

Imaging Carbon Nanotubes

Magdalena Preciado López, David Zahora, Monica Plisch

I. Introduction

In this lab you will image your carbon nanotube sample from last week with an atomic force microscope. You will also analyze Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM) images of carbon nanotubes using image analysis software. The goals are to learn more about carbon nanotube growth, develop quantitative image analysis skills, and in general to understand the advantages and limitations of AFM and SEM imaging.

Atomic Force Microscopy

You were introduced to the AFM last week during the demonstration. An AFM generates a topographic image of a surface with nanoscale resolution. It is a versatile tool that can image almost any surface in a variety of ambient environments, including air and liquids. See Appendix G for a reminder of the basic operating principles of an AFM.

The AFM has better vertical resolution than horizontal resolution. A vertical resolution of 0.01 nm ($\sim 1/20$ height of atom) can be achieved with the laser sensor. Small deflections of the cantilever are translated to relatively large displacements of the reflected laser beam on the photodiode detector.

The horizontal resolution of the AFM is limited by the radius of curvature of the tip. Commercial tips made of Si or SiN typically have a radius of 5-10 nm. They can be made using a wet chemical etch that preferentially etches along certain directions of the crystal lattice. In research labs, carbon nanotube tips can achieve a radius < 1 nm.

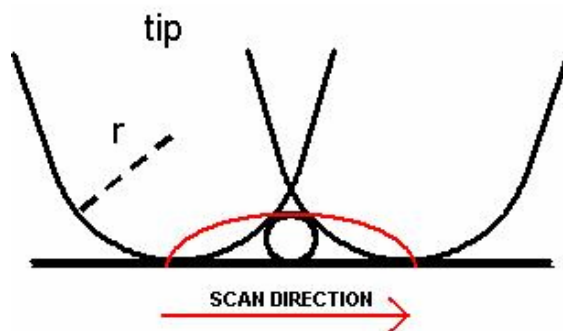


Figure 1. Tip-Sample Convolution

Figure 1 shows a tip with a radius of 5 nm scanning a nanotube of radius 1 nm. Notice that the side of the tip contacts the tube well before the bottom of the tip. This causes the profile of the tube to appear much broader than it really is. However, the height of the profile remains accurate. The sharper the tip, the better the horizontal resolution.

The AFM has a variety of modes of operation. In “contact mode,” the tip is in constant contact with the surface. The z-piezo moves the cantilever up and down to maintain constant contact force. Dragging the tip across the surface can be damaging to soft samples and to the AFM tip. For this and other reasons, “tapping mode” is more commonly used. In tapping mode, the cantilever is driven at near its resonant frequency (~100 kHz) so that the cantilever vibrates the tip with a certain amplitude. As the tip approaches the surface, damping occurs and the amplitude of the vibration decreases. When the tip scans the surface, the z-piezo adjusts the height of the cantilever to maintain a constant amplitude of vibration. We will use tapping mode in the lab.

Scanning Electron Microscopy

A complementary nanoscale imaging technique is Scanning Electron Microscopy (SEM). The SEM operates analogous to an optical microscope, but it uses electrons instead of light for imaging surfaces. Energetic electrons (1-30 keV) are focused using magnetic lenses into a beam 2-10 nm in diameter. Figure 2 shows the electron optics of a SEM.

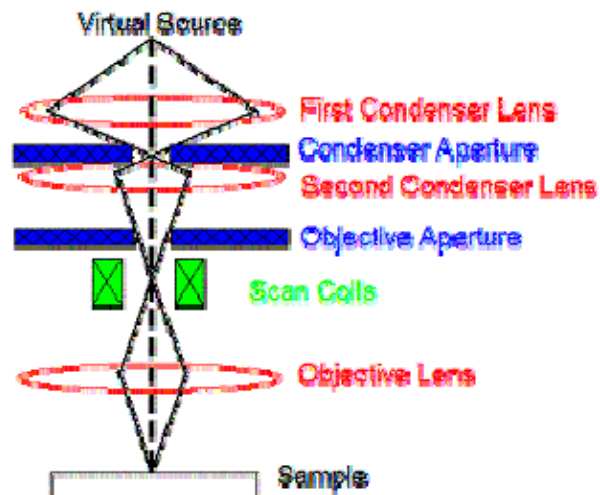


Figure 2. Scanning Electron Microscope

When high energy electrons hit the sample, they ionize nearby atoms and create “secondary electrons.” Some of the secondary electrons escape the surface and are collected and counted by a positively charged detector. To generate an image, the scan coils deflect the beam and raster it over the sample. The brightness of each pixel in the image is determined by the number of secondary electrons generated by the beam at each position on the surface.

SEM imaging requires that the electron source, lenses, and sample are all in a vacuum. Otherwise, the electrons would collide with air molecules and quickly lose their energy. Since electrons are electrically charged, the sample needs to be conductive enough to dissipate this charge. This requires non-conducting samples to be coated with a thin layer of metal before imaging.

The resolution of a SEM is determined primarily by the diameter of the beam (1-10 nm). Spreading of secondary electrons away from the beam slightly broadens the effective spot size. Information contained in a SEM image is similar to an optical microscope image; however, there are a few differences. One advantage of SEM is a large depth of focus due to the relatively small aperture angles. This allows a wide range of heights to be simultaneously in focus.

SEM images of secondary electrons show excellent topographic contrast. The “inclination effect” causes the edges of a spherical particle to appear brighter than the center. This is due to the greater number of secondary electrons generated by an electron beam striking a surface at a shallow angle. In addition, increased electric field strength at sharp edges and spikes cause these features to appear bright.







There are many other modes of imaging in SEM. Backscattered electrons approach close to a nucleus and are ejected at large energies. These electrons are sensitive to atomic number and are collected by a special detector. Characteristic X-rays are also emitted as ionized atoms return to their ground state, yielding information on elements present at the surface of the sample.








II. Procedure

A. AFM imaging

You will image your carbon nanotube sample with an AFM and search for evidence of carbon nanotubes. The lab instructor will guide you through the process. Your goal is to take at least one low resolution image ($\sim 10 \mu\text{m} \times 10 \mu\text{m}$) that shows several nanotubes and one high resolution image ($\sim 2.5 \mu\text{m} \times 2.5 \mu\text{m}$) that shows at least one nanotube clearly. Record the file names and the maximum values along the x, y and z axes. If you are unable to obtain good images, you can use the files located in the desktop folder “AFM images.”

B. AFM and SEM Image Analysis

1. Launch WSxM (v3.0 or later) located on the desktop of any of the PCs in the lab (freeware available at www.nanotec.es). An abbreviated manual is in Appendix I.
2. View all images of carbon nanotubes in the folder “SEM images” on your desktop. These images are of samples prepared using the same method you used in lab.
 - a. To open files, you may have to change the *File Type*: to *All Files (*.*)*.
 - b. Answer questions 1-3 in the Analysis section.
3. Open your high resolution AFM image or a similar resolution ($\sim 2.5 \mu\text{m} \times 2.5 \mu\text{m}$) image in desktop folder “AFM images.”
 - a. To open files, you may have to change the *File Type*: to *All Files (*.*)*.
 - b. If it is your own image, click on the *Recalibrate* tool  and if necessary change the *Z Amplitude* to match that of the original image.
4. Measure the height and width of one nanotube in several locations.
 - a. Use the *Profile* tool  to generate a profile of the tube.
 - b. Click on the profile window and use the *Measure Point*  and/or *Measure Distance*  features to generate quantitative data.
 - c. For the width, measure the Full Width of the nanotube profile at Half the Maximum height of the profile (f.w.h.m.).
 - d. For the height, subtract the average background level from the maximum value of the profile.
 - e. Repeat steps a-d for several profiles of the same nanotube.
 - f. Answer questions 4-5 in the Analysis section.
5. Open your low resolution AFM image or a similar resolution images ($\sim 10 \mu\text{m} \times 10 \mu\text{m}$) in desktop folder “AFM images.”
 - a. If it is your own image, click on the *Recalibrate* tool  and if necessary change the *Z Amplitude* to match that of the original image.
 - b. To see small nanotubes more clearly, use the *Plane Local* tool  to level the silicon surface.

- c. To see small nanotubes more clearly, also use the *Z Scale Control* feature  to adjust the vertical scaling.
 6. Measure the diameter of at least 20 different carbon nanotubes. Be sure to include small diameter tubes in addition to large diameter tubes so that you get a representative sample.
 - a. Use the *Zoom* feature  as needed to magnify regions containing nanotubes.
 - b. Use the *Profile* tool  to generate a profile of a nanotube. Avoid dirt on the Si surface to keep the profile clean.
 - c. Click on the profile window and use the *Measure Point*  and/or *Measure Distance*  features to measure the height of the tube. Remember to subtract the average background level from the maximum value of the profile.
 - d. Repeat steps a-c for at least 20 nanotubes. Be sure to get a representative sample of tubes, including small diameter tubes.
 - e. Answer questions 6-7 in the Analysis section.
 7. Open a high resolution SEM image (at least 100 kX magnification).
 - a. Use the *Profile* tool  to generate a profile of the smallest nanotube you can find.
 - b. Click on the profile window and use the *Measure Distance* feature  to measure the width (f.w.h.m.) of the profile.
 - c. Repeat steps a-c to measure the five smallest diameter carbon nanotubes you can find in the image.
 - d. Answer questions 8-9 in the Analysis section.

III. Analysis

1. What is the maximum length of carbon nanotubes grown with the method used in lab (order of magnitude)?
2. Does there appear to be a preferential growth direction for nanotubes with the method you used in lab? Explain your answer.
3. Is there any evidence that carbon nanotubes interact with each other as they grow? Hint: look for “bundles” where separate carbon nanotubes come together.
4. Using a high resolution AFM image, make several measurements of the height and width (f.w.h.m.) of a single nanotube and organize your data neatly in a table. Report the average height and width and include an uncertainty figure for each (i.e. standard deviation).
5. Of the two numbers recorded in question 4, which number (height or width) most closely corresponds to the actual diameter of the carbon nanotube? Explain your choice. Why are the height and width are different?
6. Measure the diameter of at least 20 carbon nanotubes in AFM images. Create a histogram of the tube diameters.
7. Based on your data from question 6, does the CVD method used in this lab produce primarily single-wall (0.4 to 3 nm diameter) or multiwall (1.4 to 100 nm diameter) nanotubes? Explain your answer.
8. Report the width (f.w.h.m.) of five of the smallest diameter carbon nanotubes you can find in a high resolution SEM image. How do the minimum diameters measured with SEM compare to the minimum diameters measured with AFM? Can you explain any difference? What is the resolution of the SEM used to image the nanotubes?
9. Name any advantages you can identify for SEM imaging over AFM imaging. Do the same for AFM imaging over SEM imaging.

APPENDIX G

Introduction to the Atomic Force Microscope

Since the beginning of the 17th century, physicists and others have extended the capability of humans to see small objects with microscopes. By the 18th century, instrumentation technology had reached a fundamental limit, diffraction. Lenses that used light could not image objects smaller than the wavelength of light, or a fraction of a micron (10^{-6} m).

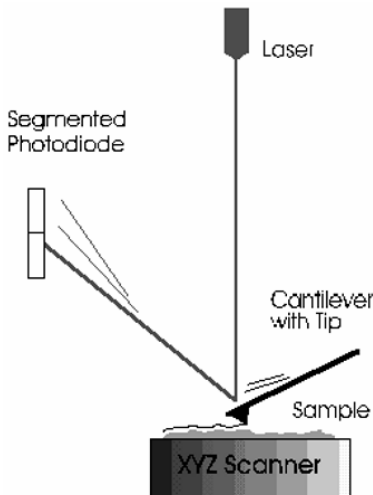
In the 20th century, the limitations of the light were overcome with the invention of the transmission electron microscope. Electrons instead of photons were used to probe specimens and magnetic and electric lenses were used to focus the beam of electrons. Eventually in the best microscopes objects smaller than 0.2 nm could be imaged, approximately the distance between individual atoms. However, there were limitations to this technique as well. The electrons that were transmitted through the sample often damaged it, especially biological materials. The sample needed to be cut in a thin enough cross-section to allow electrons through, making preparation challenging. The electron beam could only operate in an ultra-high vacuum. Despite these limitations, it was and still is an outstanding tool for the study of the structure of many types of materials.

The first imaging tool used to study the surface, or topography, of a material was the scanning electron microscope. A focused beam of high energy (~ 10 keV) electrons is scanned over the surface of an object. The number and angle of electrons ejected from the surface were used to assemble an image that appears three-dimensional. Again there were limitations. Non-conducting samples had to be coated with a thin layer of metal, which could obscure some features and modify the sample. Resolution was limited due to scattering of electrons just below the surface of the sample.

The scanning tunneling microscope invented in the early 1980's was the first instrument that could probe a surface with atomic resolution. A very sharp tip held very close (~ 1 nm) from a surface allowed a tunneling current to flow between them when a voltage was applied. Since the magnitude of the tunneling current is very sensitive to tip-sample separation, this current could be used to image the surface topography on an atomic scale. This technique is limited to conducting surfaces and to maintain surface cleanliness an ultra-high vacuum is often required.

Shortly after the invention of the scanning tunneling microscope, a new microscope called the atomic force microscope was developed. It uses a very fine-tipped probe to gently touch a surface. By measuring how much the tip moves up or down while dragging it across the surface, an image can be formed with near-atomic resolution. Its simplicity allows a wide range of materials to be studied, since it works in air and requires no special sample preparation. It even allows biological molecules to be imaged in aqueous solution, which is their natural environment. The atomic force microscope has become a very versatile tool in several fields of science and engineering.

The basic premise of an AFM can be seen in the diagram below:



Atomic Force Microscope

Source: PROBING BIOMOLECULES WITH THE ATOMIC FORCE MICROSCOPE. Helen G. Hansma, Department of Physics, University of California, Santa Barbara, CA 931106 http://www.physics.ucsb.edu/%7Ehhansma/afm-ac_s_news.htm

How the AFM works:

1. *Tip*—The tip at the end of the cantilever is the part of the AFM that actually contacts the sample. It is the key to horizontal resolution; tips with a smaller radius of curvature have better resolution. They are typically made by patterning and etching silicon, which can produce tips with a 5-10 nm radius.
2. *Cantilever*—The cantilever is like a diving board with a very small spring constant. This allows the very sharp tip at the end of it to contact the sample without dislodging atoms. The cantilever bends in proportion to the force between the tip and the sample.
3. *Laser*—In the AFM the laser shines down on the cantilever and reflects from the top surface. As tip moves up and down, the laser reflects at different angles from the cantilever. This causes the position of the laser to rise and fall on the segmented photodiode, a position-sensitive detector, allowing topographic information to be gathered.
4. *Piezo scanner*—The end of the cantilever is attached to a piezoelectric material that changes slightly with an applied voltage. The piezo tube scans the tip over the sample, and the tip rises or falls based on the topography of the sample.

Typically, the AFM is operated in constant force mode, so that the tip adjusts up and down while scanning over the surface to maintain constant force. This is accomplished by contracting and extending the piezo in order to keep the position of the laser constant on the photodiode.

APPENDIX I

Abbreviated Version of Software Help for WSxM

GENERAL



Information – Basic image information.



Recalibrate – Allows recalibration of x, y and z dimensions. Useful when WSxM does not read dimensions correctly from original data file.









Show Scale Bar, Edit Scale Bar

QUANTITATIVE ANALYSIS



Profile – Profile curve of transversal cut across image.

1) Select image, 2) Click icon, 3) Left-click and drag, 4) Right-click to apply, 5) Click on profile window to get the following options:

-  **Reset:** Restore Original Curve
-  **Reverse:** Invert Y-axis of the graph.
-  **Smooth:** Average current values.
-  **Fit Line:** Fit curve to a line and subtract, brings out features.
-  **Measure Point:** Display point values in Status Bar: (Z-coord., Profile line-coord.).
-  **Measure Distance:** Display distance between two points. 1) Click and drag crosses to select distance, 2) Status Bar displays horizontal and vertical distances between two points.



Multiple Profile – Find same profile curve on multiple images. Useful to compare the effect of filters and other modifications on an image.

1) Select image, 2) Click icon, 3) Select other images, 4) Left-Click on main image and drag, 4) Right-click to apply.

ANALYSIS OF PERIODIC IMAGES



Fast Fourier Transform – To find periodic structure and/or remove unwanted frequencies or noise.

1) Select Window (ellipse or rectangle), 2) Click Filter, 3) Select Areas on Bottom-Right image by left-clicking and dragging, 4) Right click to apply.



2D Cross Correlation – The higher the value, the more similar the two images are. Good when dealing with thermal drift to calculate the distance the point has moved.

1) Select first image, 2) Click on icon and 3) Select second image.



Lattice – Create a new layer over an image, usually a periodic atomic pattern (e.g. graphite hexagonal lattice).

1) Select image, 2) Click icon,

- Preset lattice: hexagon, nxn (for Si 111), square.
- User defined: 1) Tick vector checkbox, 2) Select 3 points by left-clicking, 1st click is the common origin for other two points; lattice displays in green lines, 3) Adjust vectors with V1/V2 length (nm) and V1/V2 angles.
- Correct: Corrects distortion to enable a better fit. 1) Left click to select all similar vertex points associated with a pattern, 2) Right click to correct.

3) Click OK to apply.

VIEWING IMAGES



2D – Displays top view of image.



3D View, 3D Settings – Displays 3D view of image; adjusts 3D view settings.



Zoom, Multiple Dynamic Zoom – Zoom in; zoom into same region of up to 4 images.

1) Select images, 2) set X and Y apertures of zoom region, 3) click on recalculate Max and Min to find hidden features in images.

BASIC IMAGE MANIPULATION



Duplicate Image



Z Reverse – Negative of image, data multiplied by -1.



Mirror – Reflect image with respect to Y-axis.



Rotate 90° – 90° CW rotation about Z-axis.



Rotate Angle – Rotate by any angle.

1) Select image, 2) Click icon, 3) Select Horizontal or vertical, 4) Select new X or Y axis by left-clicking and dragging to create a line, release.

- Rotating by an angle not multiple of 90° will place zeros in points not representing data points.

BRING OUT FEATURES



Lut Command, Lut Settings Command – Change color gradient. Sometimes new palettes bring out features that were not visible with other color gradients.

1) Select image, 2) Click icon,

- Useful Palettes: ThermicHot.lut, Flag.lut, AEP.lut

3) Select preset palette, or 4) Create own color table by modifying brightness, contrast, continuous or discrete modes, 5) Save color table in Lut file format, 6) Click OK to apply.



Z-Scale Control – Useful to bring out low features when high features are present in the image.

1) Select image, 2) Click icon, 3) Rescale max value to a lower value to find low features or 4) Click Automatic.



Derivative – Calculates derivative along the X-axis, good to find borders.

1) Select image, 2) Click icon.



Cosine – Calculates cosine of angle between slope of image and Z-axis, good to find borders.

1) Select image, 2) Click icon.



Equalize – Select range of heights to enhance contrast, features lower than left limit will be raised to left edge min height; features higher than right limit will be lowered to right edge max height.

1) Select image, 2) Click Icon, 3) Left-click for left-edge, 3) Right-click for right edge.



Contour Plot, Contour Plot Settings – Contour plot of the image, brings out ‘invisible’ features.

1) Select Image, 2) Click Icon, 3) Select number of contours, 4) Ok to apply.

TILT CORRECTIONS



Plane Global – Corrects any tilt due to tip-surface angle, applied to whole image.

1) Select image, 2) Click icon to apply.



Plane Local – Same as global, but applied to local planes.

1) Select image, 2) Click icon, 3) Left-click and drag to select as many planes as you want, 4) Right click to apply.



Find 2nd – Fits local planes to parabolic surface, then subtracts from whole image.

1) Select image, 2) Click icon., 3) Left-click and drag to select as many planes as you want, 4) Right click to apply.

CLEAN UP IMAGE



Flatten – Removes low frequency noise (seen as random darker lines along Y-direction).

1) Select image, 2) Click icon.

- Simple Flatten: Removes a function from each line, Offset (average), Line or Parabola.
- Discard Regions: Avoid flattening features you want to highlight. 1) Create, 2) Left-click and drag, 3) Right click. Select as many regions as you wish, 4) Apply.
- Path Selection: Lines that connect top with bottom of image, 1 line subtracts avg. of values crossed by path, 2 lines subtract a plane and 3 lines subtract a parabola. 1) Path1-Create, 2) Drag mouse to bottom of image through area to calculate function to remove, 3) Left-click at bottom of image. Create up to 3 paths. 4) Apply.



Popcorn – Removes peaks, by finding average of heights of whole image and subtracting.

1) Select image, 2) Click icon.

- Cutoff: Max height distance from average.
- Correlation: Global – use whole image to do average, Local – use separate regions, take local averages and filter individually; apply to XY Squares or lines in X or Y direction.
- Number: of points affected by filter.

3) Apply.



Remove Lines – Delete bad scan lines.

1) Select image, 2) Click icon.

- Removing Style: -Average, interpolates 2 closest ‘good lines’, -Set zero, replaces with zeros (black lines).
- No. of lines to be removed.
- 1st line: type or drag cursor to left of image.

3) Apply.



Spot Removal – Cleans noise (peaks) locally, remove unwanted high points in image.

1) Select image, 2) Click icon,

- Options: Copy, region into memory, Paste, copied region into selected region, Medium, replaces region with average value and Smooth, replaces each point with average of neighbors.
- Cutoff: for Medium, max height distance from average value allowed.
- Source Aperture %: size of selected region.
- Zoom Aperture %: size of region in zoom frame.

3) Apply.

SMOOTHING DATA



Redimension – Change number of columns and rows in image, maintains original ratio.



Smooth – Removes high frequency components, replaces each point with neighbors average.

EXTRA STUFF



Tip/Sample Dilation – Simulates the effect of a finite sized tip on an image. Tip used follows the equation:
 $Z = aX^2 + bY^2$.

1) Select image, 2) Click icon, X and Y Tip Radius: radius along X or Y direction in nm, 3) Click Dilate to apply.



Y Average – Profile curve of averages of all horizontal lines.