

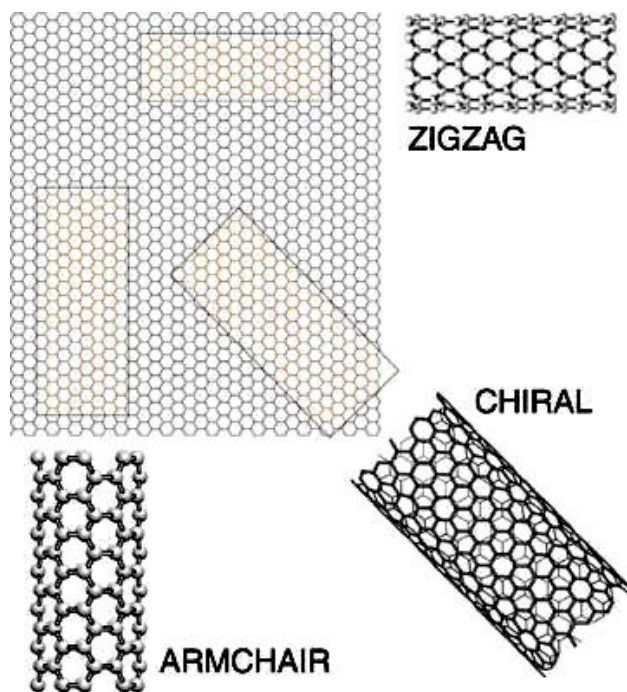
Synthesis of Carbon Nanotubes and Atomic Force Microscopy Demonstration

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I. Introduction

Carbon nanotubes are a new form of carbon discovered in 1991 by Sumio Iijima, a Japanese scientist who was examining soot in an electron microscope. He noticed nanoscale thread-like structures lying in the amorphous carbon. Since their discovery, carbon nanotubes have become the subject of intense scientific study and engineering due to their extraordinary properties. They have enormous tensile strength (45 GPa compared to 2 GPa for high strength steel alloys), are better thermal conductors than any known material, and possess unique electronic properties.

Carbon nanotubes share some structural similarities with graphite. Graphite consists of sheets of carbon atoms; each sheet has its atoms arranged in a hexagonal structure with an atom at every vertex (see Figure 1). Imagine rolling a single sheet of graphite into a tube with a nanoscale diameter. If it were possible to do this, you would have a carbon nanotube. Depending on which way the sheet is rolled, different nanotube structures result. They have been nicknamed “armchair”, “zigzag” and “chiral” (see Figure 1). The chirality of the nanotube can play an important role in determining its properties. For example, armchair tubes are metallic while others are semiconducting.



<http://www.seas.upenn.edu/mse/research/nanotubes.html>

Fig. 1 Structures of Carbon Nanotubes

Carbon nanotubes can be single-walled or multi-walled. Single-walled tubes have diameters ranging from 0.4 nm up to a few nanometers. Multi-walled tubes consist of a group of concentrically nested single-walled tubes and have diameters ranging from 1.4 nm up to ~100 nm.

There are three major methods for carbon nanotube production including carbon arc discharge, laser ablation, and chemical vapor deposition (CVD). The fundamental idea behind each method is the same: (1) heat a carbon-containing material to high temperature to release individual carbon atoms, and (2) encourage the reassembly of the free atoms into carbon nanotubes with carbon-absorbing catalyst particles (such as nickel, cobalt or iron nanoparticles).

The first published method for making carbon nanotubes was the arc discharge method. Two graphite rods are placed a few mm apart, and a high voltage across the rods creates an electrical discharge. Carbon atoms vaporize and some (up to 30%) recombine to form nanotubes. In the laser ablation method, intense laser pulses hitting a graphite surface create a hot carbon gas. In the presence of the right catalyst, up to 70% of the carbon forms nanotubes.

The method of choice for growing carbon nanotubes is Chemical Vapor Deposition (CVD). During this process a hydrocarbon gas flows through a hot furnace. As the gas decomposes, carbon atoms are absorbed by metallic catalyst nanoparticles and recombine to form nanotubes. It is possible to form nearly 100% nanotubes. The CVD method offers many control parameters, including temperature, ambient gas composition, growth time, and catalyst composition. Also, it has potential to be scaled up to industrial production.

Although much progress has been made, better control of carbon nanotube growth is highly desirable. It remains a challenge to precisely control the length, diameter, and chirality of nanotubes, all of which determine the properties of individual carbon nanotubes. Another set of challenges comes with the ability to place nanotubes in desired locations, important in applications such as nanoscale circuits.

This lab session will be split into two parts, first nanotube growth and second an introduction to Atomic Force Microscopy (AFM). In lab the following week, we will use an AFM to image our carbon nanotube samples. An introduction to AFM is included in Appendix G.

II. Procedure

A. Sample Preparation

1. Disperse catalyst nanoparticles in solution (see Appendix H for catalyst preparation)
 - a. Stir the catalyst solution on hot plate/stirrer for 5 minutes at high speed.
 - b. Sonicate the catalyst solution for 5 minutes.
2. Cleave a piece of Si wafer to make a chip approximately $1.5 \text{ cm} \times 1.5 \text{ cm}$.
3. Place a clean glass capillary tube into the catalyst solution and allow it to soak up a small amount of the solution.
4. Orient the capillary tube vertically and very briefly touch the tip to the Si chip. The solution will expand outward from the tip and wet the surface.
 - a. Make sure the solution does not wet the entire surface (the edge of the drop is best for imaging nanotubes).
 - b. Allow several seconds for the methanol to evaporate.

B. Nanotube Growth


1. Load substrate into furnace
 - a. Using tweezers place your chip with the catalyst side up in the furnace tube
 - b. Use the metal rod to carefully push the chip in to the center of the furnace. If there is more than one sample, record the position of your sample.
2. Close and seal furnace
 - a. When all samples are in place inside the tube, close and latch the furnace hood.
 - b. Wipe the o-ring of the furnace inlet connector with your fingers to remove any particles. Carefully place the connector on the open end of the quartz tube. Gently screw the connector tight to compress the o-ring.
3. Visually inspect the entire gas flow route from the gas tanks to the end of the tube in the vented hood. Make sure the hood is turned on.
4. Flow Ar through the furnace
 - a. Open the main Ar tank valve a few turns (metal knob on top of tank)
 - b. Open the valve at the outlet of the pressure regulator (small plastic knob). Do not adjust the outlet pressure of the regulator (large knob).
 - c. Check that gas is bubbling through paraffin in the flask at the furnace outlet.
 - d. Adjust the flow meter to a flow rate of 5 ($5,000 \text{ cm}^3$ per minute, or sccm).
5. Leak check the o-ring seal at the furnace inlet
 - a. Gently spray Snoop (soapy liquid) around the tube connections and look for the formation and/or growth of bubbles.
 - b. If bubbles appear, gas is leaking out. Close the Ar tank and remake the seal.
6. Raise the furnace temperature to $900 \text{ }^\circ\text{C}$
 - a. Turn on the power to the furnace controller located below the furnace.
 - b. Adjust the set point to $900 \text{ }^\circ\text{C}$ and press the "set" button.
 - c. Let the temperature rise until it reaches $900 \text{ }^\circ\text{C}$ (about 15 minutes). Then let it stabilize for 2 minutes.




7. Flow methane through furnace
 - a. Begin flow of methane gas following the same procedure as the Ar gas.
 - b. Close the outlet valve of the Ar regulator. (Do not reverse the order of 7a and 7b; this allows the flow to stagnate and hinders tube growth.)
 - c. Adjust the flow rate of the methane gas to 5,000 sccm on the flow meter.
 - d. Time methane flow for 10 minutes.
8. Resume Ar flow through furnace
 - a. Open outlet valve on Ar regulator (check tank valve is also open).
 - b. Close outlet valve on methane regulator and methane tank valve. (Do not reverse order of 8a and 8b or flow will stagnate.)
 - c. Adjust flow rate of the methane gas to 5,000 sccm on the flow meter.
9. Cool down furnace
 - a. Change the temperature controller set point to 0 °C and press the “set” button.
 - b. When the temperature falls to 700 °C, you can slightly open (2-3 cm) the top of the furnace and insert a wedge to accelerate cooling.
 - c. When the temperature falls to 500 °C, you can fully open the top of the furnace to further accelerate cooling to below 200 °C (~5 minutes).
10. Open furnace and remove sample
 - a. When the temperature is below 200°C, close all valves on gas cylinders.
 - b. Immediately after stopping gas flow, disconnect furnace inlet connector (to avoid backflow of paraffin into furnace). Wrap the end of the connector in Al foil.
 - c. Using the metal rod, drag your sample out being careful not to touch the surface.
 - d. Using tweezers place your sample in a plastic wafer carrier and close it.
 - e. Label the wafer carrier with date and sample type.

C. Optical Inspection

1. Inspect your sample visually. Place it under the optical microscope and examine it at various magnifications.
2. Answer questions 5 and 6 in the Analysis section.

D. Atomic Force Microscopy (AFM) Demonstration and Image Analysis

1. Observe the AFM demonstration of imaging the edge of an Al thin film resistor. Record the file name of the image and the maximum values of the x, y and z axes.
2. Launch WSxM (v3.0 or later) located on the desktop of any of the PCs in the lab (freeware available at www.nanotec.es).
3. Open the file containing the image of the patterned Al film acquired during the demonstration. To open the file with WSxM, you may have to change the *File Type*: to *All Files (*.*)*.
4. Click on the *Recalibrate* tool  (see Appendix I) and if necessary change the *X*, *Y* and *Z Amplitude* to match that of the original image.

5. Use the *Plane Local* tool  (see Appendix I) to level the silicon surface if it appears tilted.
6. Measure the height of the Al film in several locations.
 - a. Use the *Profile* tool  to generate a profile of the Al step. Be careful to avoid any areas with a lot of dirt on the surface.
 - b. Make the profile window active and click on the *Measure Distance* tool  to generate two cursors that you can use to measure the difference in height between the Si and Al surfaces.
 - c. Often there is dirt at the edge of the Al film. Avoid placing cursors on this or any other obvious dirt.
 - d. Repeat steps a-c to generate several measurements of the Al film thickness.

III. Analysis

1. Name the method used to synthesis the carbon nanotubes in lab and summarize the basic steps.
2. What is the source of carbon that forms the carbon nanotubes?
3. Why is Ar gas flowed through the furnace while heating up to 900 °C and cooling down?
4. Explain the role of the catalyst in the synthesis of the carbon nanotubes.
5. Can you observe individual carbon nanotubes in the optical microscope? Why or why not?
6. Describe the distribution of the catalyst on your chip. Is it uniformly distributed? Where does the catalyst appear most dense? What areas are likely to be best for imaging C nanotubes with an atomic force microscope, given that nanotubes are easiest to image on flat surface (i.e. the Si wafer)?
7. Draw a diagram of an AFM and label its parts. Briefly describe how an AFM generates a topographic image of a surface.
8. Name at least three pieces of information you can expect to learn about carbon nanotubes from an atomic force microscope image.
9. List all of your trials for measuring the aluminum film thickness and report an average thickness. Be sure to include an uncertainty figure as well (calculate the standard deviation of your trails).

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).

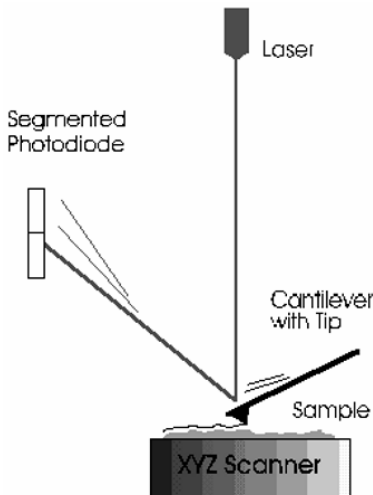
In the 20th century, the limitations of the light were overcome with the invention of the transmission electron microscope. Electrons instead of photons were used to probe specimens and magnetic and electric lenses were used to focus the beam of electrons. Eventually in the best microscopes objects smaller 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 H

Catalyst Synthesis

Catalyst Materials:

- 45 mg of Alumina Nanoparticles
- 60 mg Iron Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
- 3 mg Molybdenyl Acetylacetonate ($\text{MoO}_2(\text{acac})_2$) (chemical is air sensitive)
- 45 ml Methanol

Equipment Needed:

- Sonicator
- Magnetic Stirrer
- Stirring Bars
- Balance
- Weighing Paper
- Nitrile Gloves
- Glass Pipettes
- 50ml glass vial
- Parafilm

Safety Measures:

1. Always wear suitable protective clothing and gloves.
2. Handle substances carefully.
3. Keep an organized working space.
4. For all chemicals remember to:
 - Not breathe the vapors.
 - Not get in eyes, on skin or on clothing.
 - Avoid prolonged or repeated exposure.
 - Keep away from combustible materials, heat, sparks and open flame (only Methanol and Iron Nitrate are flammable).
5. Aluminum Oxide is a very light powder, be careful when handling it to avoid skin and eye contact.

For more information refer to the MSDS sheets in the laboratory.

Synthesis:

1. Rinse glass vial with a little bit of methanol. Dispose the methanol down the drain with plenty of water. Dry vial with compressed air tank (if available).
2. Pour 45ml of methanol in vial, close cap.
3. Use a new film of weighing paper and a new pipette to scoop out and measure each substance.

4. Each time flush away any leftover powder down the drain with plenty of water. Rinse the weighing paper and dispose in trash container.
5. Place a film of weighing paper inside the balance and calibrate.
6. Scoop out 60mg of Iron Nitrate with clean pipette and place in vial.
7. Place a new film of weighing paper on balance and calibrate. Then, using a new pipette, scoop out 3mg of Molybdenyl Acetylacetonate and place it in vial.
8. Repeat step 7 with 45mg of Alumina nanoparticles.
9. When all substances are in vial, drop in the magnetic stirring tablet and place on magnetic stirrer for 24 hours. First, be sure to label the vial since you'll be leaving it on the stirrer for a long time.
10. After stirring is done, sonicate the solution for 1 hour. **WARNING: DON'T** put your fingers in the water tank while sonicator is **ON**. Make sure the water in the sonicator tank covers all of the substance in the vial before starting it.
11. When sonicating is finished, turn sonicator **OFF** and then remove vial.
12. Wrap cap with parafilm to avoid evaporation.

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

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.