behavior of nanostructures such as isolated single
multiwalled carbon nanotubes$^{55}$ and networks of single walled carbon nanotubes.$^{56}$

The images obtained from electrostatic interaction are dependant on the shape of
the probe and the objects on the sample surface. Quantitative analysis of the force exerted
on the probe in environment of polarized objects is difficult. Later investigators have
focused on development of more precise mathematical approximations for the tip
geometry with varying success.$^{52}$ $^{57}$ $^{58}$ Some of the mathematical approximations have
include the cantilever as a factor that contributes to the contrast in EFM.$^{58}$ However the
problem of a real conical probe, terminating with a circular hemisphere and carrying a
charge, has been found to be mathematically quite difficult and no mathematical close-
formed solutions have been yet found. Hence some investigators have resorted to use of
Finite Element Modeling (FEM) to understand tip-substrate interactions during EFM.$^{59}$
Various other spin-off techniques have emerged from EFM such as Scanning
Conductance Microscopy, Surface Potential Microscopy, Kelvin probe microscopy to
name a few.

Scanning Conductance Microscopy was, first reported by Bockrath et al.,$^{60}$ used to
measure change in conductivity over very small length scales (~ 0.4 microns). The
principle behind the technique is simple. The sample consists of SWNTs deposited on the
surface of a silicon wafer capped with one-micron thick silicon dioxide. A cantilever,
with a voltage of about 2 to 8 volts applied ($V_{r}$), was scanned across the sample in
tapping mode and lift mode. In the phase image, gathered during the lift mode, the phase
lag signal was found to be dependant on the length of the SWNTs with shorter tubes
being fainter than longer tubes. It was proposed that the above results could be explained
by considering the cantilever tip, nanotube and the degenerately doped silicon as capacitor elements. The voltage applied between the tip and the doped Si produces electrostatic forces on the tip that alter the drive frequency of the cantilever and the phase. When the tip was far from a SWNT, the electrostatic forces were independent of horizontal displacements of the tip. The phase $\phi$ thus took a position-independent background value $\phi_0$. When the tip was above a tube, the tip induced charge modulation within the tube produces additional electrostatic tip-sample forces. The magnitude of the forces and hence of $\phi$ was determined by the electric field between the tip and the tubes, which in turn depended upon the division of $V_t$ between the tip-tube capacitor and the tube-ground-plane capacitor. As the shorter tubes had less capacitance to the ground plane, their potential floated near to $V_t$, yielding smaller tip-tube voltages and smaller phase shifts.

The other factor contributing to phase signal was the conductivity of the samples. A maximal phase shift signal requires the entire tube to be polarized, making the characteristic time $\tau_{RC}$ equal to $RC$ time constant of the tube, while the tip scanned over the tube in a characteristic time $\tau_{scan}$. Thus the criterion for a detectable tube depends upon the comparison of the two time scales, the tip must remain near a tube long enough for complete polarization to occur. For a wire with one-dimensional conductivity $G_0$, $\tau_{RC} = C_0L^2/\tau_{scan}$, and comparing $\tau_{RC}, \tau_{scan}$, the authors concluded,

$$G_0 \geq G_{\text{min}} = C_0L^2/\tau_{scan}$$

for a fully detectible tube. For $G_0 < G_{\text{min}}$, the measured signal would be reduced to zero. Thus scanning conductance microscopy can map out change in conductivity.
Polymer coated carbon nanotube modified SCoM probes

Among the first applications of polymer-coated carbon nanotube modified AFM probes investigated by us was in SCoM. By mounting the carbon nanotube on electrically conductive AFM probe, (achieved by sputter deposition of a thin layer of metal) followed by subsequent polymer coating with exposed nanotube probe end leads to polymer coated carbon nanotube modified SCoM probe. The advantage of such a probe would be a simpler geometry compared to cone, increase in the separation distance of the cantilever and sample surface thus reducing the contribution of the cantilever to the EFM signal. CNT grown on silicon dioxide layer were used as a sample to quantify any changes in resolution or contrast (as compared to a standard SCoM probe).

Preparation of probe

Soft tapping mode tips from Olympus (AC240TS), having a nominal resonant frequency of 80 kHz and force constant of 4 N/m, were first UV ashed for 15 minutes to ensure removal of any organic contamination layer. The tips were then immediately transferred to high vacuum deposition system in which chromium, as adhesion layer (5 nm thick) and Pt-Ir (30 nm) were sputter deposited with 5-mTorr argon pressures at 12 watts.

Long thin single MWNT was mounted on such a metalized AFM probe and laser shortened to required lengths (~3 to 5 micron). Among the important requirements was that the carbon nanotube should have an ohmic contact resistance (as small as possible). The contact resistance was measured by dipping the free end of the mounted nanotube into a small droplet of mercury, which was mounted at the end of a fine gold wire. The advantages of using mercury are (since it is a liquid metal) nanotubes can be dipped repeatedly without changing the orientation of the nanotubes, and the liquid state of
mercury ensures that a oxide free surface is in contact with the tube. While applying a triangular voltage pulse across the circuit, the potential drop across the nanotube and current flowing were measured to determine the value and nature of the contact resistance.

![AFM tip](image1.png)

![Nanotube](image2.png)

![Hg droplet](image3.png)

Figure 4-1. Measurement of contact resistance.

Typical contact resistance obtained with freshly deposited Pt-Ir was 20 to 40 $k\Omega$, and could vary from 100 $k\Omega$ to 1 $M\Omega$ for Pt-Ir coated tips which were exposed to air. For fat bundles of the MWNTs the contact resistance was typically ohmic. For thin bundles and single MWNTs, out of ten tubes mounted six tubes showed the contact resistance to be ohmic in nature, while the rest were non ohmic in nature.

The next step in processing was polymer coating of the carbon nanotube modified SCoM. As discussed in earlier, the thickness of the polymer coating (which is determined by the required buckling force of the composite column) is controlled by the mass of the
charge dimer introduced in the deposition system. For a nanotube of 3 \( \mu \)m in length, 130 nm of parylene (wall thickness) was typically used.

Post deposition of the polymer selective removal of the polymer was carried out using the laser method, which removes nanotubes to the lengths of 100 nm upwards. A crucial requirement in preparation of polymer coated carbon nanotube modified EFM probes, was that the exposed length of nanotube to be as short as possible, so as to avoid bending instability (that would be encouraged by the forces exerted on the probe due to the lateral components of the electric force of interaction).

**Sample preparation**

The sample consisted of CVD grown CNTs grown on the surface of a degenerately doped Si wafer, which is capped with a 600 nm thick silicon dioxide layer. The oxide layer of the bottom side of the silicon wafer was removed via treatment with buffered HF, to ensure intimate contact between the grounding plate and the degenerately doped silicon. The wafer was then mounted on a polished AFM metallic puck, held in place with silver paint, to ensure electrically conductive path.

![Diagram of sample](image)

**Figure 4-2. Sample used for Scanning Conductance Microscopy.**
**Experiment**

The sample was imaged in lift mode, with a voltage of 1.2 volts applied to the probe with respect to the grounded metal.

Figure 4-3. Experimental layout for SCoM.

Figure 4-4 is the topographical image, obtained in the first pass of the scan, and the phase image obtained in the lift mode pass (lift height was 10 nm). To ensure a qualitative comparison of the images obtained with the polymer coated carbon nanotube modified AFM probes with standard EFM probes, the same area of the sample was scanned with a brand new soft tapping mode tip (AC240TS) sputter coated with identical amount of chromium and platinum-iridium alloy with all other factors such as lift height, tip to sample voltage, gains, scan rate being same. The standard tip was moreover chosen
to have a resonant frequency, quality factor and hence slope of its phase shift vs. frequency curve (in the cantilever tune mode) very similar to that of the nanotube tip used.

Figure 4-4. Topographical image of the nanotubes on silicon dioxide surface.

Results

As seen from the SCoM images (Figure 4-5, Figure 4-6) the nanotube tip exhibits a dramatic sensitivity advantage showing a phase shift 2.5 times greater, on an average, that the standard tip. This signal enhancement for the nanotube tip may be understood as
arising from its sharper end profile, and correspondingly larger field gradient in the vicinity of the tip. SCoM probes the conductivity of the nanotubes lying on the insulating layer through their polarizability.

A polarizable object in a gradient field interacts with the induced dipole to generate a force that is directed towards the high field region. Since the polarizable object is bound to the surface in this case, it is the tip that reacts to the interaction force.

The phase shift arises because this force also depends upon the tip height above the surface

\[ \Delta \phi \propto \frac{dF}{dz} \]  

(4.5)

and that height is modulated through the cantilever oscillation cycle concentration.
Figure 4-6. Phase image with polymer coated CNT modified SCoM probe.

The sharper field around the nanotube tip increases the field gradient, increasing the force rate of change with height above the surface, thereby increasing the phase shift.

Compared to the short uncoated nanotubes, the long polymer-stabilized nanotube tips have the advantage of placing the probing end far from the screening effects of the pyramidal standard tips, to which the nanotubes are attached, hence maximizing the benefit.

**Modeling**

To confirm the above hypothesis, computer modeling of above situation was carried out using the software Maxwell SV\textsuperscript{®} from Ansoft. Maxwell SV is a program that is used for modeling 2 dimensional electrostatic problems by Finite Element Modeling
(FEM). The program was used to model and give numerical solutions because of the radial symmetry of the problem (which allowed for use of a 2D model).

Figure 4-7. Flux lines from a CNT probe and Standard probe (with potential applied).

The physical dimensions and properties that were used in the software, such as the thickness of the silicon oxide layer (600 nm), the metal coating on the AFM probe, physical dimensions of the probe (40 nm radius of the standard and 7 nm for nanotube probe) were kept close to the actual physical dimension and properties to ensure a good numerical approximation. However due to the limitations of the software, which was available as a free copy from the Ansoft website, the pyramidal cone of the AFM cantilever couldn’t be modeled as a cone terminating in a hemispherical cap.

Hence the pyramidal probe was modeled as a cone that apex terminated in a flat plane with dimensions equal to the radius of the hemispherical cap of the real probe, while the nanotube probe was modeled as a solid rod of equivalent dimensions to a multiwalled nanotube probe.
To obtain the force of interaction as a function of $z$ (distance from the sample surface), numerical solutions for various values of $z$ (at constant potential applied to the probe cone or nanotube probe with grounded metal) were calculated. Upon plotting the
rate of change of force for a standard pyramidal tip and that for a carbon nanotube modified tip, it is evident that the first derivative of the force with respect to \( z \) for a nanotube is larger for small values of \( z \) as compared to a standard probe.

The following force plot was obtained for a metalized cone with 30 nm radius and a CNT tip with a radius of 7.5 nm. The particle on the surface has a radius of 10 nm.

![Force plot](image)

Figure 4-10. Comparative plots of \( \frac{dF}{dz} \) for a CNT tip and standard conical EFM probe.

It is evident that the CNT probe has a larger phase shift than a standard conical probe for equivalent potentials at smaller tip-sample separation distance (20 nm and less).

**Conclusions**

It is clear from the experimental results, from the use of polymer coated CNT probes as SCoM probes, there is an enhancement in contrast of the phase signal by a
factor approximately of 2.5. This enhancement is due to the larger field gradient of the nanotube tip and hence such a tip would be able to detect smaller polarizable objects than those by a standard EFM probe. By increasing the separation between the sample surface and the metalized cantilever, there has been reduction in the contribution of the metalized cantilever to the phase signal. The above nanotube probes also retain the advantages like the ability “resharpen and reuse”, extended lifetime due to higher resistance to wear and tear (as compared to standard silicon probe).
CHAPTER 5
MAGNETIC FORCE MICROSCOPY

Introduction

Magnetic force microscopy (MFM), first reported by Martin et al.,\textsuperscript{61} involves measurement of the spatial variation of magnetic force of interaction, between a magnetic tip and sample, by using non-contact force microscopy.

Magnetic force microscopy is done in a two-pass method where in the surface topography is measured in the first pass in tapping mode. In the second pass the tip is lifted to a user defined height from the sample surface and the same line scan is carried out, while maintaining a constant height separation.

![MFM Illustration](image)

Figure 5-1. Magnetic force microscopy.

Within a distance of 10 to 500 nm of tip-sample separation, magnetic interaction of the tip with the stray field emanating from the sample becomes noticeable and the interaction strength can be determined by various methods such as phase shift, frequency modulation or amplitude change. These detection methods,\textsuperscript{62} that usually probe the long-range magnetic dipole interaction, are sensitive to force gradients rather than magnetic dipole forces.
MFM has now become a well-established technique that is used for non-destructive, fast mapping of magnetic features on a sample. MFM has also found many industrial applications since magnetic and magneto-optic media are of interest. The most common application is mapping of magnetic topography (of the sample), which requires that the sample stray field be not affected by the probe magnetization and vice versa.

**Principles of MFM**

MFM in the non contact-imaging mode is sensitive to magnetostatic dipole-dipole interaction between the tip and sample. The total magnetic force acting on the tip in $z$ direction can be obtained by summing the forces between each dipole in the tip and each dipole in the sample:

$$F_z = \int_{\text{tip}} d^3r_{\text{tip}} \int_{\text{sample}} d^3r_{\text{sample}} f_z(r_{\text{tip}} - r_{\text{sample}})$$

where $f_z(r)$ is the interaction between two magnetic dipoles $m_1$ and $m_2$ at a distance

$$r = r_{\text{tip}} - r_{\text{sample}}$$

$$f_z(r) = \frac{\mu_0}{4\pi} \frac{\partial}{\partial z} \left( \frac{3(r \cdot m_1)(r \cdot m_2)}{r^3} - \frac{(m_1 \cdot m_2)}{r^3} \right)$$

Model calculations of the MFM response can be performed either analytically or numerically for given magnetization distributions of tip and sample. However, usually neither the magnetization distributions of the tip and the sample are known. Also the magnetization distributions of tip and sample might change due to the proximity of two magnetic bodies, which complicates the theoretical analysis of MFM data. A significant perturbation of the magnetic structure of tip and sample can be expected if the magnetic stray field $H_s$ exceeds the anisotropy field $H_k$. 
The contrast observed in MFM depends upon the length of the magnetic domain at the foremost end of the sensor tip. If the length of the effective domain at the tip apex is sufficiently small compared with the extension of the stray magnetic field then the sensor tip can be approximated as point dipole with total magnetic moment $m$. Then the force acting on the tip in the sample stray field $B_s$ by

$$F_{dipole} = \nabla (m \cdot B_s) = (m \cdot \nabla)B_s$$

where absence of current ($\nabla \times B = 0$) has been used. And thus in point dipole limit the MFM images are related to the spatial distribution of magnetic stray field gradient rather than the stray field itself. And the above equation implies that the component of the stray magnetic field gradient sensed depends upon the orientation of the tip moment.

The other limiting case is of a long magnetic domain at the tip apex, in which only the front part of the tip domain interacts with the sample stray field, leading to a magnetic monopole response.

The measured magnetic force is then directly related to the sample stray field through the magnetic charge $q_m$, which found on the probing tip.

$$F_{monopole} = q_m B_s$$

and the MFM images reflect the spatial distribution of $B_s$.

**Resolution in MFM**

The spatial resolution achieved in MFM depends upon the properties of the tip as well as that of sample stray field distribution. Even for a point dipole tip and a point dipole object on the sample surface the width of the measured sample stray field distribution will be finite and would be dependant upon the tip sample surface separation. Thus the reducing the tip sample would increase the resolution, however there are
practical limitations to the minimum tip sample separation possible. Among the limitations is the influence of the tip stray field on the sample. At very close separations the tip stray field may “pole” the sample features, thus preventing non-destructive imaging. The other limitation is placed by the spring constant of the cantilever. If the derivative of the attractive forces becomes too large at small tip-surface separation, exceeding the spring constant, the tip would snap into the sample (crashing). Using cantilevers with a higher spring constant prevents instabilities, but concomitantly causes drop in the sensitivity. And hence the optimum value of $k$ (spring constant) is a tradeoff between the sensitivity and minimum tip-sample spacing.

![Figure 5-2. Active probe volume in Magnetic force microscopy.](image)

The other limitation of a conical probe structure is the increase in the lateral interaction volume as the tip-sample separation is decreased. With decreasing tip sample separation the magnetic force of interaction increase (thus the contrast increases), however the stray field from the magnetic material on the sidewalls of the cone starts contributing in the signal (increasing the lateral interaction volume) and reducing the
resolution. Thus for a given tip-sample surface separation, the spatial resolution obtained depends upon the shape and magnetic structure of the tip.\textsuperscript{65} The maximum spatial resolution that can be achieved is on the order of the radius of the effective magnetic tip volume, and hence the effective magnetic tip volume should be as small as possible.\textsuperscript{66} A multi-domain tip could lead to additional features that complicates the interpretation of the MFM image.\textsuperscript{67}

The MFM probes have following requirements for a high spatial resolution non-destructive MFM imaging:

- The spatial extent of the effective magnetic tip volume should be as small as possible which minimizes the long range dipole magnetic interactions, maximizing the spatial resolution of MFM.
- The magnetic stray field of tip should be small and spatially confined, minimizing undesirable influences on the magnetization of the sample.
- A large total magnetic moment is desirable, leading to larger measurable forces and concomitant higher sensitivity.
- A magnetically well-defined structure that would allow quantitative interpretation of the MFM data.

An ideal MFM probe could be a rigidly attached ferromagnetic particle at the probing end of non-magnetic tip. There are several different methods of preparation of magnetic force sensors. Initial MFM probes consisted of bent electrochemically etched nickel, iron or cobalt wire.\textsuperscript{66} Such probes had the disadvantage that the iron or cobalt oxidized rapidly, leading to the degradation of MFM data as function of time. And due to the long-range interaction of the magnetic dipole, the magnetic interaction between the probe and the sample was not limited to a small volume of the probing tip, but also included the shaft of the tip. Alternate route consists of a sharp non-magnetic tip, which can be electrochemically-etched tungsten\textsuperscript{68} or a microfabricated silicon cantilever,\textsuperscript{69}
which is subsequently coated with a thin layer of ferromagnetic material. After deposition, the layer is magnetized along the tip axis. This method allows for minimization of the volume of the magnetic tip materials that interacts with the sample. The average resolution reported with a brand new microfabricated silicon cantilever, sputter coated with cobalt, is 30 nm.

In the quest for increasing the spatial resolution, various investigators have tried to reduce the interaction volumes by somehow trying to confine the active probe volume. Leinenbach et al.,\textsuperscript{70} in an attempt to reduce the active probe volume, tried a novel approach. Carbon, induced by the cracking of residual gases in a SEM, in the form of a tiny tip was deposited on the apex of a standard microfabricated tip that was coated with a thick magnetic film (Figure 5-3). In the last step of processing the carbon tip acted liked a etch mask during Ar ion milling of the cantilevers front side. The etching time and ion flux was adjusted such that on one hand the exposed magnetic material was completely removed from the cantilever, while the carbon tip was not completely etched away.

![Figure 5-3. Electron beam deposition magnetic force microscopy probes.\textsuperscript{70}](image-url)
Figure 5-4. Preparation process of Electron Beam Deposition magnetic force microscopy tips.

The result of the whole procedure was a cantilever without a complete magnetic coating but with a magnetic particle of typically $100 \times 100 \times 100 \text{ nm}^3$. It was reported that such probes have a better contrast and resolution.

The limitations of Electron Beam Deposition MFM probes are

- The tip-sample separation height (between the magnetic probe and sample surface) are increased by additional thickness of the carbon needle (about 100 nm)
- The size of the magnetic particle is quite large.

Among the other interesting approaches, Arie et al.\textsuperscript{71} used a multiwalled carbon nanotube terminating in a magnetic particle. Such a structure is possible to obtain via CVD growth of the nanotubes in which nickel is used as a catalyst. The tube, which was grown with the nickel particle at the base, was then mounted with the catalyst particle on
a standard tapping mode cantilever. The length of the nanotube was about 1000 nm while the diameter of the nickel nanoparticle was 50 nm. Though the entire probe did satisfy the definition of an ideal magnetic probe (a small magnetic particle at the end of a non-magnetic probe), the authors reported back very poor resolution compared even to a standard magnetic probe.

Figure 5-5. CNT modified MFM probe. A) TEM image of the CNT terminating in Ni nanoparticle. B) SEM image of the mounted CNT probe.

Based on our experience with CNT modified probes, the reasons for the reported poor resolution is that the nanotube was too long (in non contact mode the tube was laterally deflected by the magnetic dipole interaction forces), compounded by the fact that the cantilever chosen was of an high spring constant (40 N/m) which reduced the sensitivity of the probe.

**Sputter Coated Carbon Nanotube Modified MFM Probes**

If soft tapping mode cantilever, with a suitable MWNT (stable for imaging) attached to the probing end, is sputter coated with a thin layer of magnetic material then such a carbon nanotube modified MFM probe would be superior to a standard microfabricated MFM probe for the following reasons.

- As compared to the standard microfabricated silicon tip, with a pyramidal probe, the lateral magnetic interaction volume of a sputter coated MWNT would be smaller with a concomitant increase in spatial resolution
• The sputter coated MWNT modified MFM probe, due to a high aspect ratio, would be able to follow the topography better than a conical probe.

Figure 5-6. Reduction of lateral interaction volume for a sputter coated CNT MFM probe as compared to a standard conical probe.

**Preparation**

Soft tapping mode tips, Olympus AC240TS, with nominal resonant frequency of 80 kHz and spring constant of 4 N/m, were UV ashed for 15 minutes to clean up any organic contamination layer present on the cantilever. Thin long MWNT were mounted on the tips of the probes on the Nano Workbench by the method outlined in chapter 3. The nanotube was shortened to about 3 microns with help of the laser. The entire structure was sputter deposited with titanium as an adhesion layer (about 5 nm) and cobalt as the magnetic coating (about 15 nm). The radius of the probing tip is approximately 30 nm, which is equivalent to the radius of a standard microfabricated MFM tip, which also has about 5 nm for adhesion layer, typically chromium, and about 30 nm of ferromagnetic metal. Since cobalt doesn’t form a passivating oxide layer, the sputter coated MWNT modified MFM probes have to be stored in an inert environment, otherwise a slow but steady degradation in the MFM data is visible.
Figure 5-7. SEM image of a sputter coated carbon nanotube modified soft tapping mode probe.

**Experiment**

To compare between a standard MFM tip and the sputter coated MWNT modified MFM probe, a brand new soft tapping mode tip (Olympus AC240TS) was taken, UV ashed and sputter coated (for identical time and setting) with titanium and cobalt. To obtain a qualitative comparison between the resolution and contrast of the two types of probes, it was essential to scan identical area of a magnetic sample, with all of the rest of parameters such as lift height, scan rate, gains kept identical. Any sort of fiduciary marks needed to be large enough that they would be visible under the optical microscope of the AFM, while small enough to be mapped by the AFM probe. Such fiduciary marks were laid down on the sample surface with help of the SEM, making use of the fact that under high magnification; a contamination layer is put down. Switching the SEM to a line scan at high magnification, fiduciary marks (contamination layers) that were about 1 micron in length and half micron in width were laid down.
Figure 5-8. Fiduciary marks laid down on the samples via SEM.

Once having fiduciary marks, locating and imaging identical area of the magnetic sample, though time consuming, was easy. The magnetic samples used were a piece of computer hard drive (Seagate U80) and a piece of audiotape (supplied by DI instruments).

**Result**

The sputter coated MWNT modified MFM probes were found to be structurally stable, able to withstand a very large number of large area-scans without loss of the cobalt coating. Figures 5-9 and 5-10 are the phase shift images of identical areas of magnetic hard disk and audiotape with a brand new standard MFM tip and a sputter coated MWNT modified AFM tip with all of the scanning parameter such as lift height at 15 nm scan rate and gains being identical.

The sputter coated MWNT modified MFM probes show a higher contrast as compared to standard MFM tips with the phase contrast signal larger on an average by a factor of 2.5. Attempts to measure the resolution of the sputter coated MWNT modified MFM probes were inconclusive due to a lack of locally available suitable samples.
Figure 5-9. MFM signal obtained from *same* region by standard and sputter coated NT tips.

Figure 5-10. Comparison between MFM signal obtained from same regions on a HDD disk by standard and sputter coated MFM probes.
The superior contrast is due to the lack of increase of lateral interaction volume (upon reduction of tip sample separation) and ability to follow the topography of the sample surface more faithfully.

Though the sputter coated MWNT modified MFM probes have shown to have superior contrast, and are easy to prepare they suffer from important limitations.

- Though reduction in lateral interaction volume of the MFM probe was achieved, as compared to a standard conical MFM probe, there was no reduction in the probe radius.
- There is a continuous oxidation of the cobalt, thus reducing the shelf life and viable use time of the probe. This can be prevented by applying a thin coating of chromium on top of the cobalt, however with the concomitant increase in the probe radius.
- These probes are susceptible to damage due to crashing. Typically the cobalt layer fractures, exposing the bare nanotube. The exposed nanotube cannot be removed by currently known methods without damaging the remaining cobalt layers.

**Polymer Stabilized Cobalt Nanowire MFM Probes**

While the sputter coated CNT modified MFM probe structure has addressed the problem of increase of lateral magnetic interaction volume, the magnetic probe radius is comparable to the standard MFM probe. Increase in resolution can be obtained only by reduction of physical magnetic probe radius.

If cobalt nanowire (or any ferromagnetic metal) is deposited inside a polymer pore (formed by removal of a CNT coated by the polymer), there would be a reduction in the magnetic probe radius by five orders of magnitude. The encapsulated cobalt nanowire would be protected from oxidation by the polymer, which would resolve the limitations encountered with sputter coated MWNT modified MFM probes.

This structure, termed as Polymer stabilized cobalt nanowire MFM probes (PCoNMFm), satisfies most of the requirements of an ideal MFM probe as in there is
small magnetic “particle” at the end of a non-magnetic probe. There are few unpublished reports in which attempts were made to increase the resolution of MFM by mounting nanoparticles of ferromagnetic material at end of the SWNT modified MFM probes.

However the radius of the ferromagnetic particle is constrained by the superparamagnetic limit (below a certain volume, a ferromagnetic particle can no longer maintain the orientation of its magnetic dipole in presence of another magnetic dipole, thus becoming “paramagnetic”. This effect is called as superparamagnetic limit). This limit is overcome in the PCoNMFM probes, by the large magnetic anisotropy (which is due to the high aspect ratio of the nanowire). The cobalt nanowire has a large magnetic moment (along the length) due to shape anisotropy, thus satisfying another requirement of an ideal MFM probe.

Figure 5-11. Polymer stabilized Cobalt nanowire MFM probe.
**Preparation**

The initial method of preparation, which looked simple on paper, was to mount a MWNT on a metalized soft tapping mode cantilever, coat with parylene. The polymer cap would be removed, exposing the MWNT. This was to be followed by removal of some length of MWNT, resulting in the formation of a nanopore. By introducing ionic solution of cobalt in the nanopore, a cobalt nanowire would be grown by electrochemical deposition.

![Diagram](image)

**Figure 5-12.** Nanopore created by partial removal of the CNT.

The important step for growth of the cobalt nanowire is partial removal of the nanotube without affecting the physical shape of the polymer. Chemical dissolution of nanotube was thought to be most promising, however the chemical and procedures used for carbon dissolution consist of strongly reactive chemicals\(^ {72,73,74} \) and preliminary results such as effect of hot piranha etch on carbon fibers was not encouraging. Further literature survey pointed out to the existence of electrochemical etching techniques for carbon
fibers, since carbon fibers have been used to as nanoelectrodes.\textsuperscript{75,76,77} Chen et al.\textsuperscript{78} report a comparatively easy method for electrochemical etching of carbon fiber with 0.01 molar NaOH solution at room temperature with a graphite counter electrode and ac voltage (50 Hz and 5.5 Volts peak to peak). This technique, with some modifications was applied by me for etching of the carbon nanotube and was found to some times.

Initial etching runs proved to be complete failures, in which, upon inspection it was found that the polymer-coated tubes had flopped over (Figure 5-13). After much experimentation it was inferred during the electrochemical etching of the nanotube in the 0.01M NaOH solution with a peak to peak voltage of 5.5 volts that the polymer was, somehow, losing structural stability and stiffness. Thus upon transfer from the etching solution to DI water or the cobalt solution, while passing through the surface layer (with the resultant surface tension) the polymer tube collapsed, pinching off the pore and hence preventing the growth of nanowire.

Figure 5-13. TEM image of a flopped polymer cylinder.
By reducing the electrochemical etching rate (by reducing the peak to peak voltage from 5.5 volts to 3 volts) it was found to solve the problems of loss of structural stability of the polymer nanocylinders.

Figure 5-14. Electrochemically etched polymer coated MWNT.

The next step was to achieve electrodeposition inside the pore, caused by etching of the nanotube. There are numerous obstacles of such as, since the etching is carried out in a dilute sodium hydroxide solution, and electrodeposition in cobalt sulphate or cobalt chloride solution, there are chances of formation of cobalt salt crystal at the apex of the polymer pore, resulting in plugging of the pore with no electrodeposition of cobalt inside the pore.

Dipping the etched probe in hot de-ionized water for sufficient period can circumvent this problem. This allows for the exchange of sodium hydroxide solution and the resultant products from etching to diffuse into de-ionized water. A concomitant step is
the soaking of the probe in cobalt solution for a suitable time to allow for exchange of cobalt solution and water.

Figure 5-15. Salt crystal terminating polymer-coated nanotube.

A far more critical limitation is the selectivity of deposition of parylene C on transition metals. Vaeth et al. reported inhibited parylene deposition on substrates exposed to transition metals, metal salts and organometallic complexes, such as iron, platinum, palladium and silver. In that paper, the authors speculate that the transition metal layer suppresses both initiation and propagation reactions of polymerization on the surface by “deactivation” of p-xylylene rendering it unavailable for polymerization. It was also reported that the selectivity (amount of the parylene that was deposited on an untreated substrate to a metal coated substrate) was greatest for platinum, followed by iron, silver, and palladium in decreasing order.

And since either platinum-iridium alloy or palladium is used to metalize the silicon cantilever and probe tip, so as to achieve very low contact resistance between the CNT
and metal surface, the amount of parylene deposited on the CNT and on the cantilever are different. More so over the parylene film on the metalized cantilever is not conformal with pinholes and cracks. Thus on carrying out electrodeposition of cobalt on such probes resulted in large growth of cobalt on the cantilever (due to pin holes and cracks). If the deposition was carried out for more than 3 minutes, the deposited buried the entire cantilever and probe.

In order to negate the selectivity of parylene with respect to transition metal surface, we investigated, the effect of A-174 silane, an adhesion promoter used by industry. An initial thin layer of polymer was put down on a CNT modified palladium coated tapping mode tip. The entire probe was then dipped in A-174 silane. The silane layer negates the selectivity of any exposed Pd. The entire probe was then coated with another thick layer of parylene, thus forming a conformal layer on the entire probe structure.

Electrodeposition of cobalt and of cobalt nanowires has been topic of much investigation. Bantu et al. have reported growth of cobalt nanowires inside track etched polycarbonate membranes with a pore diameter of about 200 nm and pore length of 6 microns via electrodeposition using a potentiostat in quiescent conditions at room temperature.

For the present work, electrolyte for cobalt electrodeposition is standard sulphate solution containing 400 g/L of CoSO$_4$ 7H$_2$O and 400 g/L of H$_3$BO$_3$ in deionized water was used. The deposition was done at room temperature, with three-electrode setup where in the MFM probe is working electrode, platinum wire as counter and Ag/AgCl$_2$ as reference.
Experiment

Used blunt tapping mode tips were UV ashed for 15 minutes to remove any organic contamination layer present. Following which, they were transferred immediately into a high vacuum sputter deposition system. 5 nm of chromium as adhesion layer and 40 nm of palladium were sputter deposited on the silicon cantilevers and probe tips at 12 watts and 5 mTorr of argon gas pressure.

MWNT were attached to the probe end. It was ensured that the nanotubes have an ohmic contact with the palladium with a low contact resistance (typically 20 kΩ). A thin layer of polymer, about 50 nm wall thickness was put down on the entire MFM probe. Following this the entire MFM probe was dipped in A-174 silane and left to dry. The silane soaked MFM probes were then transferred to the parylene deposition system where another layer of parylene was put down, approximately 250 nm. The controlled removal of the polymer from the very tip of the nanotube was carried out using the optical method described earlier.

The probes were then dipped in side NaOH solution (0.01M) and pulsed etching was carried out (15 seconds on with 2 minutes off with peak to peak voltage of 3 volts and frequency of 50 Hz). The probes were then transferred into hot DI water for 30 minutes, following which the probes were transferred into cobalt solution where electrodeposition of cobalt was carried.

Results

In most of the cases, there was successful growth of cobalt nanowires inside the pore (created by etching by the nanotube). Each of the nanowires terminated with a large cobalt ball (Figure 5-16).
As the resolution depends upon the physical magnetic probe radius, the ideal resolution would be achieved by terminating the growth of nanowire before growth of the cobalt ball occurs.

During the deposition of the cobalt inside the pore (a diffusion limited process) the value of current is nearly constant. The current increases exponentially during the three dimensional growth of the ball. Thus by monitoring the rate of change of current, it is possible to stop the growth at appropriate time instant.
Such a step is possible, though difficult. A simpler solution is to knock of the cobalt ball from the end. This can be done under the optical microscope by using the peizoactuators, which have a minimum incremental displacement of 60 nm.

![Figure 5-17. Removal of the cobalt ball from tip. A) As grown. B) After knocking off the ball.](image)

A critical factor for cobalt nanowire growth is the pore (etched inside the polymer cylinder) remaining open. Another common failure mode is the closing of the pore by a polymer flap. The polymer is removed from the very end of the nanotube via laser heating, as explained earlier in chapter 3. An ideal polymer removal is a clean exposure of the nanotube without any thin sheath of polymer left behind on the nanotube. However this is not easy to guarantee because of the varied interaction of the nanotube with the laser beam. The amount of heat generated, and consequently the shape of the terminating polymer tip is complex function depending upon various factors such as the nanotube diameter, the focal spot size of the laser, and the thickness of the polymer film. Thus in such a case, the thin polymer shell (created upon etching away of the CNT) collapses sealing off the pore (completely or partially).
Figure 5-18. Formation of the polymer sheath of “flap” upon laser heating A) polymer structure post laser heating. B) Polymer flap post electrochemical etching.

Figure 5-19. TEM images of polymer flap that prevented electrodeposition of cobalt.

In the cases where polymer flap did not seal of the pore, cobalt growth did occur. In such probes the polymer flap, which is at the probing end, is not stable for topographical imaging and the flap increases the tip sample separation (between the magnetic probe and sample) thereby decreasing the contrast and resolution.
Thus all of the major problems in the preparation of polymer stabilized cobalt nanowire MFM probes have been identified and addressed and a method for preparation of polymer stabilized cobalt nanowires MFM probes has been demonstrated. While the diameter of the grown nanowires is about 40 nm, further refinement of the preparation method would allow growth of nanowires with diameters as small as 10 nm. Such probes
(cobalt nanowires with 10 nm diameter) would show significant improvement in resolution.

Figure 5-21. TEM image of the a perfect polymer stabilized cobalt nanowire MFM probe end.

**Conclusions**

The sputter coated carbon nanotube modified MFM probes have been demonstrated to have superior contrast, in comparison with standard MFM probes by virtue of reduction in the lateral magnetic interaction volume, a higher aspect ratio and possibly a more spatially confined magnetic field. Lacking the experimental setup for determining the resolution of the probes, it cannot definitely stated if there is any increase in the
spatial resolution of MFM data. These probes have the advantage of ease of preparation and are structurally stable, but suffer from degradation of the magnetic signal due to the continuous oxidation of the sputtered cobalt over a period of time.

The polymer stabilized cobalt nanowire modified MFM probes would be able to address all of the above shortcoming and meet the requirements of an ideal MFM probe. All of the major factors and problems in preparation of such probes have been identified and addressed, and a method of preparation has been successfully demonstrated. The techniques developed for characterization of the sputter coated nanotube modified MFM probe can be readily applied for the polymer stabilized cobalt nanowire modified MFM probes.
CHAPTER 6
CONCLUSION

Future Work and Directions

In the scope of our work, it has been demonstrated, polymer stabilization is an improvement in SPM by addressing the shortcomings of carbon nanotube modified probes and standard probes. Apart from unusual advantages like “resharpen and reuse” and near indestructibility, these probes can be applied for various applications.

Polymer Stabilized Cobalt Nanowire MFM Probes

A large amount of work still needs to be done especially in the area of the polymer stabilized cobalt nanowire modified MFM probes. While a method for preparation of polymer stabilized cobalt nanowires MFM probes (with a cobalt nanowire diameter of ~50 nm) has been successfully demonstrated, increase in spatial resolution of MFM signal can be achieved only by growing cobalt nanowires of less than 30 nm on soft tapping-mode cantilevers. Such probes would have very small magnetic probe radius, spatially confined magnetic field and a low interaction volume. Growth of such thin cobalt nanowire can be achieved by mounting single MWNT (diameter 12 nm) and carrying out the process as described in chapter 5. There could some challenges in growth of such small diameter nanowires due to the narrow diameter of the pore. The problem of creation of the polymer flap can be solved by using method of abrasion (to expose the nanotube prior to electrochemical etch of the nanotube). The resolution and contrast for such probes can be measured with the help of techniques already developed for characterization of the sputter coated CNT modified MFM probes.
**Other Possible Probe**

Since the polymer (Parylene C) is electrically insulating, there are some other novel probes for scanning probe microscopy that can be designed such as nano electrodes which could have a significant applications in the study of cell physiology.

**Nanoelectrode**

A polymer coated MWNT modified metalized AFM probe is also a functional “nanoelectrode”. Such nanoelectrode would have applications in study of cell physiology. Currently microelectrodes, using carbon fibers, are used to probe exocytotic processes.

![Figure 6-1. Nanoelectrode for cell physiology.](image)

Since the “nanoelectrode” is a functional scanning probe, spatial resolution in locating areas of interest in a biological AFM should be good and carrying out experiments should be easy. In the current carbon fiber microelectrodes, detection of chemical species (with current signal magnitude being in picoamps), is often masked in the larger capacitative current. The nanoelectrode would have very small capacitative
current, a superior spatial resolution (due to a very small active area), in detection of chemical species would be better. And thus such probes would be able to gather topographical knowledge and physiological information simultaneously.

Conclusions

In conclusion of our work, it can be stated that polymer-coated carbon nanotube modified probes are an improvement in the current probe technology for SPM, by the virtue of having a nearly infinite use life (due to ability to resharpen and near indestructibility). Enhanced sensitivity was demonstrated for scanning conductance measurements, an improvement by a factor of 2.5. Similar increase in contrast was demonstrated for sputter coated CNT modified magnetic force microscopy tip.

All of the major problems and factors in the preparation of polymer stabilized cobalt nanowire MFM probes have been identified and a successful method of production has been demonstrated conclusively. Exciting applications and results can be expected of these probes in various areas including cell physiology, electrochemistry measurements, and magnetism to name a few.
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BIOGRAPHICAL SKETCH

Amol Virendra Patil was born on 24\textsuperscript{th} of December 1975 in Mumbai (formerly known as Bombay) India. He was admitted to Sir Parshurambhau College for Bachelors in Science in Physics and was ranked as third in his May 1996 graduating class.

After earning his bachelor’s degree, he was admitted to the Department of Physics, University of Pune. He worked for Dr. Kiran Adhi on pulsed laser deposition system and fractal growth in viscoelastic media, receiving Master’s degree in Physics in May 1999.

He was admitted to the graduate program of Material Science and Engineering, (University of Florida, Gainesville FL) in fall of 1999. He joined the group of Dr. Andrew Rinzler (Department of Physics), working on applications of carbon nanotubes as probes for scanning probe microscopy. He received his master’s degree in summer 2002. In the spring of 2004 he received his PhD in material science and engineering under advisement of Dr. Pearton.