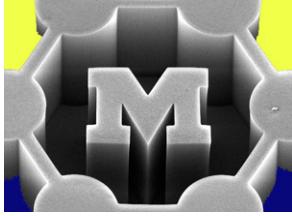
Nanomanufacturing
University of Michigan
ME599-002 |Winter 2010



02: Techniques for characterizing nanostructures

January 13, 2010

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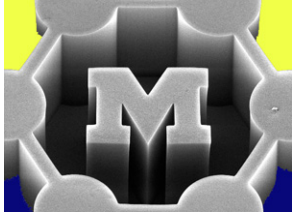
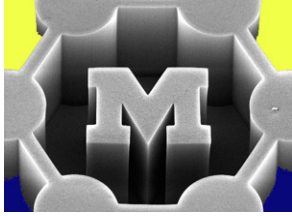
Announcements

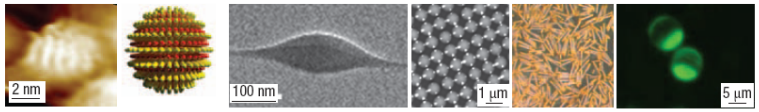


- Please fill out the info sheet if you are new
- How many plan to take the GCC?
- No class next M (Jan/18)

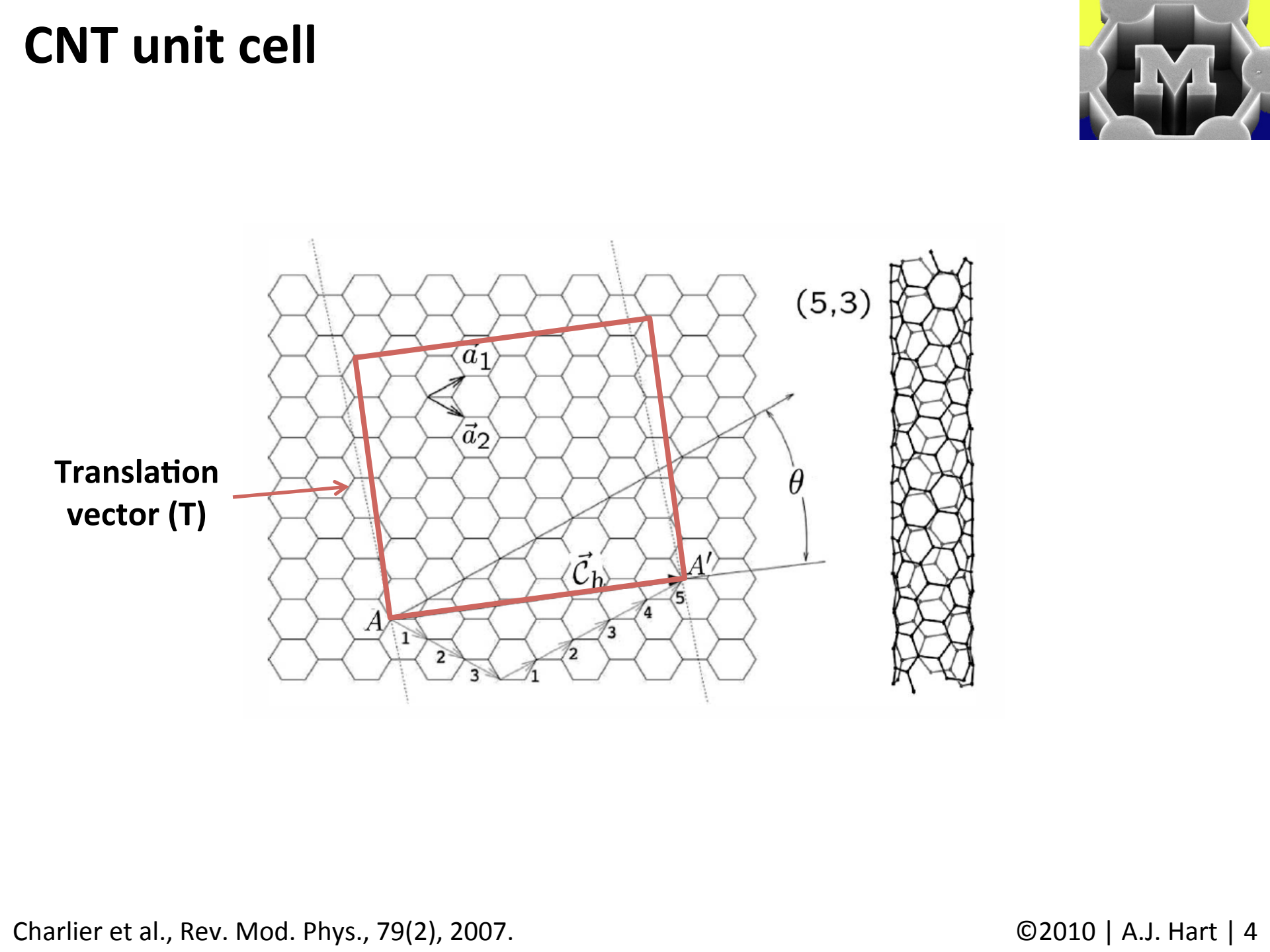
Recap: nanoscale structures



- **Taxonomy**: nano-clusters, -wires, -tubes, sheets, heterostructures
  - 0D, 1D, 2D – how many degrees of freedom would you have if you were inside the structure?
  - Emphasis on structural diversity
  - We will see effects of size and shape on properties



CNT unit cell



Charlier et al., Rev. Mod. Phys., 79(2), 2007.

Periodic Table of Carbon Nanotubes

zigzag ($m = 0$)

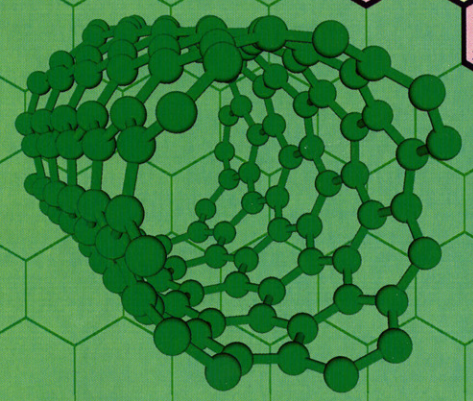
armchair ($n = m$)

(n,m)	(1,0)	(2,0)	(3,0)	(4,0)	(5,0)	(6,0)	(7,0)	(8,0)	(9,0)	(10,0)	(11,0)	(12,0)	(13,0)	(14,0)	(15,0)	(16,0)	(17,0)
d_t (Å) $d{:}d_R$	0.78 1:1	1.57 2:2	2.35 3:3	3.13 4:4	3.92 5:5	4.70 6:6	5.48 7:7	6.27 8:8	7.05 9:9	7.83 10:10	8.62 11:11	9.40 12:12	10.18 13:13	10.97 14:14	11.75 15:15	12.54 16:16	13.32 17:17
E_g (eV)	5.484	1.078	0.740	1.494	1.348	0.185	1.087	0.986	0.082	0.827	0.764	0.046	0.663	0.622	0.030	0.552	0.523
T (Å) θ	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°
N	4	8	12	16	20	24	28	32	36	40	44	48	52	56	60	64	68
(1,1)	1.36 1:3	2.07 1:1	2.82 1:1	3.59 1:3	4.36 1:1	5.14 1:1	5.91 1:3	6.69 1:1	7.47 1:1	8.25 1:3	9.04 1:1	9.82 1:1	10.60 1:3	11.38 1:1	12.16 1:1	12.94 1:3	13.73 1:1
	0.0	4.880	1.839	0.267	2.199	1.166	0.110	1.346	0.865	0.058	0.961	0.686	0.036	0.746	0.568	0.024	0.608
	2.46 30°	11.28 19.1°	15.37 13.9°	6.51 10.9°	23.74 8.9°	27.95 7.6°	10.73 6.6°	36.42 5.8°	40.67 5.2°	14.97 4.7°	49.16 4.3°	53.42 4.0°	19.22 3.7°	61.92 3.4°	66.18 3.2°	23.48 3.0°	74.69 2.8°
	4	28	52	28	124	172	76	292	364	148	532	628	244	844	964	364	1228
(2,2)	2.71 2:6	3.41 1:1	4.15 2:2	4.89 1:3	5.65 2:2	6.41 1:1	7.18 2:6	7.95 1:1	8.72 2:2	9.50 1:3	10.27 2:2	11.05 1:1	11.83 2:6	12.61 1:1	13.39 2:2		
	0.0	1.975	2.146	0.114	1.139	1.380	0.067	0.836	0.990	0.041	0.665	0.766	0.027	0.553	0.623		
	2.46 30°	18.58 23.4°	11.28 19.1°	8.87 16.1°	15.37 13.9°	34.89 12.2°	6.51 10.9°	43.26 9.8°	23.74 8.9°	17.23 8.2°	27.95 7.6°	60.14 7.1°	10.73 6.6°	68.61 6.2°	36.42 5.8°		
	8	76	56	52	104	268	56	412	248	196	344	796	152	1036	584		
(3,3)	4.07 3:9	4.77 1:1	5.48 1:1	6.22 3:3	6.96 1:1	7.72 1:1	8.47 3:3	9.24 1:1	10.00 1:1	10.77 3:9	11.54 1:1	12.31 1:1	13.09 3:3	13.86 1:1			
	0.0	1.509	1.269	0.057	0.980	0.885	0.043	0.744	0.691	0.030	0.604	0.569	0.021	0.510			
	2.46 30°	25.93 25.3°	29.84 21.8°	11.28 19.1°	37.89 17.0°	41.99 15.3°	15.37 13.9°	50.26 12.7°	54.43 11.7°	6.51 10.9°	62.80 10.2°	67.00 9.5°	23.74 8.9°	75.42 8.4°			
	12	148	196	84	316	388	156	556	652	84	868	988	372	1252			
(4,4)	5.43 4:12	6.12 1:1	6.83 2:2	7.56 1:3	8.29 4:4	9.04 1:1	9.79 2:6	10.54 1:1	11.30 4:4	12.06 1:3	12.83 2:2	13.59 1:1					
	0.0	1.302	1.056	0.032	0.999	0.779	0.028	0.788	0.624	0.022	0.644	0.523					
	2.46 30°	33.30 26.3°	18.58 23.4°	13.70 21.1°	11.28 19.1°	49.16 17.5°	8.87 16.1°	57.35 14.9°	15.37 13.9°	21.88 13.0°	34.89 12.2°	73.96 11.5°					
	16	244	152	124	112	532	104	724	208	316	536	1204					
(5,5)	6.78 5:15	7.47 1:1	8.18 1:1	8.90 1:3	9.63 1:1	10.36 5:5	11.11 1:3	11.86 1:1	12.61 1:1	13.36 1:3	14.12 5:5						
	0.0	1.000	0.978	0.020	0.749	0.788	0.020	0.604	0.649	0.016	0.521						
	2.46 30°	40.67 27.0°	44.51 24.5°	16.14 22.4°	52.38 20.6°	11.28 19.1°	20.15 17.8°	64.51 16.6°	68.61 15.6°	24.24 14.7°	15.37 13.9°						
	20	364	436	172	604	140	268	916	1036	388	260						
(6,6)	8.14 6:18	8.83 1:1	9.53 2:2	10.24 3:3	10.97 2:2	11.70 1:1	12.44 6:6	13.18 1:1	13.93 2:2								
	0.0	0.853	0.780	0.013	0.667	0.623	0.014	0.550	0.521								
	2.46 30°	48.04 27.5°	25.93 25.3°	18.58 23.4°	29.84 21.8°	63.66 20.4°	11.28 19.1°	71.71 18.0°	37.89 17.0°								
	24	508	296	228	392	892	168	1132	632								
(7,7)	9.50 7:21	10.18 1:1	10.88 1:1	11.59 1:3	12.31 1:1	13.04 1:1	13.77 1:3	14.51 7:7									
	0.0	0.764	0.688	0.009	0.646	0.564	0.011	0.553									
	2.46 30°	55.42 27.8°	59.22 25.9°	21.03 24.2°	67.00 22.7°	70.95 21.4°	24.98 20.2°	11.28 19.1°									
	28	676	772	292	988	1108	412	196									
(8,8)	10.86 8:24	11.54 1:1	12.24 2:2	12.94 1:3	13.66 4:4	14.38 1:1											
	0.0	0.658	0.639	0.007	0.545	0.552											
	2.46 30°	62.80 28.1°	33.30 26.3°	23.48 24.8°	18.58 23.4°	78.26 22.2°											
	32	868	488	364	304	1348											
(9,9)	12.21 9:27	12.90 1:1	13.59 1:1	14.30 3:3	15.01 1:1												
	0.0	0.590	0.556	0.005	0.498												
	2.46 30°	70.18 28.3°	73.96 26.7°	25.93 25.3°	81.67 24.0°												
	36	1084	1204	444	1468												
(10,10)	13.57 10:30	14.25 1:1	14.95 2:2														
	0.0	0.542	0.507														
	2.46 30°	77.56 28.4°	40.67 27.0°														
	40	1324	728														
(11,11)	14.93 11:33	15.61 1:1															
	0.0	0.489															
	2.46 30°	84.94 28.6°															
	44	1588															

metallic tubes | semimetallic tubes | semiconducting tubes

The semi-empirical bandgap E_g is calculated according to H. Yorikawa and S. Muramatsu, Phys. Rev. B **52**, 2723 (1995) for the semiconducting tubes (no curvature effects) and A. Kleiner and S. Eggert, Phys. Rev. B **63**, 073408 (2001) for the metallic and semi-metallic tubes (includes curvature). All other values are evaluated from the expressions below.

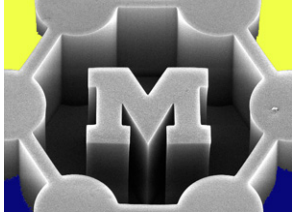
$a_{C\text{–}C}$	carbon–carbon distance		1.421 Å (graphite)
a	length of unit vector	$\sqrt{3}\, a_{C\text{–}C}$	2.461 Å
$\mathbf{a}_1,\ \mathbf{a}_2$	unit vectors	$\frac{a}{2}(\sqrt{3}, 1),\ \frac{a}{2}(\sqrt{3}, -1)$	in (x, y) coordinates
$\mathbf{b}_1,\ \mathbf{b}_2$	reciprocal unit vectors	$\frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1),\ \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$	in (x, y) coordinates
$\mathbf{C}_h$	chiral vector	$n\mathbf{a}_1 + m\mathbf{a}_2$	n, m integer
L	circumference of tube	$L = \lvert\mathbf{C}_h\rvert = a\sqrt{n^2 + m^2 + nm}$	$0 \le m \le n$
d_t	diameter of tube	$d_t = L/\pi$	
θ	chiral angle	$\tan\theta = \frac{\sqrt{3}m}{2n+m}$	$0° \le \theta \le 30°$
d	highest common divisor of (n, m)		
d_R	highest common divisor of $(2n + m, 2m + n)$	$d_R = \begin{cases} d & \text{if } n - m \text{ is not a multiple of } 3d \\ 3d & \text{if } n - m \text{ is a multiple of } 3d \end{cases}$	
$\mathbf{T}$	translational vector of 1D unit cell	$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$ $t_1 = (2m + n)/d_R$ $t_2 = -(2n + m)/d_R$	t_1, t_2 integer
T	length of $\mathbf{T}$	$T = \sqrt{3}L/d_R$	
N	number of atoms per 1D unit cell	$N = 4(n^2 + m^2 + nm)/d_R$	$N/2$ = hexagons/unit cell



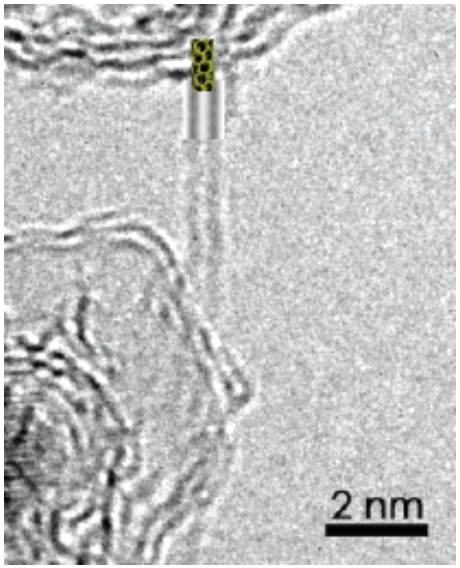
atomistix
www.atomistix.com

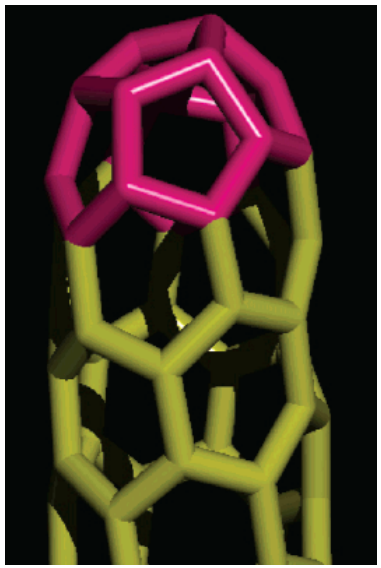
$a_{\mathrm{C\text{–}C}}$	carbon–carbon distance		1.421 Å (graphite)
a	length of unit vector	$\sqrt{3}\, a_{\mathrm{C\text{–}C}}$	2.461 Å
$\mathbf{a}_1,\ \mathbf{a}_2$	unit vectors	$\frac{a}{2}(\sqrt{3}, 1),\ \frac{a}{2}(\sqrt{3}, -1)$	in (x, y) coordinates
$\mathbf{b}_1,\ \mathbf{b}_2$	reciprocal unit vectors	$\frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1),\ \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$	in (x, y) coordinates
$\mathbf{C}_h$	chiral vector	$n\mathbf{a}_1 + m\mathbf{a}_2$	n, m integer
L	circumference of tube	$L = \lvert\mathbf{C_h}\rvert = a\sqrt{n^2 + m^2 + nm}$	$0 \le m \le n$
d_t	diameter of tube	$d_t = L/\pi$	
θ	chiral angle	$\tan\theta = \frac{\sqrt{3}m}{2n+m}$	$0° \le \theta \le 30°$
d	highest common divisor of (n, m)		
d_R	highest common divisor of $(2n + m, 2m + n)$	$d_R = \begin{cases} d & \text{if } n - m \text{ is not a multiple of } 3d \\ 3d & \text{if } n - m \text{ is a multiple of } 3d \end{cases}$	
$\mathbf{T}$	translational vector of 1D unit cell	$\mathbf{T} = t_1\mathbf{a_1} + t_2\mathbf{a_2}$	t_1, t_2 integer
		$t_1 = (2m + n)/d_R$	
		$t_2 = -(2n + m)/d_R$	
T	length of $\mathbf{T}$	$T = \sqrt{3}L/d_R$	
N	number of atoms per 1D unit cell	$N = 4(n^2 + m^2 + nm)/d_R$	$N/2$ = hexagons/unit cell

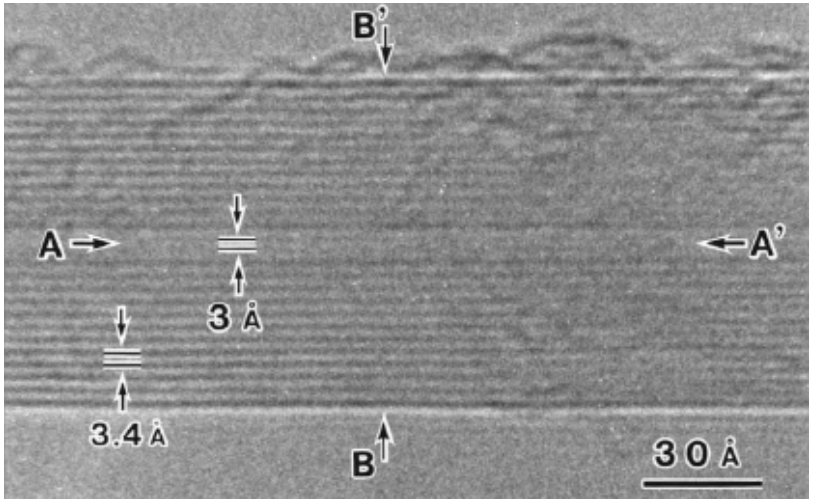
What is the smallest CNT?



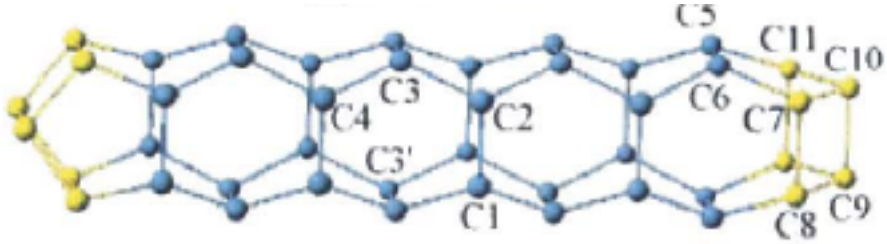
4A







3A

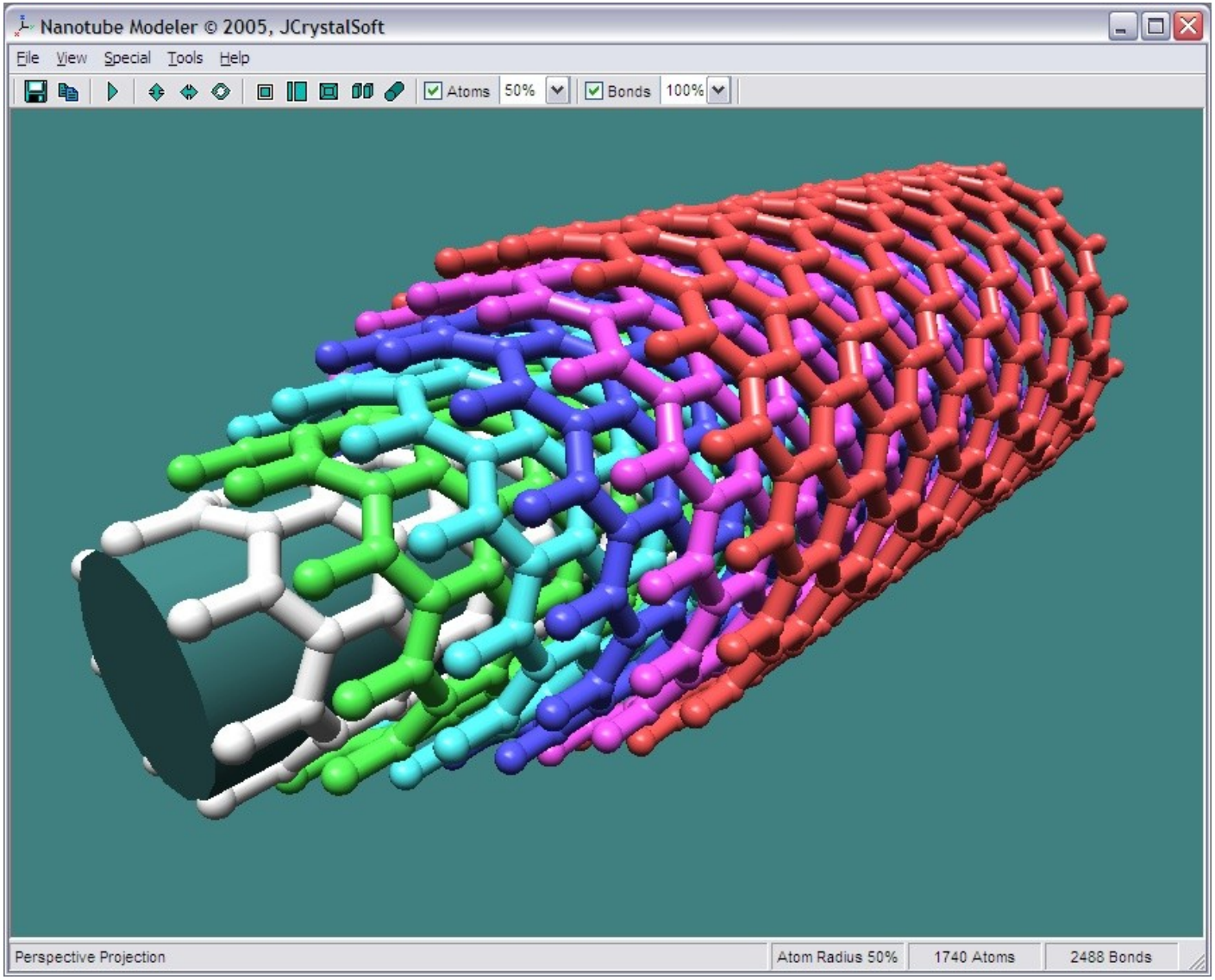


(d) 0.17 eV/atom

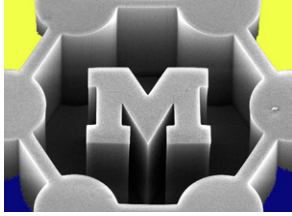
Hayashi et al., Nano Letters 3(7):887-889, 2003
Zhao et al., Phys Rev Lett 92(12):125502, 2004.

Nanotube modeler

http://www.jcrystal.com/products/wincnt/



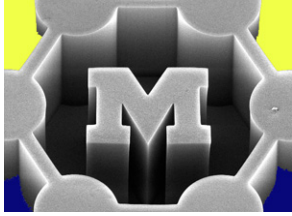
Today's agenda



- Microscopy: techniques and limits
  - Optical
  - Electron
  - Scanning probe (AFM/STM)
- Surface/structural analysis: electron and X-ray techniques
- Optical spectroscopy
  - Raman
  - UV/visible light
  - Infrared

- **This lecture could be an entire course (or more); our goal is to know the very basics of techniques we'll refer to in later topics.**
- **We'll overview how to measure properties in the coming lectures (mechanical, electrical, thermal, optical)**

Today's readings



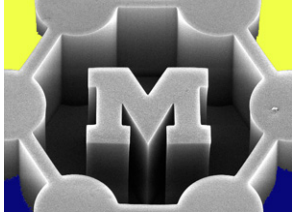
Nominal: (on ctools)

- Binning, Quate, and Gerber, **Atomic Force Microscope**
- Rao, **Characterization of Nanomaterials by Physical Methods**

Extras: (on ctools)

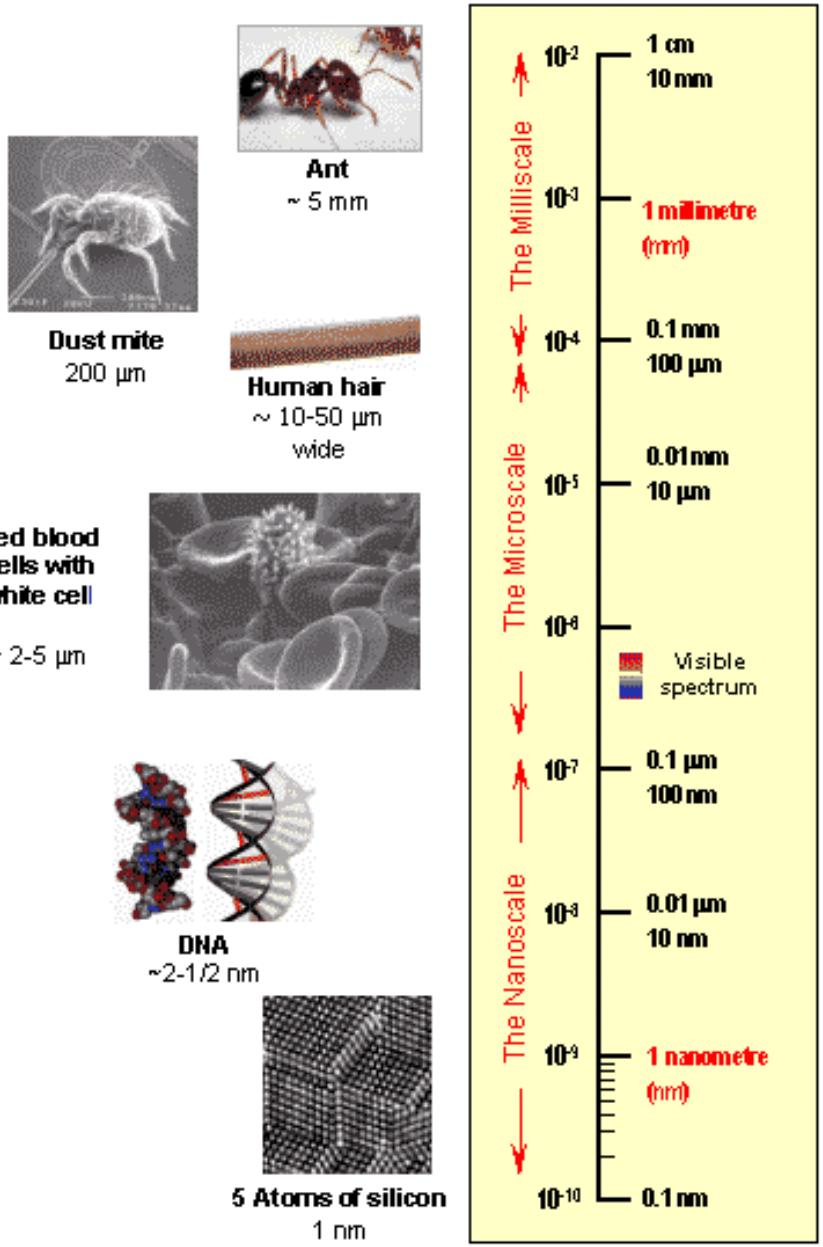
- Several papers on dynamic characterization, e.g., time-resolved electron microscopy

Additional resources



- References listed on these slides
- Internet search!
- Review papers (in journals)
- Many good books, e.g.,
  - Grasserbauer and Werner (eds.), Analysis of Microelectronic Materials and Devices, ISBN 0471950130
- Courses at UM:
  - Structural and chemical characterization of materials, Prof. Steve Yalisove (MSE465 W10)
  - Experimental methods in solids, Prof. Samantha Daly (ME599 was offered in W09)

Calibration



1 micrometer = 10^{-6} m

1 nanometer = 10^{-9} m

1 angstrom = 10^{-10} m

so…

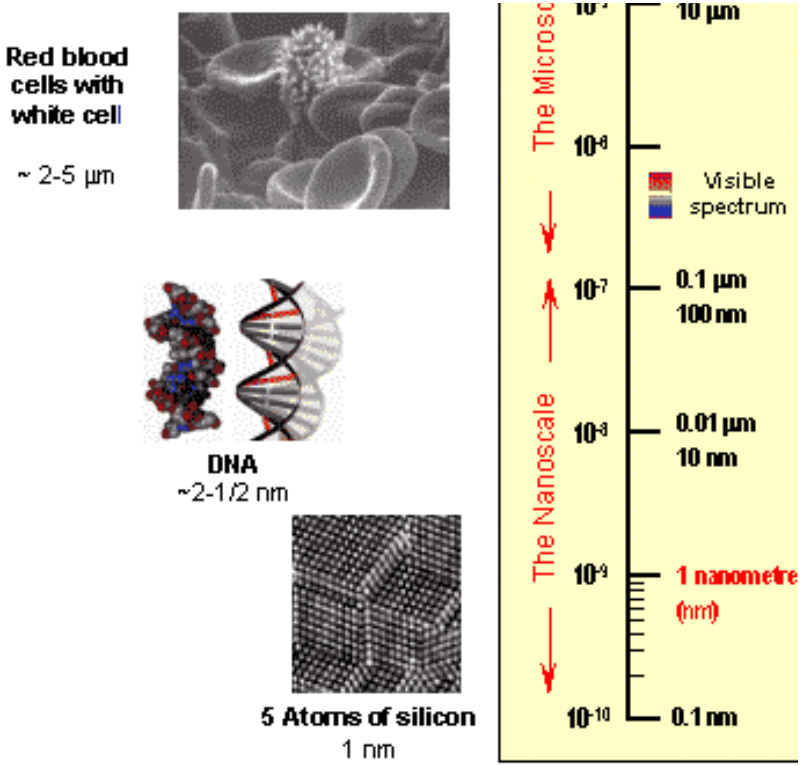
1 mm = 1,000,000 µm

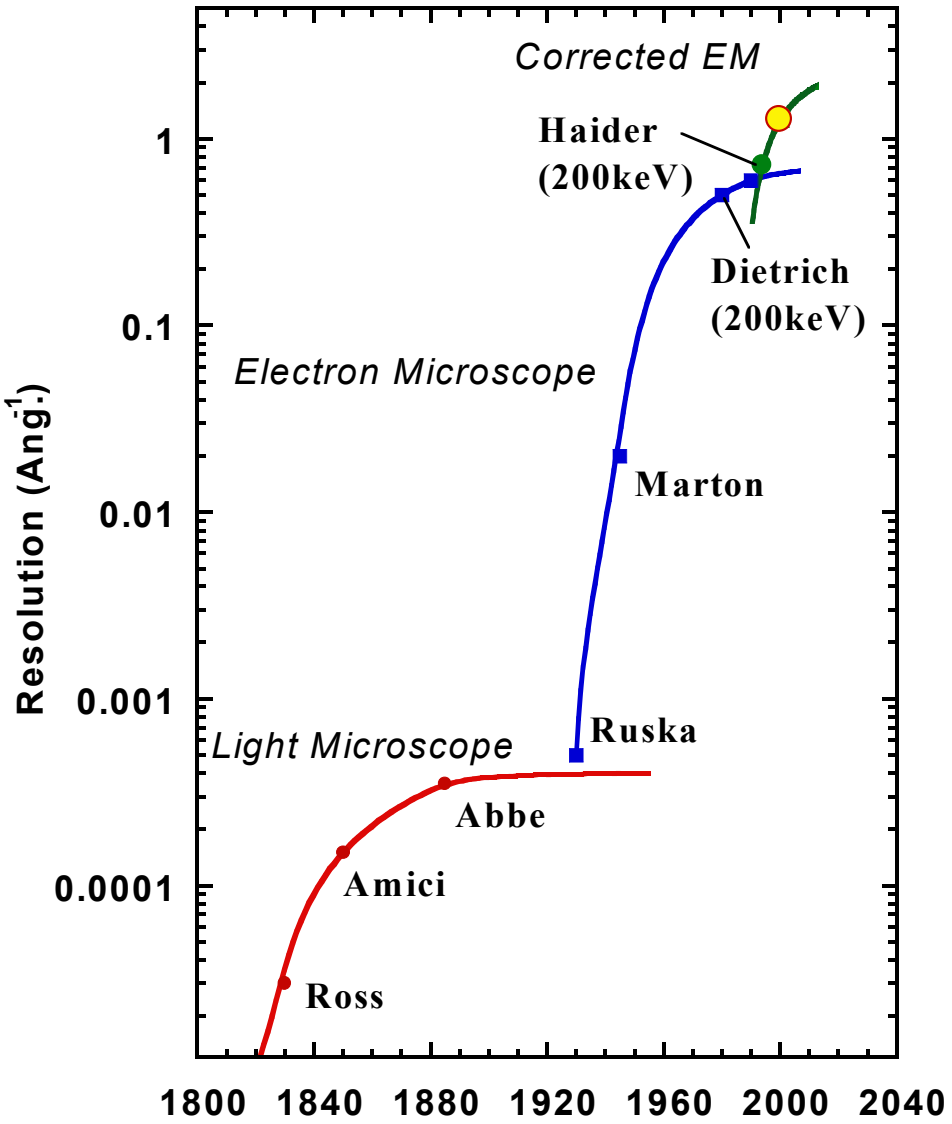
1 µm = 1000 nm

1 nm = 10 A

http://www.sustainpack.com/nanotechnology.html

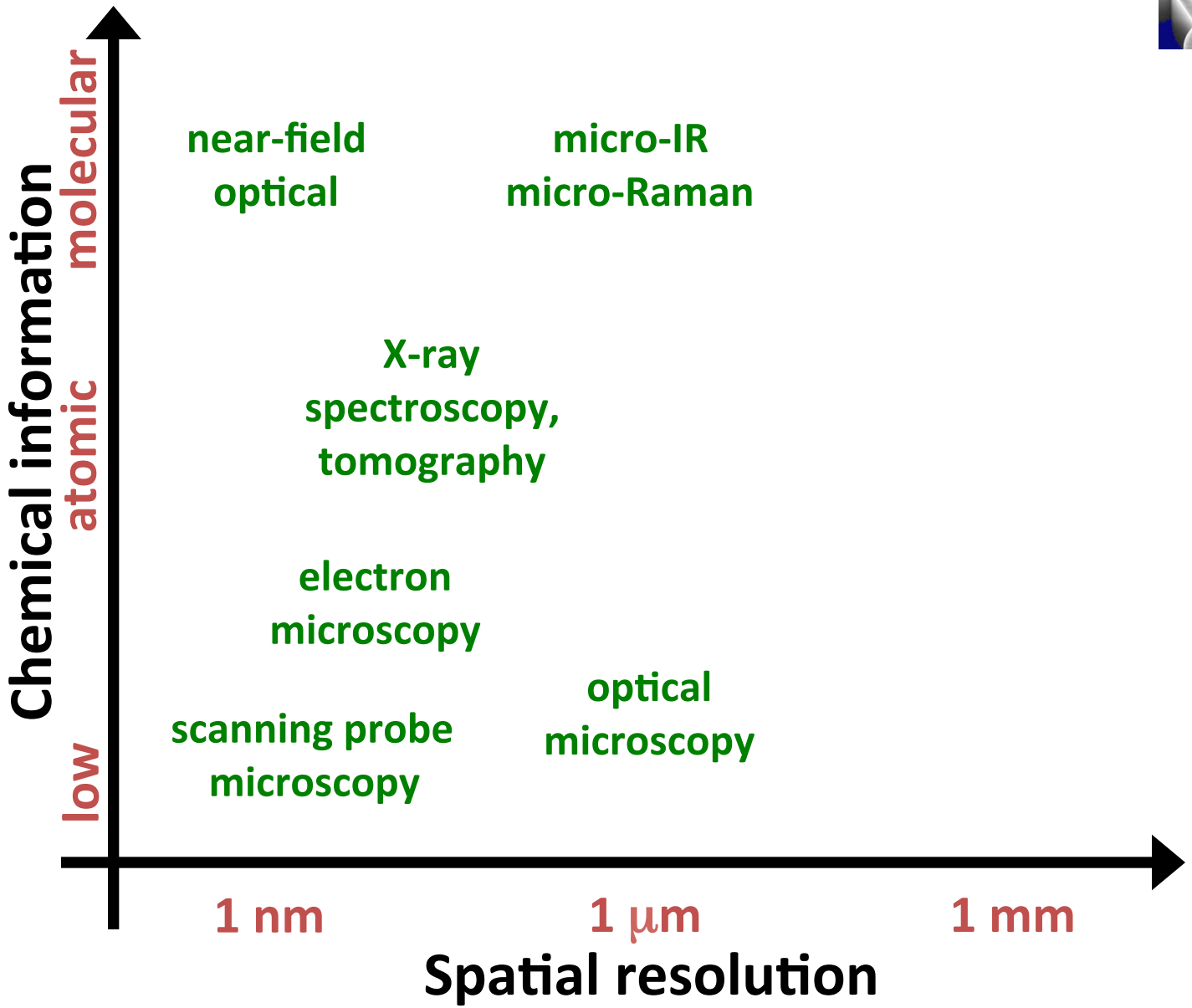
Resolution versus time



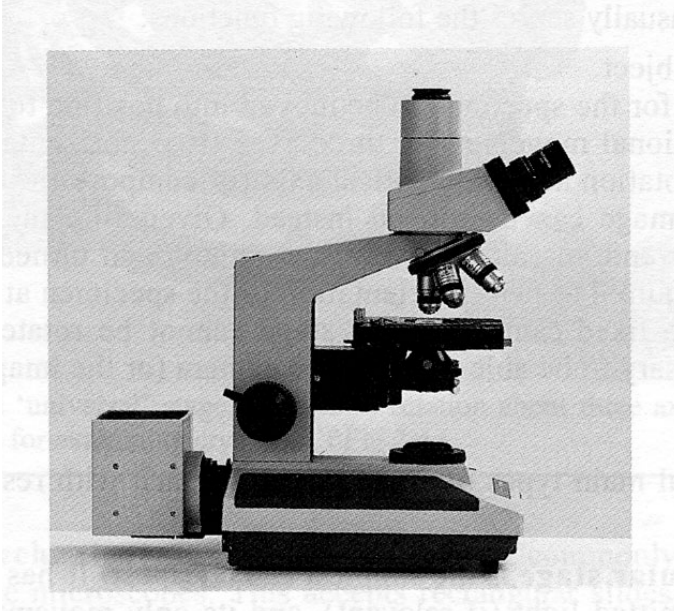


http://www.sustainpack.com/nanotechnology.html

What types of information do we want?



Optical microscope



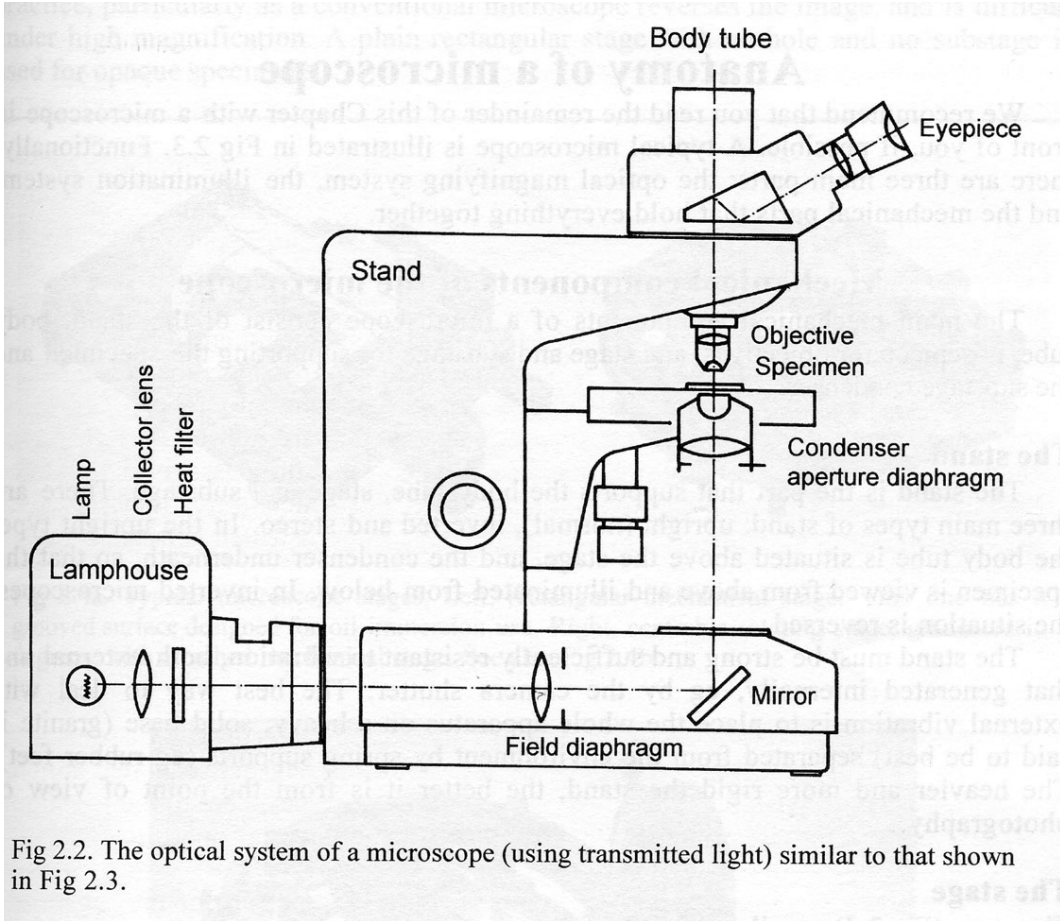
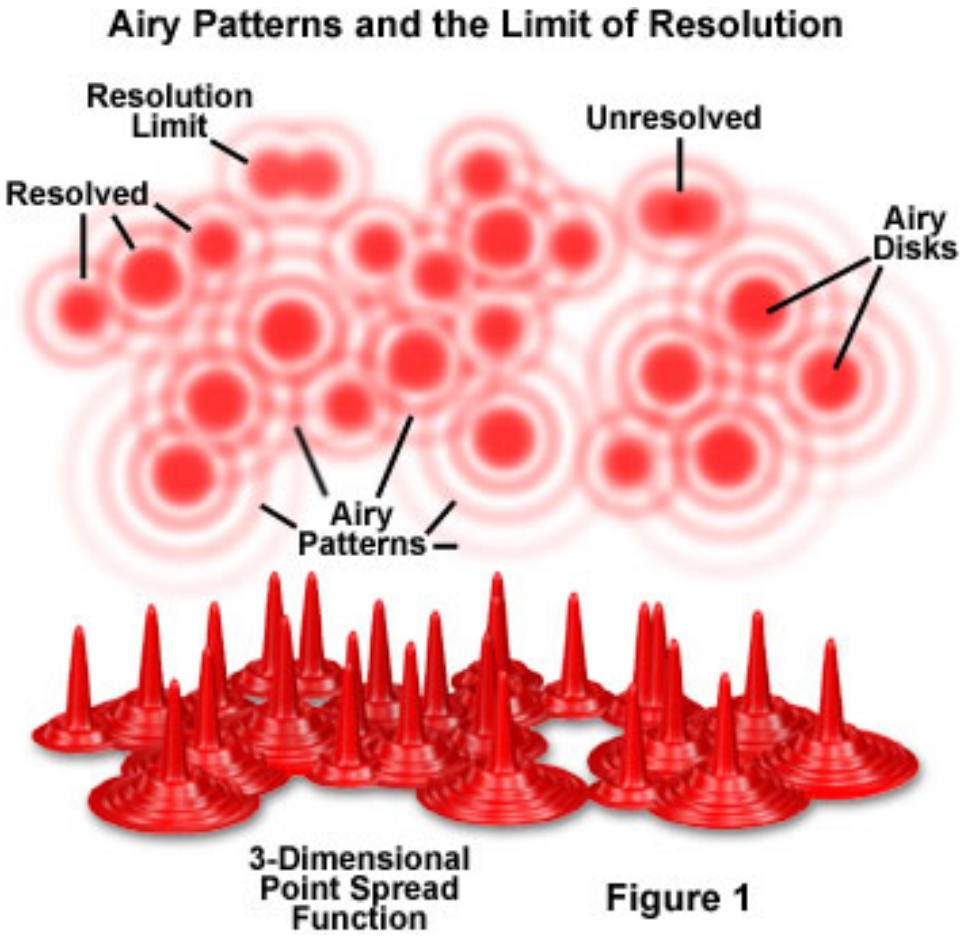


Fig 2.2. The optical system of a microscope (using transmitted light) similar to that shown in Fig 2.3.

Limits of optical microscopy

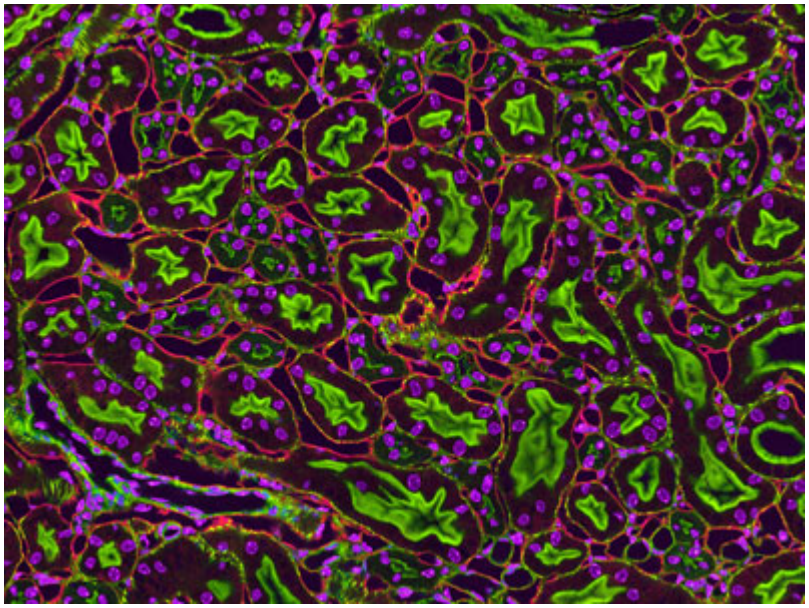
- Diffraction limit defines spatial resolution, $d = \lambda/NA$
- Ability to fit spread (airy) function determines point-to-point resolution of ideal emitters



http://www.microscopyu.com/articles/formulas/images/resolutionfigure1.jpg

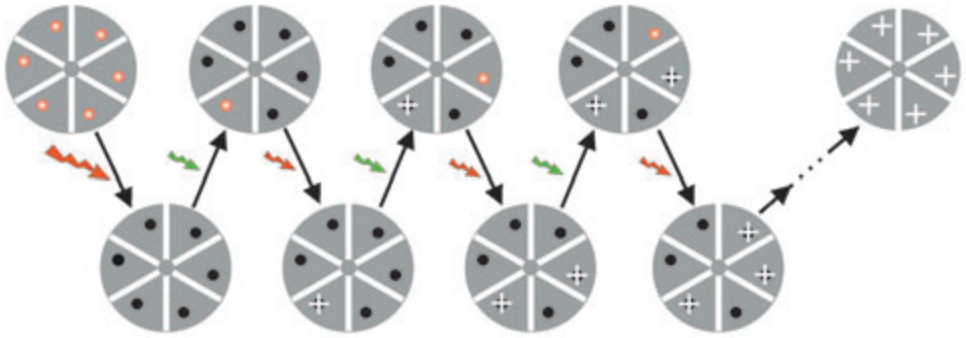
Limits of optical microscopy

- Ways to beat the diffraction limit
  - Immersion optics (e.g., increase *NA*)
  - Prior knowledge of what should be in the image
  - Surface and tip-enhanced methods
  - Use fluorescent beacons (e.g., quantum dots) to tag specific locations

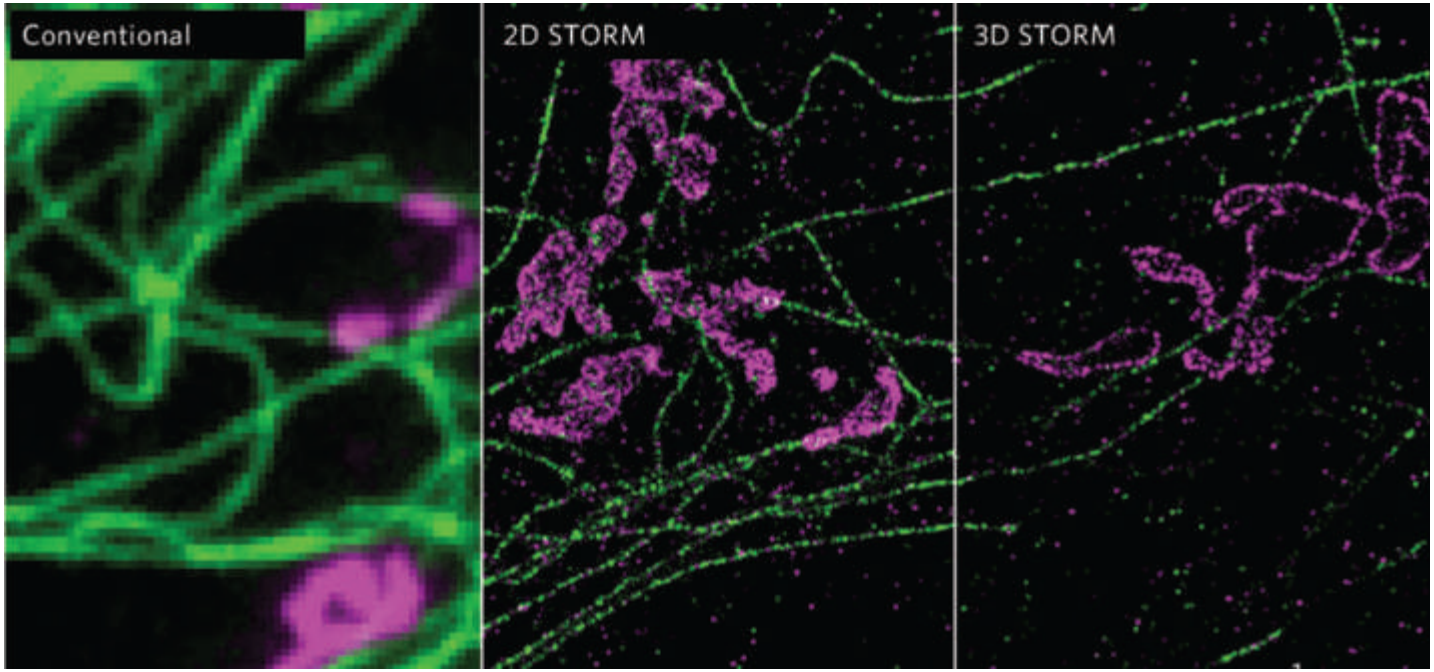


Thomas J. Deerinck
National Center for Microscopy & Imaging Research
University of California - San Diego
La Jolla, California, USA
Quantum dot fluorescence image of mouse kidney section (240x)

Stochastic optical reconstruction microscopy (STORM)



Switchable fluorophores



Zhuang group at Harvard, http://zhuang.harvard.edu/

Scanning electron microscope (SEM)

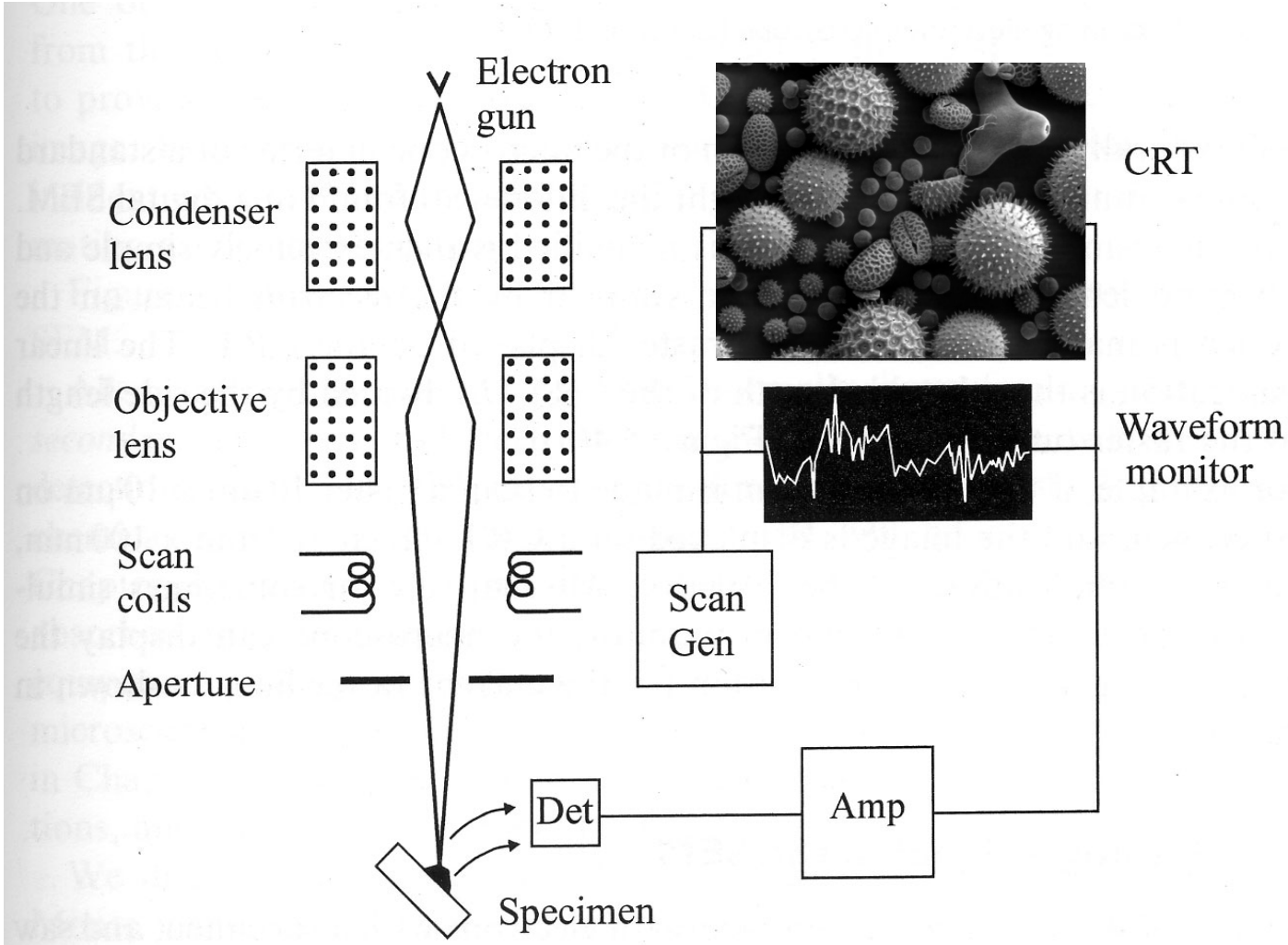
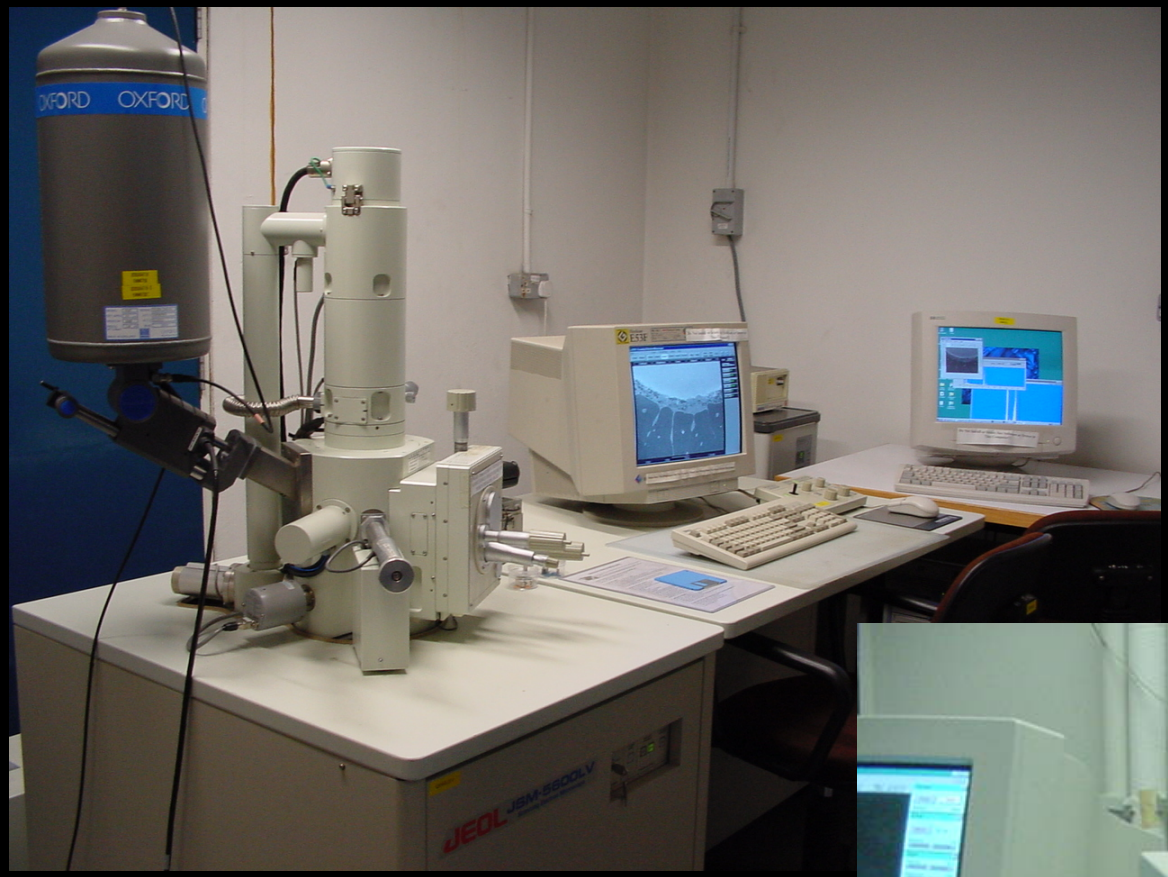
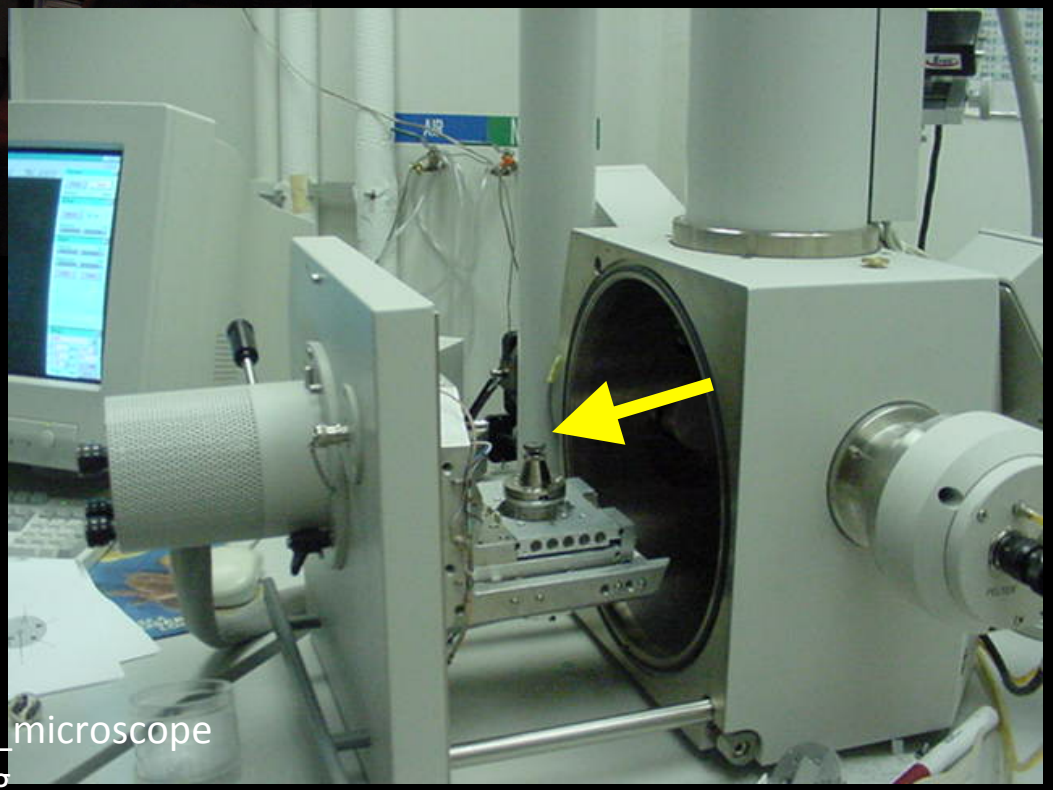


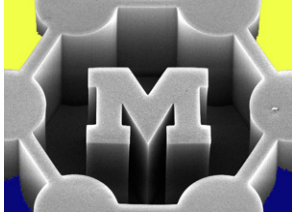
Figure 5.2 Schematic diagram showing the main components of a scanning electron microscope.





http://en.wikipedia.org/wiki/Scanning_electron_microscope
http://serve.me.nus.edu.sg/mat/images/sem.jpg

SEM



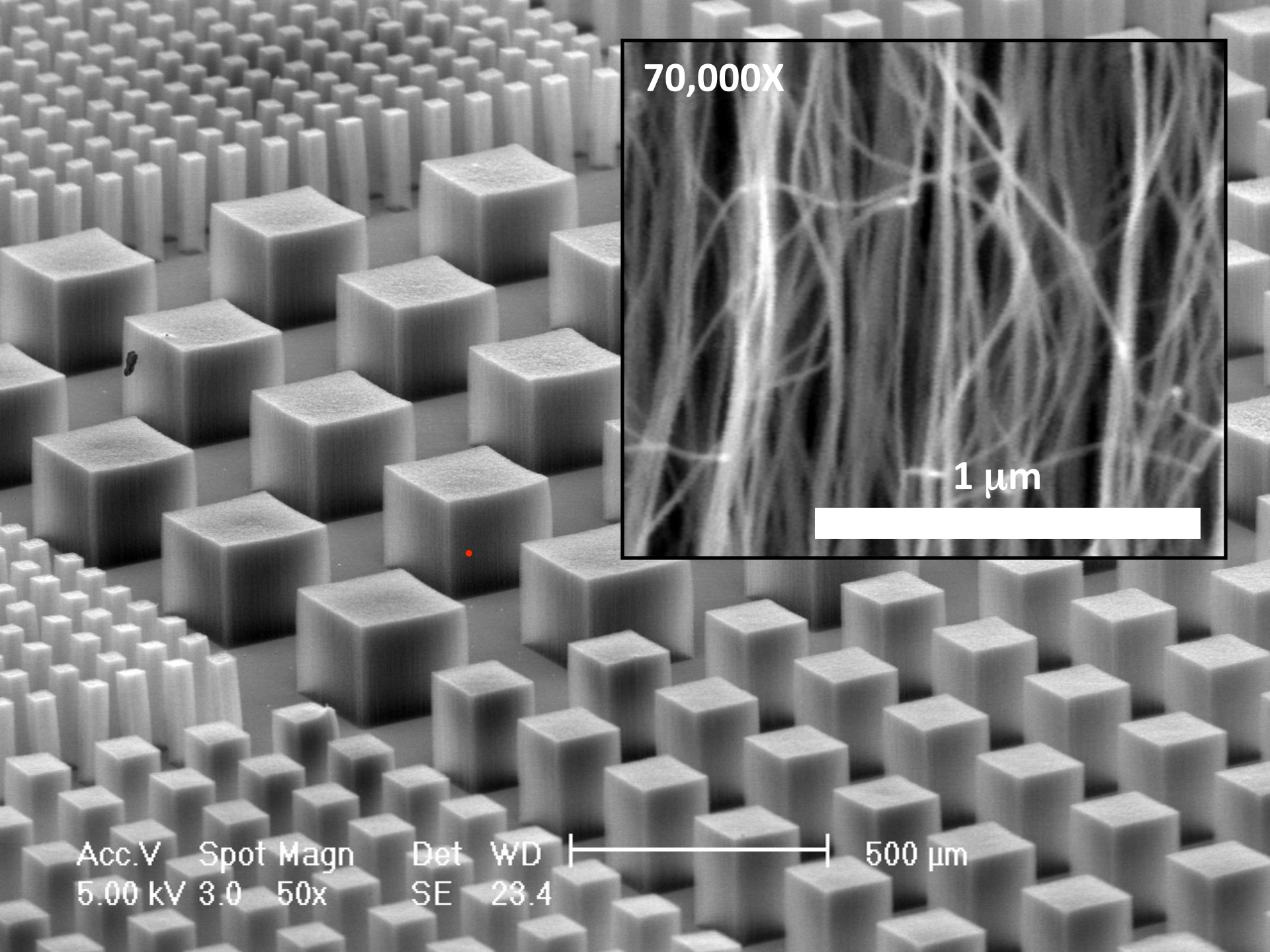
JEOL Conventional Tungsten High Vacuum SEMs

- Ideal for failure analysis, inspection, and characterization.

Available Models

	Resolution	Accelerating Voltage	Magnification	Stage
JSM-6390	3.0nm	0.5 to 30 kV	x5 to 300,000	X=125mm, Y=100mm
JSM-6390A				
JSM-6490	3.0nm	0.3 to 30 kV	x5 to 300,000	X=125mm, Y=100mm
JSM-6490A				

http://www.jeol.com


70,000X
1 µm
Acc.V Spot Magn Det WD
5.00 kV 3.0 50x SE 23.4
500 µm

SEM sample preparation

- Electrically conductive sample surface required
- Affix to sample stage with conductive tape (e.g., carbon) or conductive epoxy (e.g., polymer and Ag particles)
- Coat non-conductive samples with a thin metal layer (typically 10-100 nm), OR use **environmental-SEM (E-SEM)**

It's cold outside!

NANO LETTERS

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Nanometer Patterning with Ice

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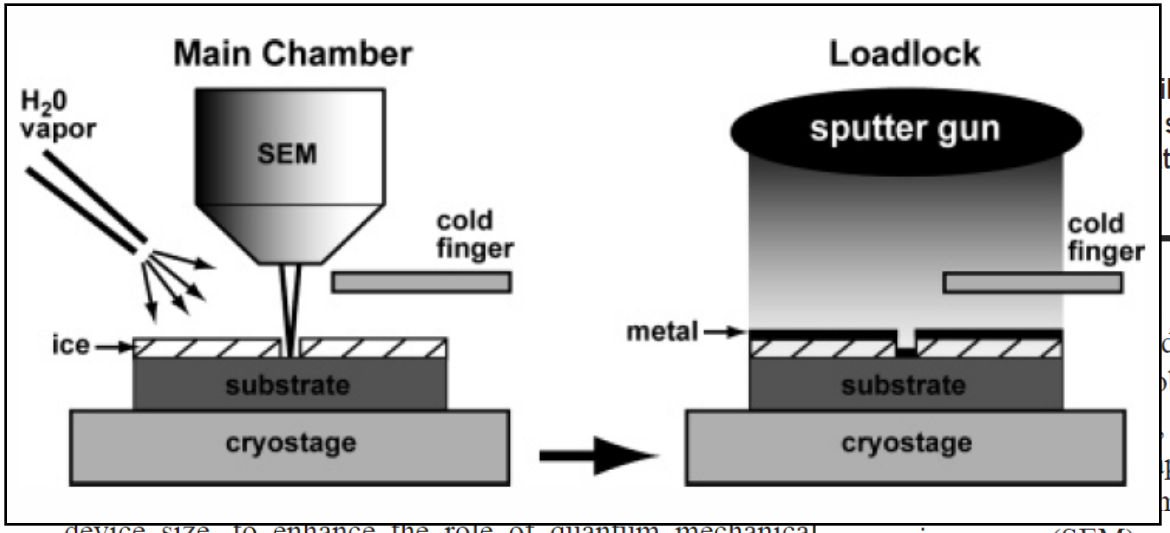
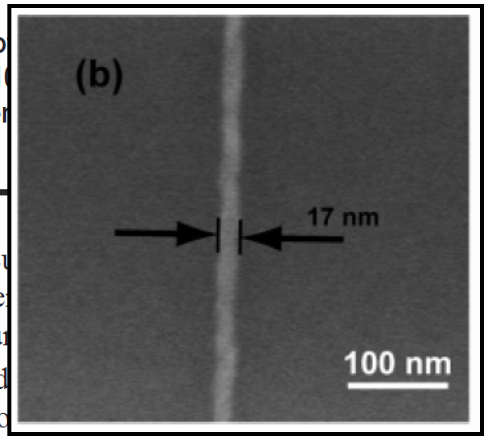
Department of Physics, Department of Molecular and Cellular Biology, and Division of Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

Received March 3, 2005; Revised Manuscript Received April 12, 2005





device size, to enhance the role of quantum mechanical device characteristics, and to pattern increasingly complex substrates requires new lithographic approaches to define nanometer scale structures. Here we demonstrate a new approach to nanoscale e-beam patterning based on the condensation and beam stimulated sublimation of water ice

mber of a combined scanning electron microscope (SEM) and focused ion beam (FIB) apparatus (FEI Co., Hillsboro, Oregon). Subsequent exposure of the ice surface to focused energetic electron or gallium ion beams stimulates local removal of ice and ultimately exposes the underlying silicon substrate in whatever patterns the beams

Transmission electron microscope (SEM)

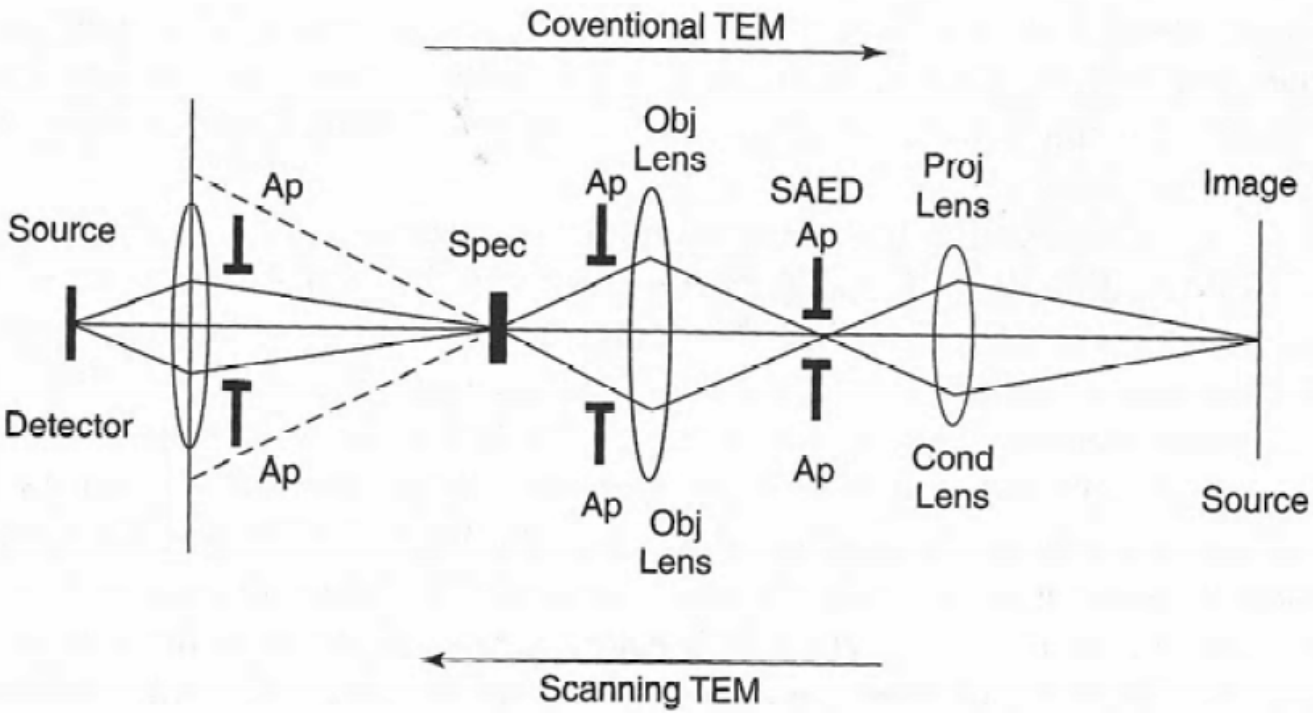


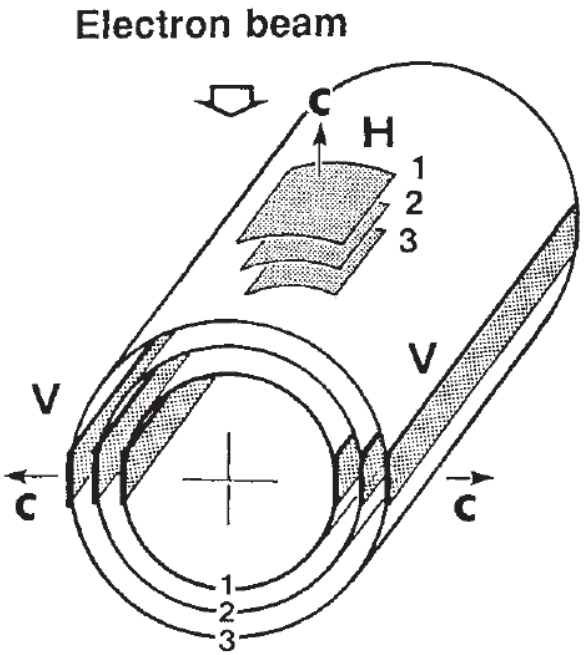
Figure 3.10. Ray diagram of a conventional transmission electron microscope (top path) and of a scanning transmission electron microscope (bottom path). The selected area electron diffraction (SAED) aperture (Ap) and the sample or specimen (Spec) are indicated, as well as the objective (Obj) and projector (Proj) or condenser (Cond) lenses. (Adapted from P. R. Buseck, J. M. Cowley, and L. Eyring, *High-Resolution Transmission Electron Microscopy*, Oxford Univ. Press, New York, 1988, p. 6.)

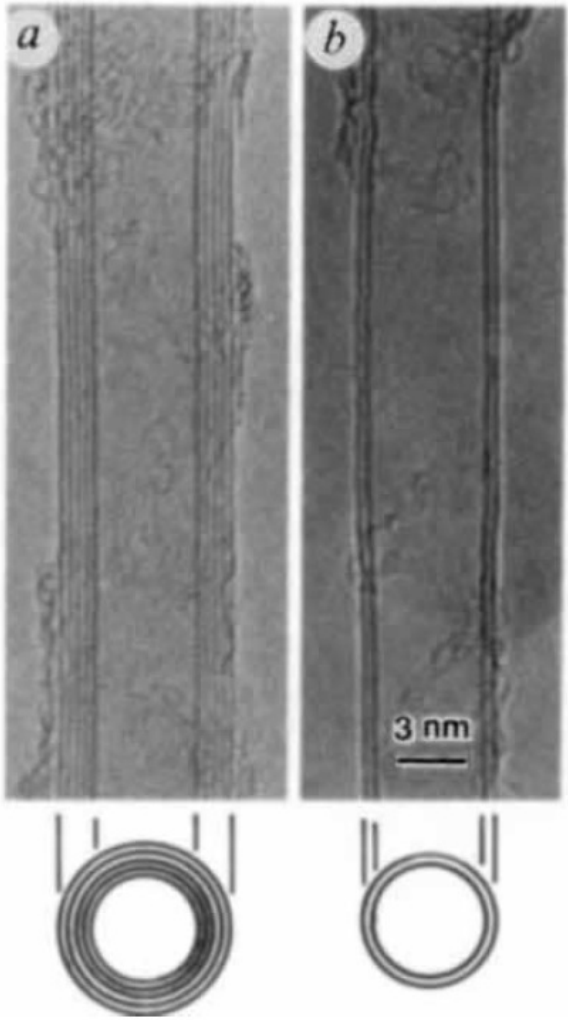
NATURE · VOL 354 · 7 NOVEMBER 1991

Helical microtubules of graphitic carbon

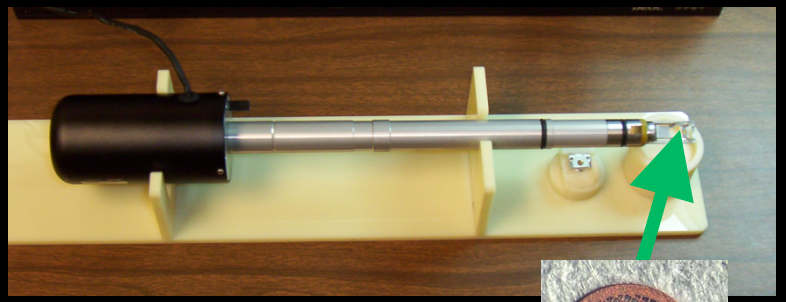
Sumio Iijima

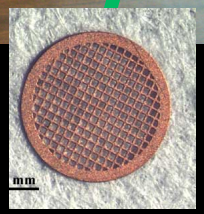
NEC Corporation, Fundamental Research Laboratories.





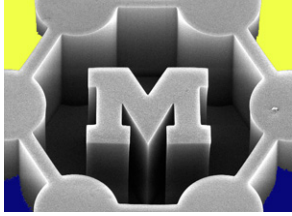
Iijima, Nature 354:56-58, 1991.





http://www.jeol.com
http://www.fei.com

TEM



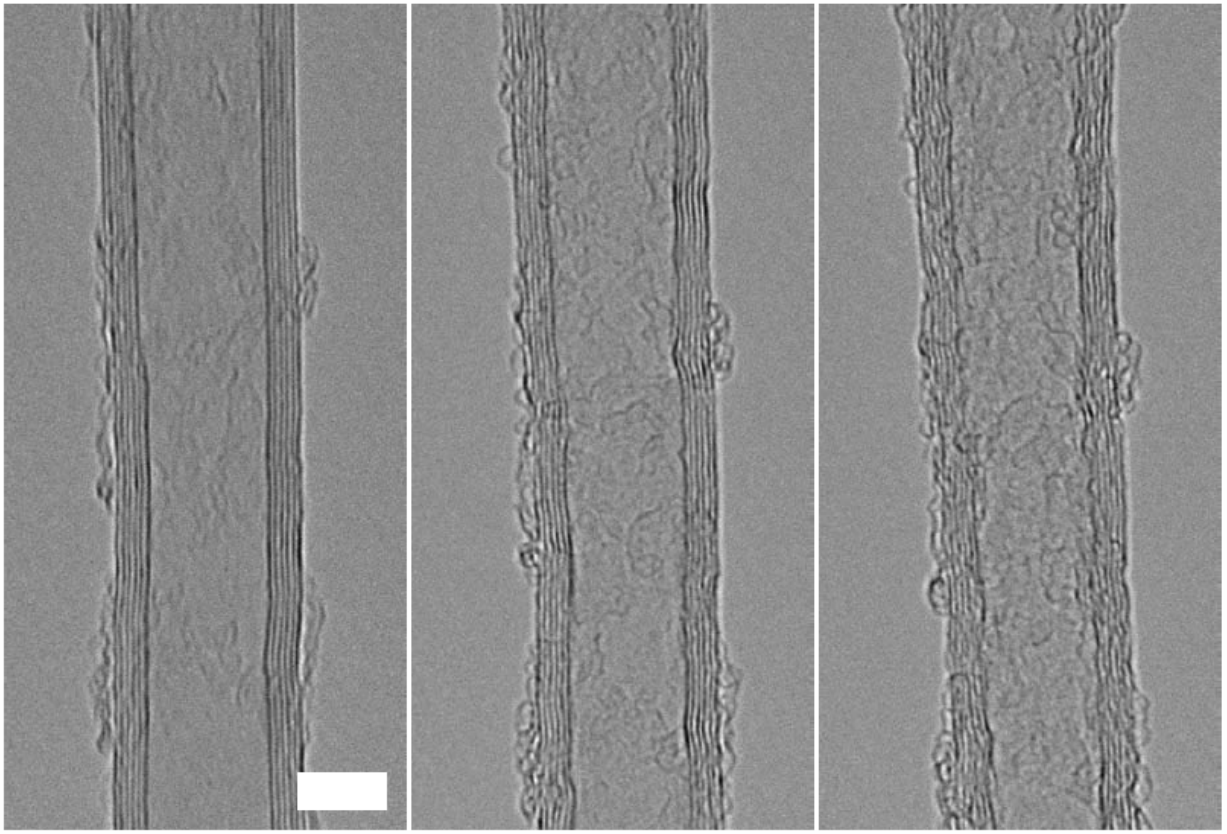
JEOL 200 kV Transmission Electron Microscopes

Available Models

	Resolution	Accelerating Voltage	Magnification
JEM-2100F	0.14nm Lattice	80 to 200 kV	x50 to 1,500,000
JEM-2100 LaB_6	0.10nm Lattice	80 to 200 kV	x50 to 1,500,000
JEM-2200FS	0.14nm Lattice	80 to 200 kV	x50 to 1,500,000
JEM-2500SE	STEM 0.2nm Lattice TEM 0.14nm Lattice	80 to 200 kV	x100 to 20,000,000

http://www.jeol.com

Electron beam can damage a structure

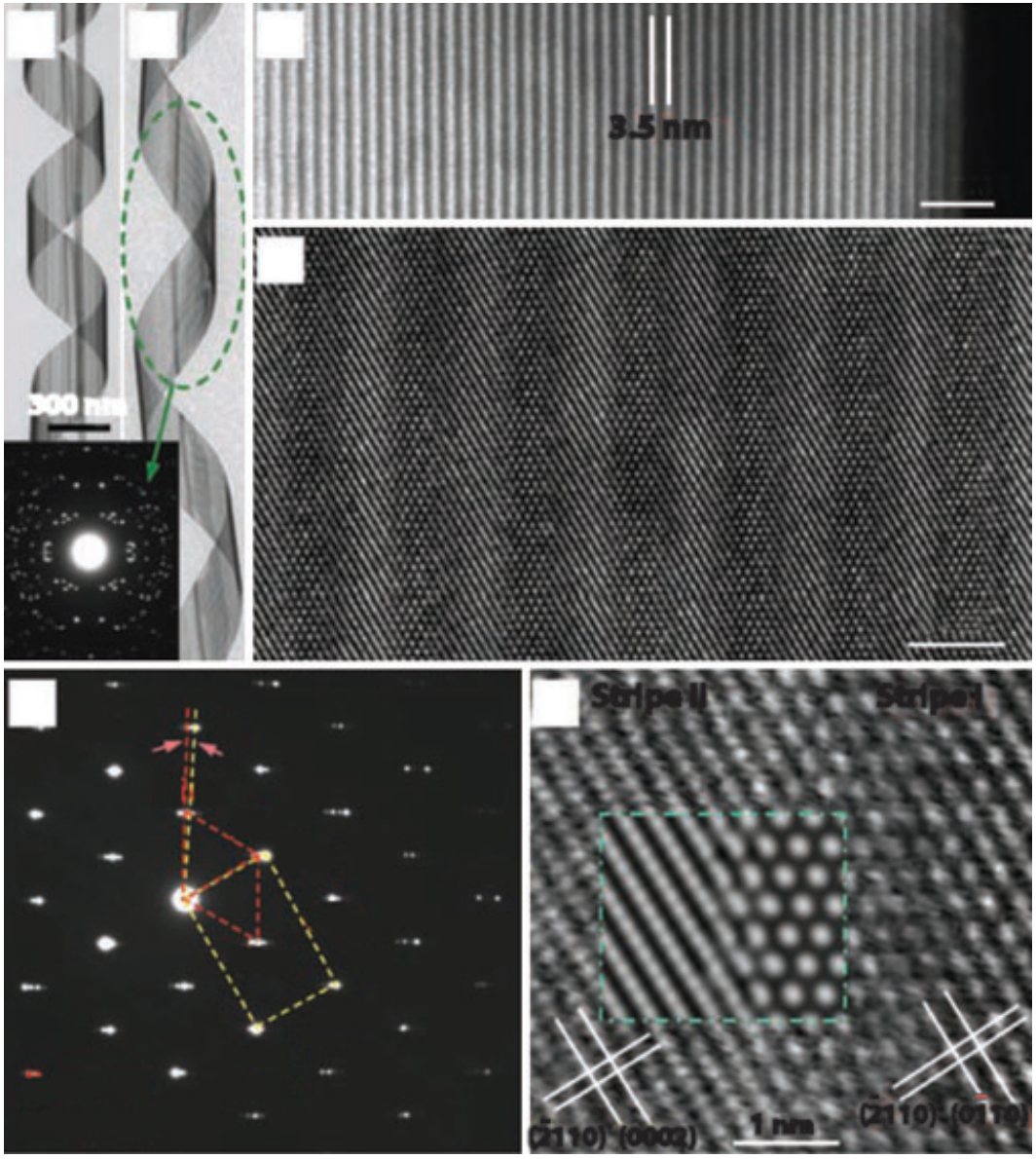


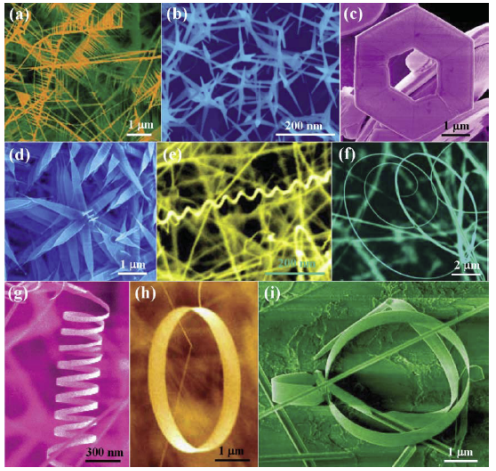
(a) $t = 10\,s$ (b) $t = 30\,s$ (c) $t = 180\,s$

Figure 4-22. Damage to a MWNT by electron beam exposure during TEM imaging (JEOL-2011 at 200 keV). Scales 5 nm.

A.J. Hart, Ph.D. thesis, 2006.

TEM characterization of ZnO helices

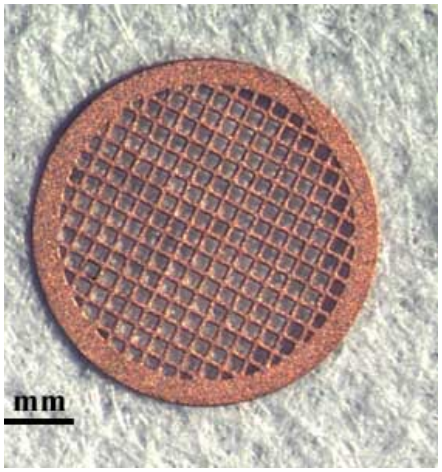


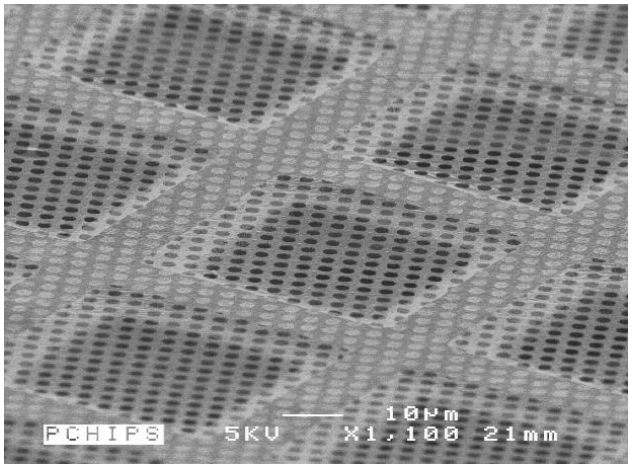


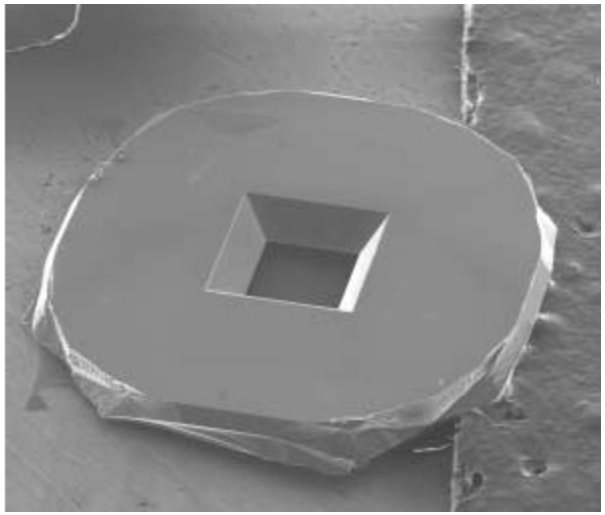
Gao et al., *Science* 309:1700-4, 2005.

TEM sample preparation

- Grid, typically 3 mm diameter
- Membrane (< 10 nm thick) often suspended over grid
- Fabricate thin sections by ion milling or microtoming

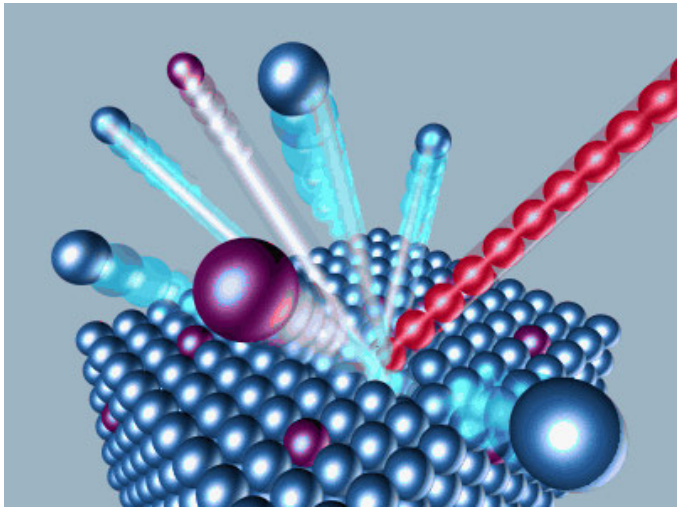






various online sources: e.g., Quantifoil, SPI

Sample prep using a focused ion beam (FIB)



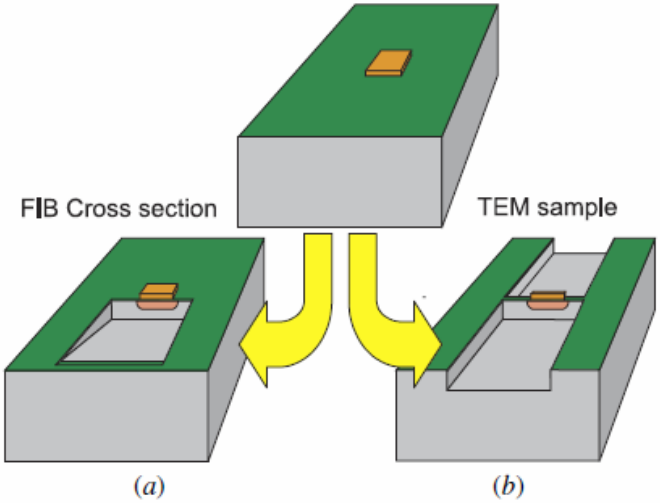
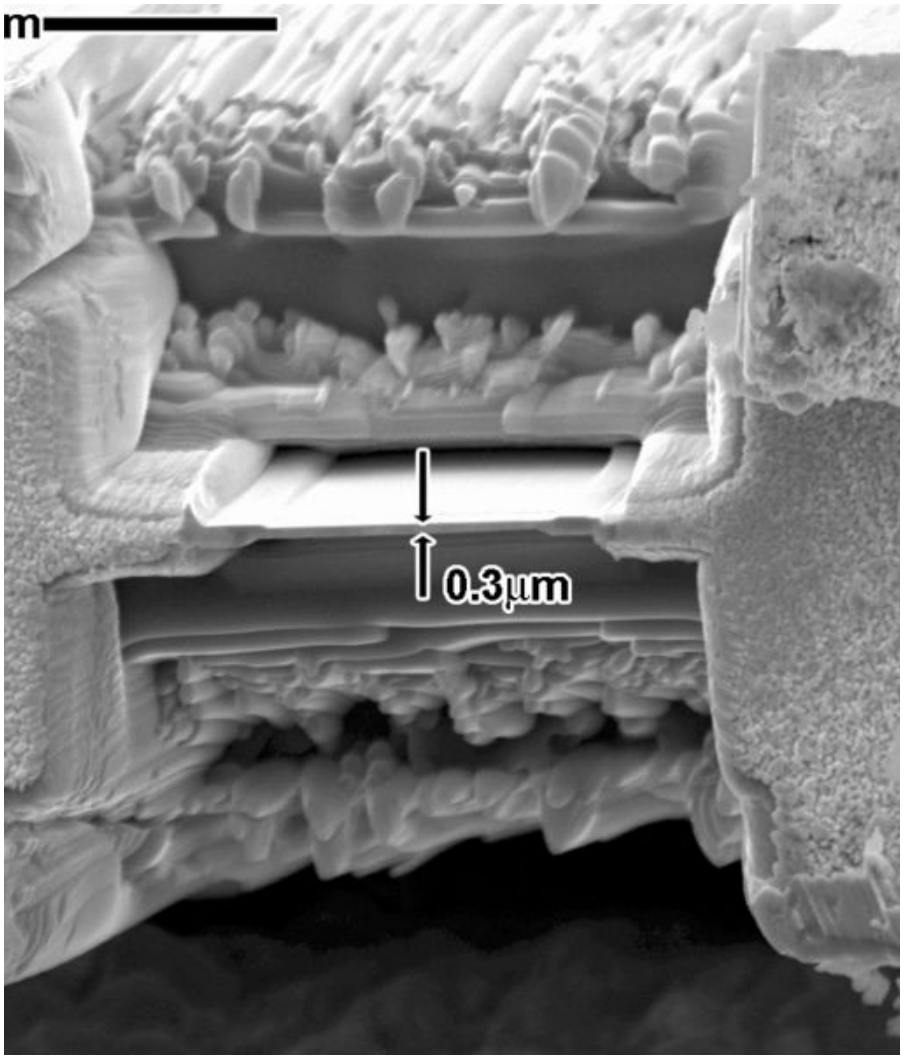


Figure 9. Sample with feature of interest can be (*a*) cross sectioned in the FIB. The section can be advanced until desired feature appears or (*b*) it can be prepared for inspection in a TEM.

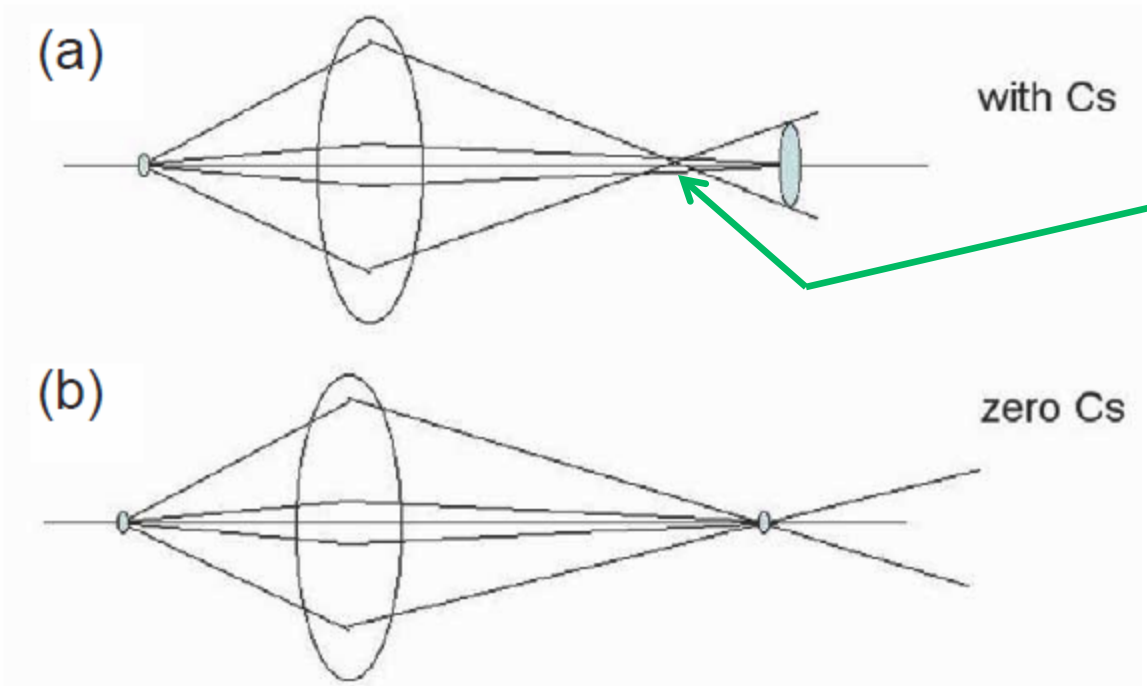


http://commons.wikimedia.org/wiki/Image:Fib_tem_sample.jpg

Reyntjens and Puers, J. Micromechanics and Microengineering, 11:287-300, 2001.

Lens aberrations determine the practical resolution limit

- It's difficult to eliminate aberrations in metallic lenses

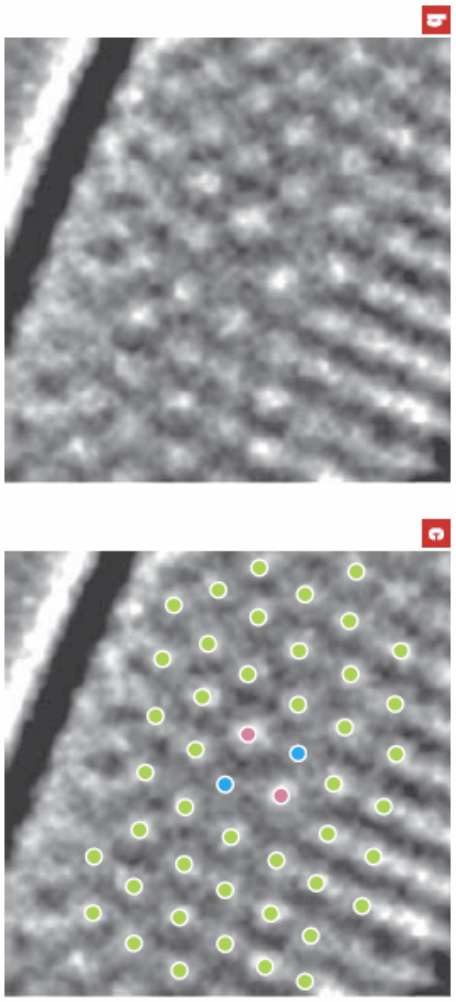


Rays focus at different points
-due to non-uniformities in focusing fields, diffraction at apertures

Fig. 1 (a) In a standard electron lens with spherical aberration, rays at different angles to the optic axis are brought to a focus at different points. (b) The effect of correcting the spherical aberration is to bring all rays into focus at the same point. The small blue area on the right of the lens represents the aberration disc.

Hetherington, Materials Today, December 2004.

Aberration-corrected TEM can show individual atoms (0.1 nm resolution)



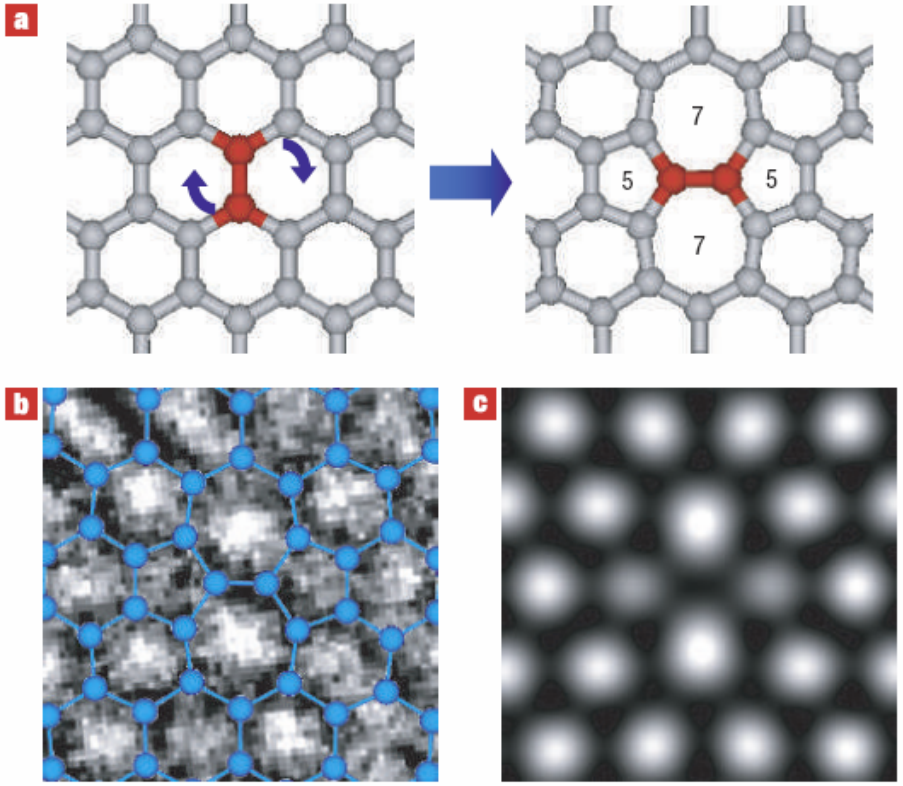
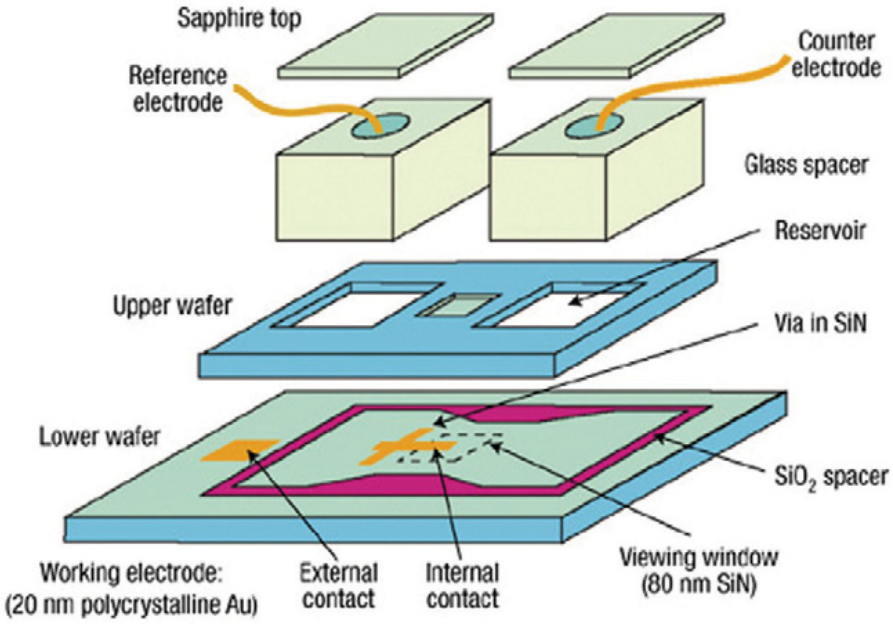
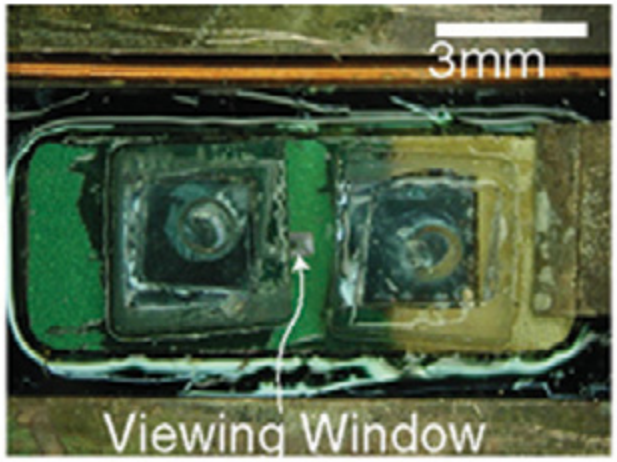


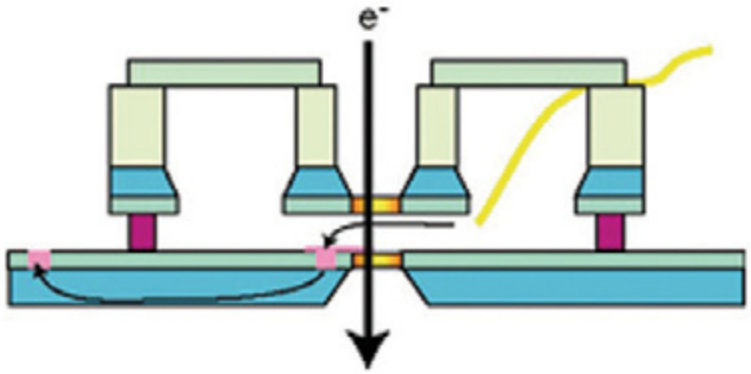
Figure 2 Atomic arrangement of the Stone–Wales (SW) model. a, The SW transformation leading to the 5–7–7–5 defect, generated by rotating a C–C bond in a hexagonal network. **b**, HR-TEM image obtained for the atomic arrangement of the SW model. **c**, Simulated HR-TEM image for the model shown in **b**.

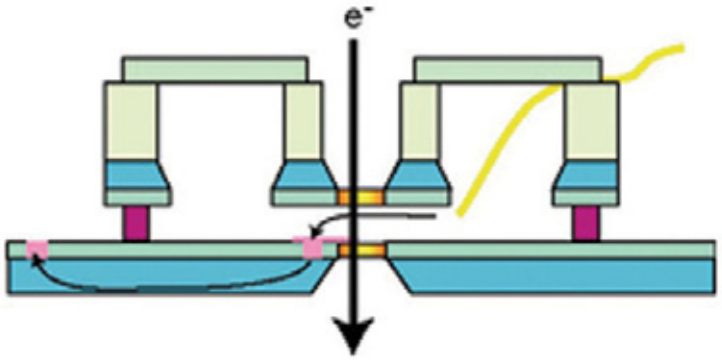
Suenaga et al., Nature Nanotechnology, 2:358, 2007.

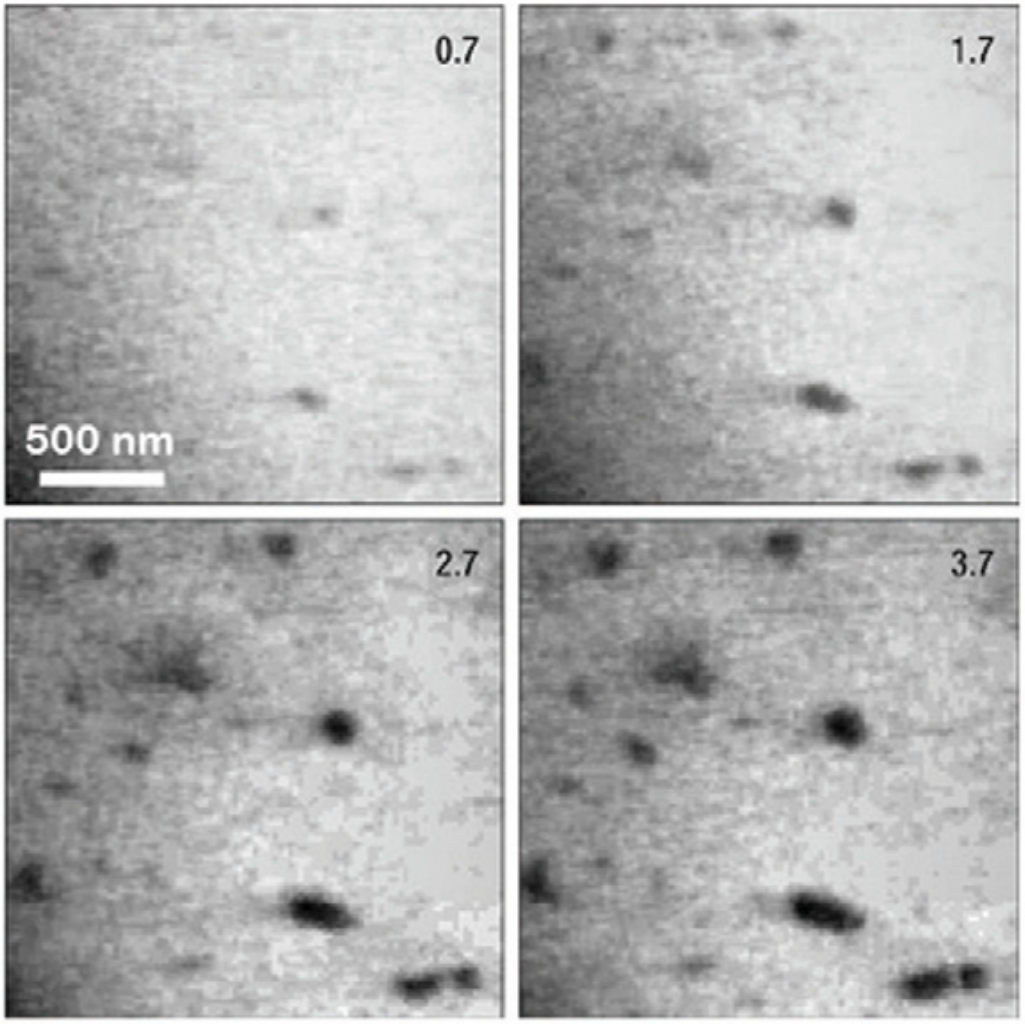
Environmental TEM (E-TEM) shows material dynamics





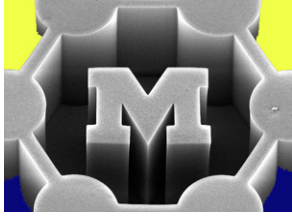




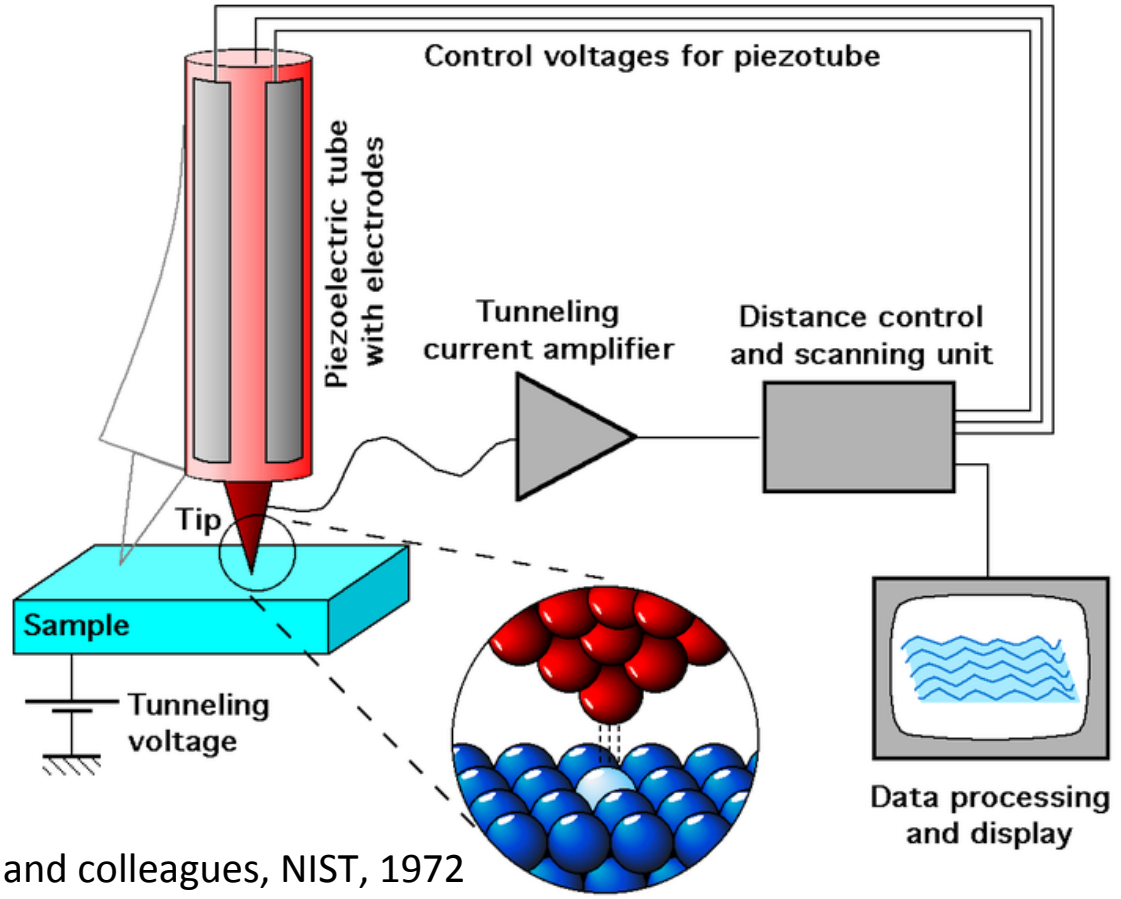


A sequence of images of the nucleation and subsequent growth of individual Cu crystallites during galvanic deposition at 5 mA/cm2. The numbers in the upper right-hand corner indicate the number of seconds after the initiation of the current flow.

Scanning tunneling microscopy (STM)



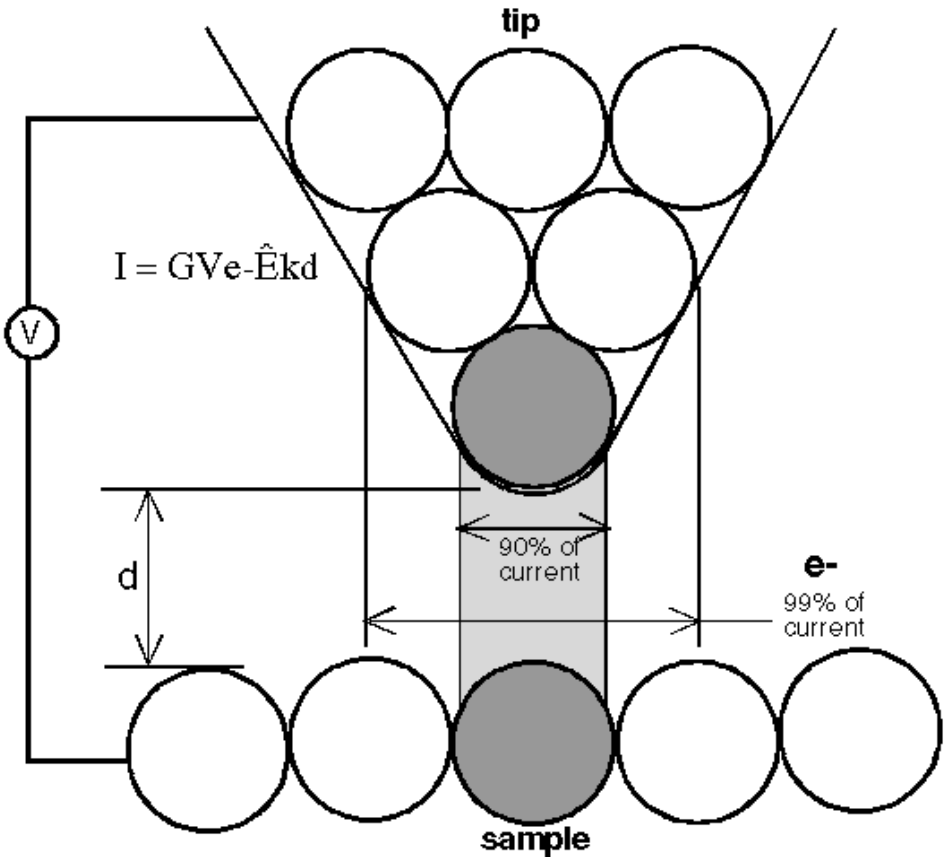
- First to give real-space atomic resolution images
- ~10A gap between conductive tip and conductive sample, using tunneling (exponential) current to measure displacement

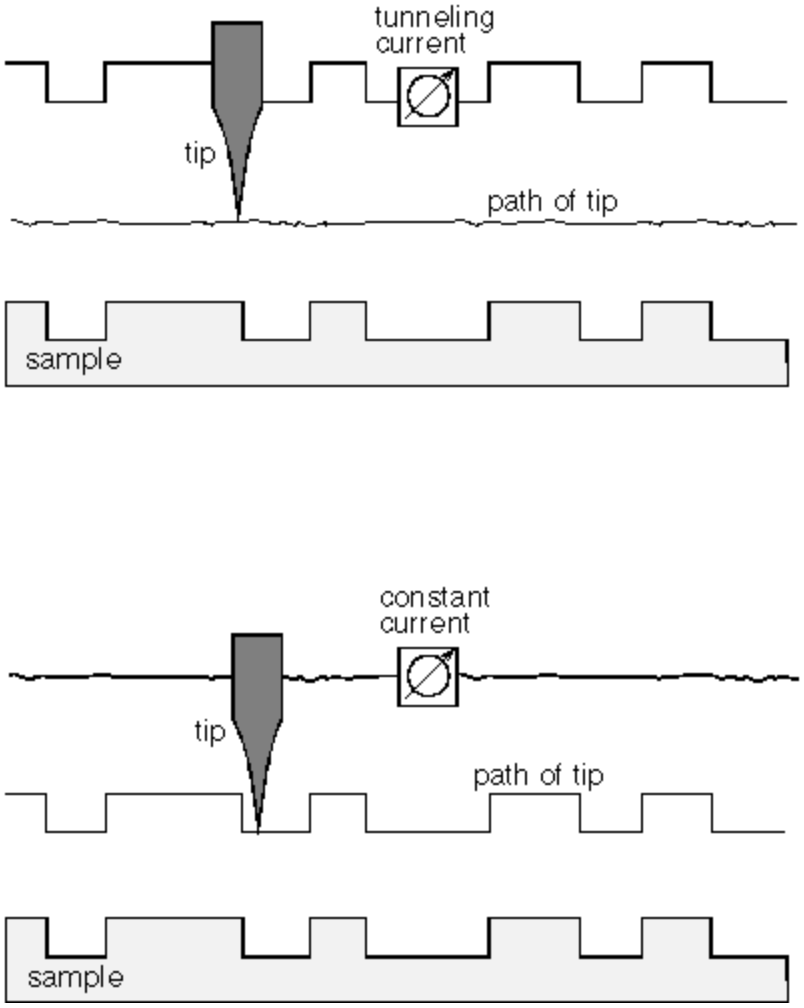


"topografiner" invented by Young and colleagues, NIST, 1972
http://nvl.nist.gov/pub/nistpubs/sp958-lide/214-218.pdf

Binnig and Rohrer (IBM), Nobel Prize, 1986

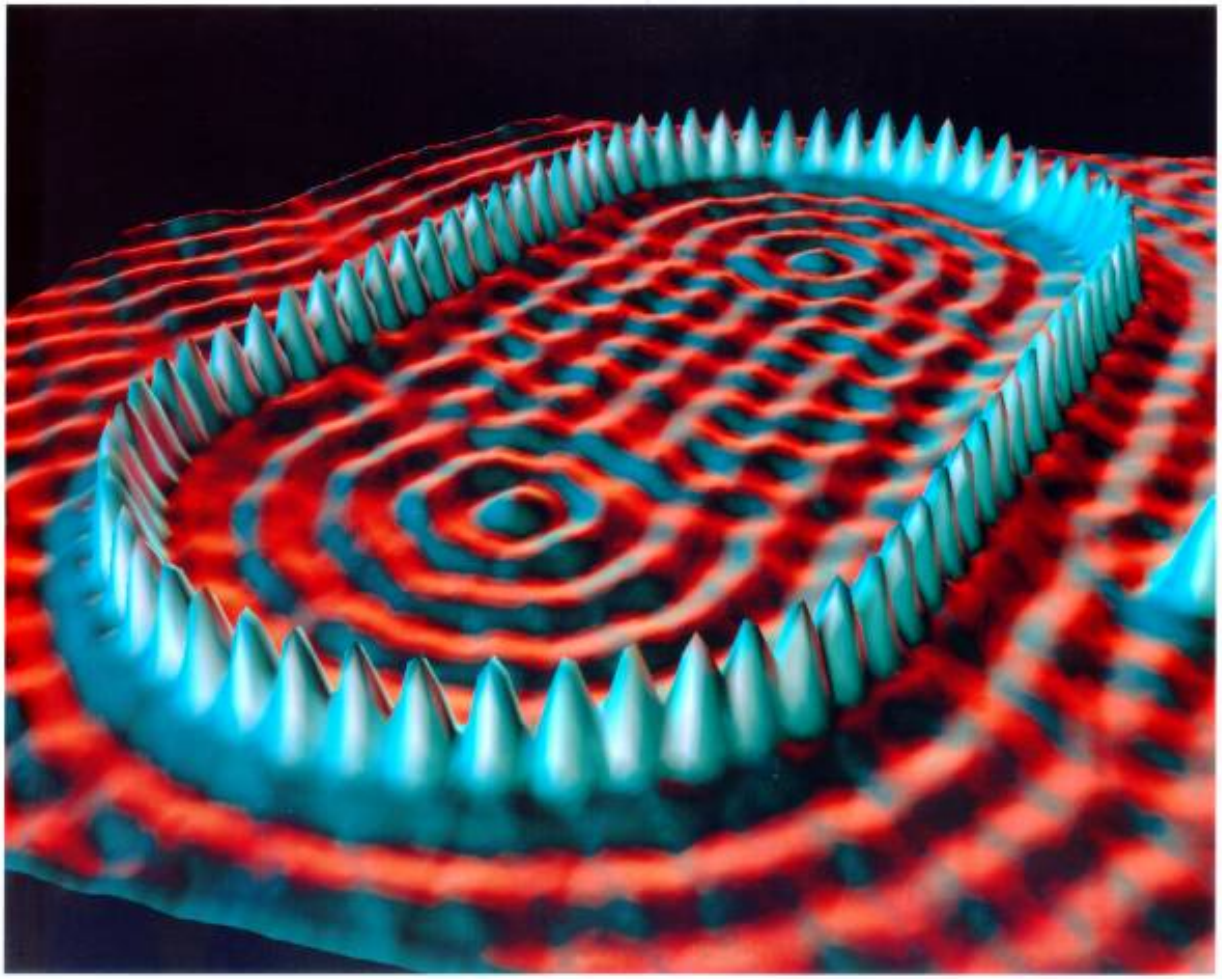
STM: scanning modes





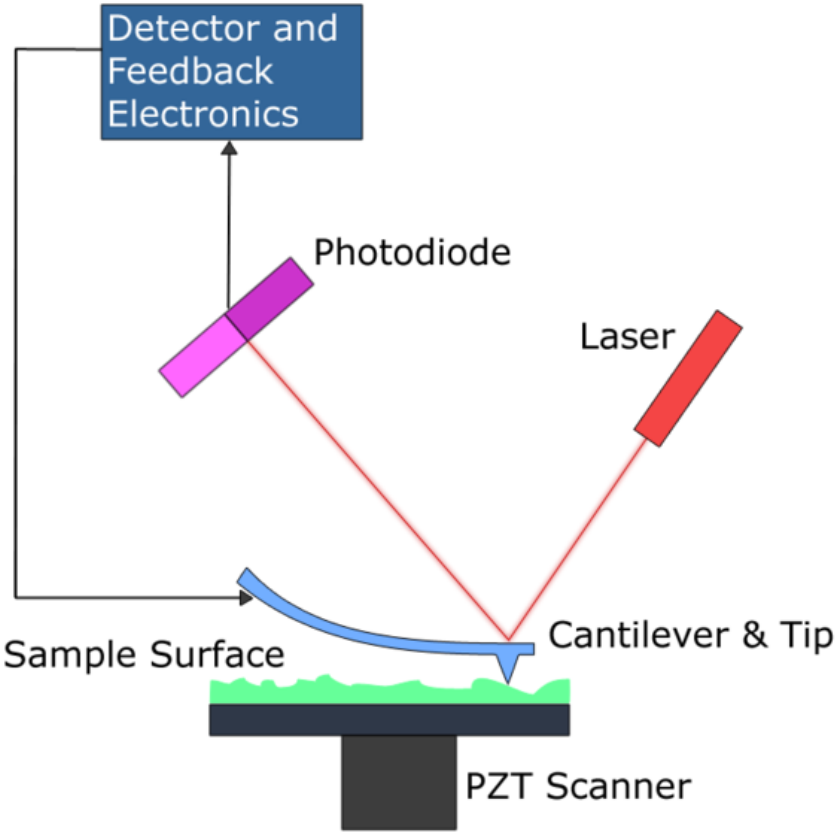
invented by Young and colleagues, NIST, 1972
Binnig and Rohrer, Nobel Prize, 1986
Figure from park.com, A practical guide to scanning probe microscopy

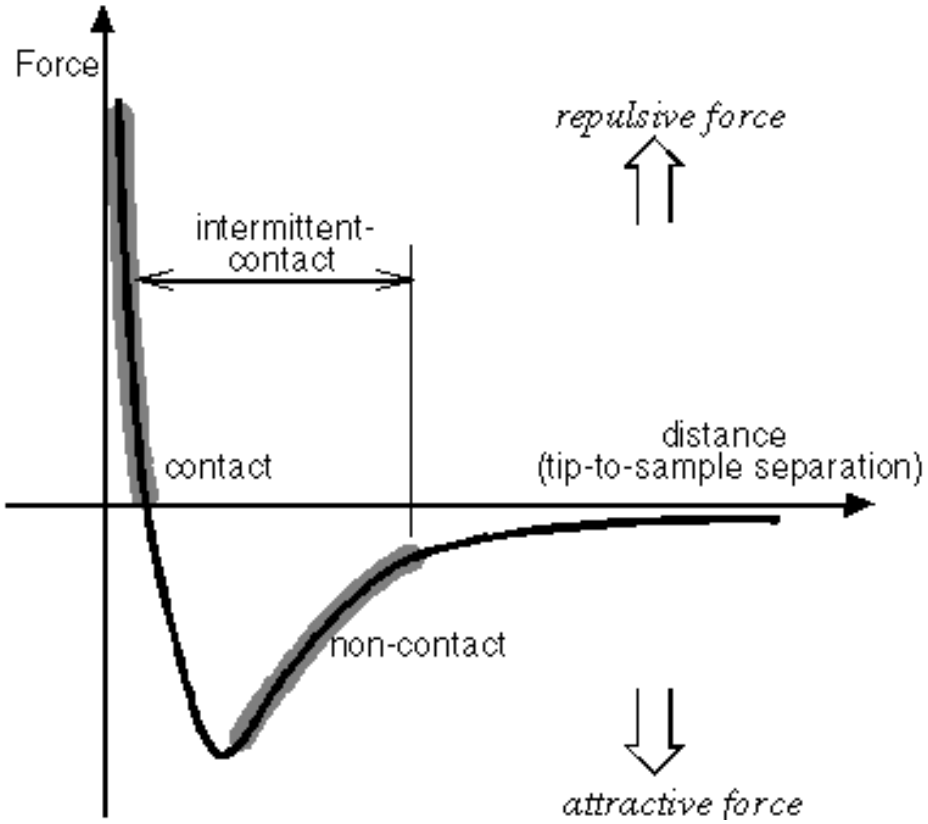
Quantum corral



Crommie et al., Science 262:218-220 1993.

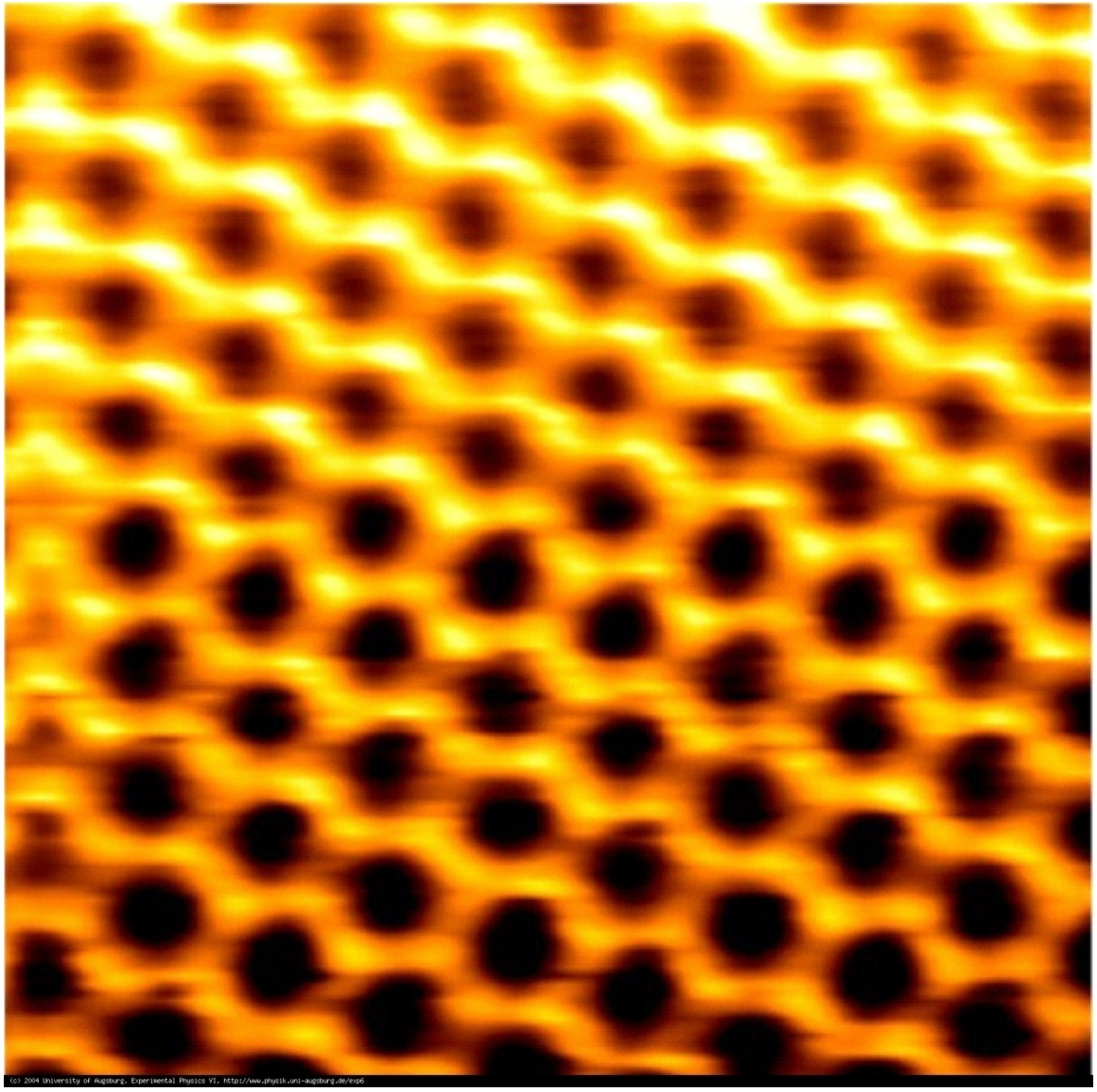
Atomic force microscopy





invented by Young and colleagues, NIST, 1972
Binnig and Rohrer, Nobel Prize, 1986
Park.com, A practical guide to scanning probe microscopy

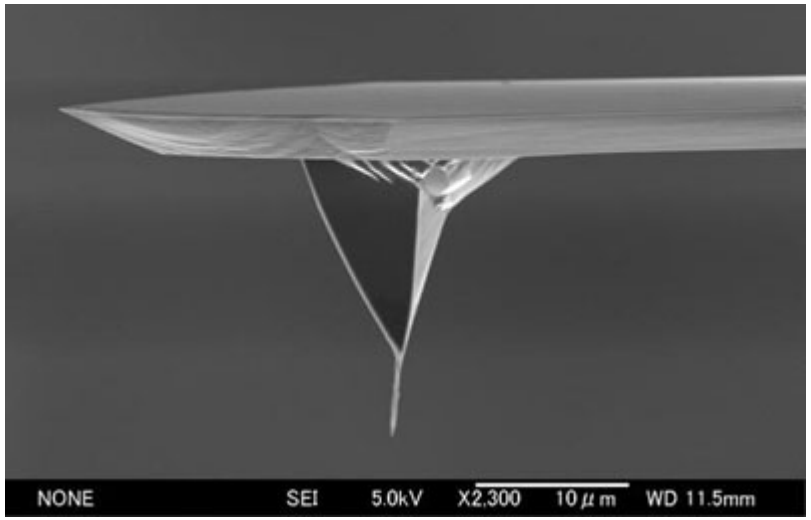
AFM image of graphite



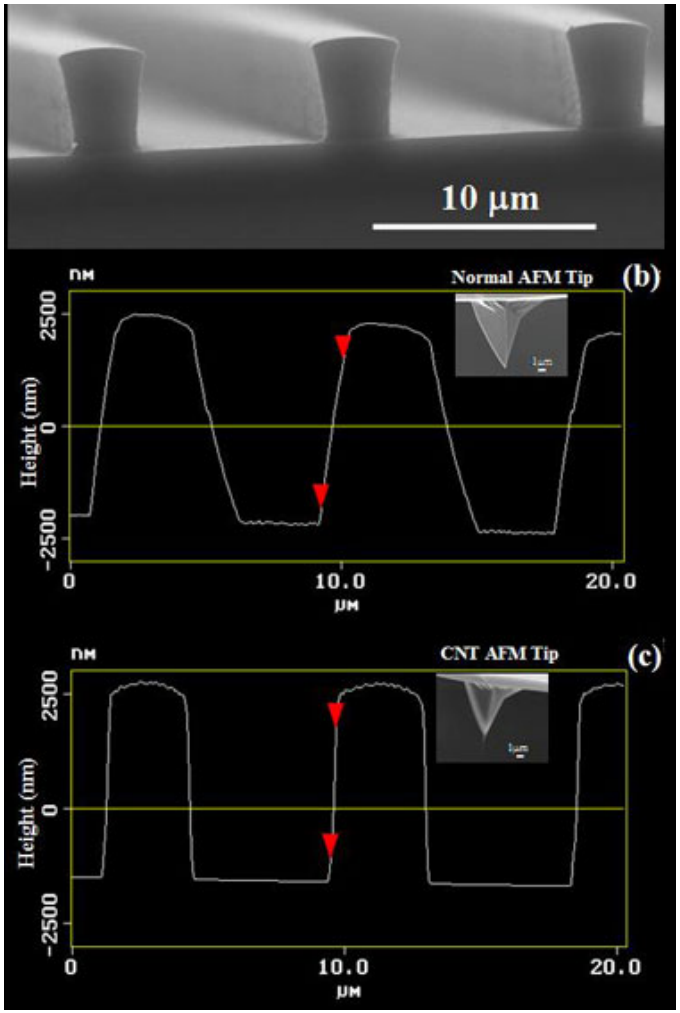
http://www.physik.uni-augsburg.de/exp6/imagegallery/afmimages/afmimages_e.shtml

AFM cantilevers and tips

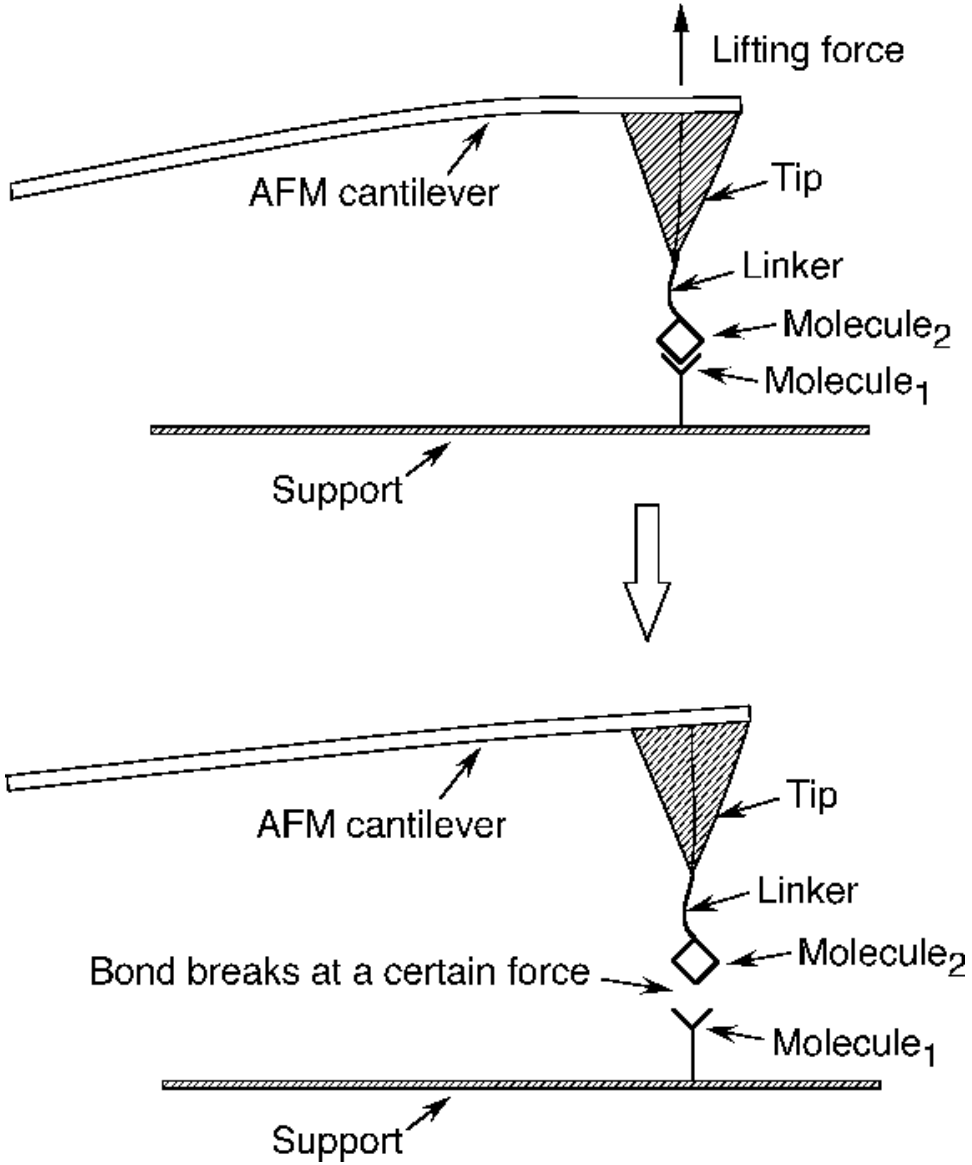
- Etched pyramids
- Oxide/etch sharpening
- Growth of nanostructured tips

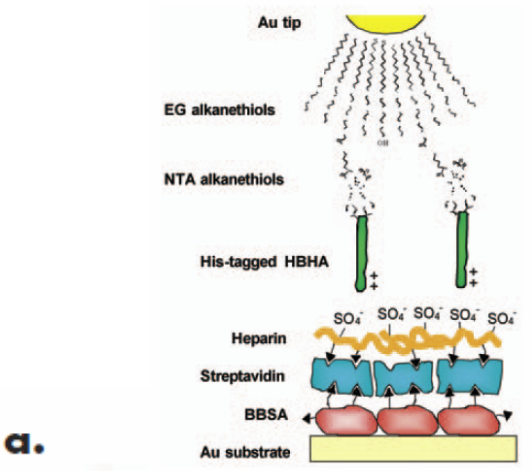


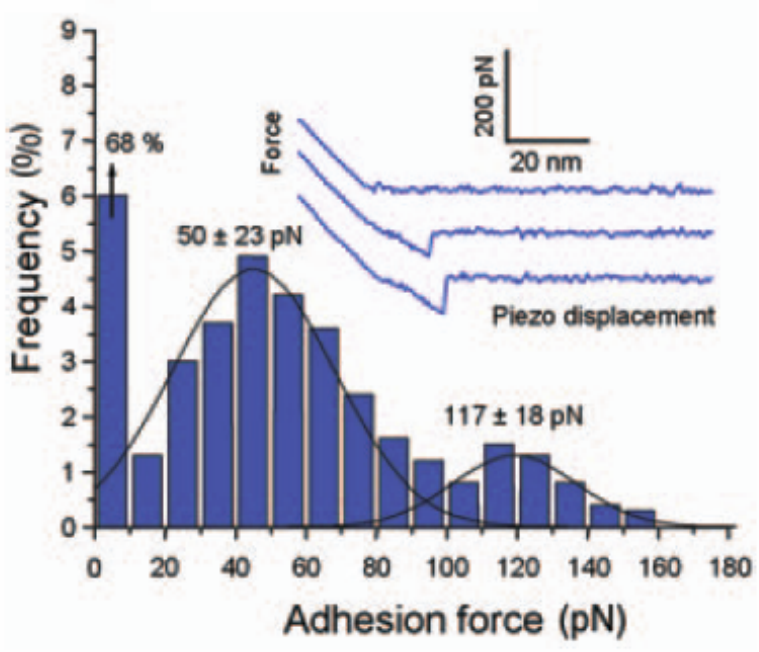
Tip/sample convolution



Actuating single molecules using AFM







http://www.pitb.de/nolting/biophysics_methods/nanobiotech.html
http://www.veeco.com/pdfs/appnotes/AN92-BacterialAdhes_02176_rf_251.pdf

High-speed (video-rate) AFM

- Key: resonant scanning in two axes

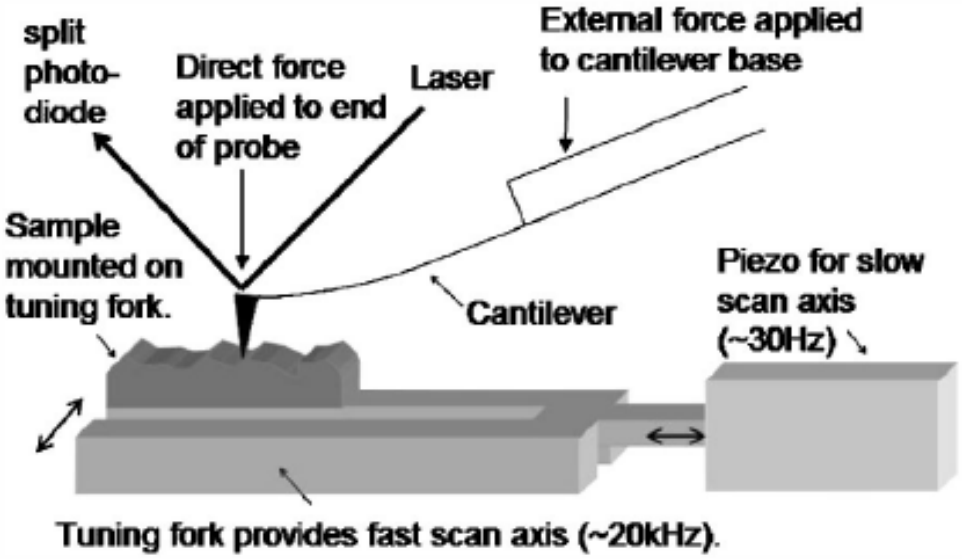


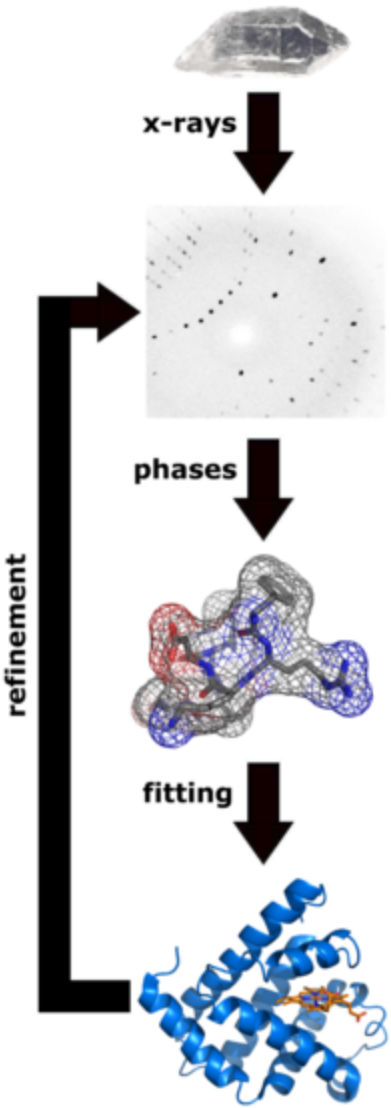
FIG. 1. A schematic of the HSAFM. The sample is mounted on a quartz crystal resonator that generates the fast scan axis and is driven in the orthogonal slow scan axis by a piezo actuator. An optical lever is used to measure the deflection of the microcantilever. An additional "direct force" is applied to the end of the cantilever, forcing the tip to maintain contact with the surface. By tuning the magnitude of the "direct force" and the degree of damping of the cantilever, a high bandwidth passive feedback loop is created.

VIDEOS

http://www.infinitesima.com/VideoAFM-download.html

http://www.s.kanazawa-u.ac.jp/phys/biophys/roadmap.htm

Structure determination using X-rays

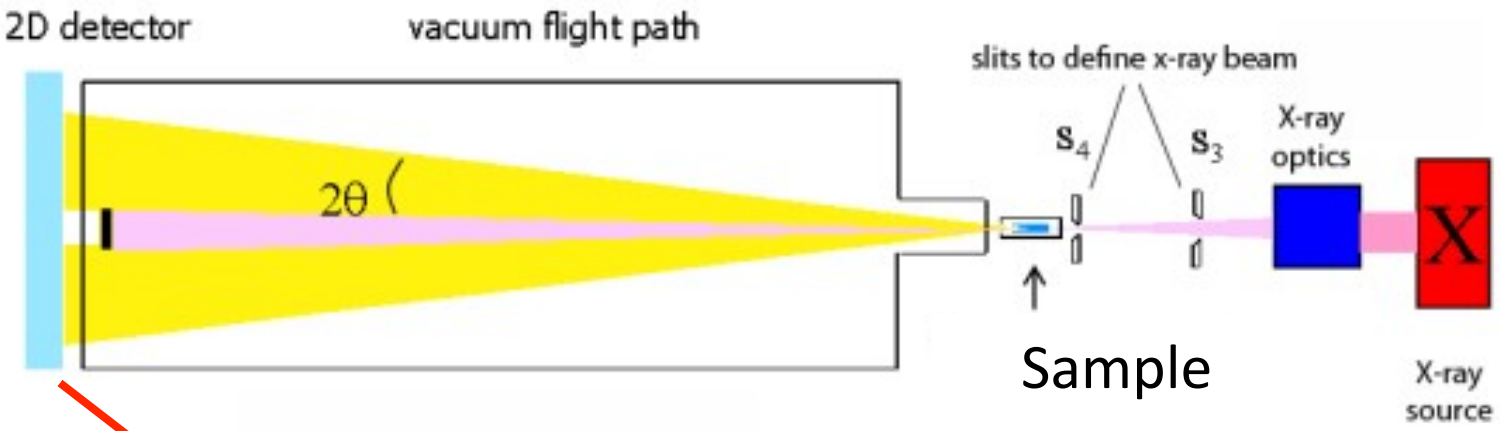


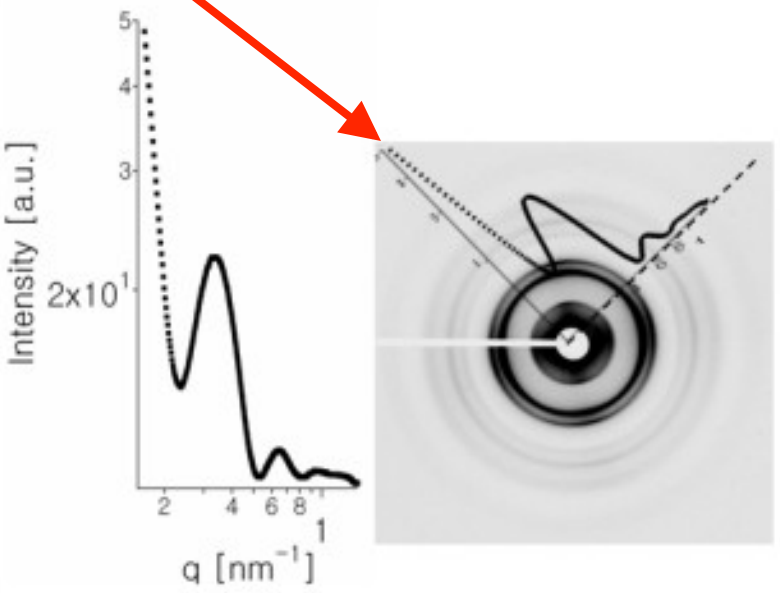
Reciprocal space

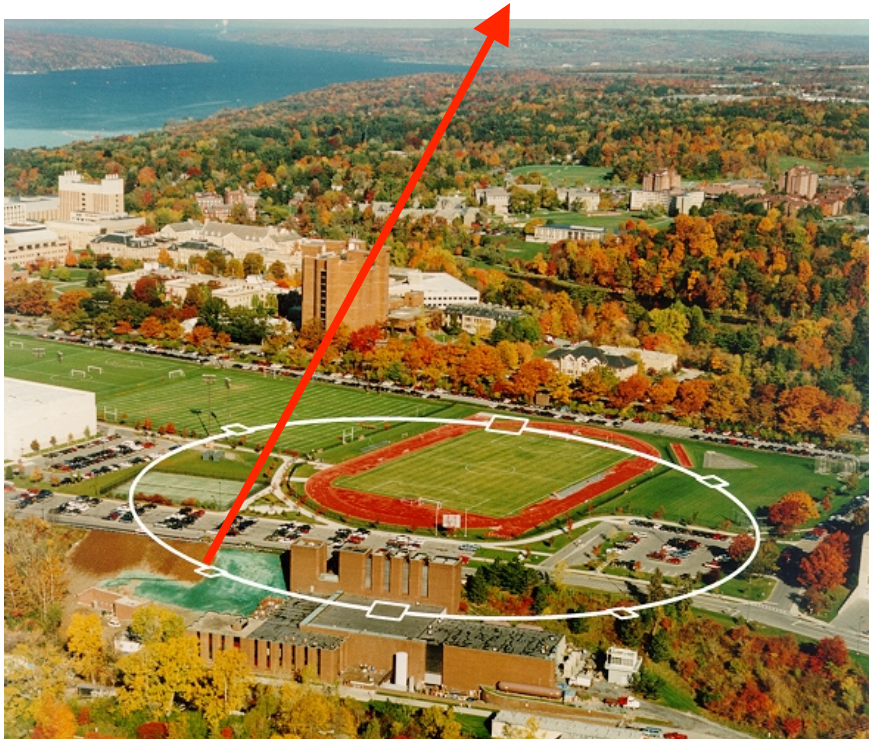
Real space

http://en.wikipedia.org/wiki/X-ray_crystallography

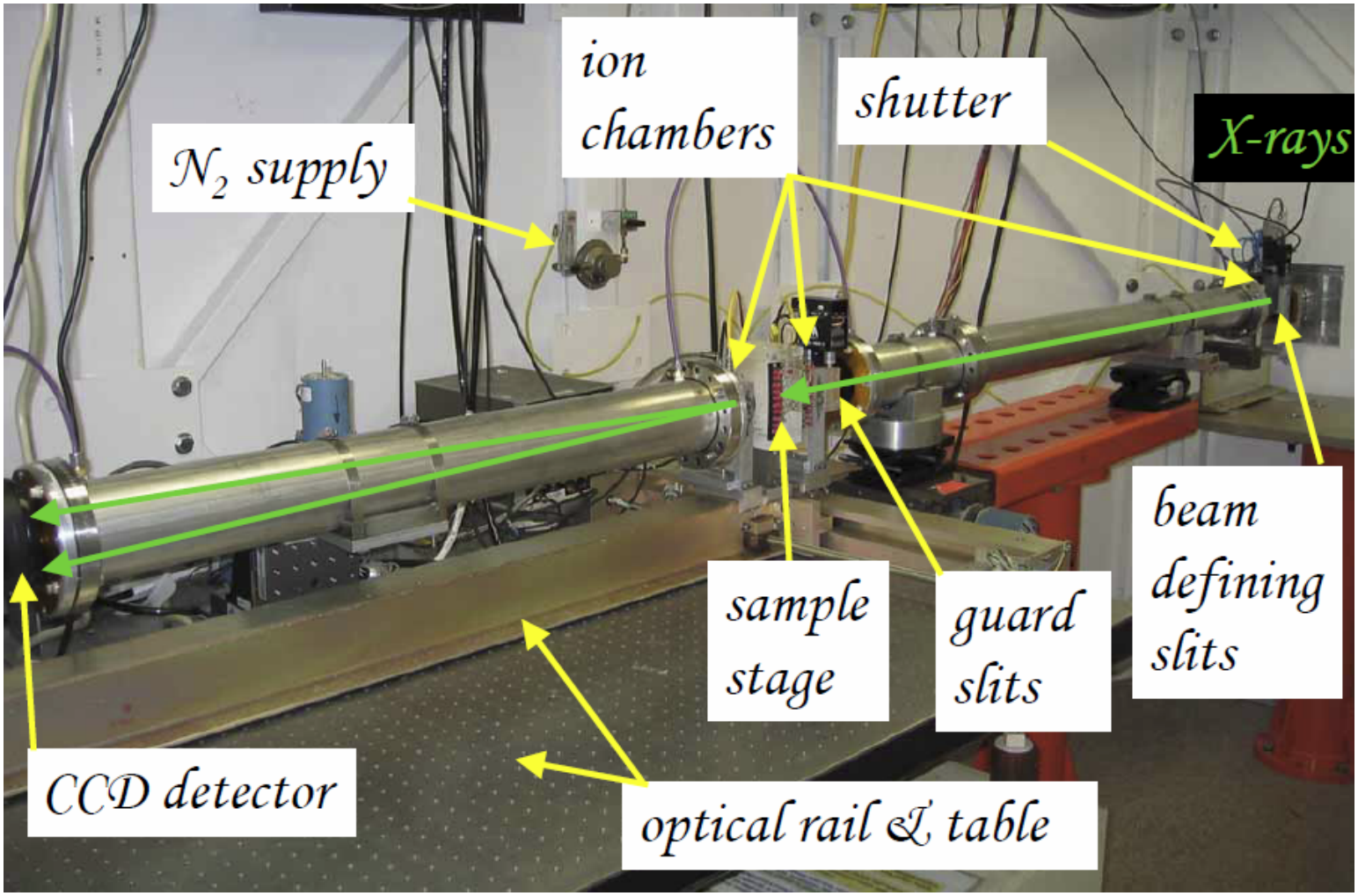
X-ray scattering (diffraction)







Typical SAXS beamline



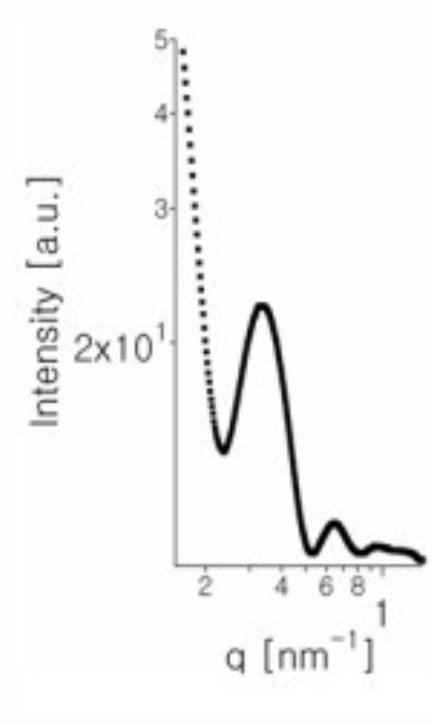
http://www-ssrl.slac.stanford.edu/conferences/workshops/scatter2006/talks/pople_saxs_work hop_060522.pdf

Scattering angles and feature sizes

Bragg's law:

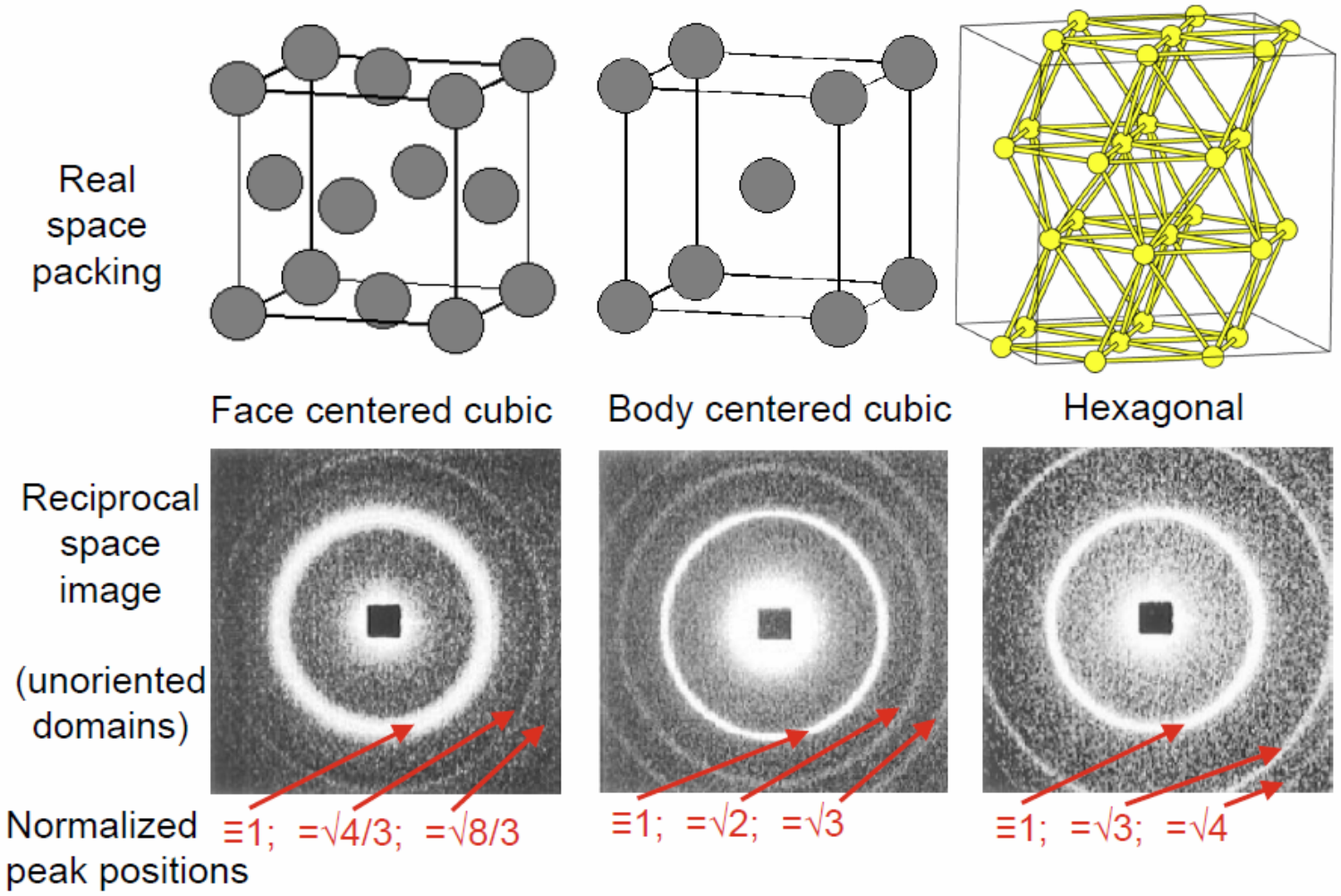
$$\lambda = 2d \sin\theta$$

$$q = \frac{2\pi}{d}$$



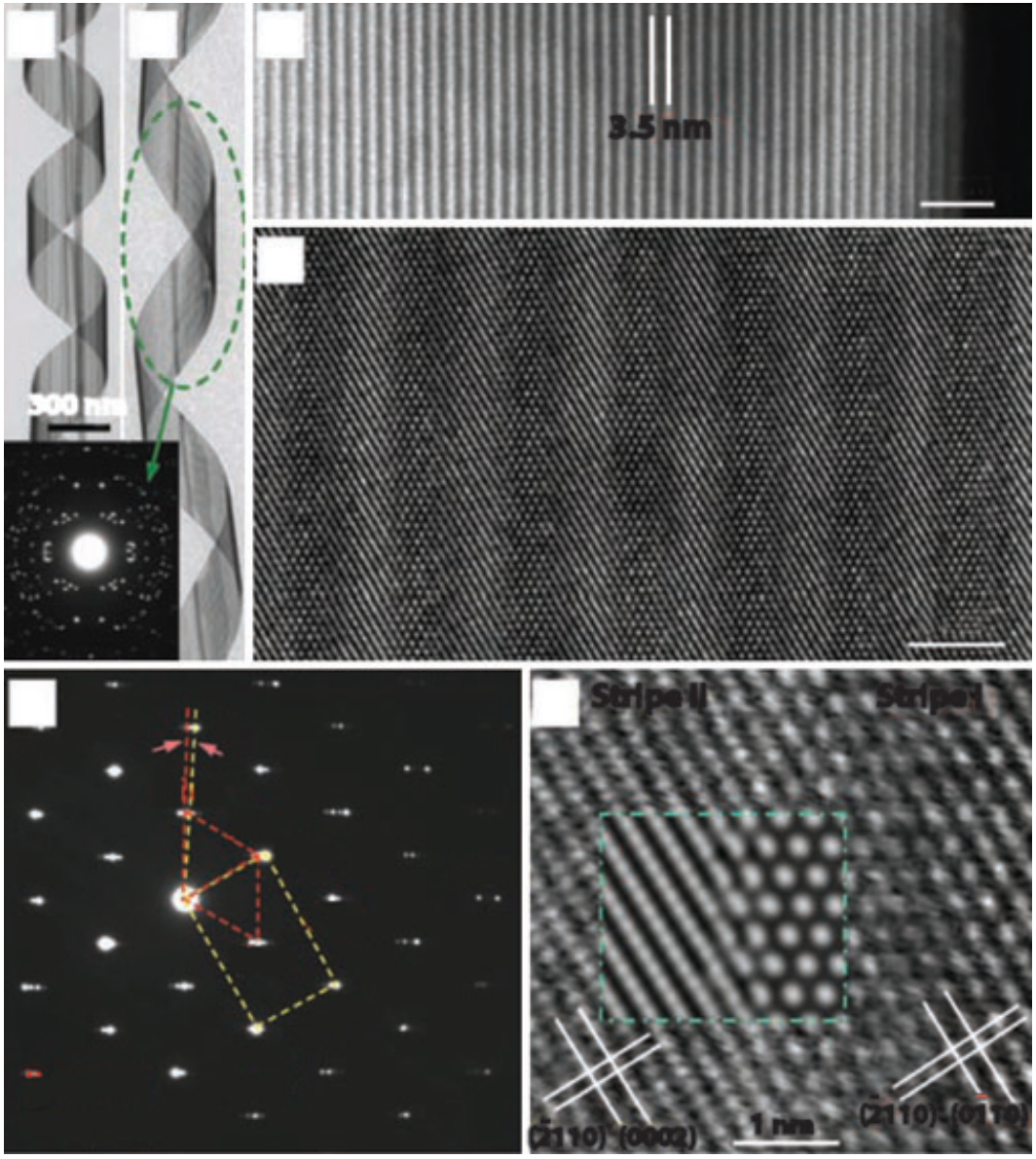
- Small-angle (SAXS): ~5-50 nm
- Wide-angle (WAXS): smaller features than SAXS, to lattice spacing and below
- Ultra small-angle (USAXS): larger features than SAXS, e.g., structure-structure interactions

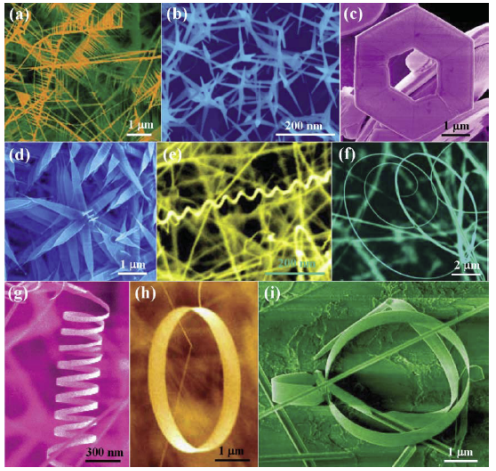
Diffraction rings → atomic spacings



http://www-ssrl.slac.stanford.edu/conferences/workshops/scatter2006/talks/pople_saxs_workshop_060522.pdf

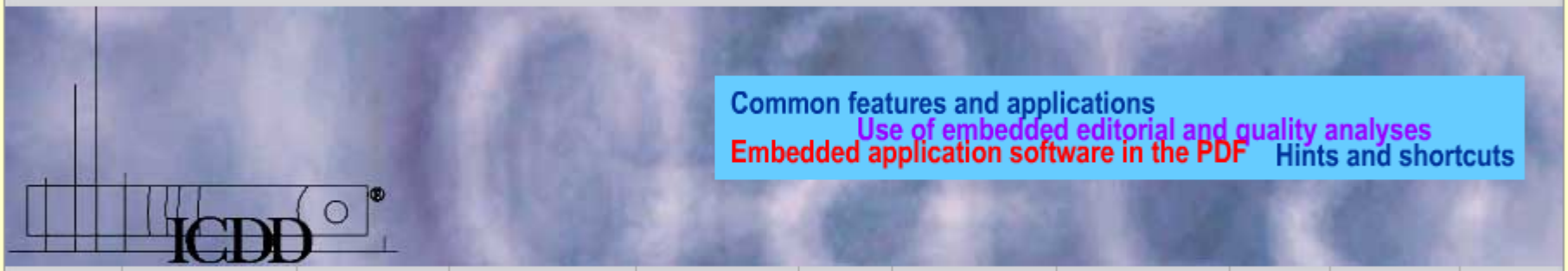
Electron diffraction in TEM





Gao et al., *Science* 309:1700-4, 2005.

ICDD
The International Centre for Diffraction Data



Frequently Visited Pages:

- **Events Calendar**
  - ICDD Events and Conference Schedule
- **Advances in X-ray Analysis**
- **2007 Public Report (PDF)**
- ***Powder Diffraction* Journal**
- **Grant-in-Aid Program**
- **ICDD Awards**
- **ICDD Product Tutorials**

The International Centre for Diffraction Data

ICDD

Our Mission and Vision

The International Centre for Diffraction Data® (ICDD®) is a non-profit scientific organization dedicated to collecting, editing, publishing, and distributing powder diffraction data for the identification of crystalline materials. The membership of the ICDD consists of worldwide representation from academe,

PPXRD-7

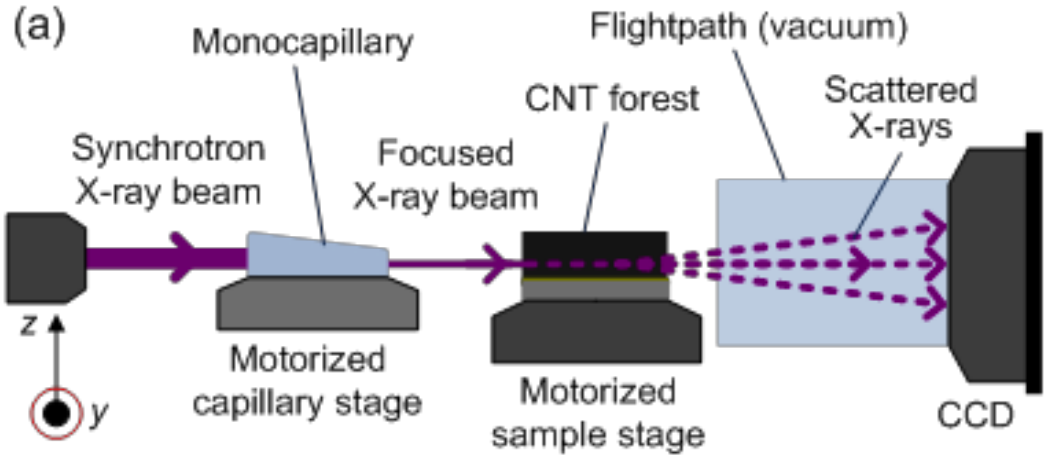
The 7th Pharmaceutical Powder X-ray Diffraction Symposium will be held in Orlando, FL, U.S.A.

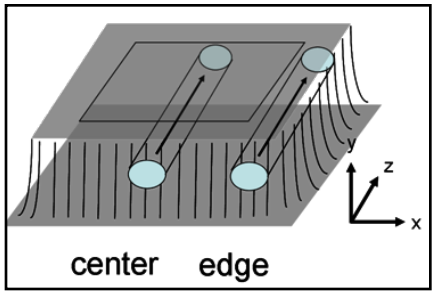
Learn more @ **www.icdd.com/ppxrd**

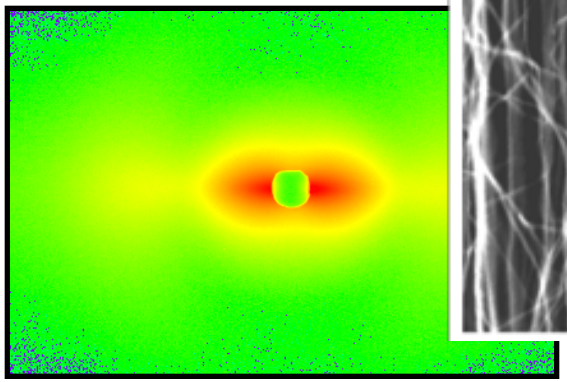
Upcoming Events:

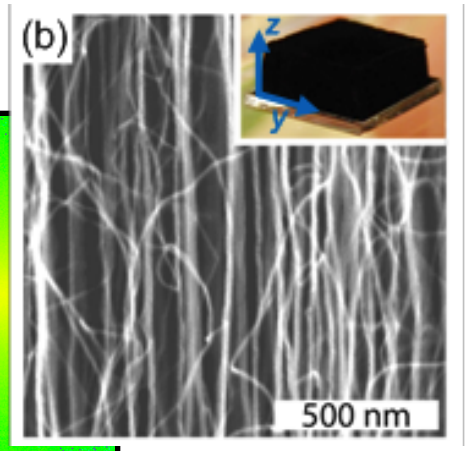
ICDD Clinics on X-ray Powder Diffraction - Session I - Fundamentals of X-ray Powder Diffraction: 2-6 June 2008

Characterizing CNT forests by SAXS

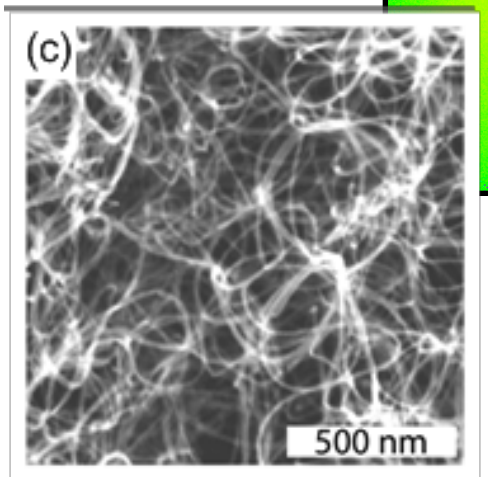


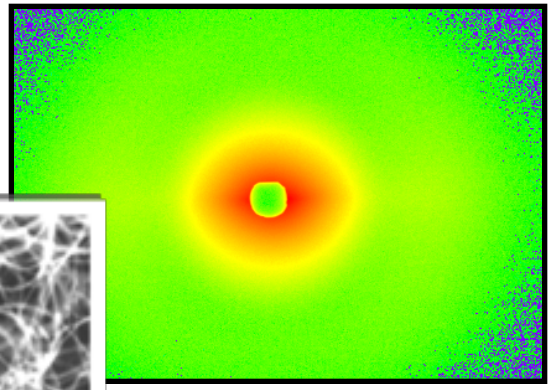






Aligned

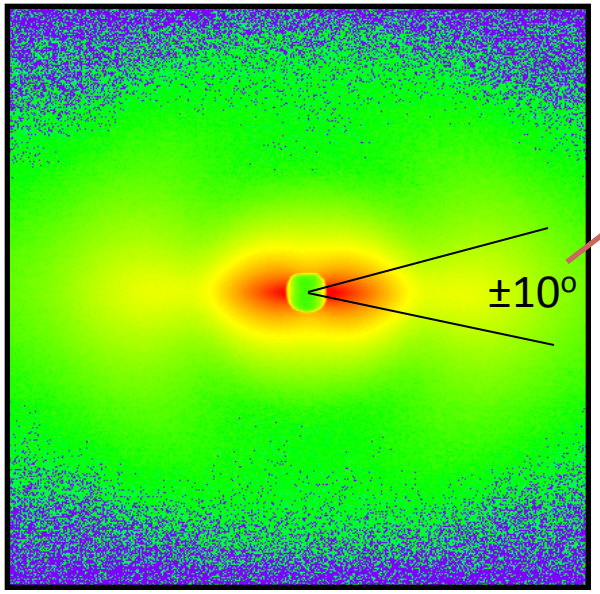




Unaligned

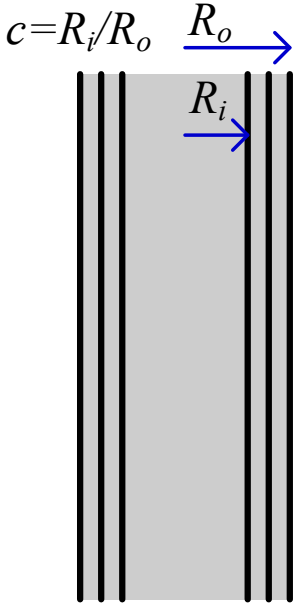
Bedewy, Meshot, Wang, Verploegen, Hart, et al.

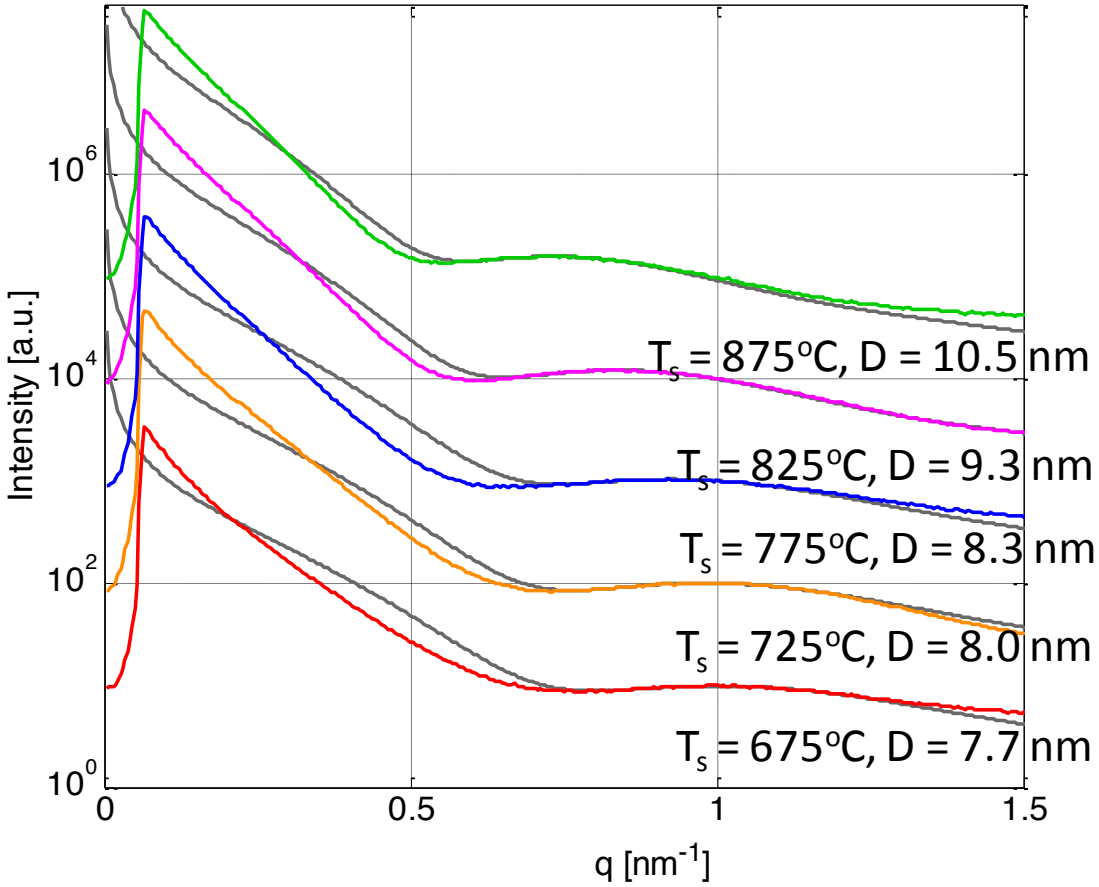
Measuring CNT diameter using SAXS



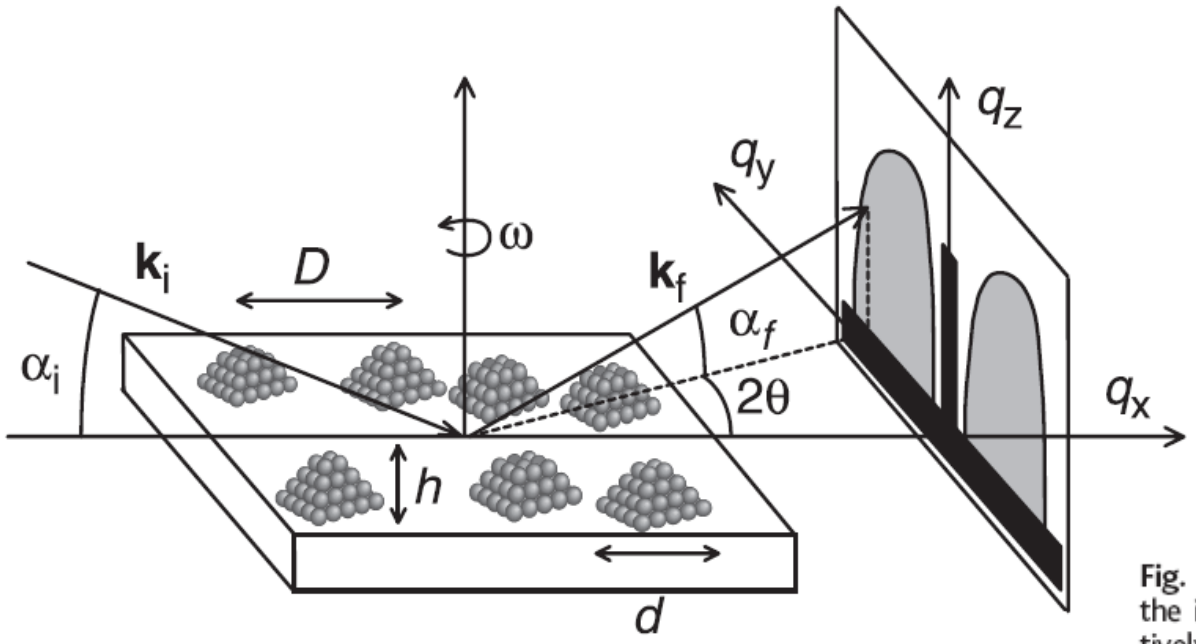
$$\int_{-\pi/18}^{\pi/18} I(q,\theta)\,d\theta$$

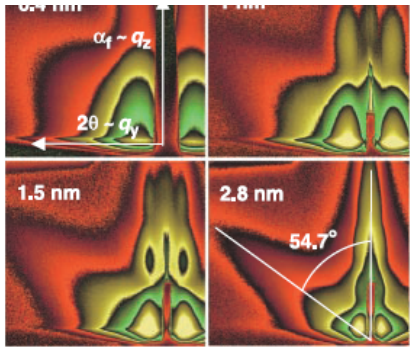
$$f(q,R_o) = \Delta\rho R_o \frac{2\{J_1(R_o q) - cJ_1(cR_o q)\}}{qR_o(1-c^2)}$$





Grazing incidence SAXS (GI-SAXS)





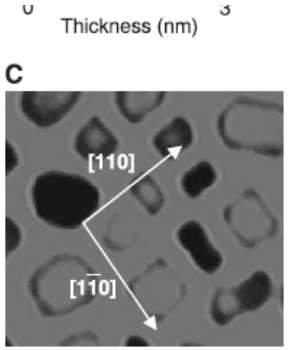
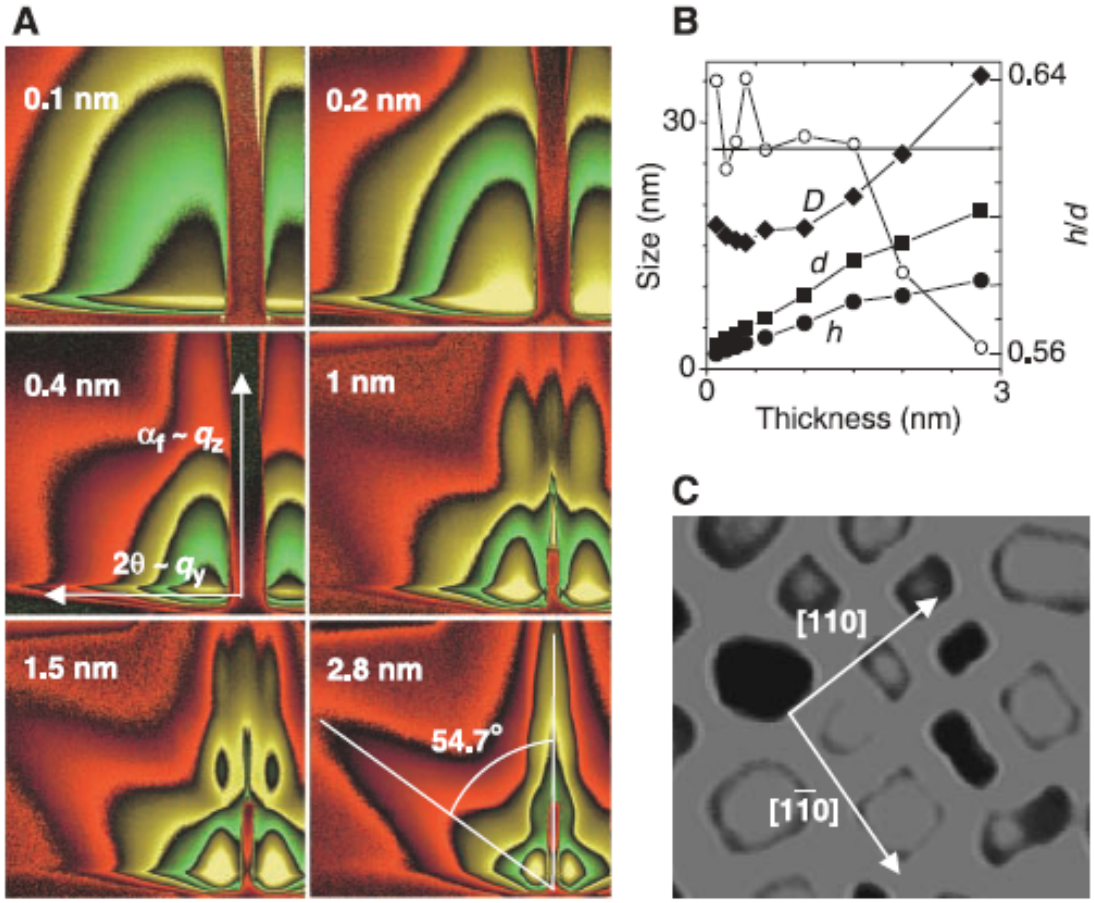


Fig. 1. The principles behind GISAXS. $\mathbf{k}_i$ and $\mathbf{k}_f$ are the incident and scattered wave vectors, respectively, yielding the momentum transfer (i.e., the reciprocal space vector) $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. The angles α_i, α_f, and 2θ are related to the components of the momentum transfer, either parallel (q_x and q_y) or perpendicular (q_z) to the sample surface, by the equations $q_x = |\mathbf{k}_i|[\cos 2\theta \cos\alpha_f - \cos\alpha_i]$, $q_y = |\mathbf{k}_i|[\sin 2\theta \cos\alpha_f]$, and $q_z = |\mathbf{k}_i|[\sin\alpha_f + \sin\alpha_i]$. Close to the origin in reciprocal space because they are small, the in-plane and out-of-plane scattering angles, 2θ and α_f scale with the components q_y and q_z of $\mathbf{q}$. The sample can be rotated around its surface normal by an ω rotation, which defines the orientation of the incident x-ray beam with respect to the in-plane crystallographic directions. A beam stop protects the bidimensional detector from the direct and reflected beams.

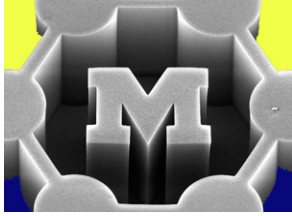
Renaud et al., Science 300:1416, 2003.

Grazing incidence SAXS (GI-SAXS)



Renaud et al., Science 300:1416, 2003.

Chemical analysis

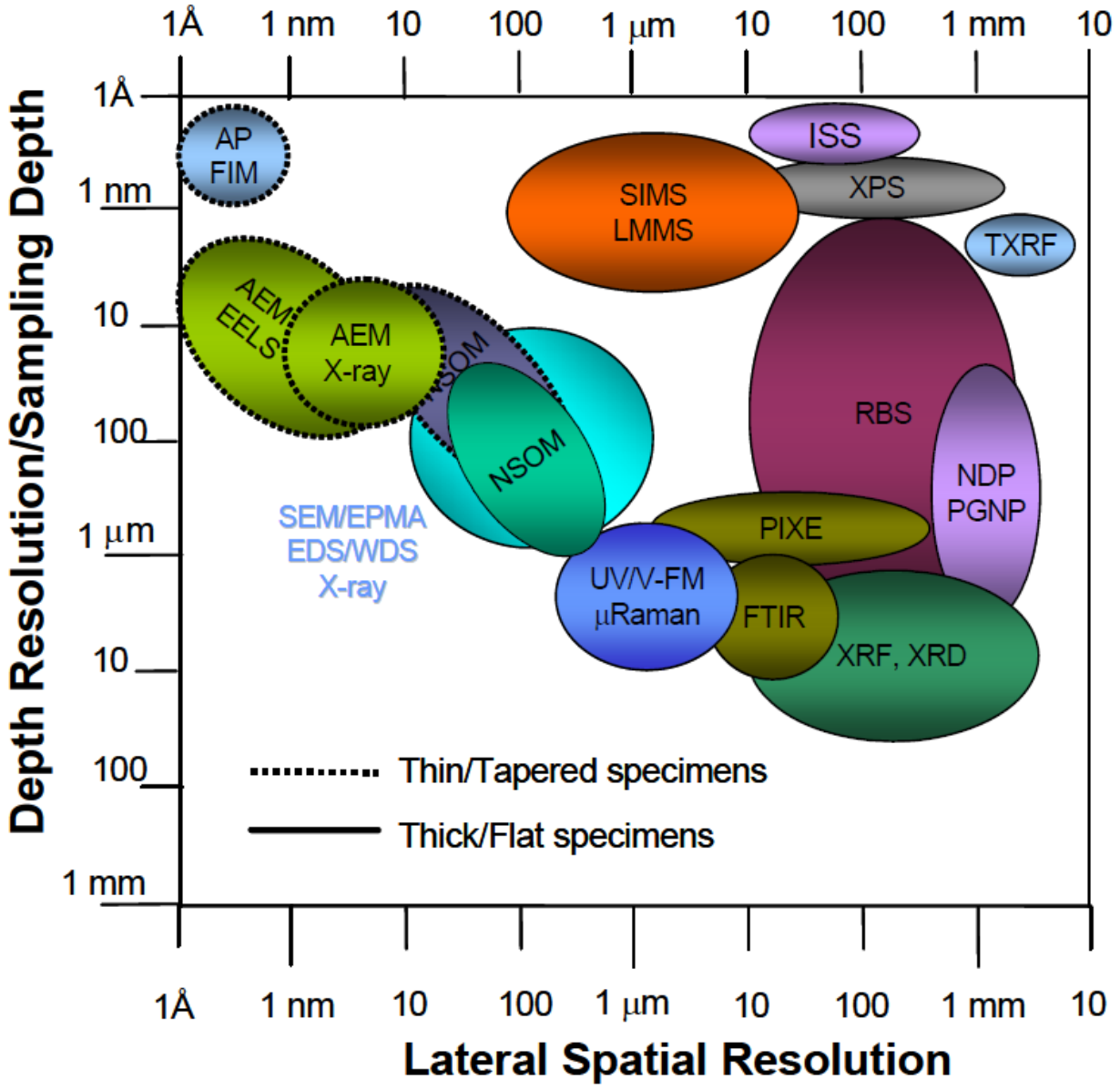


- **X-ray photoelectron spectroscopy (XPS)** → compounds
  - X-rays in, electrons out
- **Energy-dispersive X-ray spectroscopy** → elements
  - electrons in, X-rays out
- Auger electron spectroscopy → elements
  - Electrons in, electrons out

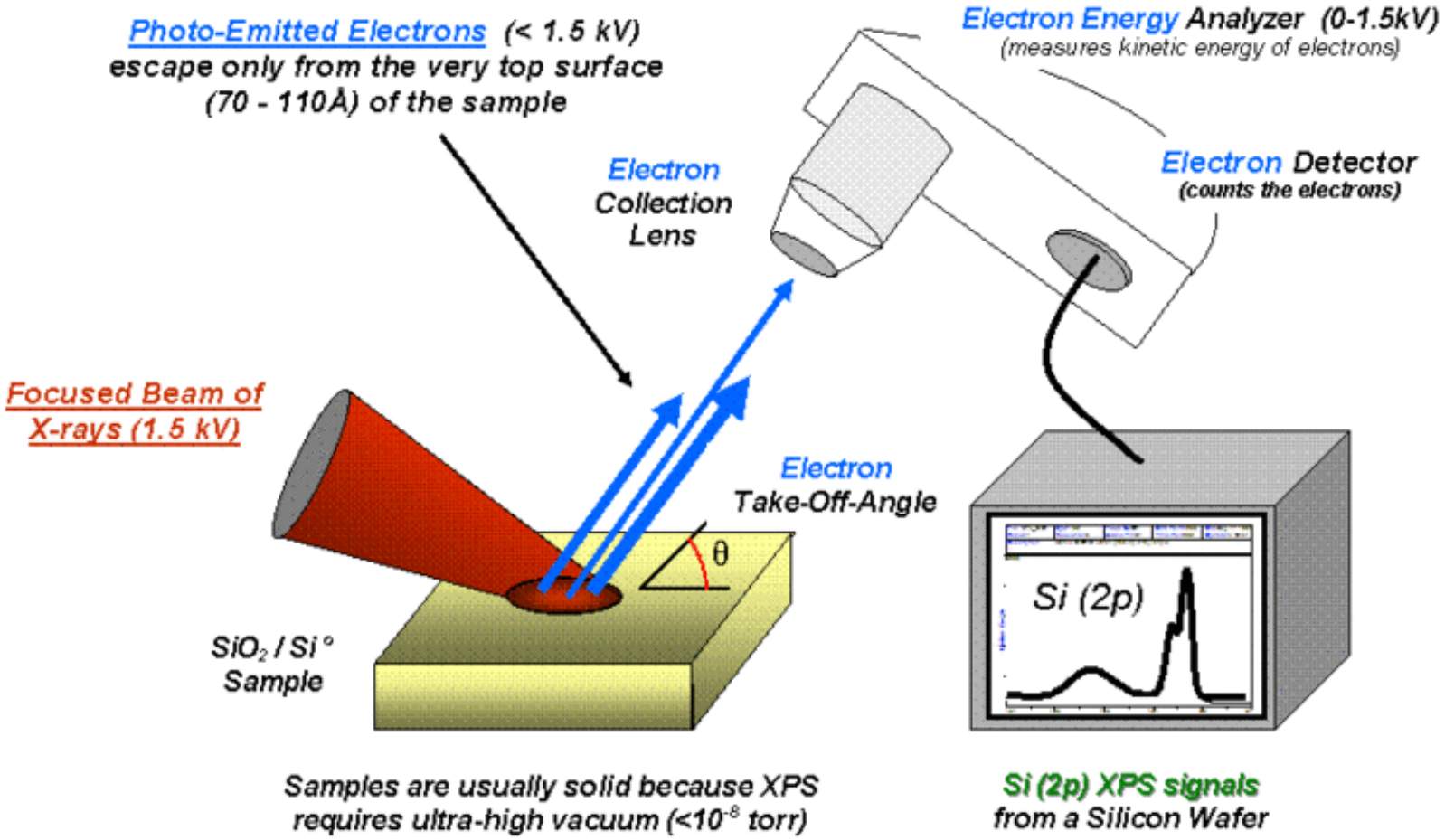
- **Optical spectroscopy: peak → vibrational mode**
  - Resonant Raman spectrometry
  - IR spectroscopy
- Mobility-based measurements of gases and liquids, e.g., mass spectrometry

- **Electron and X-ray techniques = VACUUM**
- **Optical techniques = AMBIENT**

Lateral resolution vs. depth resolution



X-ray photoelectron spectroscopy (XPS)



X-rays in

Measured

Work function of spectrometer (calibrated)

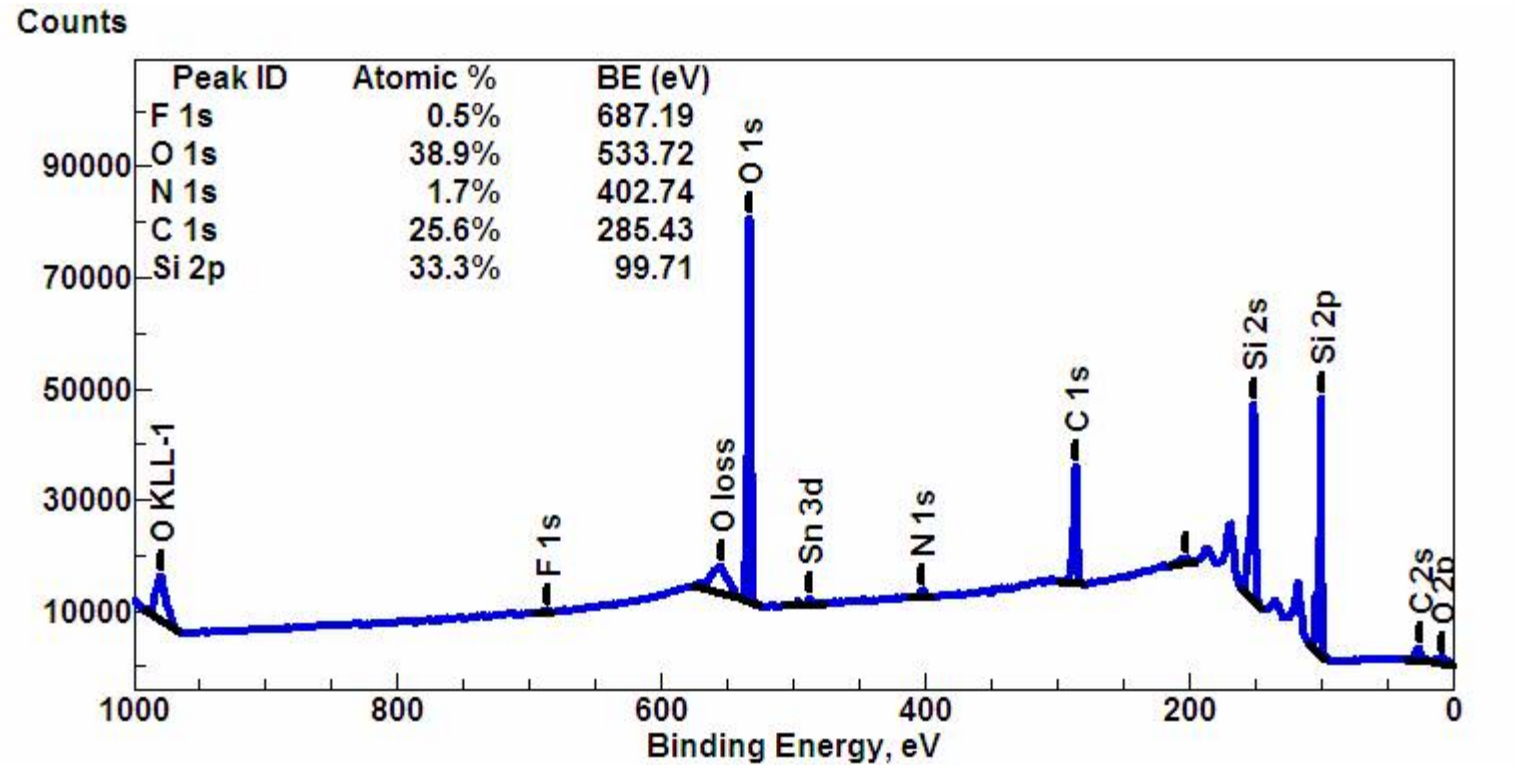
Output used to determine material

$$E_{binding} = E_{photon} - E_{kinetic} - \phi$$

http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy

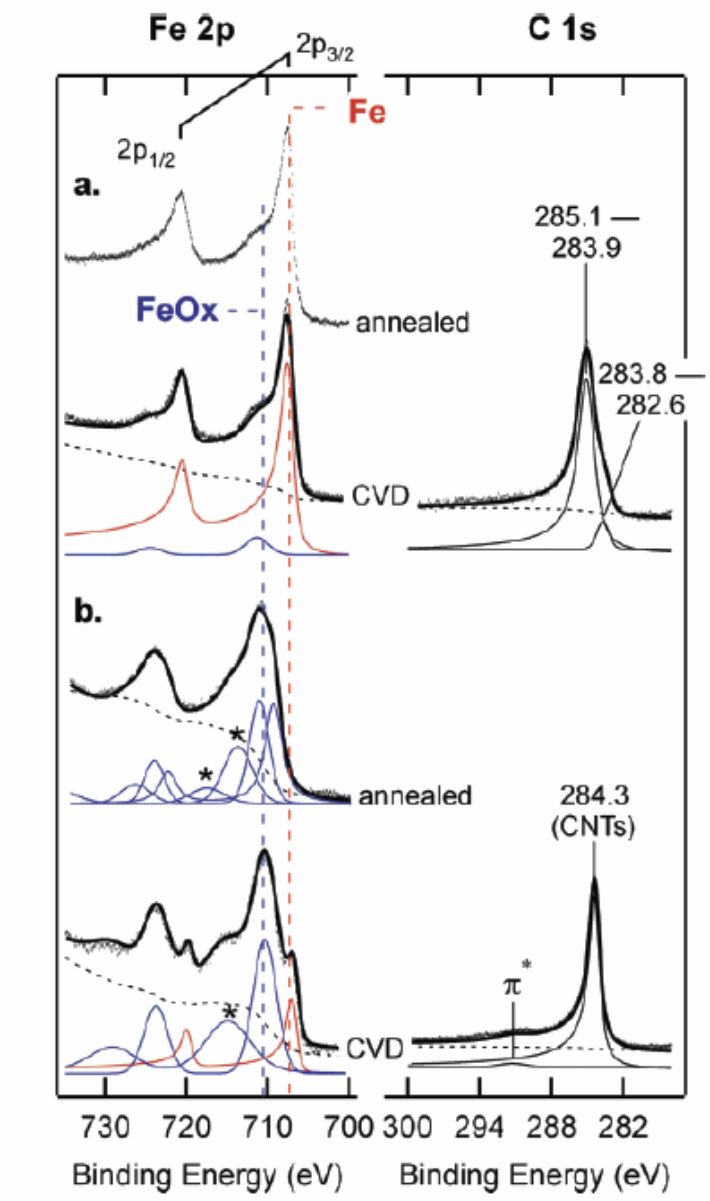
Work function of the spectrometer: http://www.rikenkeiki.com/pages/AC2.htm

XPS

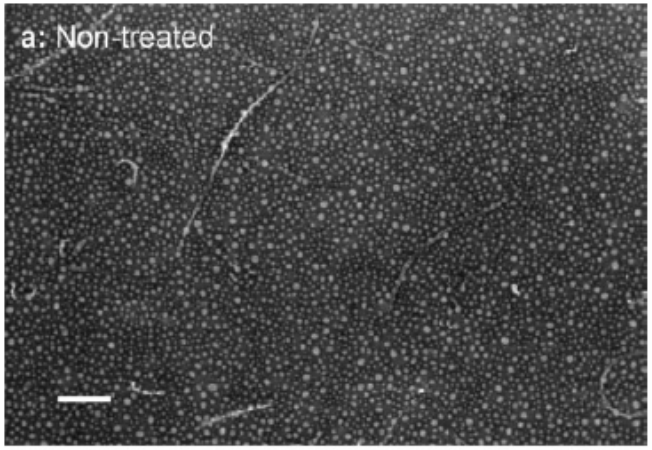


http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy

Is the CNT growth catalyst metal or oxide?



metallic Fe on Al_2O_3



Fe-oxide on Al_2O_3

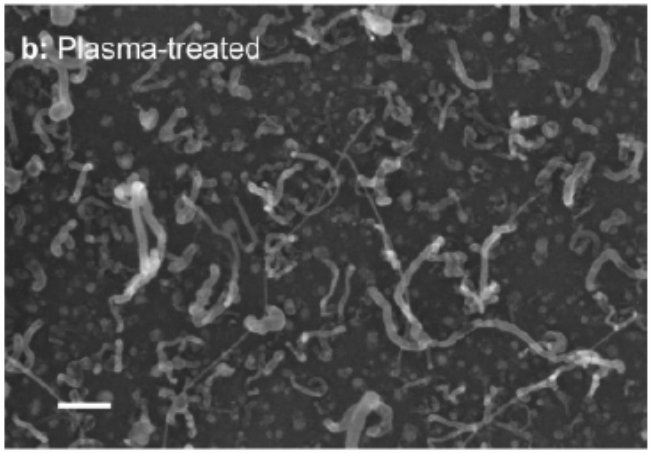
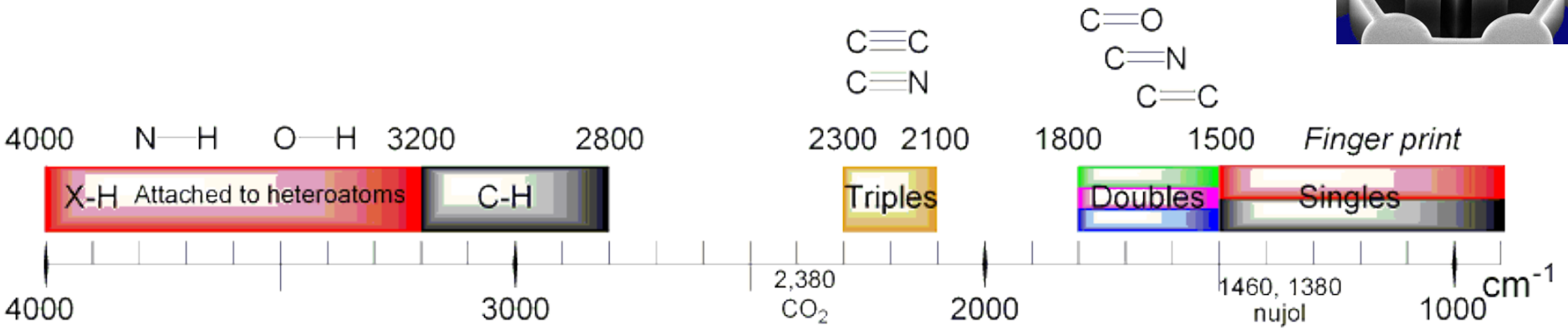
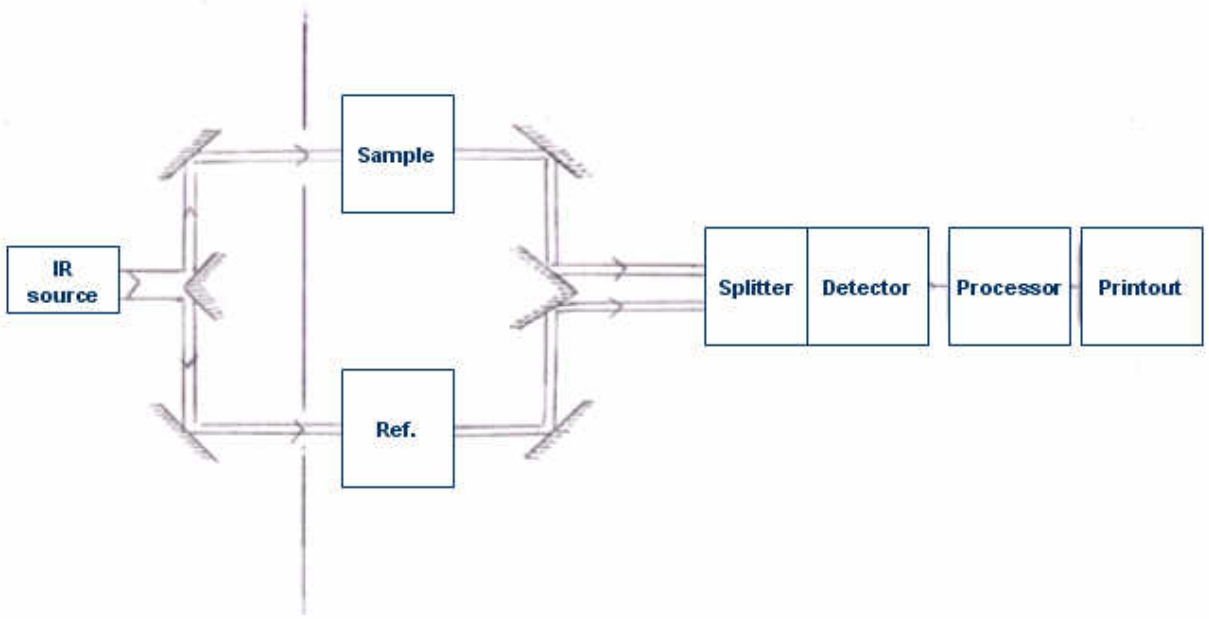
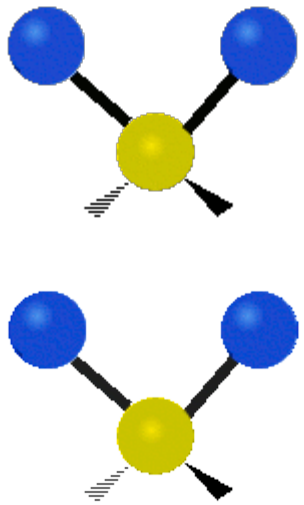


Figure 3. SEM images after CVD onto substrates with Al_2O_3 buffer layers. (a) CVD performed without previous O_2 plasma treatment; (b) CVD performed after O_2 plasma treatment. Scale bars are 100 nm.

Infrared (IR) spectrometry

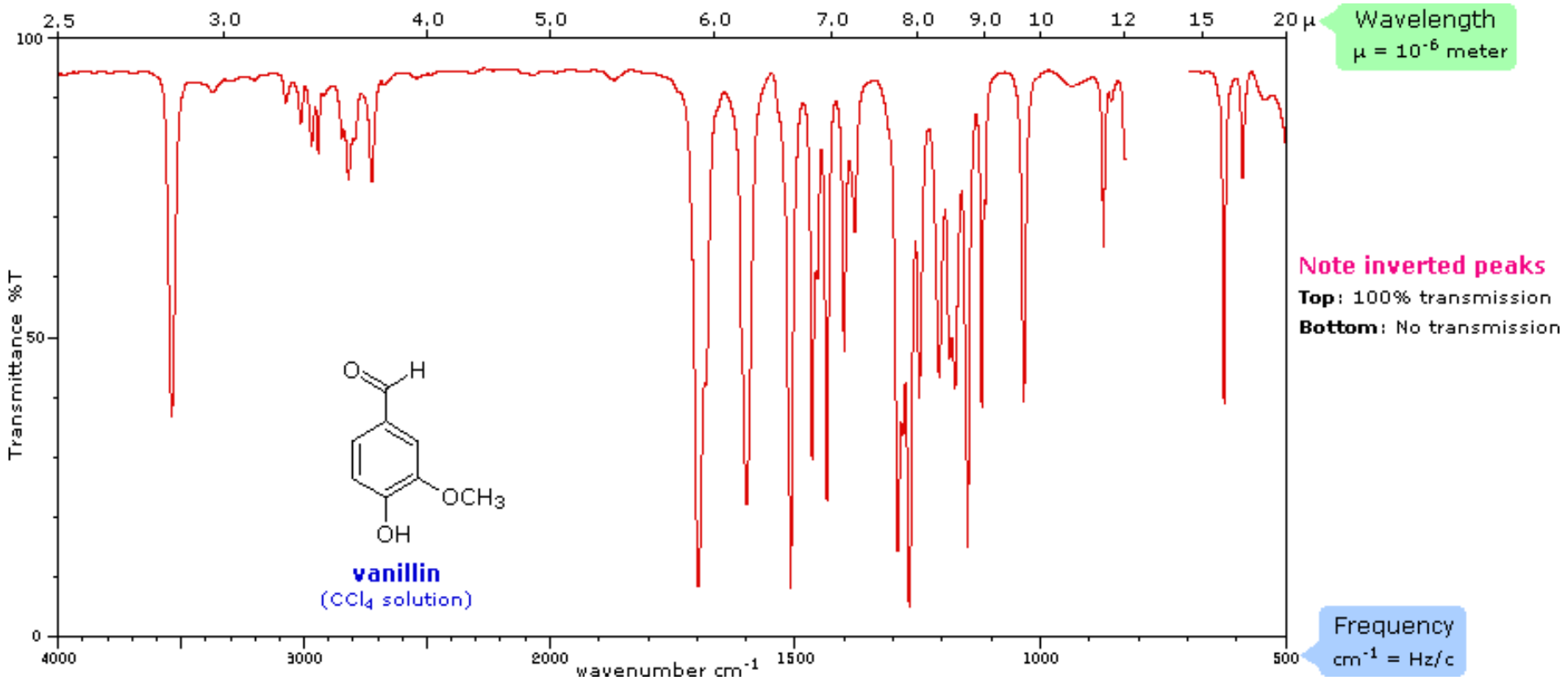






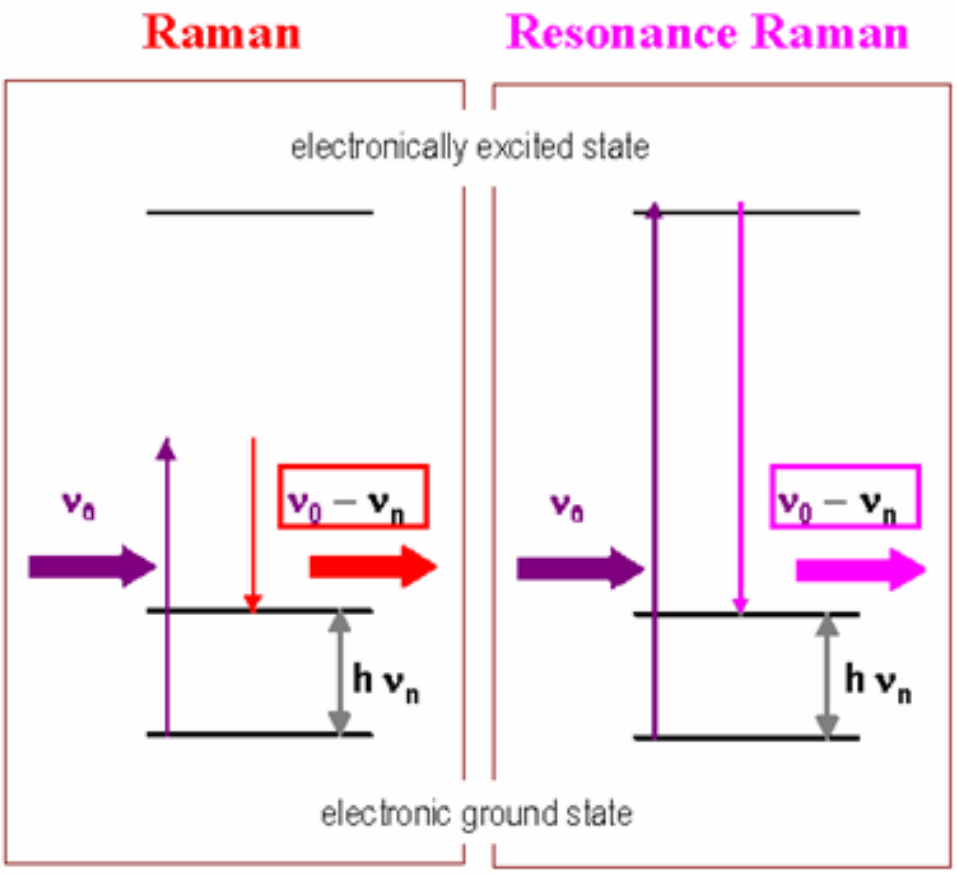
http://en.wikipedia.org/wiki/Infrared_spectroscopy

Infrared (IR) spectrometry

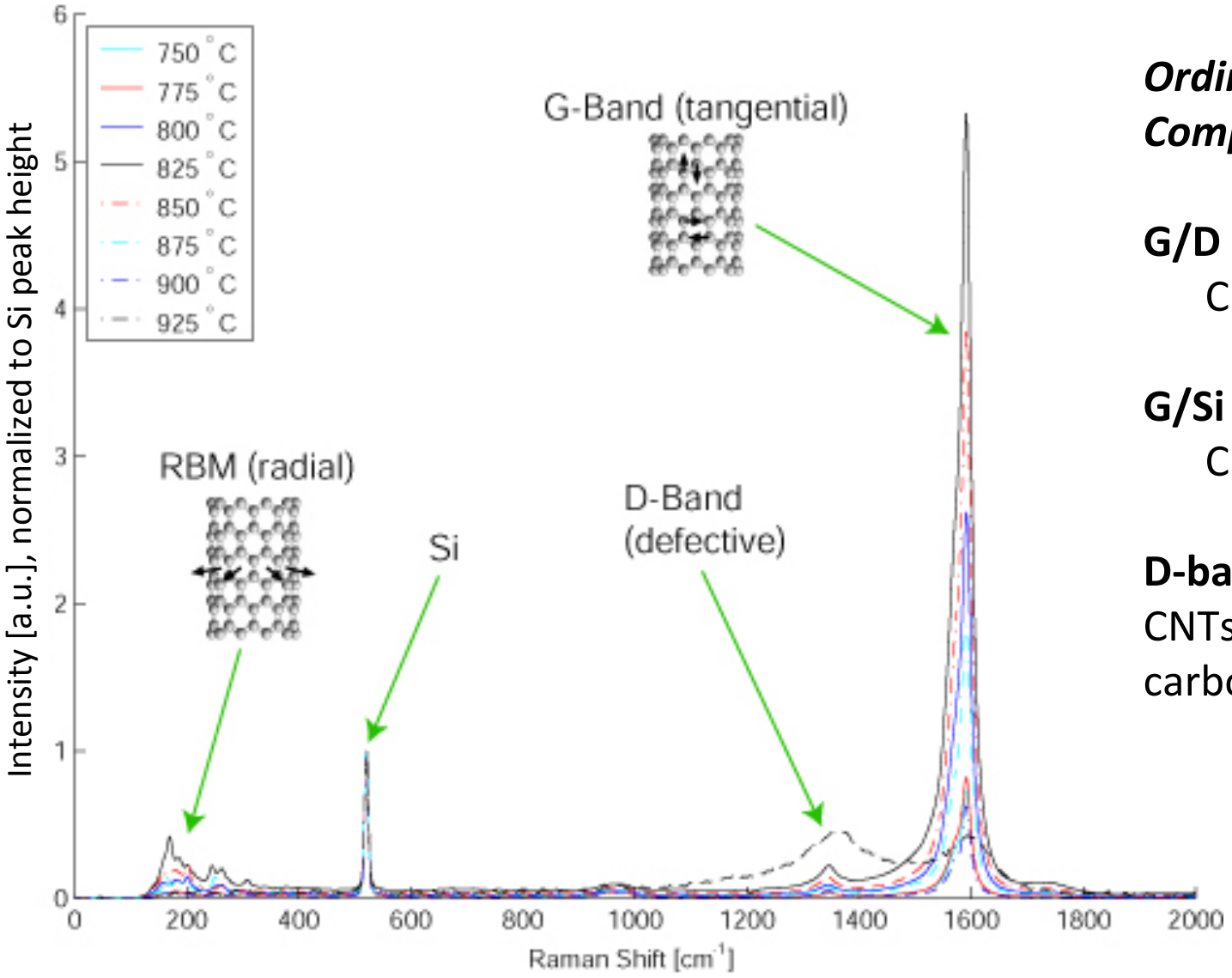


Raman spectroscopy

- Raman shift: scattered light shifts in frequency when it excites a molecular vibration; tuning this excitation to an electronic transition in the sample gives a huge enhancement



Raman spectroscopy of CNTs



Ordinal Comparisons:

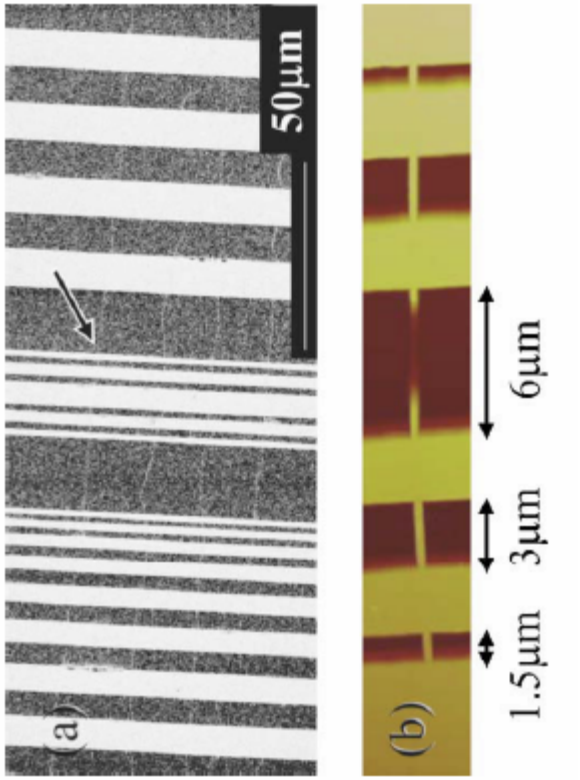
G/D Ratio =
CNT quality

G/Si Ratio =
CNT yield

D-band = Defects in CNTs and defective carbon on substrate

after Jorio et al., New Journ. Phys., 5:139.1–139.17, 2003

Raman peak of a SWNT shifts with strain …like a guitar string



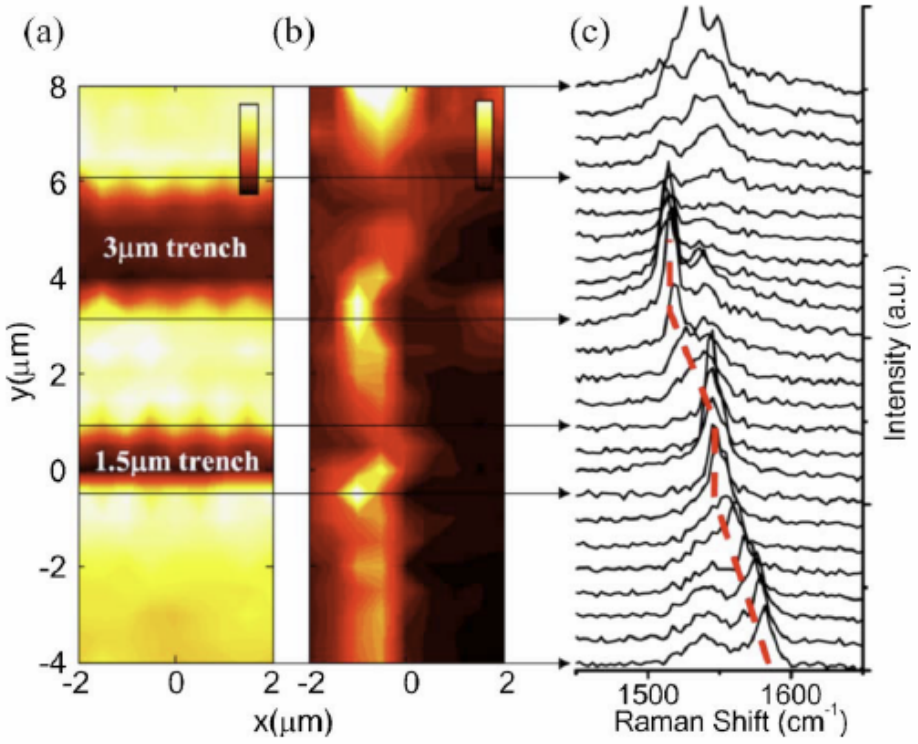
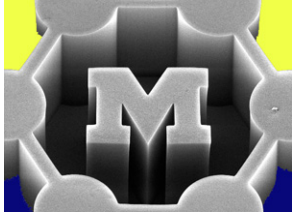


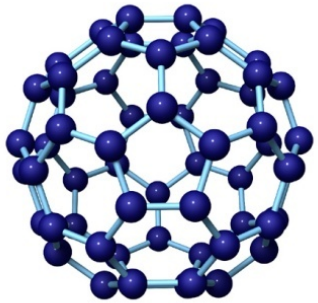
FIG. 3. (Color online) (a) 2D integrated intensity map of the silicon peak at 520 cm^{-1}. The dark regions correspond to the trench regions. (b) 2D integrated intensity map of the *G* band between 1500 and 1600 cm^{-1} taken from a SWCNT in the same region as in (a). (c) Actual *G*-band spectra along the length of the SWCNT shown in (b). The peak frequency of the most intense peak is observed to shift linearly with respect to the position on the substrate and remains constant across the trenches.

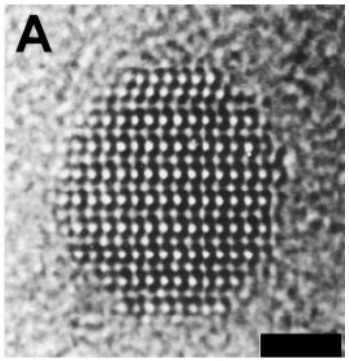
Son et al., *Appl. Phys. Lett.* 90:253113, 2007.

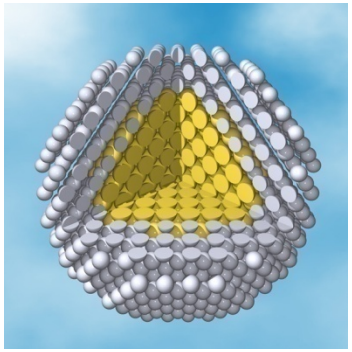
How were these pictures taken?



0-D







Nanoclusters

Magic #'s of atoms

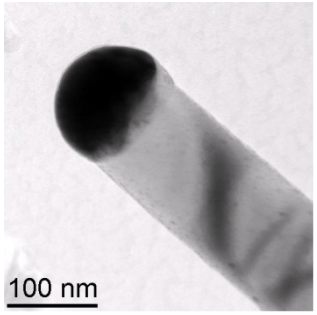
≤1 nm size

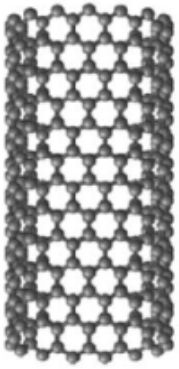
Nanoparticles

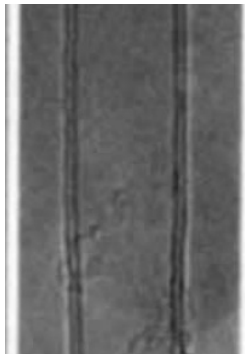
100's-1000's of atoms

~1-100 nm diameter

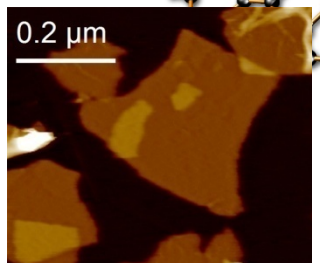
1-D







2-D



Nanowires

Filled

Nanotubes

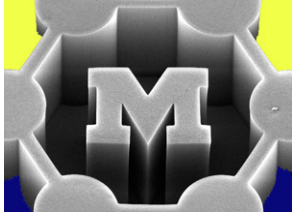
Hollow

Nanosheets

~1 atom thick

~1-100 nm dia, up to mm long and beyond!

Characterization facilities at UM



Electron Microbeam Analysis Laboratory (EMAL)
http://www.emal.engin.umich.edu/
Facilities: Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray Photo-electron Spectroscopy (XPS), Focused Ion Beam (FIB), and others.

X-Ray MicroAnalysis Laboratory (XMAL)
http://www.mse.engin.umich.edu/research/xmal
Facilities: X-ray Diffraction and X-ray Scattering

Michigan Ion Beam Laboratory (MIBL)
http://www-ners.engin.umich.edu/research/Mibl/index.html
Facilities: Rutherford Backscattering Spectroscopy, Ion Implantation