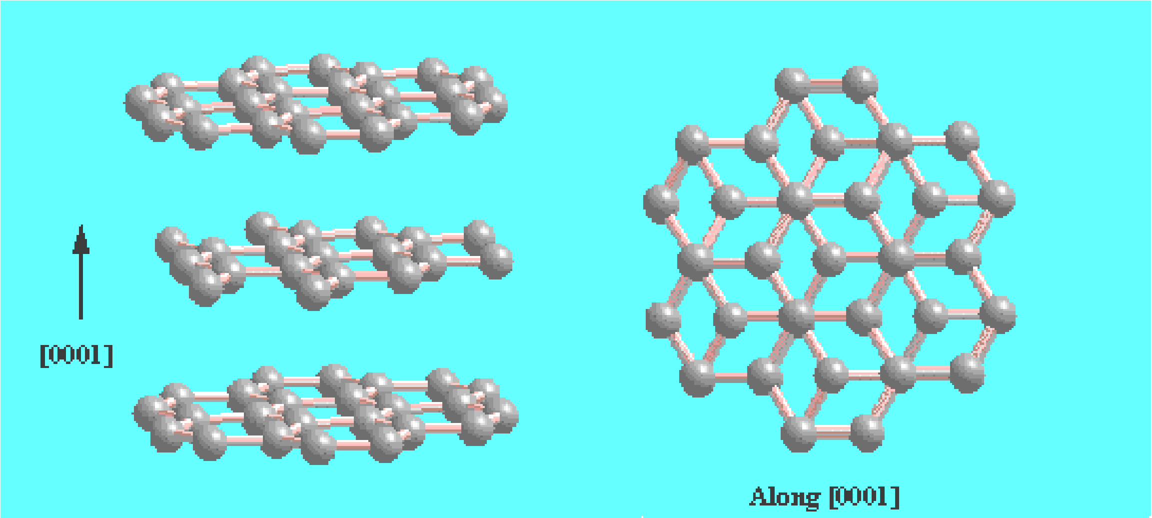
Structure and Mechanical Properties of sp^2-bonded Nanotubes

B. G. Demczyk

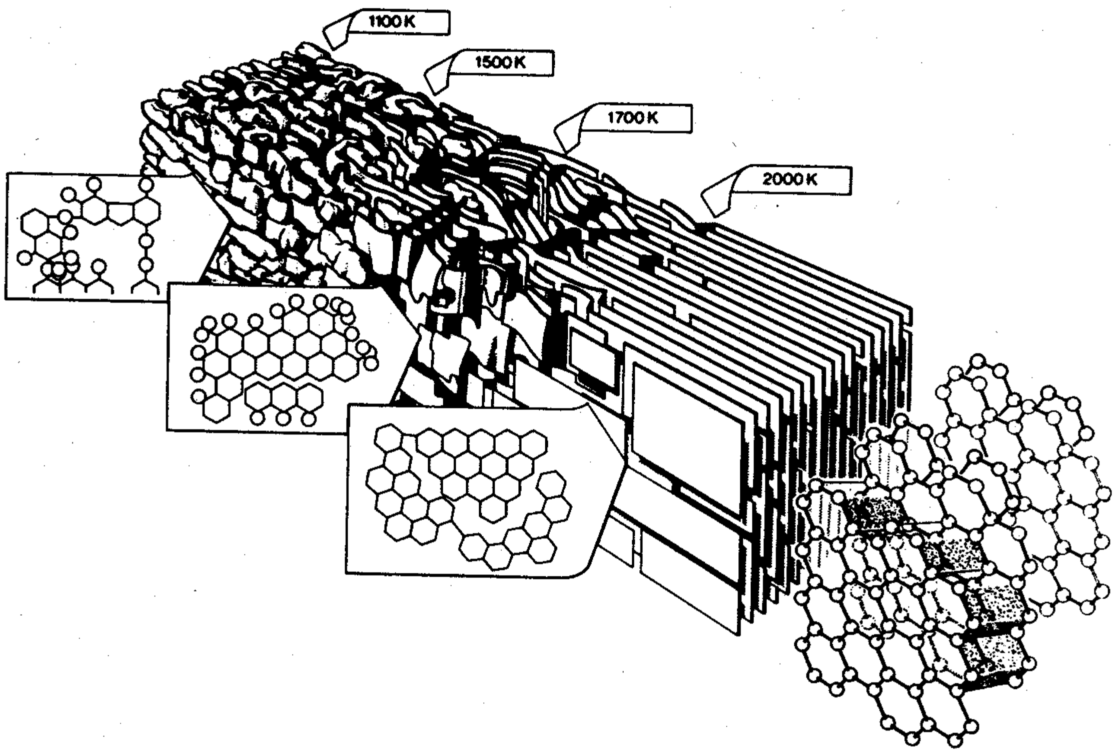
Graphite Structure



B.L. =0.142 nm (diamond, 0.154nm)

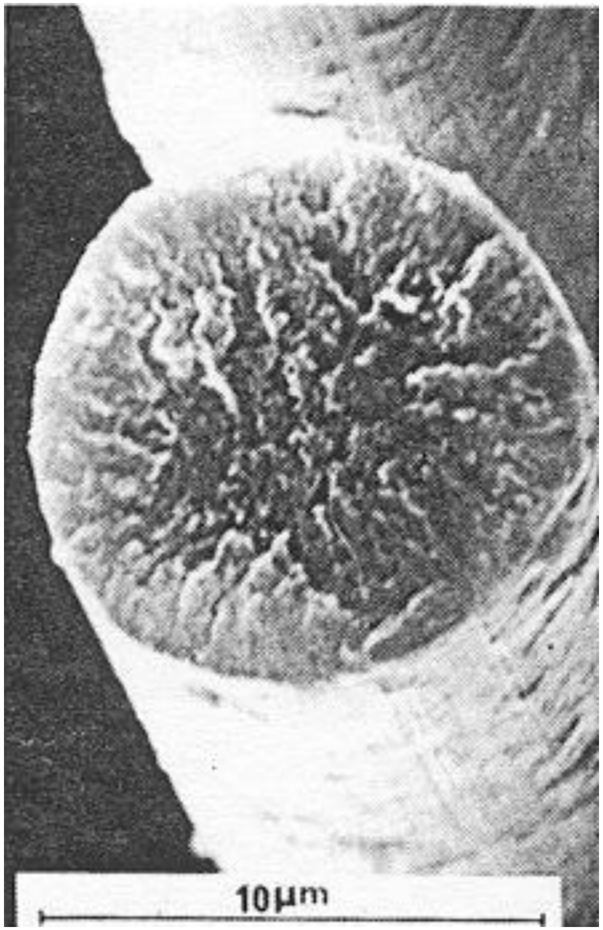
Crystal structure of graphite. The in-plane C-C covalent bond strength is the highest found in nature, but the van der Waals layer to layer bonds are weak.

Carbon Fiber

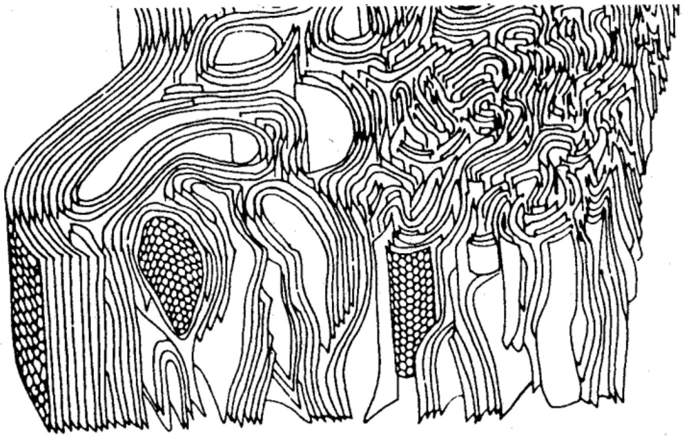


Schematic idealized structure of a carbon fiber,
where the strong C-C bonds lie along the length of the fiber.

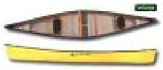
Carbon Fibers



SEM Image



Defect Structure



Tensile Strength

Cohesive Strength

(0.33 TPa) $\sigma_c = E\lambda/2\pi a_o\ (\approx E/\pi)$

E = Young's Modulus (1026 GPa)

λ = interatomic force period ($\sim a_o/2$)

a_o = interatomic separation (0.213 nm)

Fracture Strength (Orowan-Polanyi)

(0.14-0.18 TPa) $\sigma_f = \sqrt{E\gamma/a}\ (\approx E/7\text{-}E/5)$*

γ = Surface energy (4.2 J/m^2)

a = interplanar separation

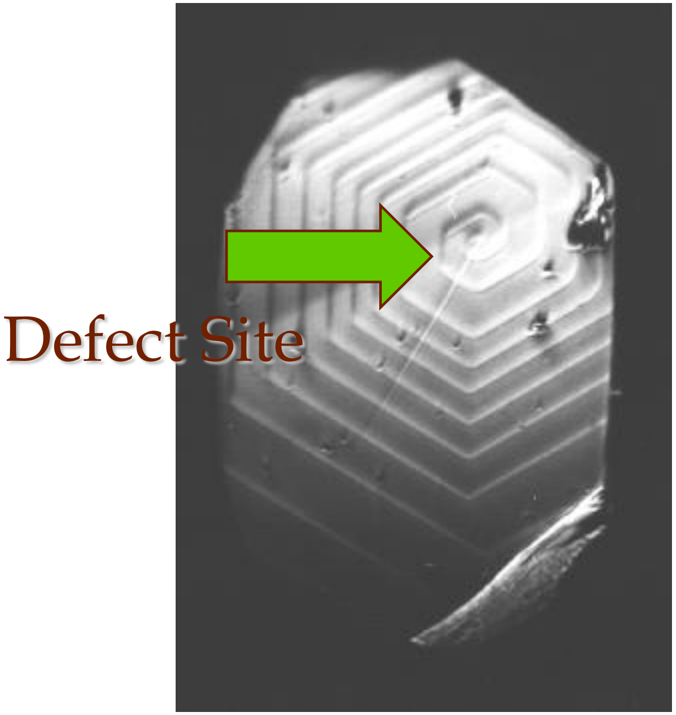
*Rep. Prog. Phys. 12 185 (1949).

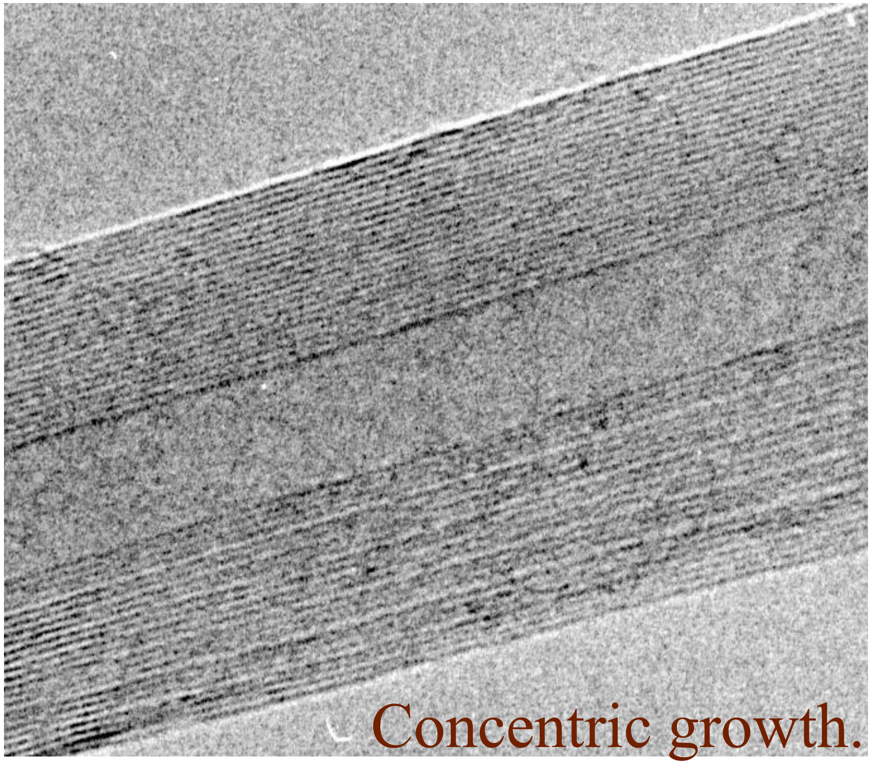
Relative Strengths of Carbon Fibers

Steel	1-2 GPa
Carbon Fiber	2-5 GPa
Carbon Whisker	up to 20 GPa
Carbon Nano tube	~ 300 GPa
Theoretical (C-C bond) Strength	>1000 GPa

=> structural defects limit U.T.S

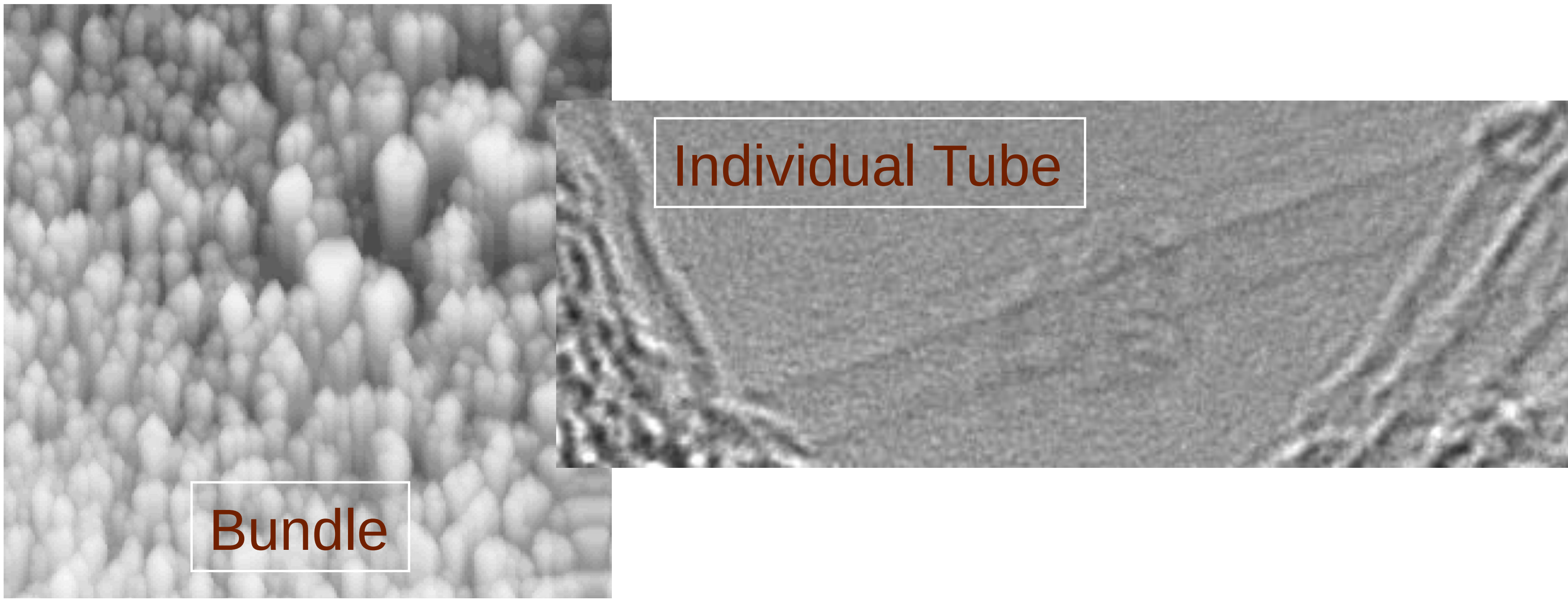
Fine Fibers (Whiskers) and Nanotubes





The continuity of atomic planes along the tube axis enhance the mechanical strength.

Single Wall Carbon Tube



CVD grown(~600 °C): C_2H_4 -> (Fe(Mo))-> C(s) + H_2

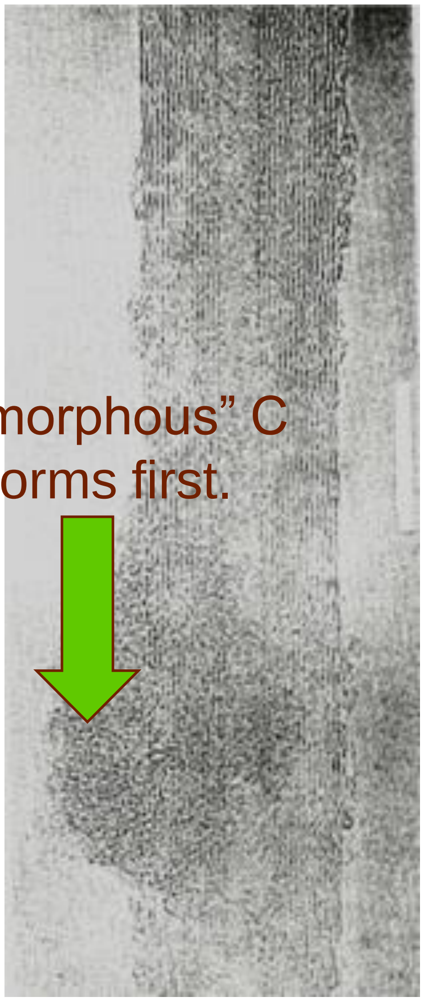
-"nanoswitch" (Nantero); transister (Nanõmix)

Ia. Multi-Walled C Nanotube Structure (Historical-U. Mich.)

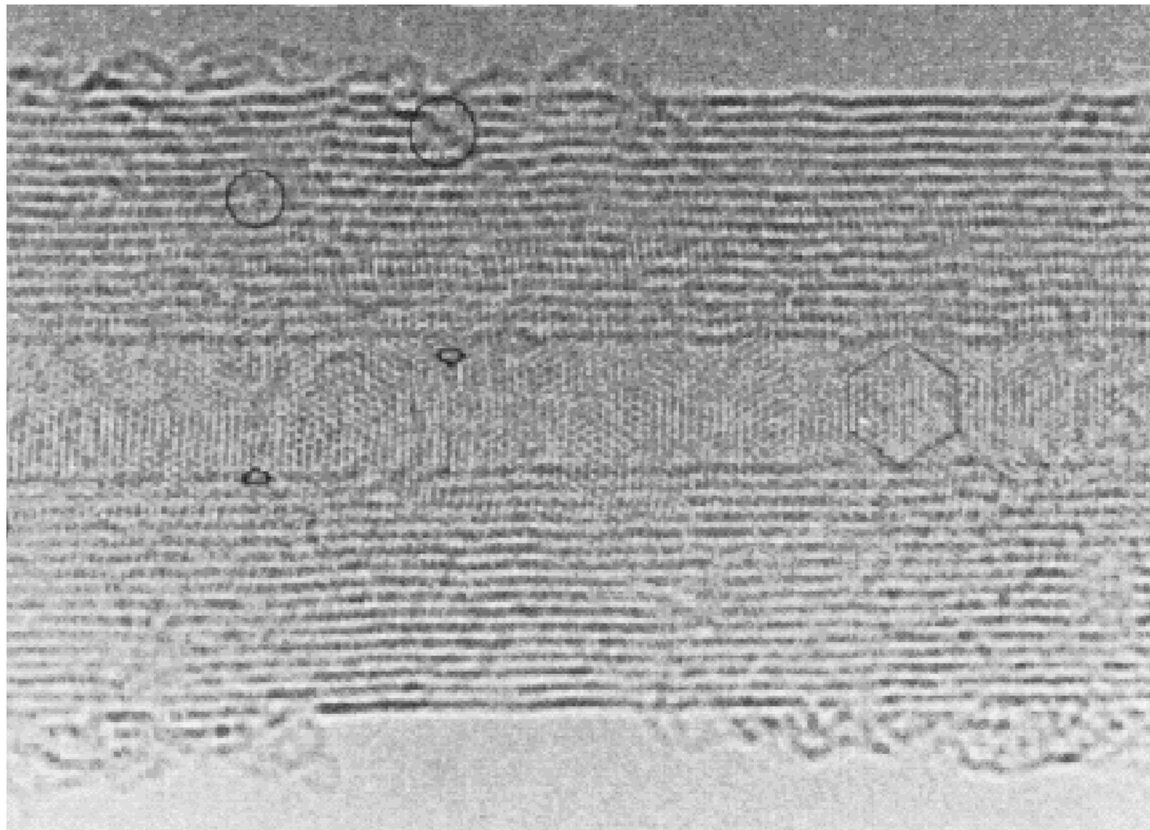
- Nanotube Growth:
  - ➢ Arc (110A, 30-45VDC) between graphite rods in He atm (320 Torr)
    - (J. Cryst. Gwth. 141 304 (1994))
- Nanotube HRTEM Characterization
  - ➢ JEOL 4000EX* LaB_6 (400 kV)
    - – 0.175 nm point resolution

*-commercial ARM

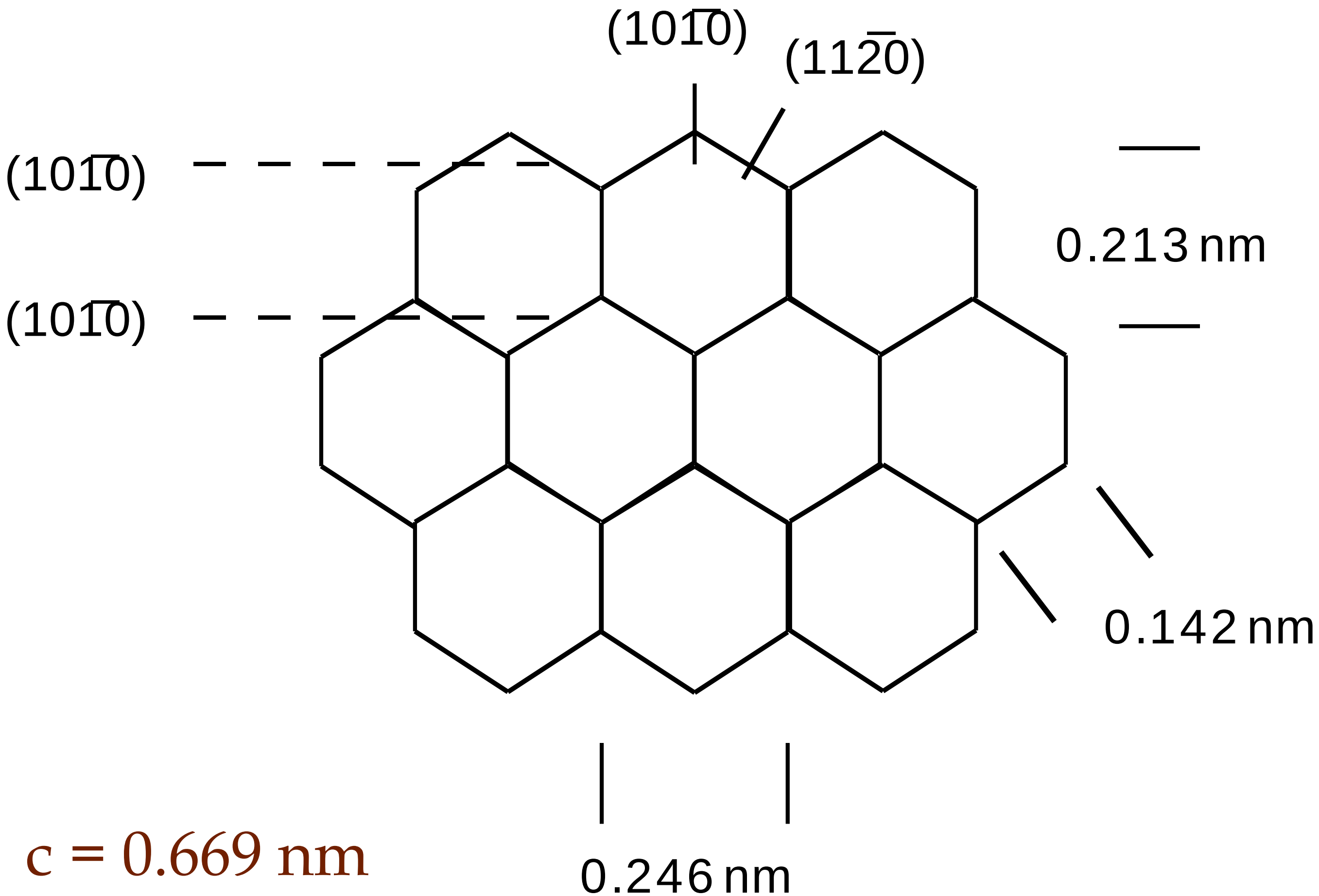
Nanotube HREM Images



"Amorphous" C forms first.



Graphene Structure

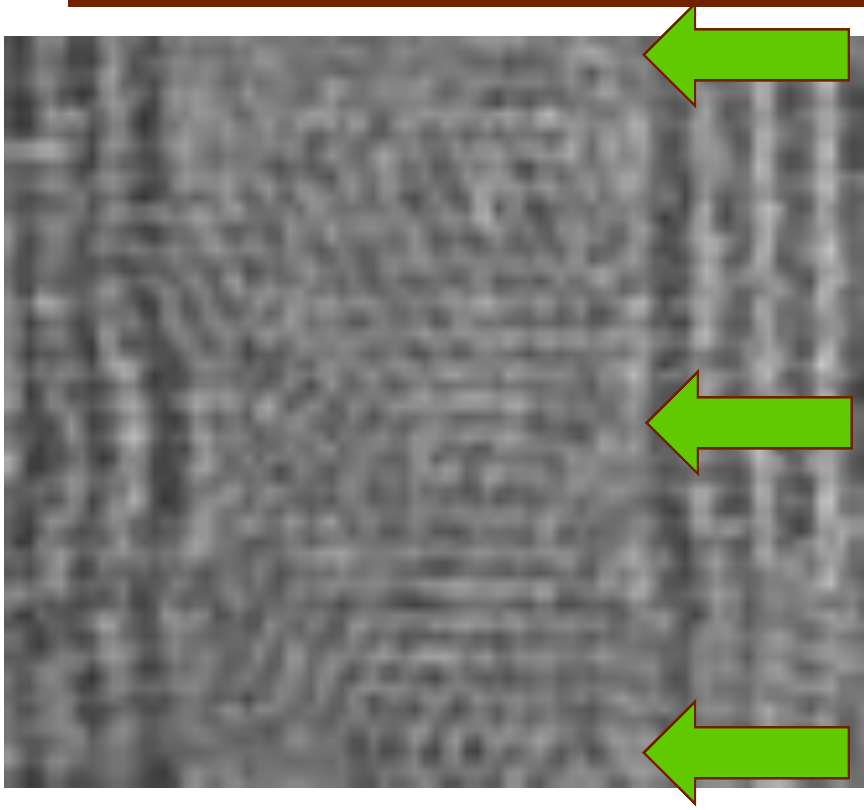


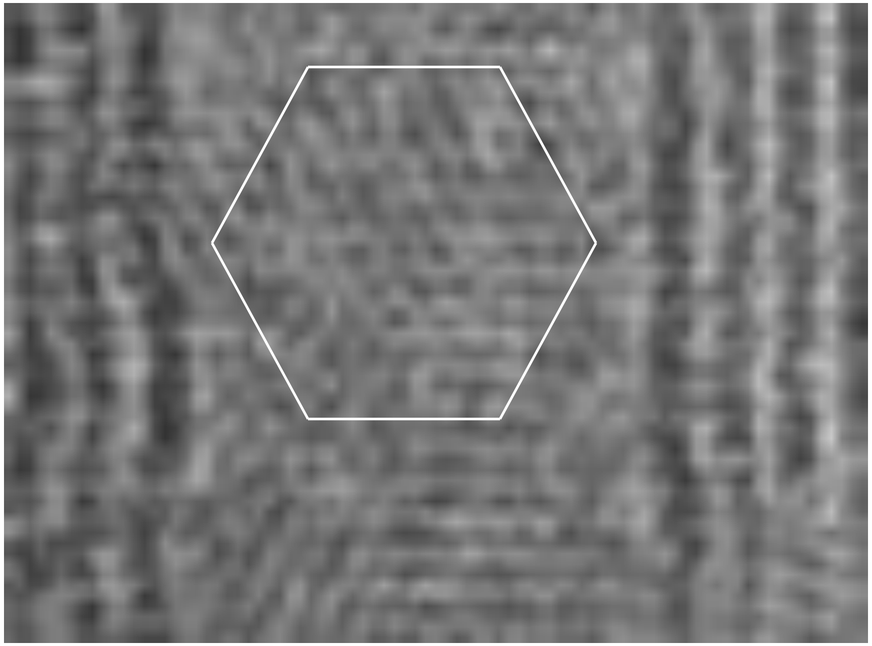
c = 0.669 nm

But in the Microscope...

… due to instrument resolution limit (0.175 nm)

Moire Patterns





$$D = \frac{d_1 d_2}{(d_1^2 + d_2^2 - 2d_1 d_2 \cos\alpha)^{0.5}}$$

=>Evidence of helicity variation ($\pm$3°) within tube.

Helicity (to maintain closure)

- Initial cylinder circumference

  (OX_1) : $2\pi r_o = n_o a$

  - r_o - radius of inner cylinder
  - n_o - # of edge sharing hexagons

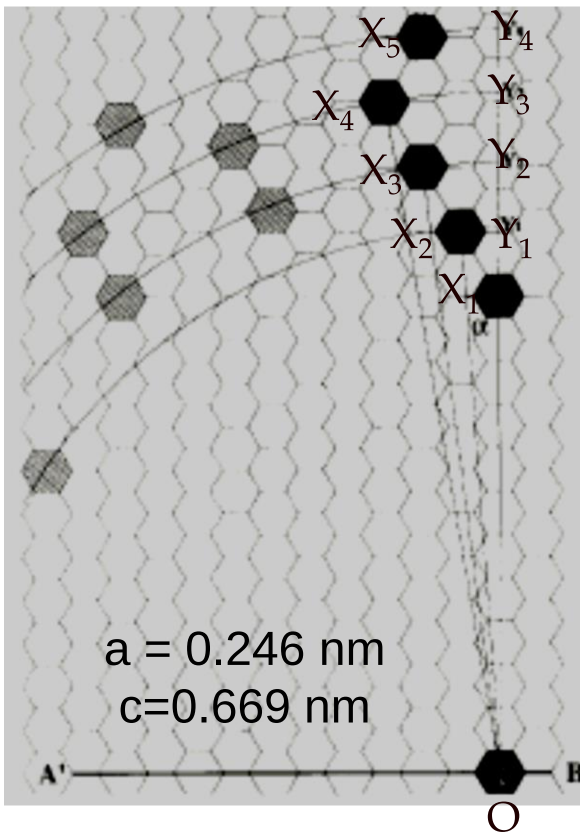
  - Next:

  $OY_1 = n_o a + \pi c$ $(O \text{ -> } X_2)$

  - $\alpha_1 = \tan^{-1}(X_2Y_1/OY_1)$ = helicity

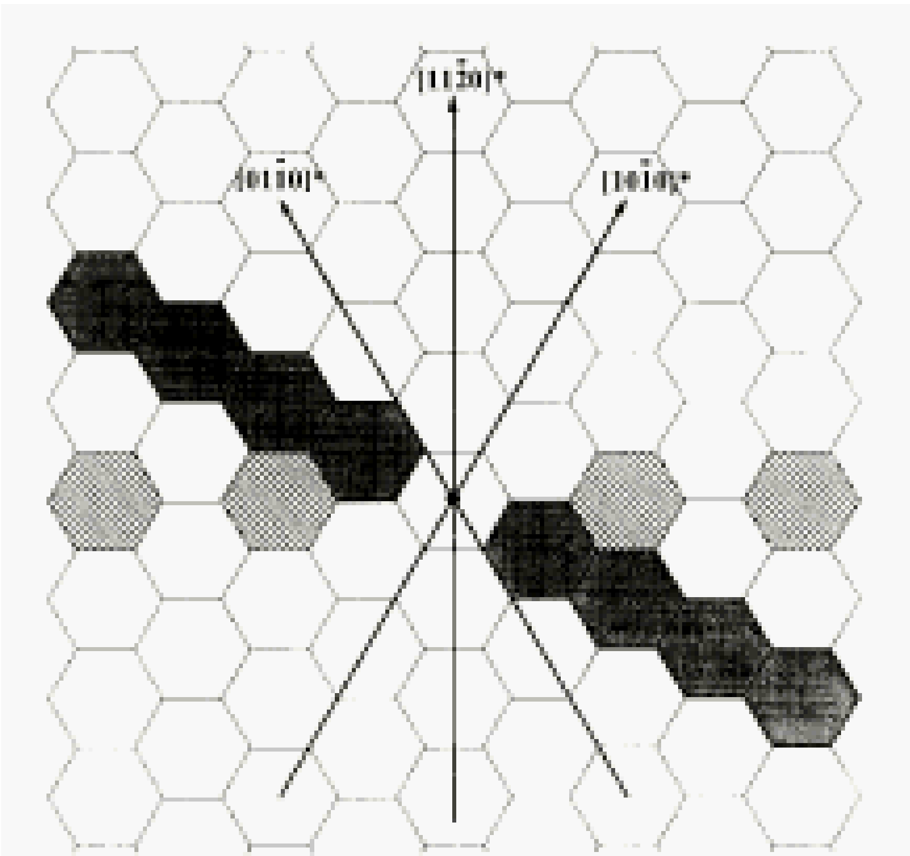
  - Then:

  $OY_2 = n_o a + 2\pi c$ $(O \text{ -> } X_3)$



=> Get both nonhelical and helical tubes

2 Ways to "Roll-up" Graphene



"Zig-Zag" $(10\bar{1}0)$

$n_z = \pi c/a$ (=8.43)

"Armchair" $(11\bar{2}0)$

$n_a = 2\pi c/a\sqrt{3}$ (=9.86)

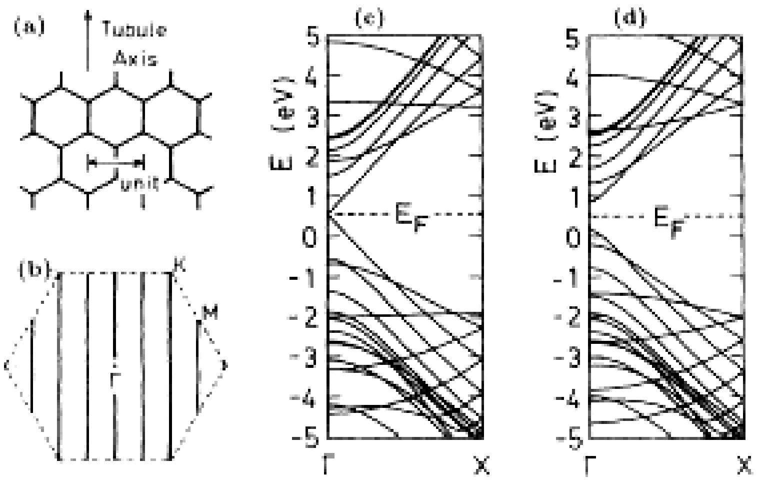
J. Cryst. Gwth. 130 368 (1993).

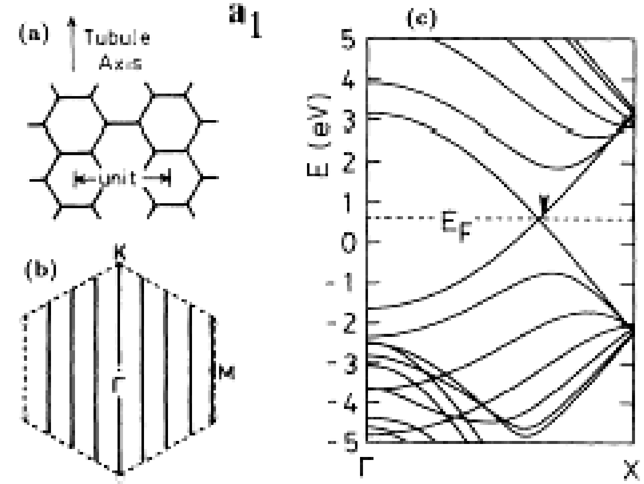
n_i = # extra hexagon rows/tube

CNT Brillion Zone

"Roll-up" determines conducting properties

$C = na_1 + ma_2$





n or m = 0 ("zig-zag")
=> metallic or semiconductor

n = m ("armchair")
=> metallic

Phys. Rev. Lett. <u>68</u>(10) 1579 (1992).

(Local) Diffraction Information from HREM

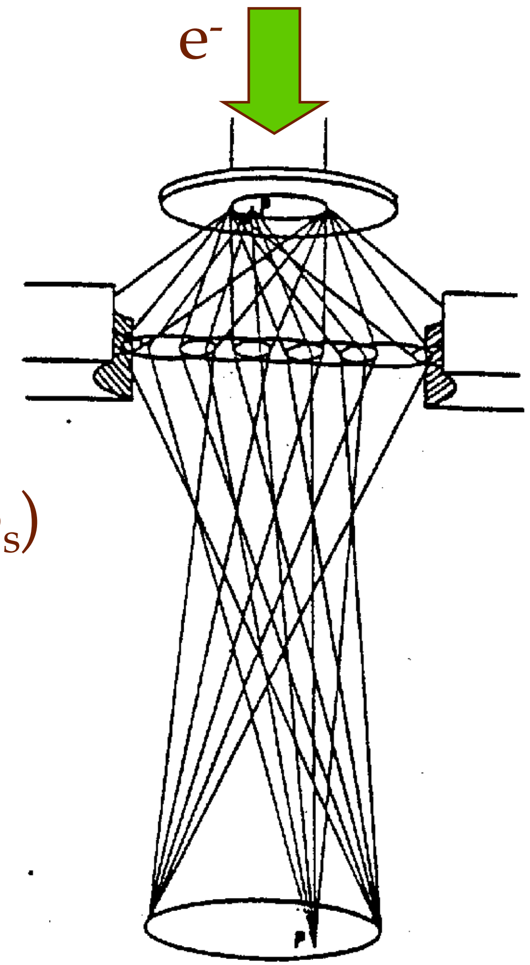
In-situ

Specimen, φ

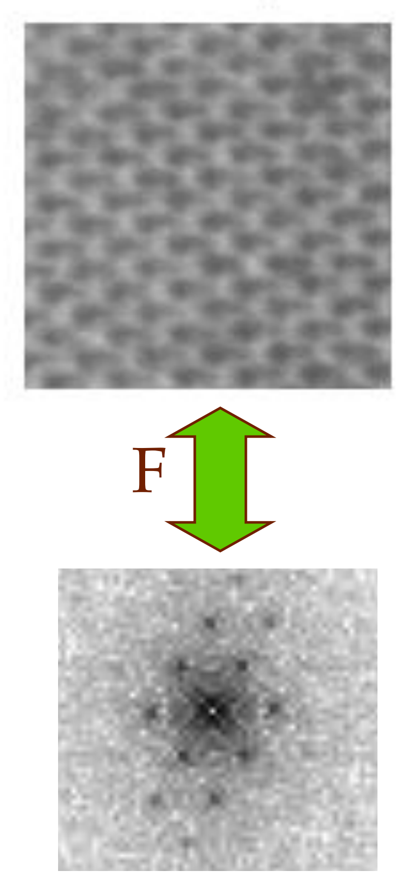
Objective Lens, φ_s

Diffraction Pattern, $f \approx F(\varphi_s)$

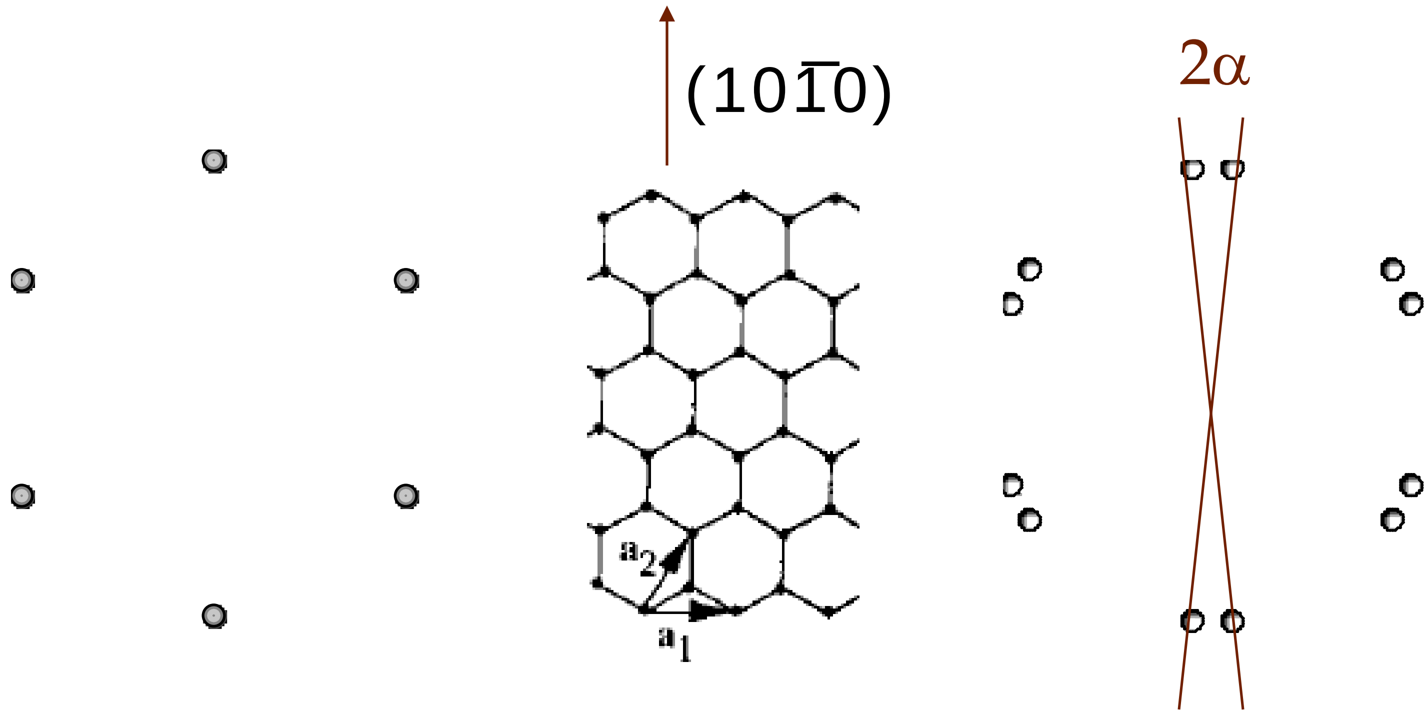
Image, $\varphi_m \approx F^{-1}(f)$



Ex-situ



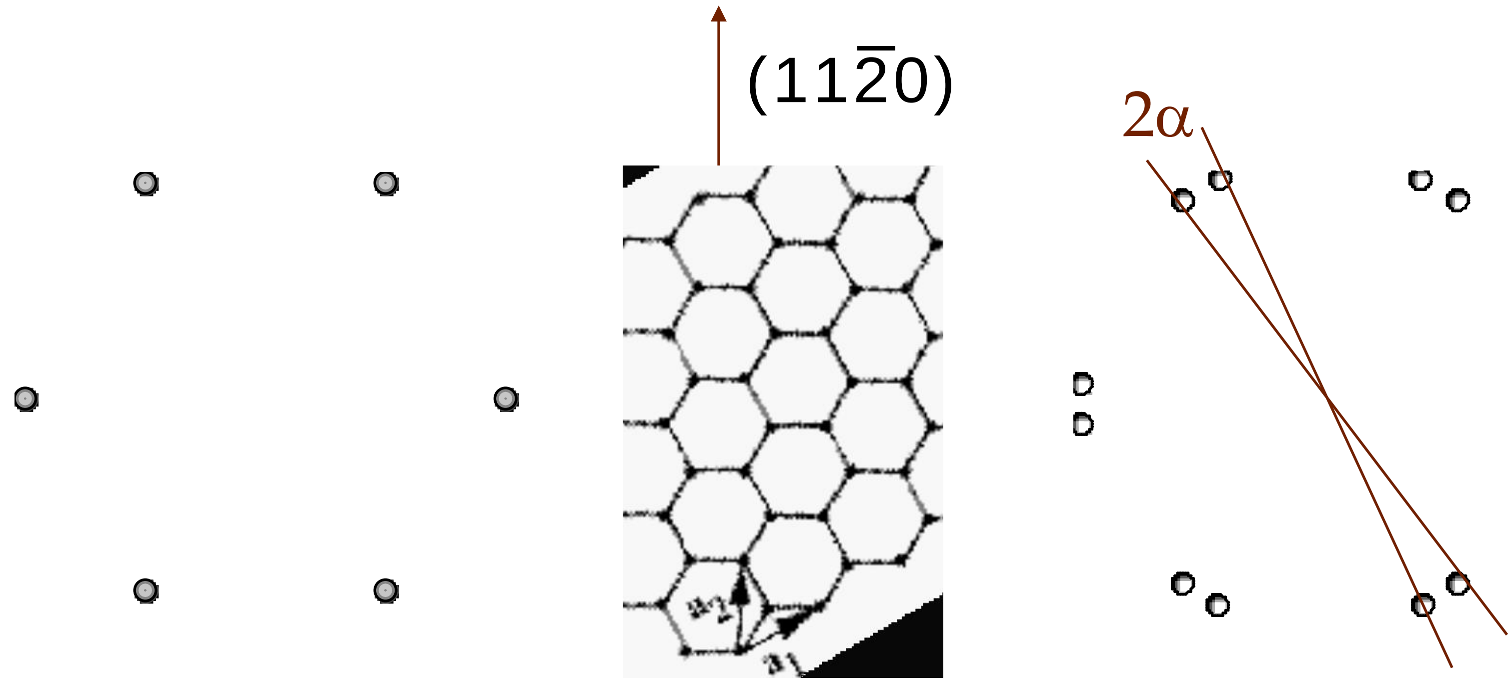
Diffraction-”Zig-Zag” Tubes



Non-Helical

Helicity, α

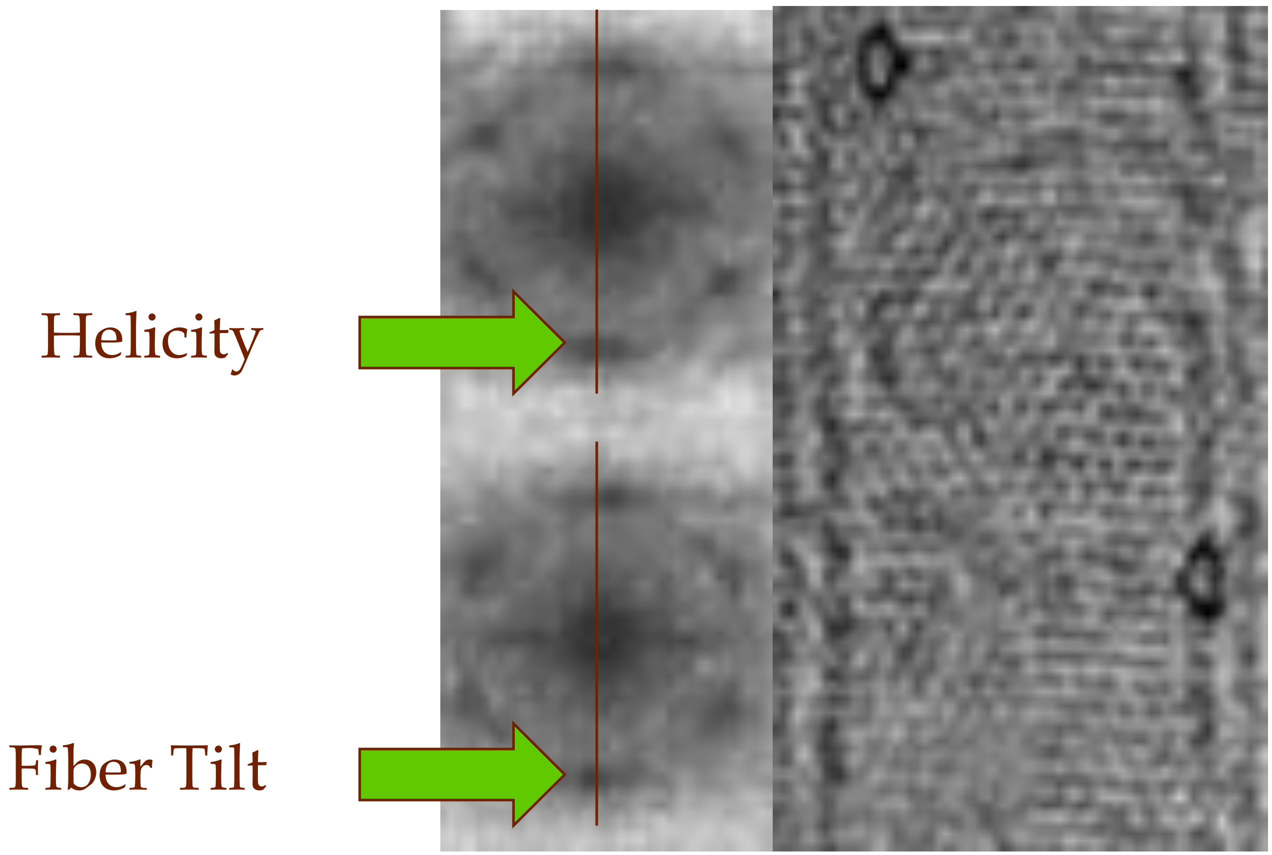
Diffraction-"Armchair" Tubes



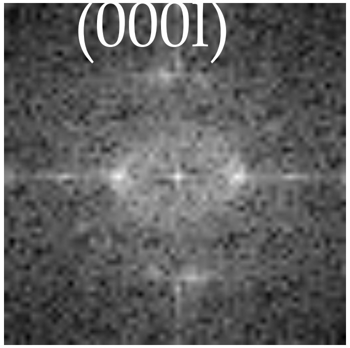
Non-Helical

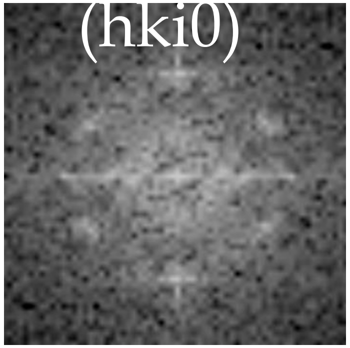
Helicity, α

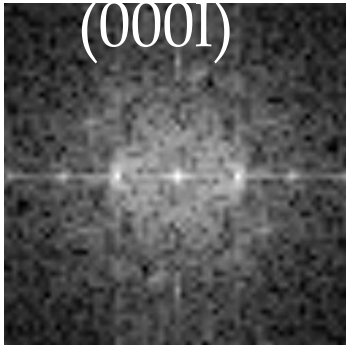
Axially...

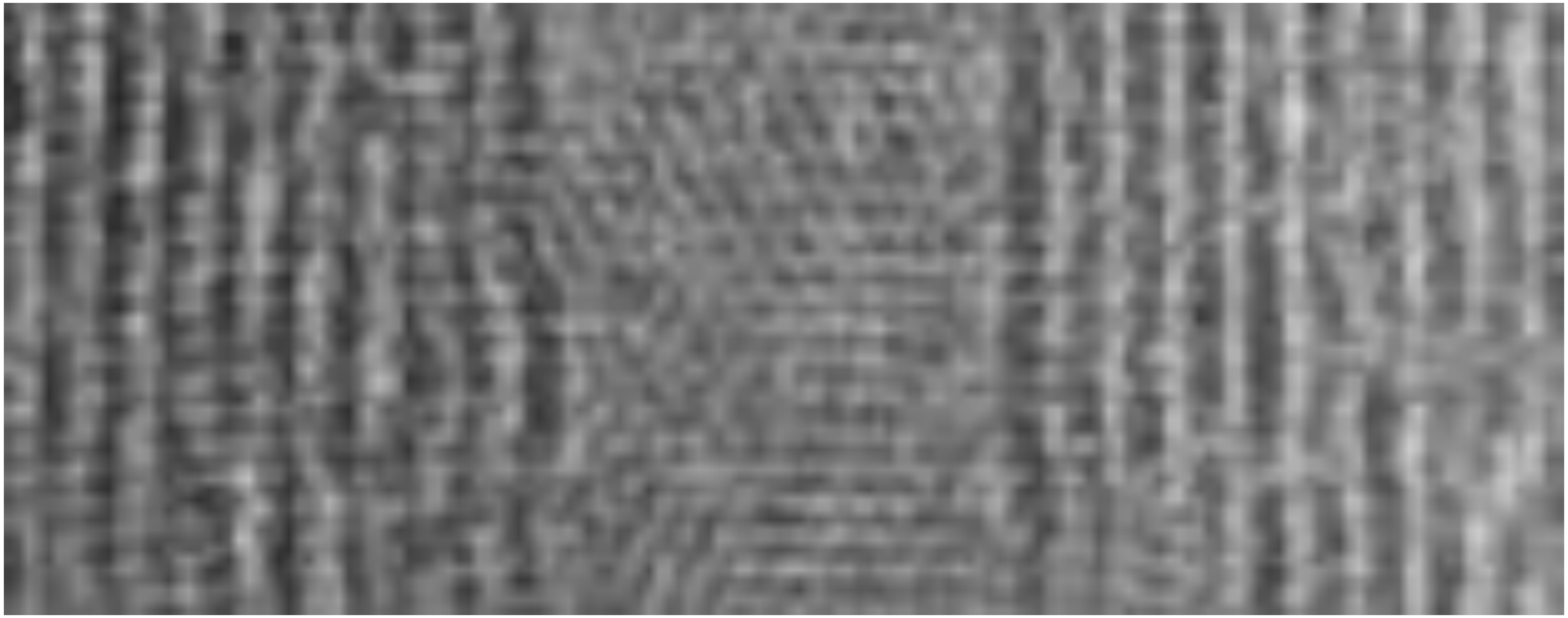


Radially...

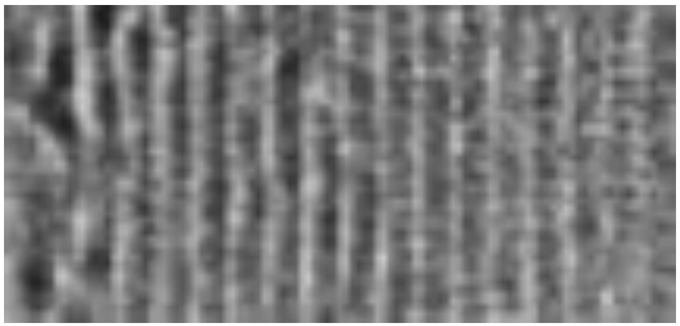








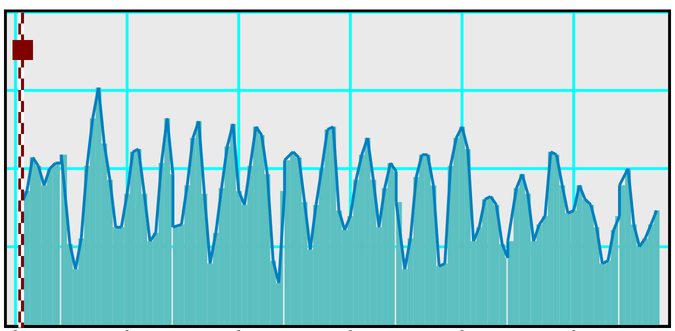
Spacing Variation



Over 300 pixels,
c = 0.375±0.004 nm

=> gives overall nonhelical fiber

every second tube has slight helicity



Tube #	d (nm)	n (=$\pi d/a$)	α (=$\tan^{-1}[\pi d/a]$)
1	3.17	40.5	1.2
2	3.91	50	0
3	4.66	59.5	0.8

CNT Structure Summary

- 10.0 (zig-zag) growth axis
- 0.375nm *c-axis* spacing
  - To maintain overall zero helicity
- Helicity can vary not only in succesive nanotubes, but also locally within a single tube

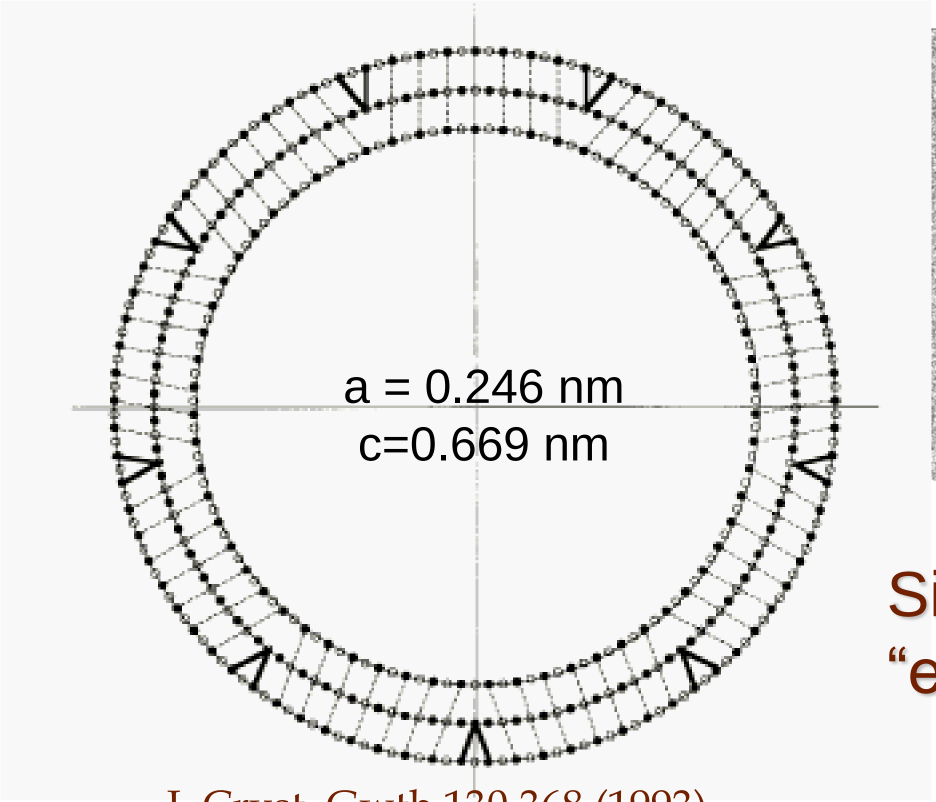
1b. CNT Structure (NCEM)

- Nanotube Growth:
  - Arc (60A, 30-45VDC) between B-doped C anode N_2 atm (380 T)
    - (Chem. Phys. Lett. 260 465 (1996))
- Nanotube HRTEM Characterization
  - Philips CM300 FEG (300 kV)
    - 0.17 nm point resolution
  - Philips CM200 FEG (120 kV)
    - 0.24+ nm point resolution

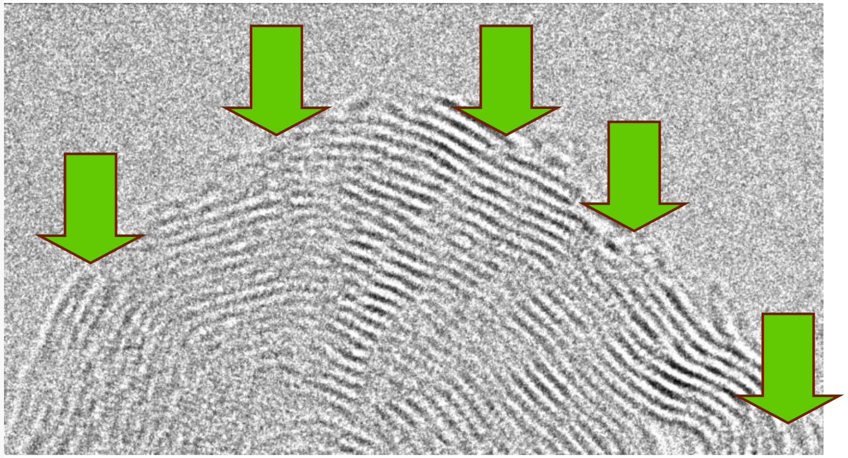
Defect Formation

-in general, "πc" is unrelated to "a"

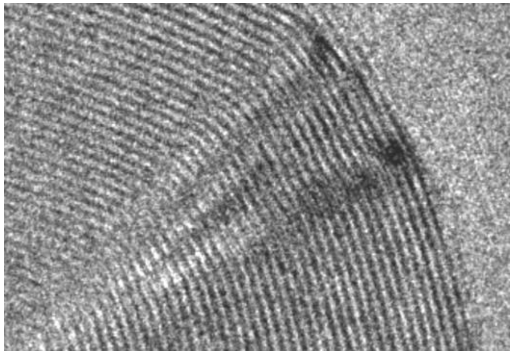
=> "interfacial" dislocations required for closure



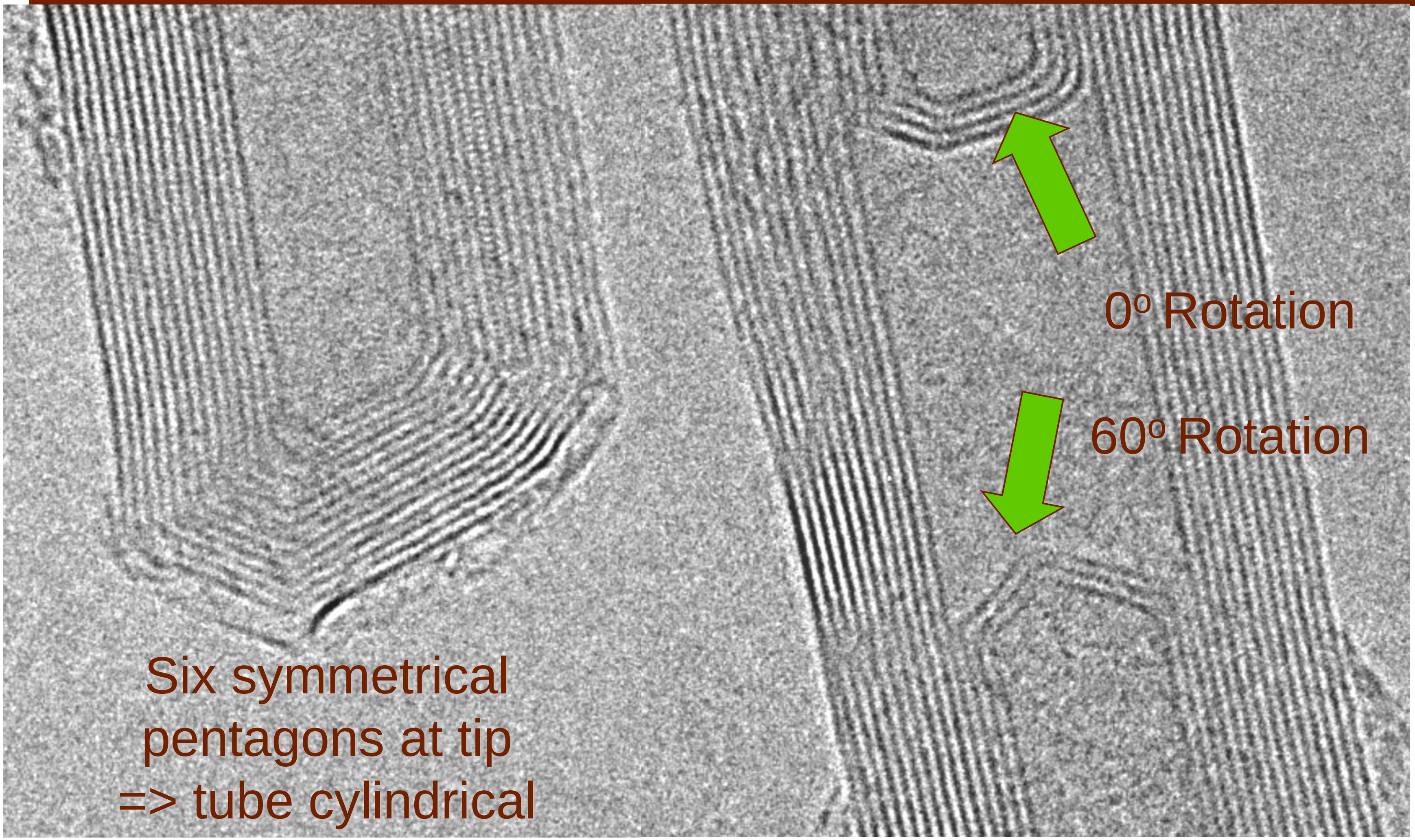
J. Cryst. Gwth. 130 368 (1993).



Sideview of "endcaps"

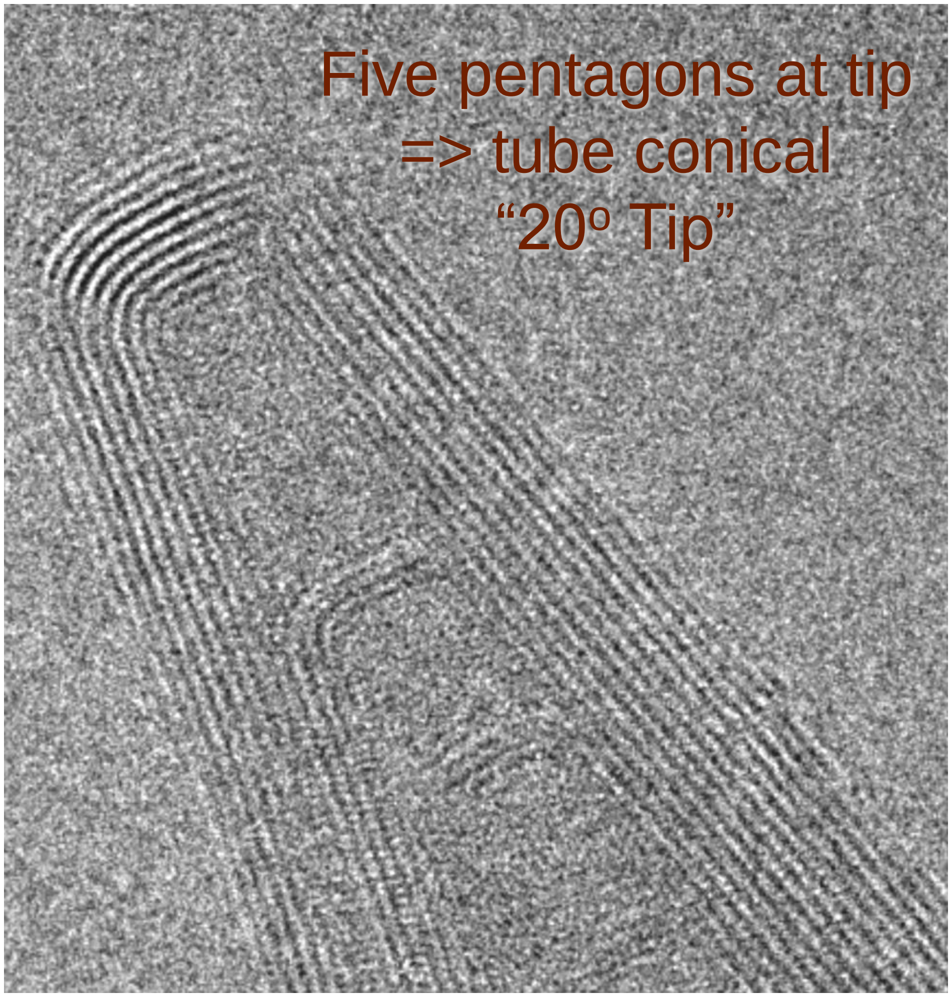


CNT Growth Termination-Normal

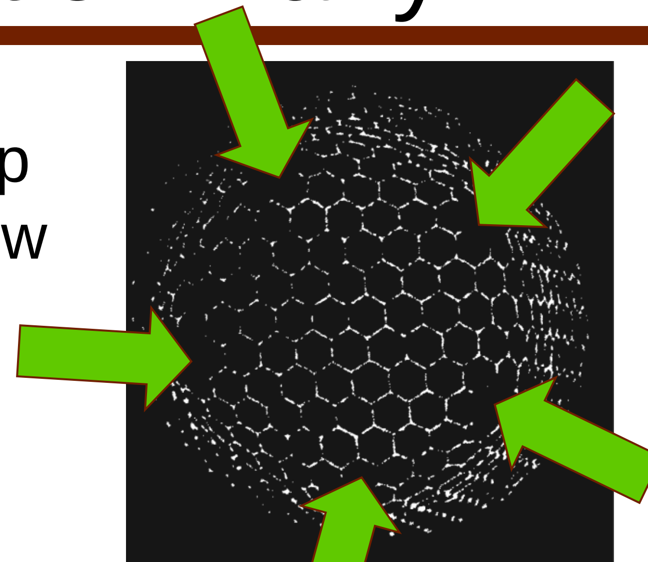


V + f = e + 2 (Euler)

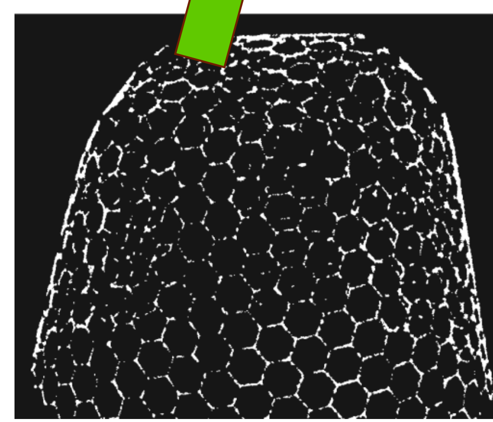
CNT Growth Termination-Early



Top View

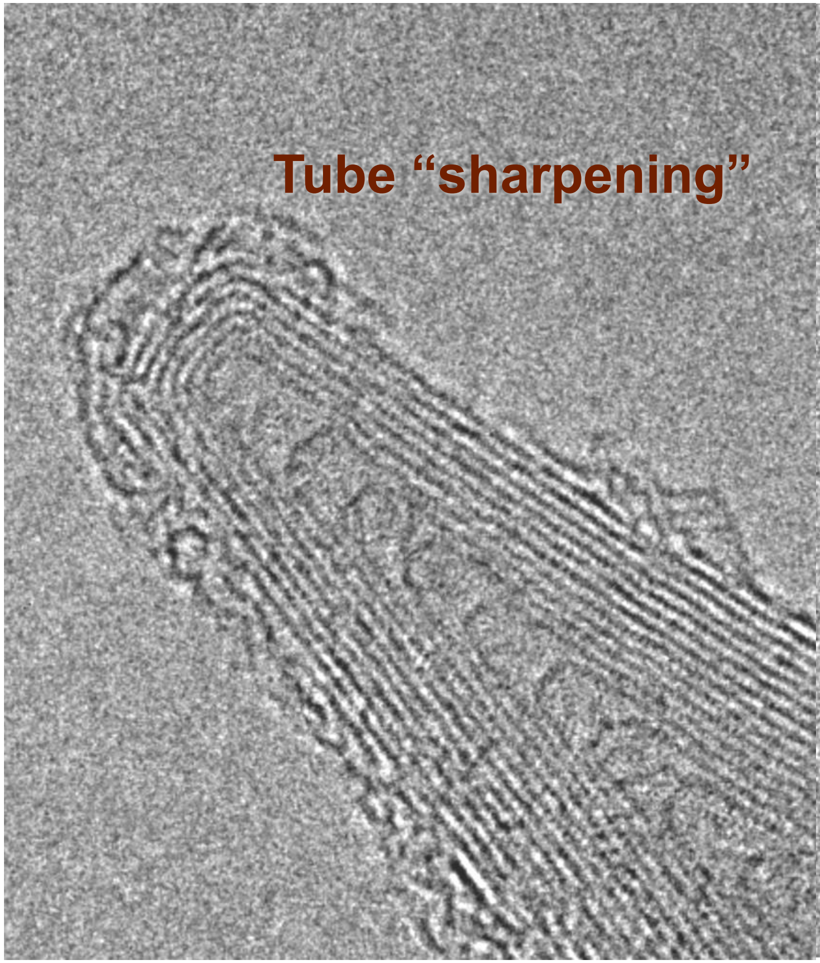


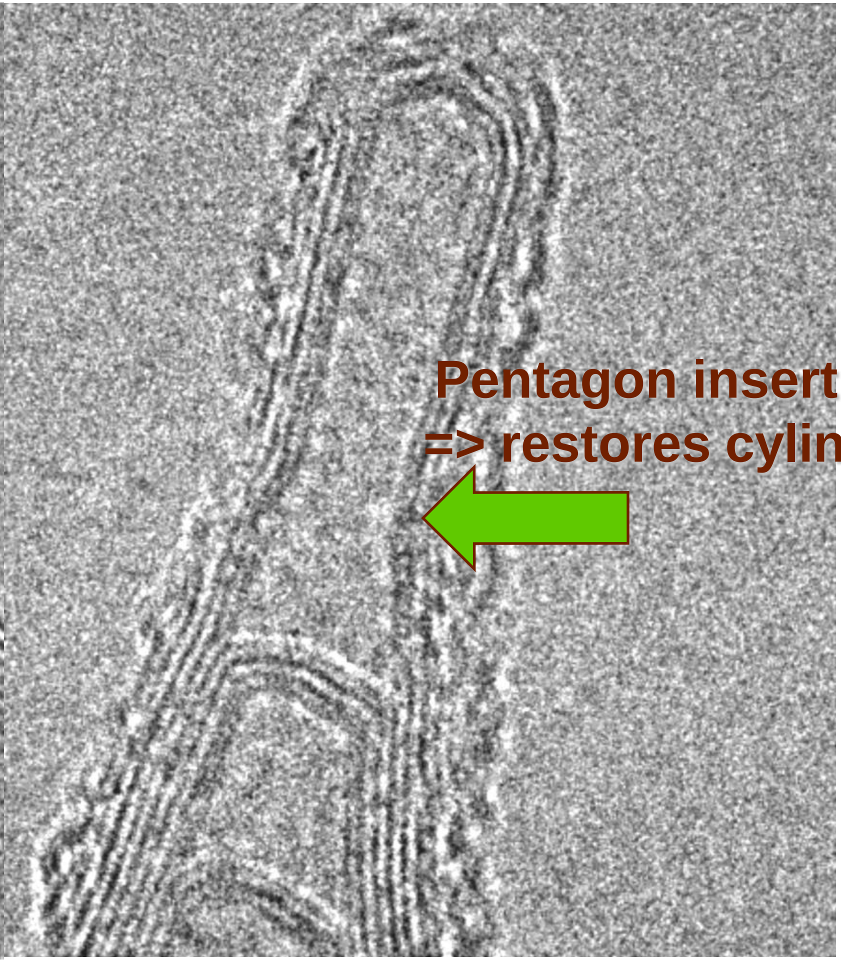
Side View



Elect. Micro. VIII 117 (1998).

CNT Growth Termination-Early

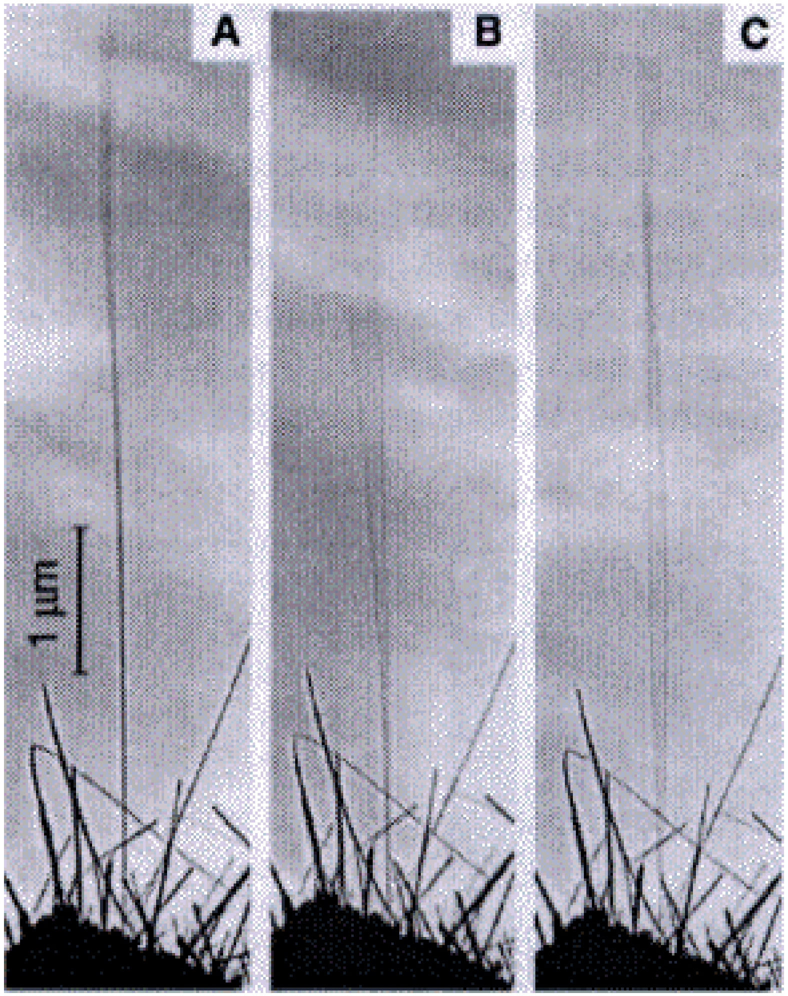


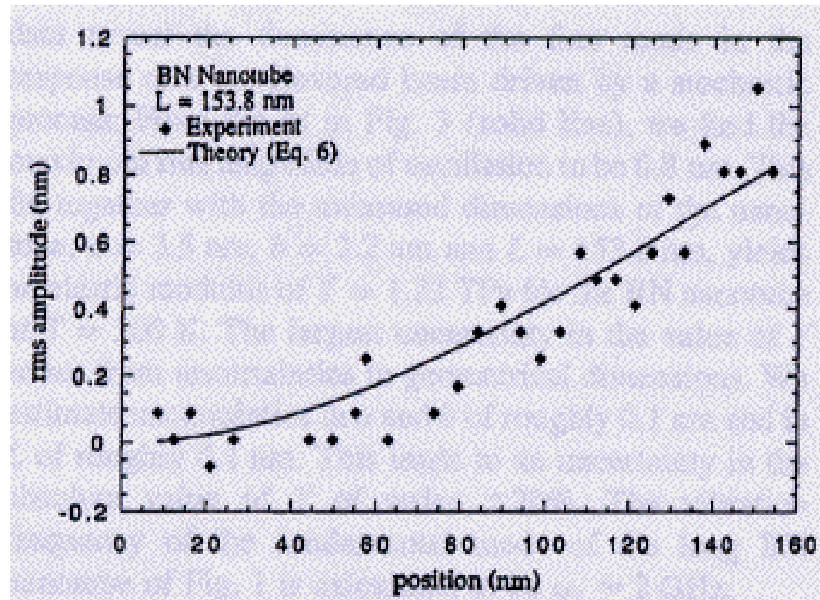


II.Tensile Testing of Multiwall C Nanotube

- Nanotube Growth:
  - Arc (60A, 30-45VDC) between B-doped C anode N_2 atm (380 T)
    - (Chem. Phys. Lett. 260 465 (1996))
- Nanotube TEM Characterization
  - Topcon 002B (200kV)
  - Piezoelectric Manipulation Stage

CNT Thermal Vibration (TEM)

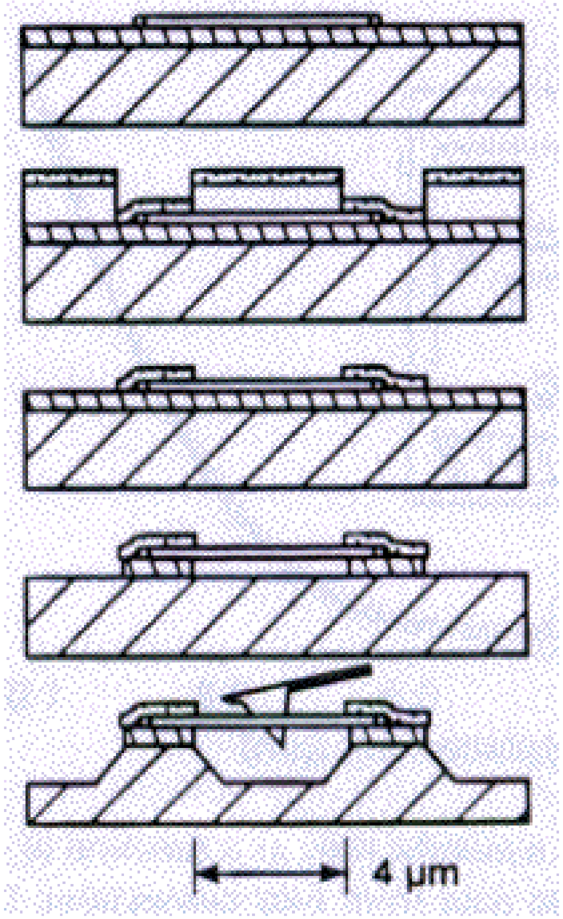


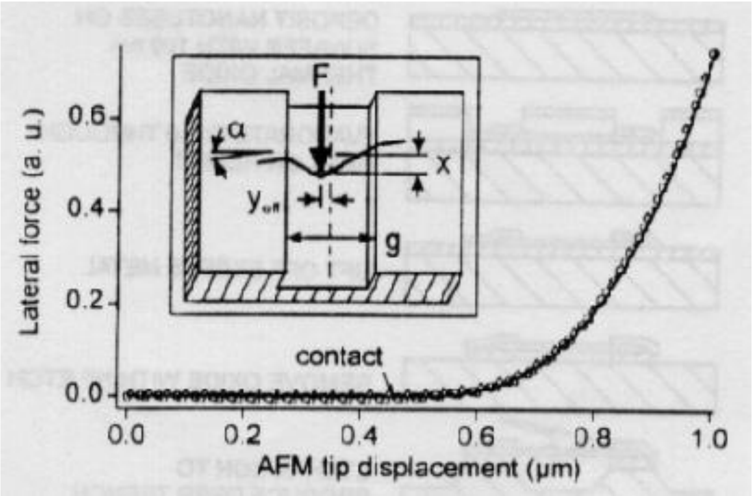


$$\nu = \frac{\beta^2 D \sqrt{E}}{8\pi L^2 \sqrt{\rho}}$$

Sol. St. Comm. 105(5) 297 (1998).
J. Phys. Chem. Sol. 61 1025 (2000).

CNT Bending (AFM)

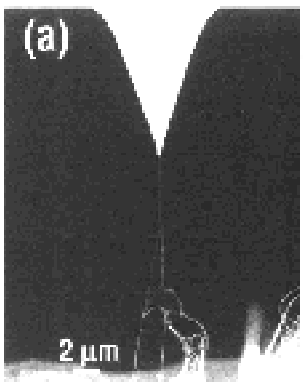




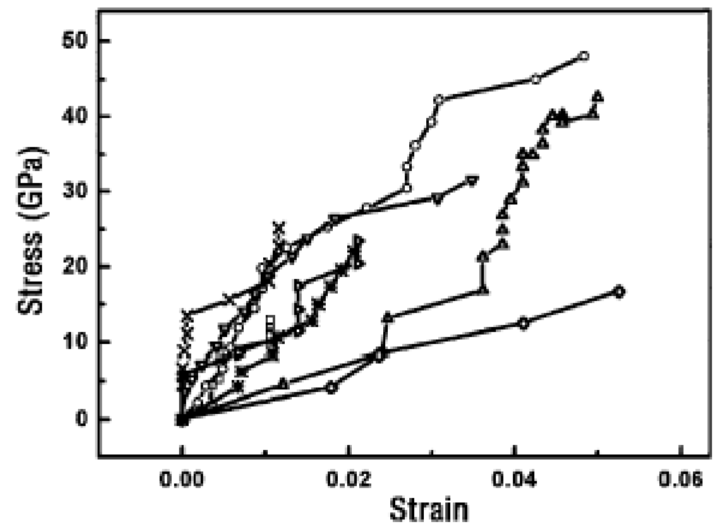
Force applied with probetip
=>strain (to failure) measured
- But section not round

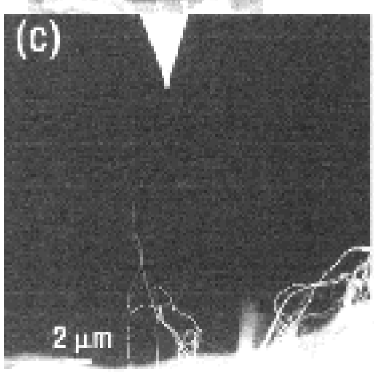
Appl. Phys. Lett. 74 (25) 3803 (1999).
Phys. Rev. Lett. 82 (5) 944 (1999).

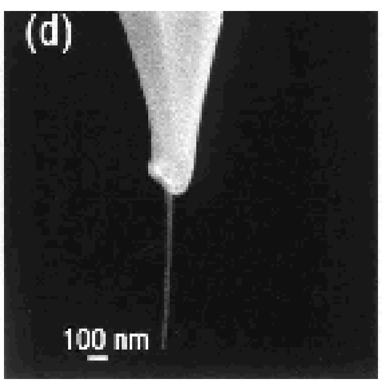
CNT Pulling (AFM/SEM)



< Before
After
v



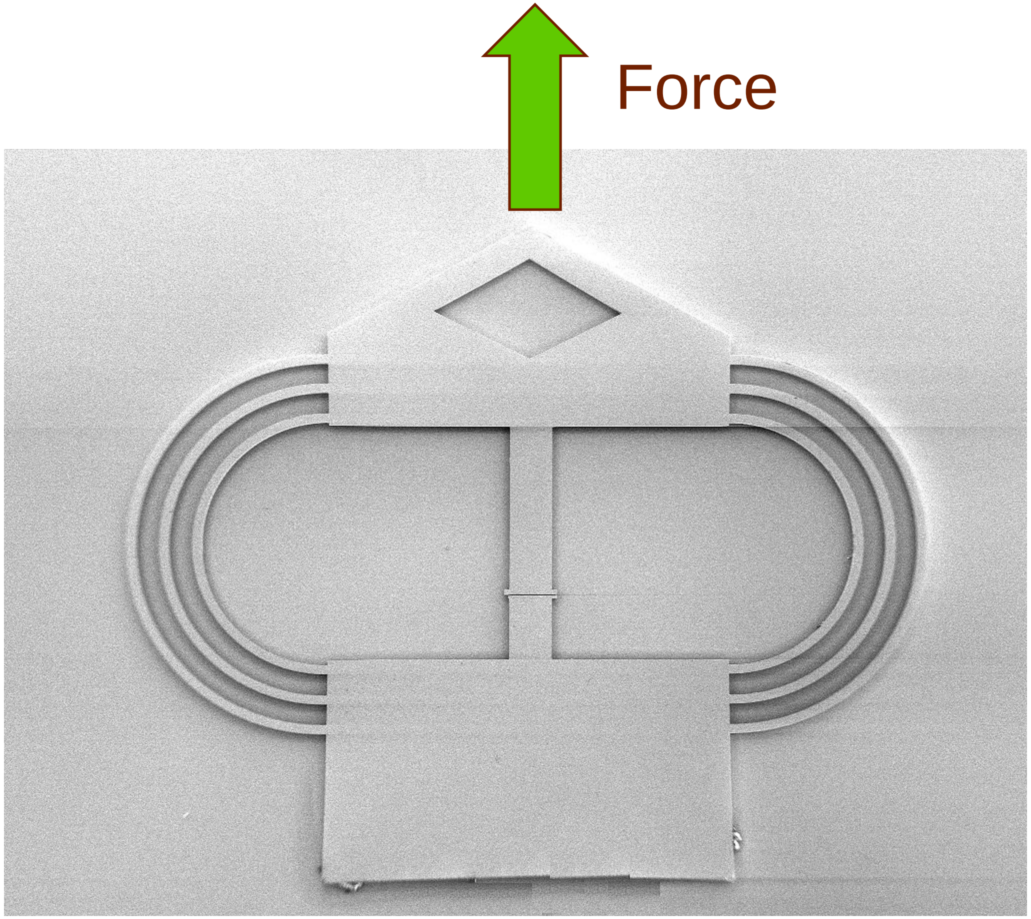


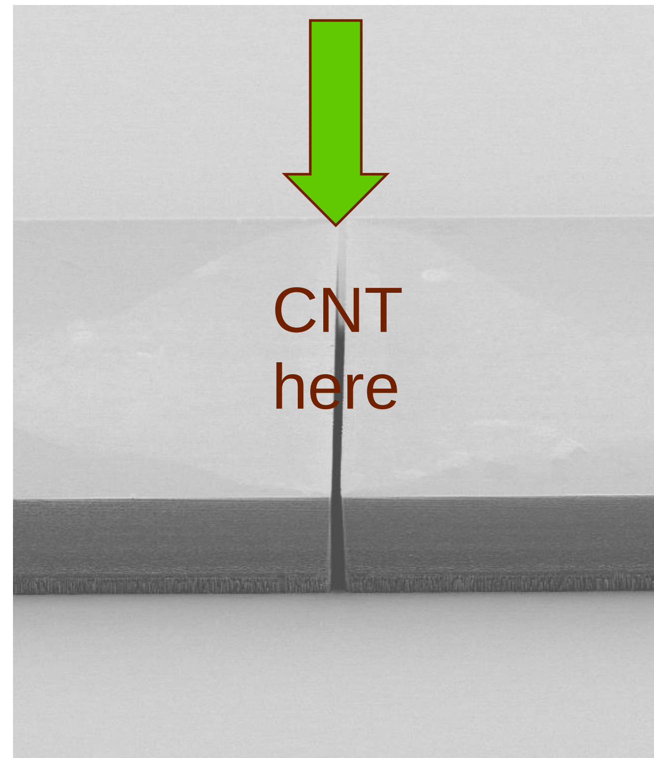


Tube pulled with probetip
=>strain (to failure) measured
- But both ends moving.

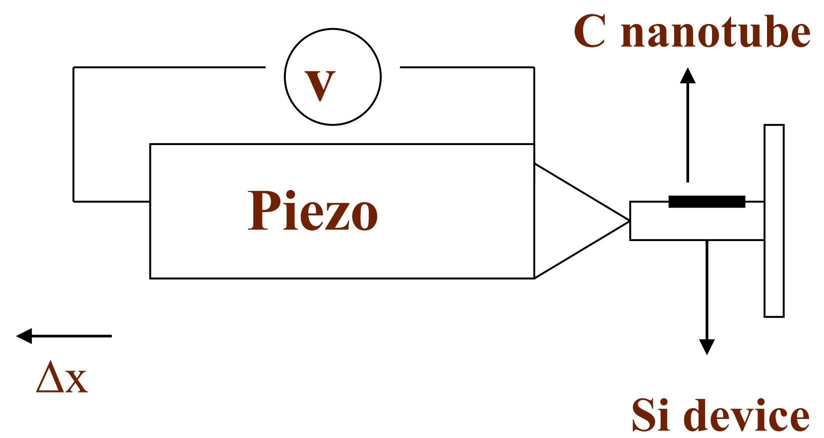
Phys. Rev. Lett. 84 (24) 555, (2000).
Science 287 637 (2000).

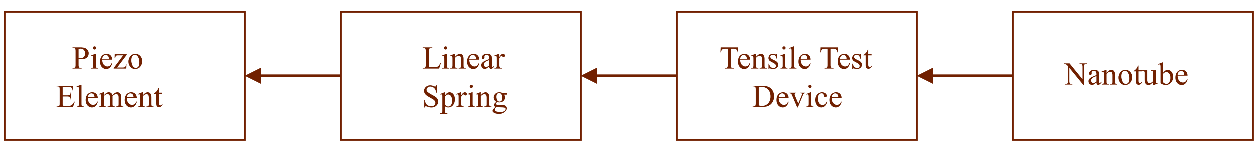
Microfabricated Tensile Stage





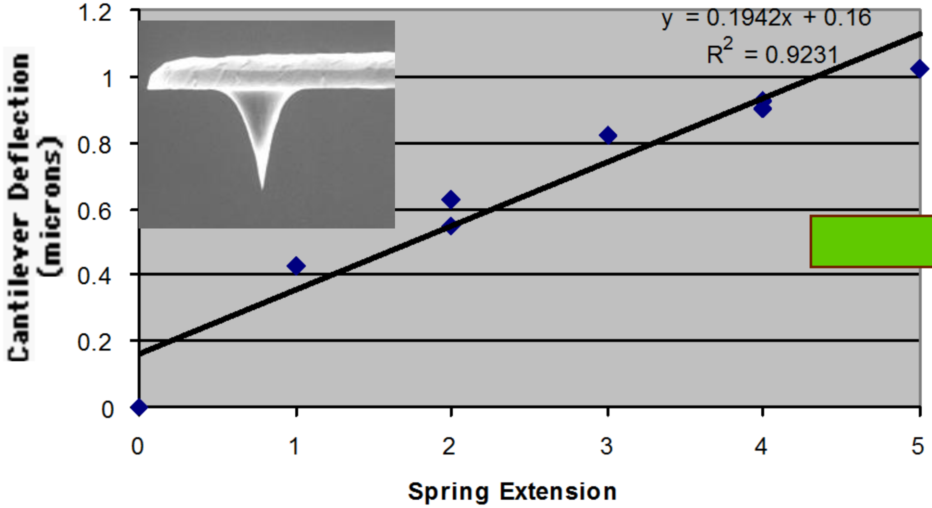
Experimental Setup



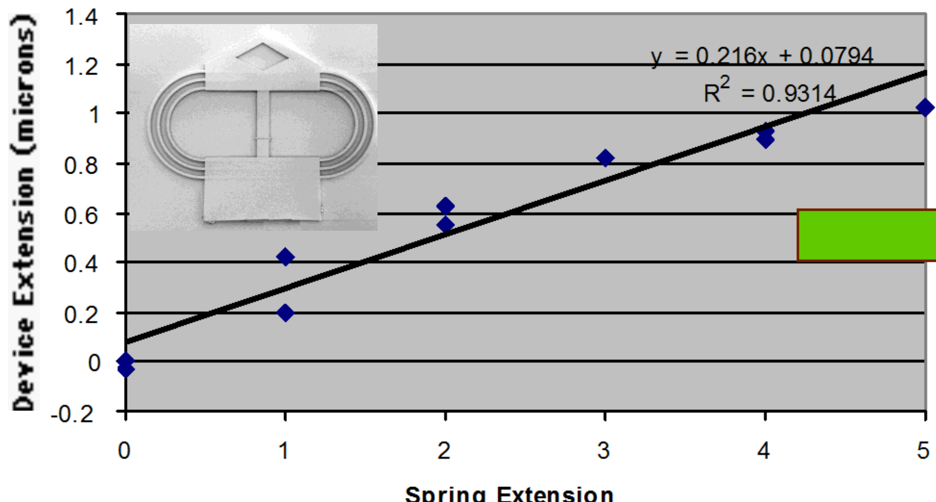


$<= F$ $\quad$ $k_S\, x$ $\quad$ $-k_D\, x$

Force Calibration



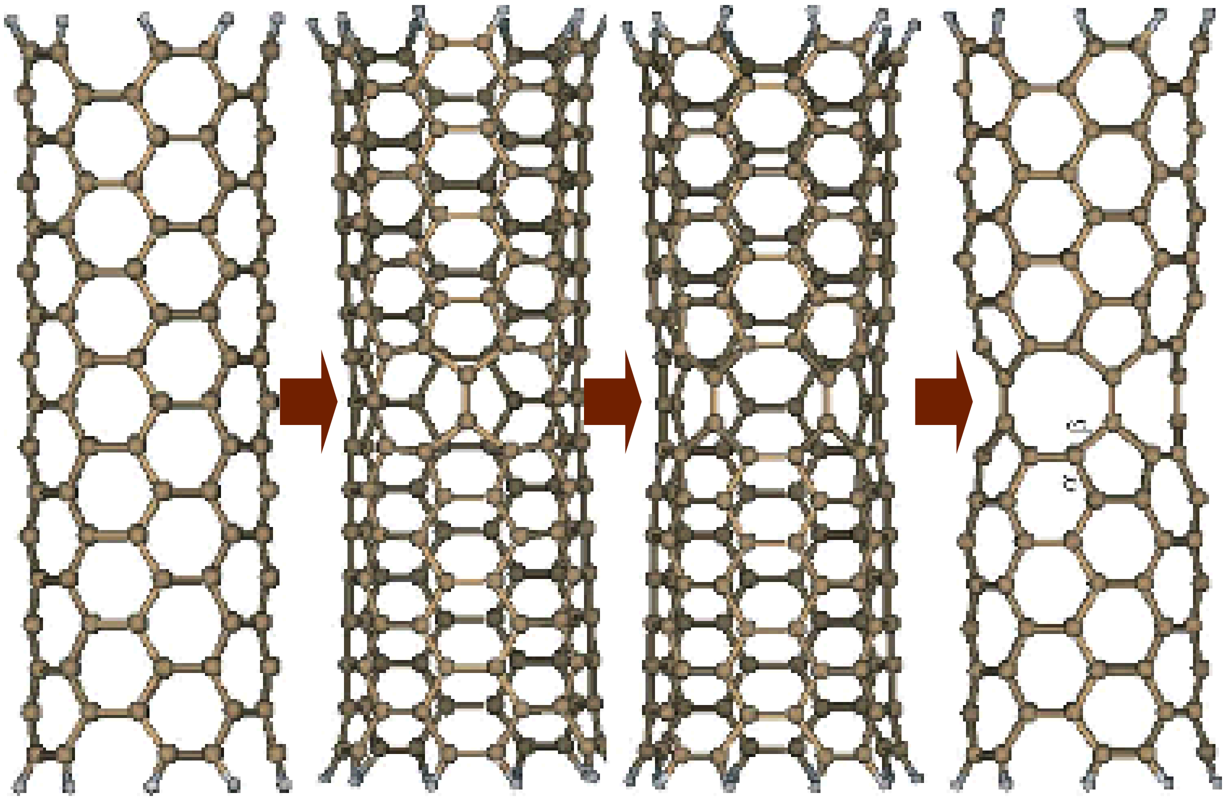
k_{spring}



k_{device}

CNT Fracture- Stone-Wales Transformation

- C-C bond ruptured in 4 hexagons
=>2pentagon/heptagon pairs created
then larger (octagon) rings formed

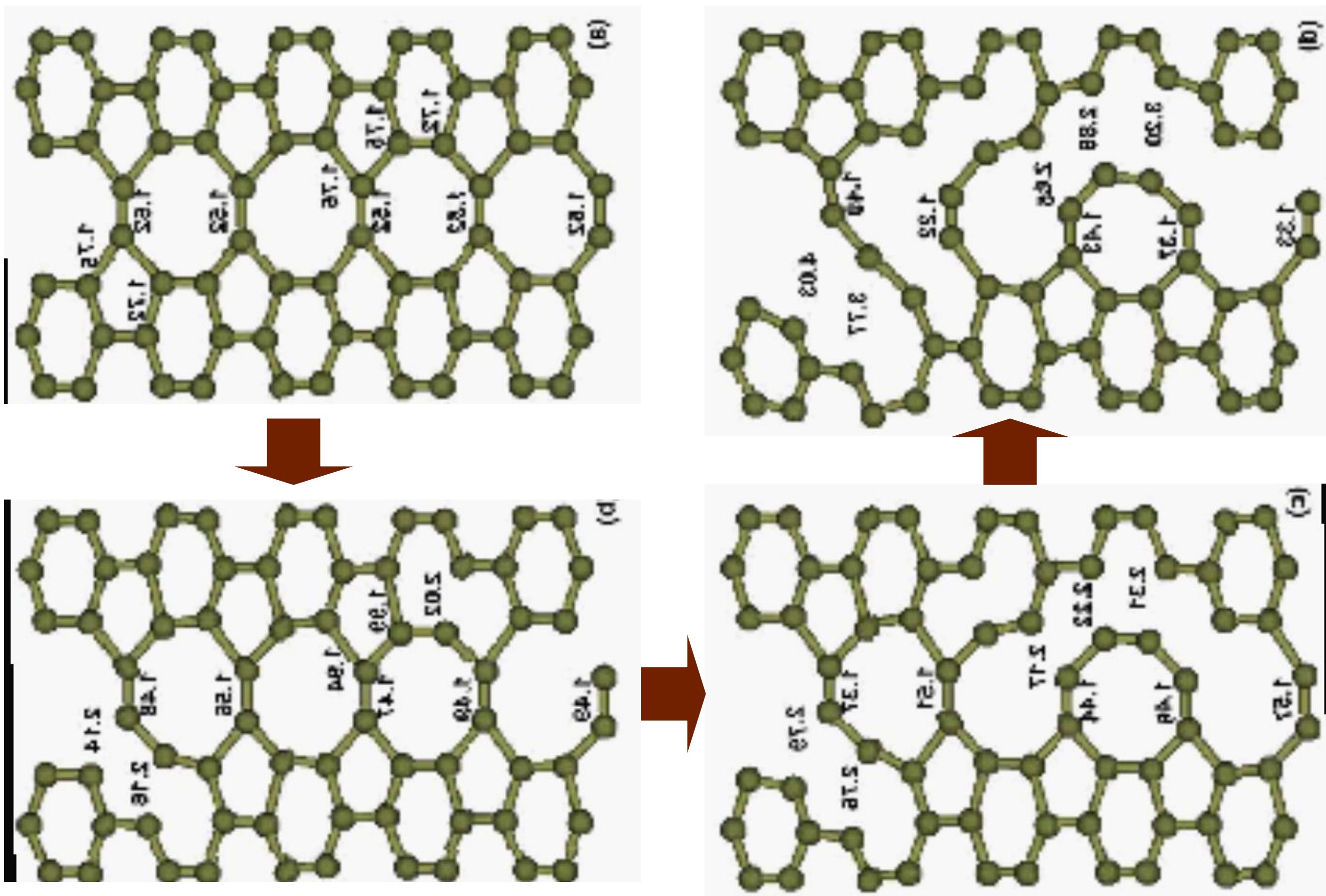


Energetically favored for $\varepsilon \sim 5\%$

Chem. Phys. Lett. 382 133 (2003).

CNT Fracture-Bond Breaking

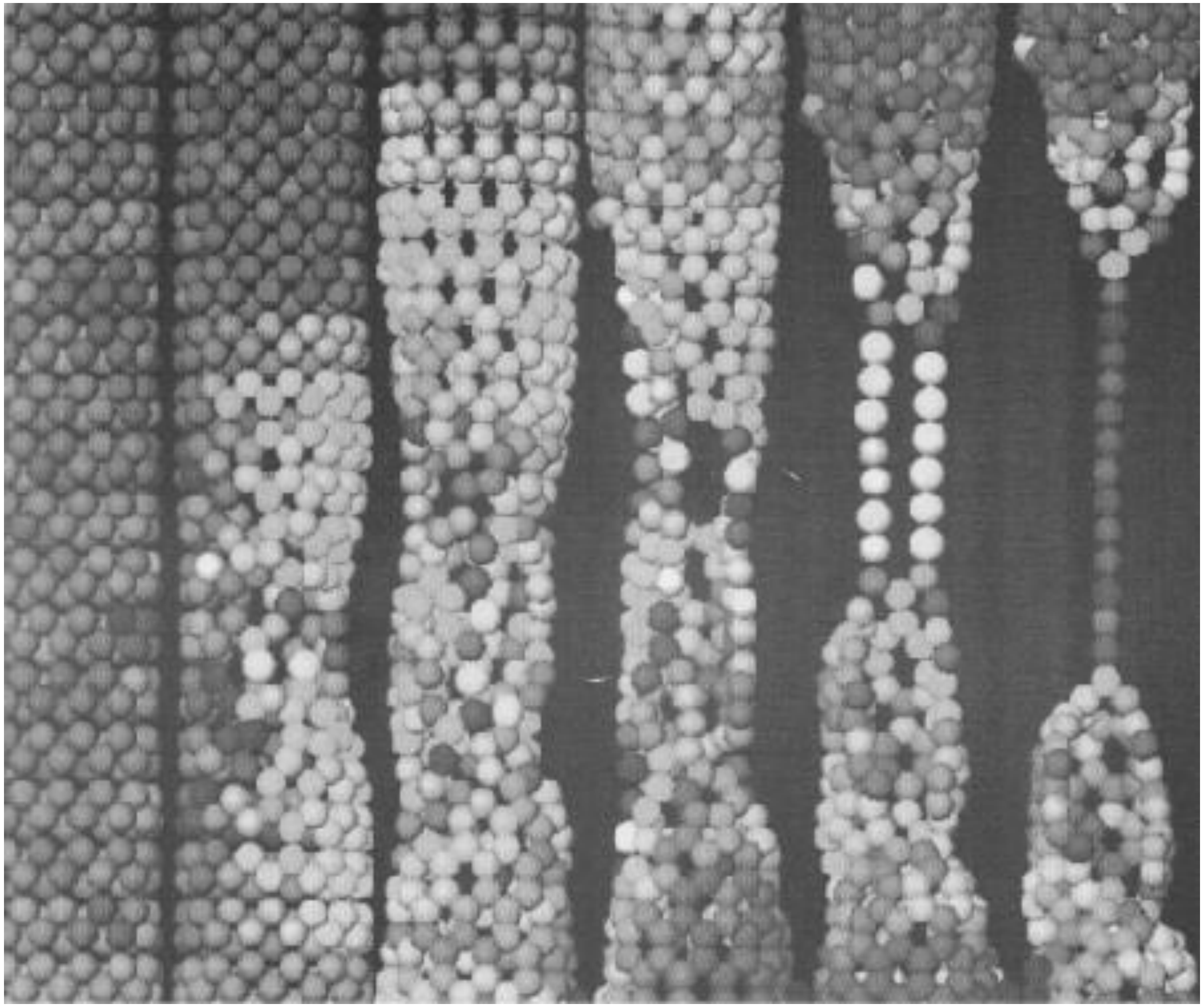
Octagon ring bonds break => tube narrows



Mechanism gives E=1.16TPa

Chem. Phys. Lett. 382 133 (2003).

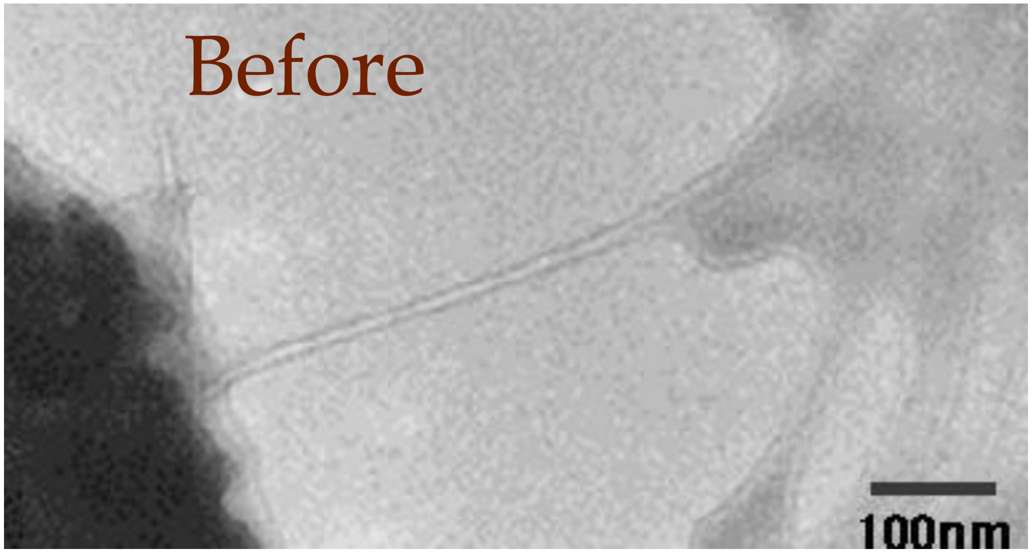
CNT Fracture-Narrowing to Failure



Tube narrows to monatomic layer (in ~ 10^{-10} sec)

J. Chem. Phys. 99 6923(1993)

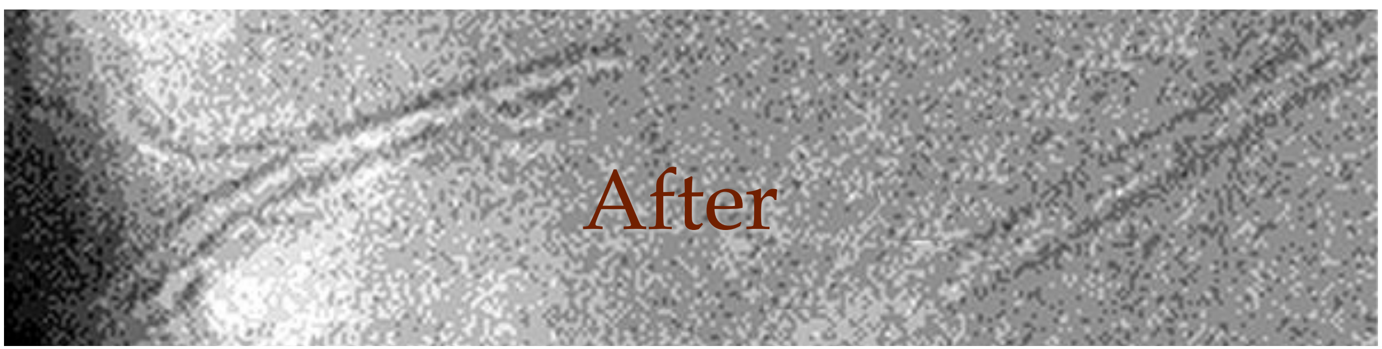
NanotubeTensileTest



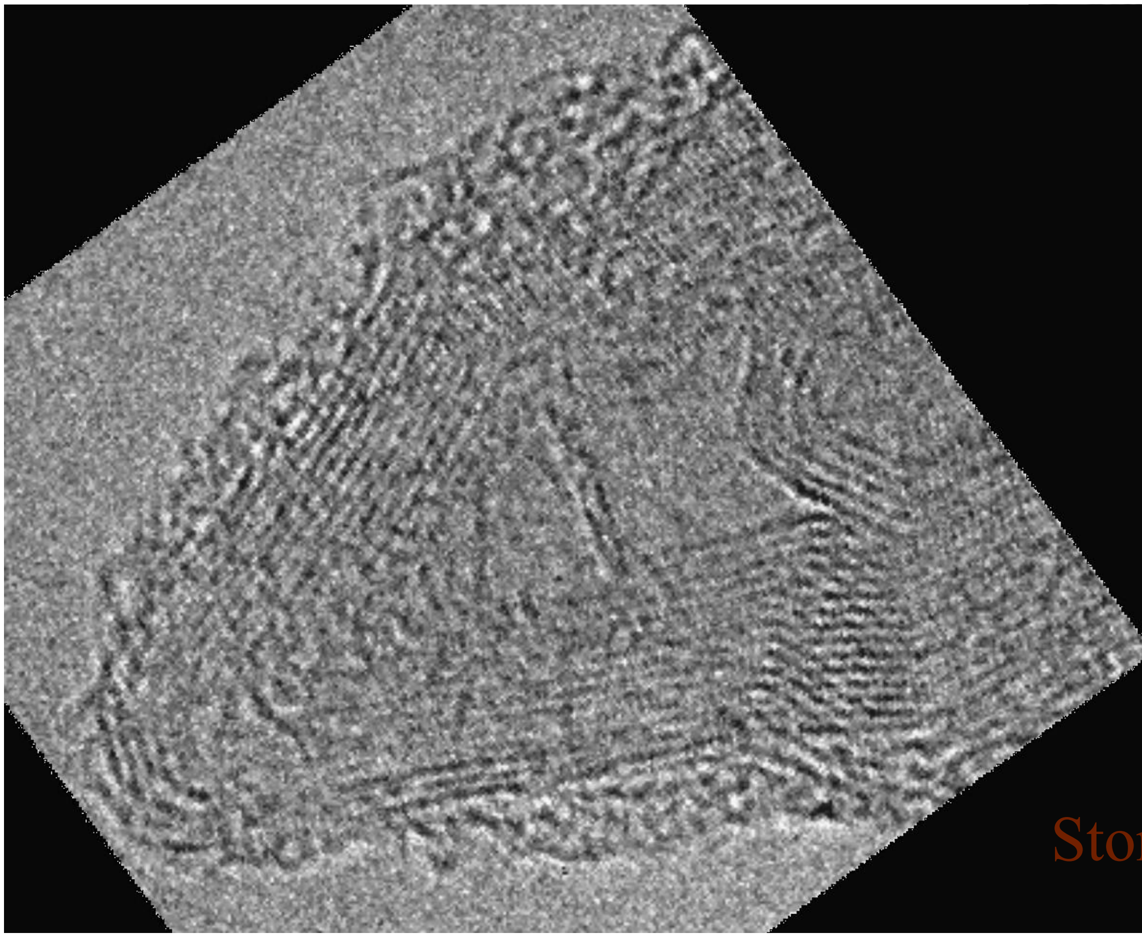
-for F = 18 μNt, A=123 nm^2

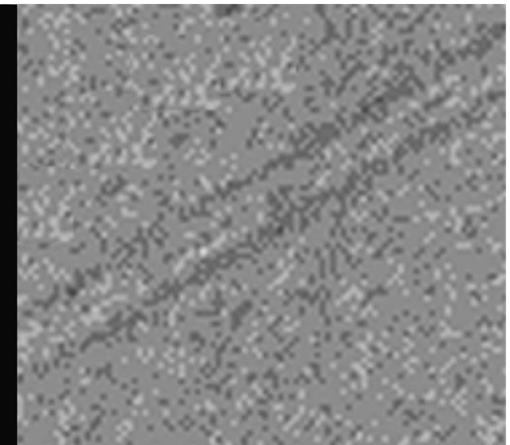
=>σ = 0.15 TPa

-consistent with predictions and Stone-Wales mechanism



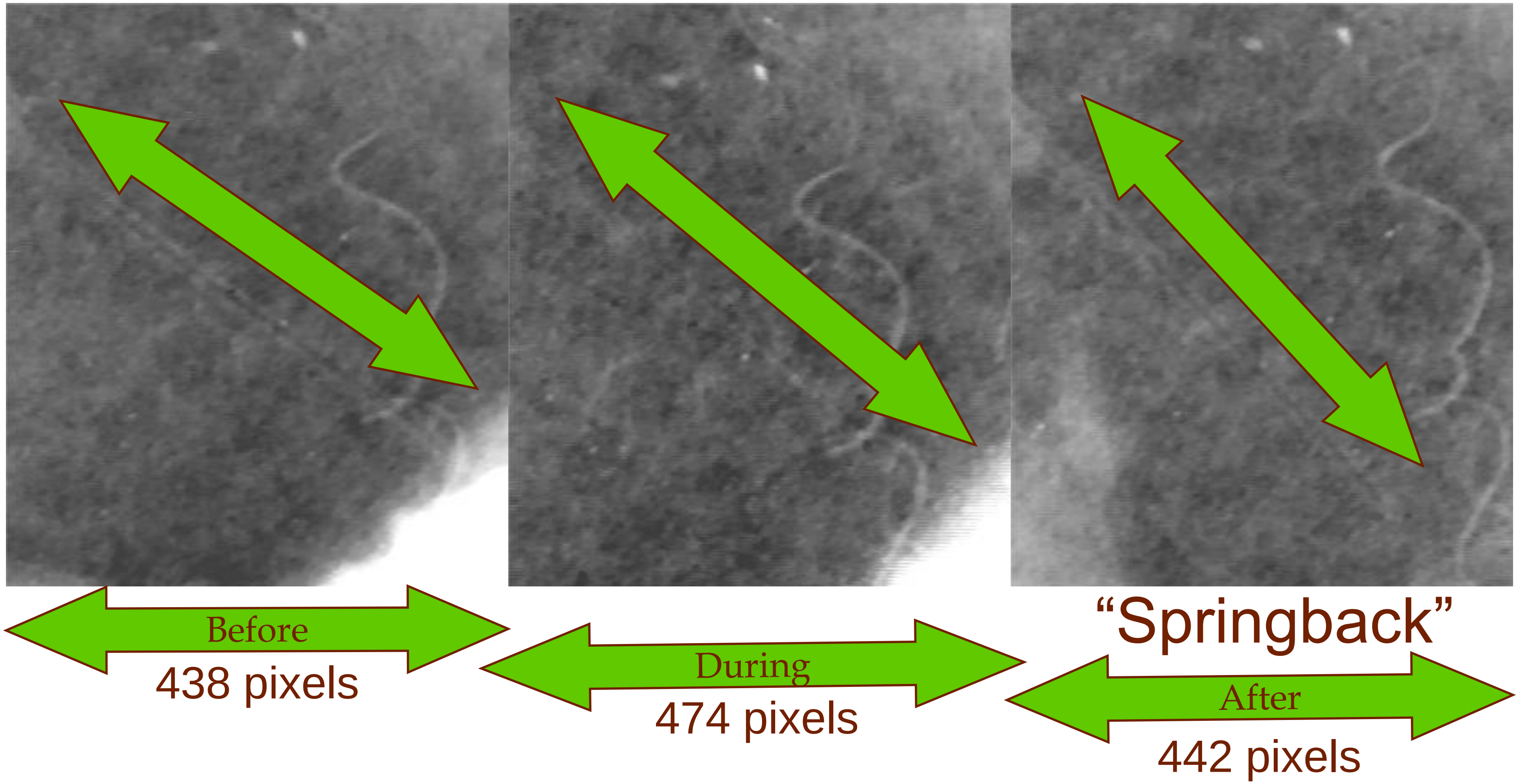
“Healed” Endcap





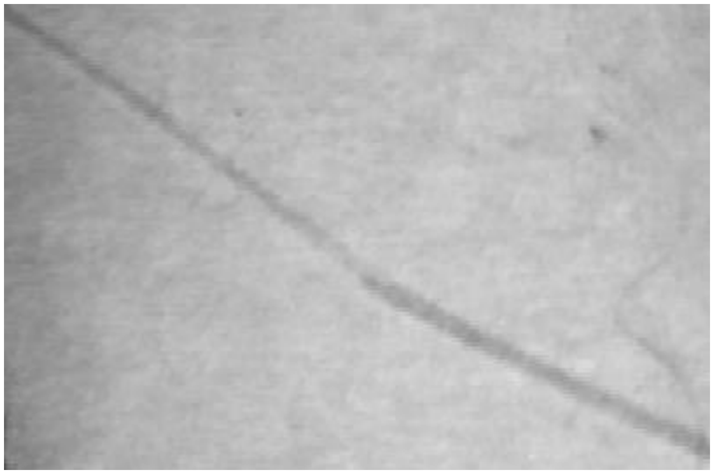
Consistent with
Stone-Wales mechanism

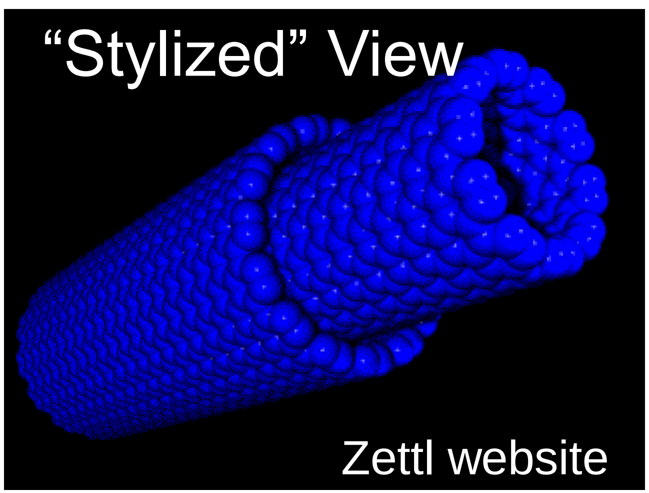
Elongation (major section)

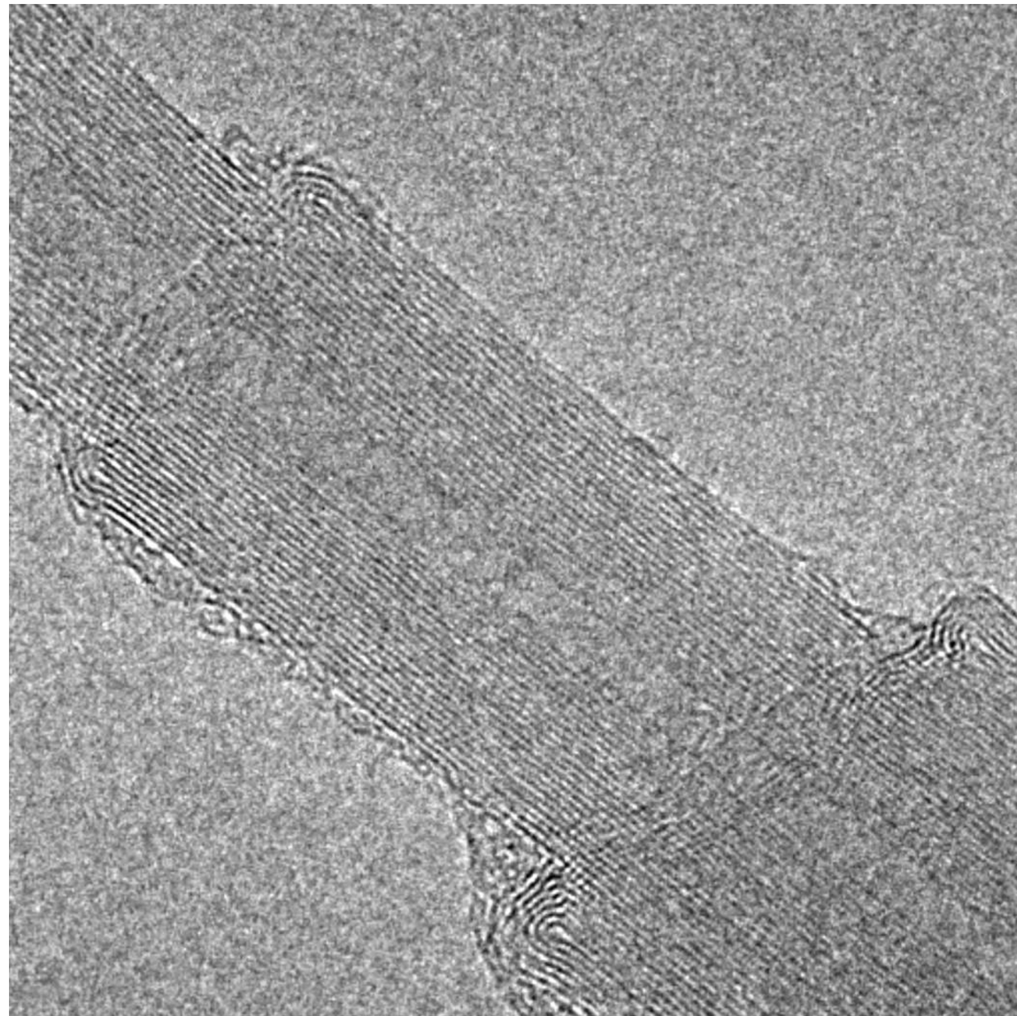


Elongation = 8.2%

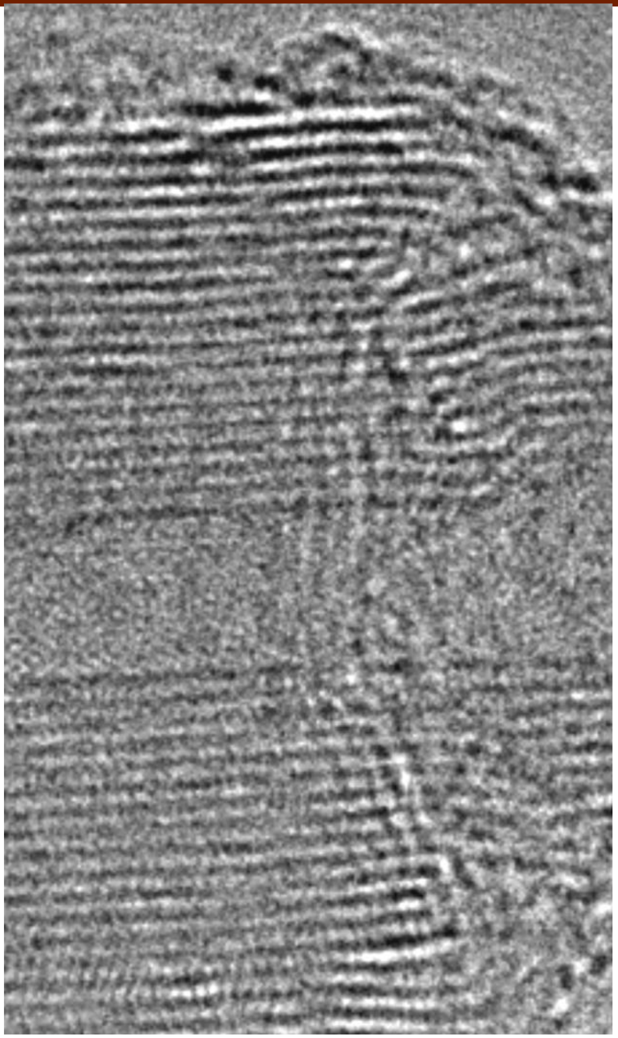
“Telescoping” Tubes

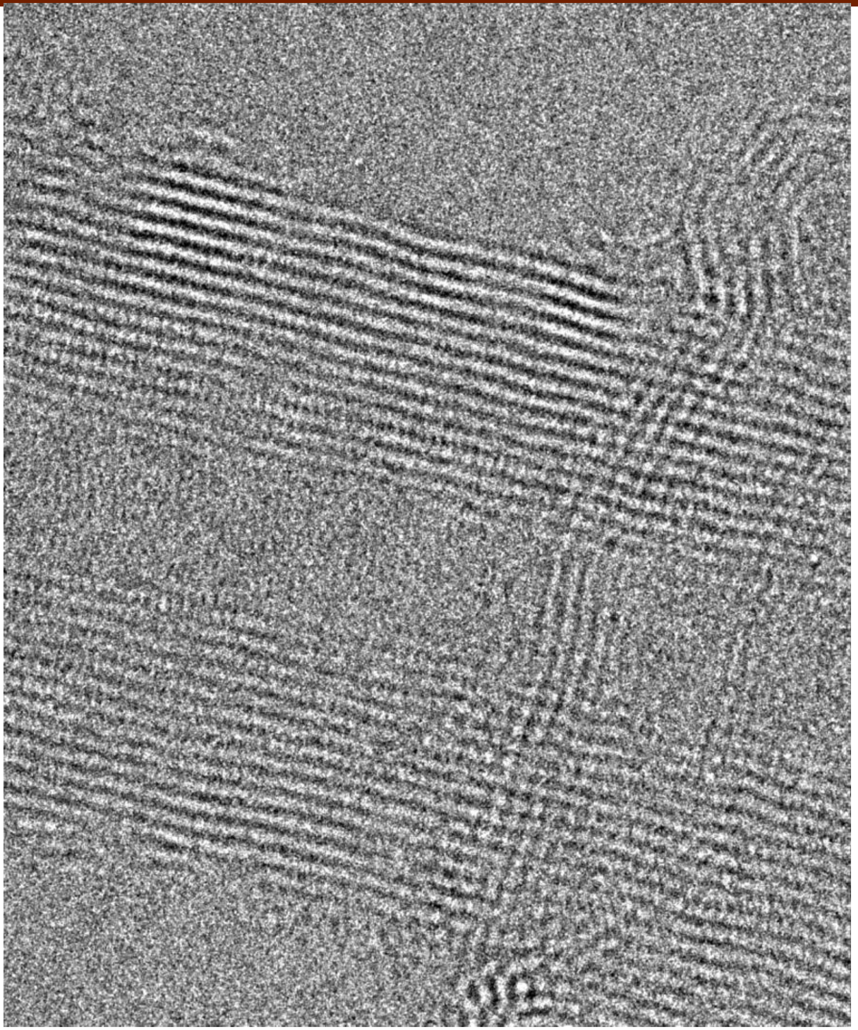




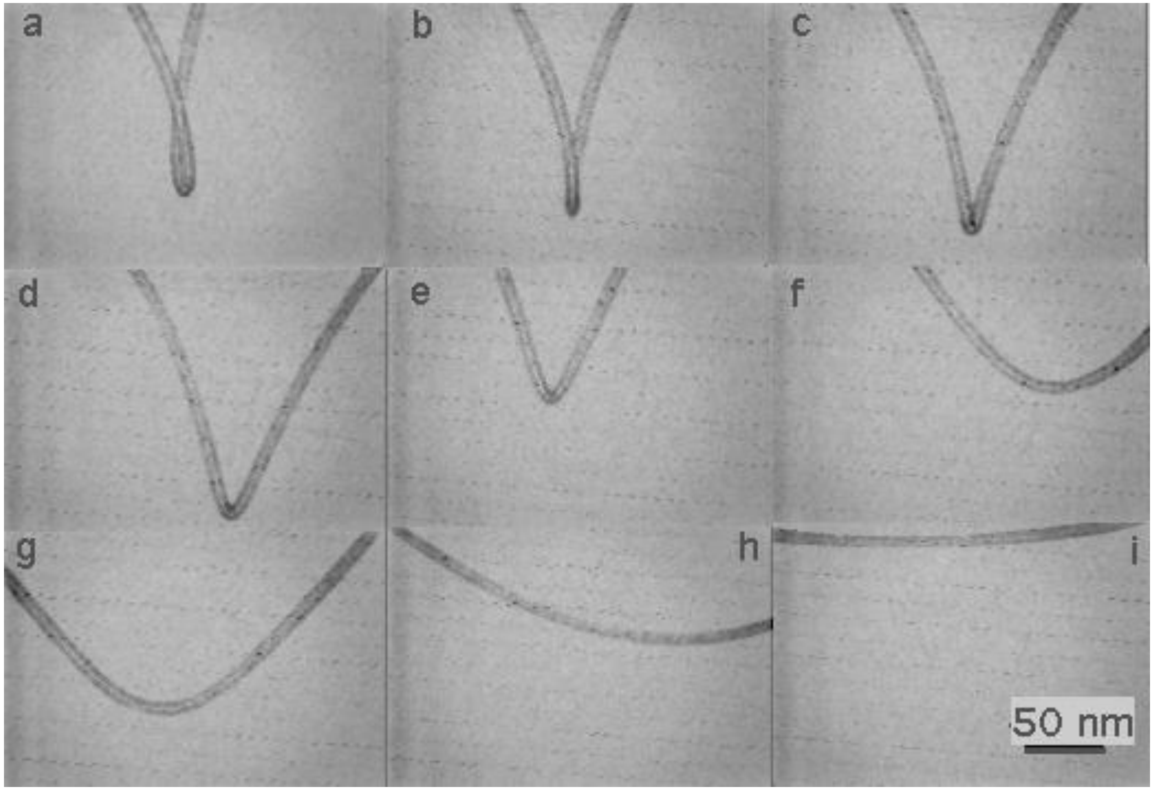


“Telescoping” Tubes (Grown-In)



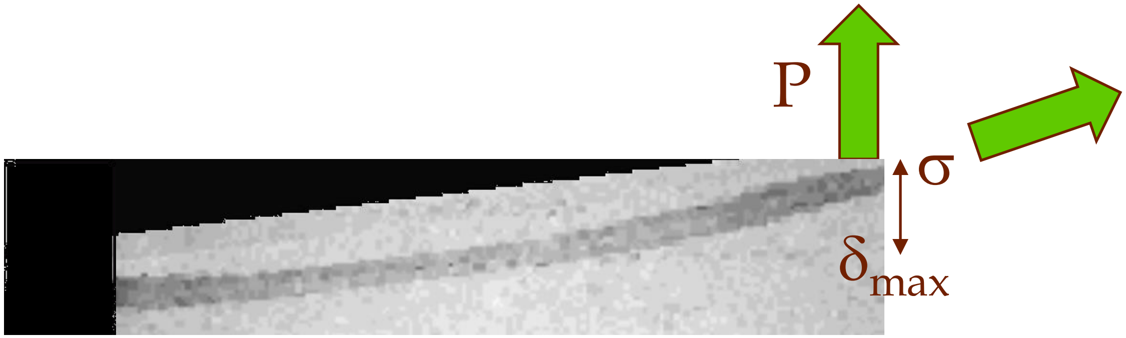


CNT Bending Sequence



Note strain contrast at sharp bends (b-e) and the lack of the same in the straightened tube (i).

Young's Modulus



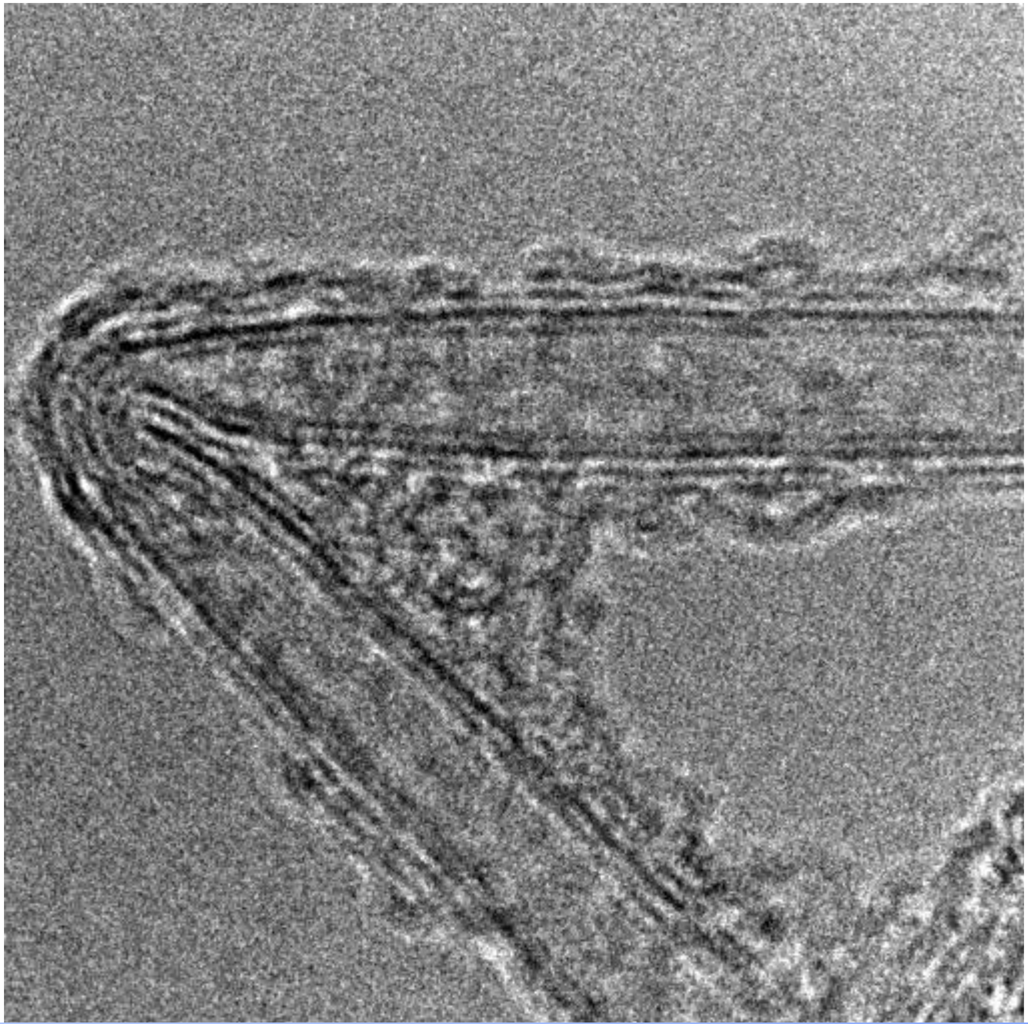
$$P = \sigma \tan\alpha$$

$$E = PL^3/3I\delta_{max} \qquad I = \pi t r^3$$

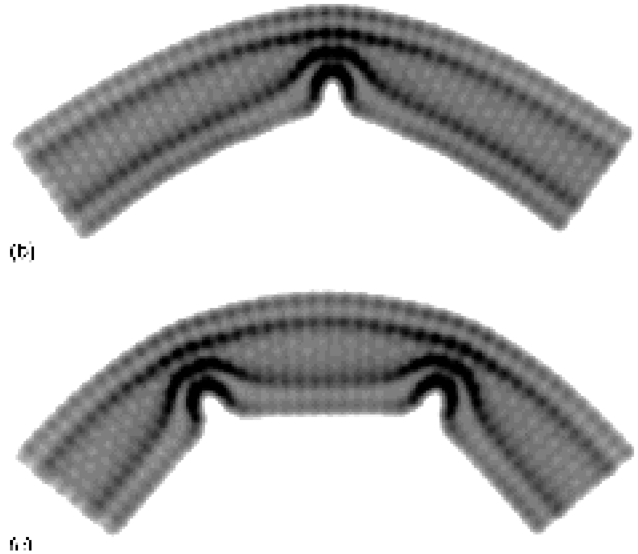
-for P=10.9 μNt, r=5.6 nm, t=333 nm (10 walls)

=>E = 0.91 TPa

Bent Tube



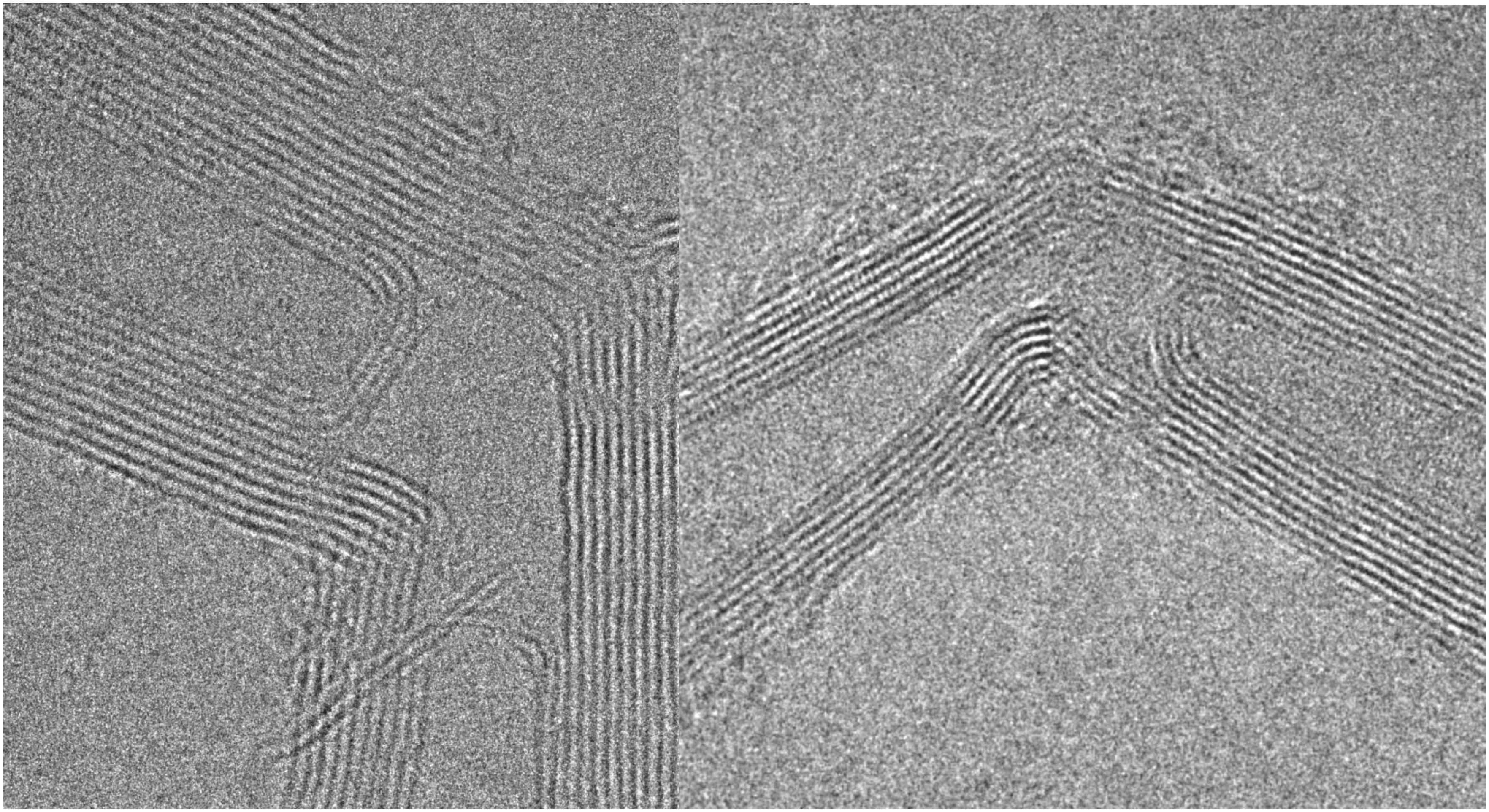
High Strain



Higher Strain

J. Chem. Phys. 104(5)2089 (1996.

Bent Tubes (Grown-In)



Multiwall CNT Mechanical Measurements

E (TPa)	σ_T (TPa)	Method
0.81 (50%)	----	AFM-2ends clamped [33]
1.28 (40%)	----	AFM-1end clamped [21]
1.26 (20%)	----	TEM- thermally vibrating beam [22]
0.1-1 (~1/R) (30%)	----	TEM-electrostatic deflection [15]
0.27-0.95	0.01-0.06	Dual AFM cantilevers [34]
0.91 (20%)	**0.15 (30%)**	**TEM-direct tension [this work]**

E = Young's Modulus, σ_T = tensile strength, R = nanotube radius, ( ) = uncertainty

Summary of *In-Situ* CNT Observations

- Mechanical Properties:
  - ➢ σ_T = 0.15 TPa, E = 0.91 TPa
- Deformation Mechanisms:
  - ➢ high strain rate
    - – outer tubes fracture
    - – partial pullout of inner tubes
  - ➢ Low strain rate
    - – Full "telescoping"
  - ➢ Reversible (>90^{o}) bending

But CNT….

- Not chemically inert
  - React with metals (carbides)
- Cannot withstand shock loading
  - Form nanodiamonds
- Unstable at high T
- **EXPENSIVE**
  - $1500./gm (gold $450./gm)

Inorganic tubes attractve

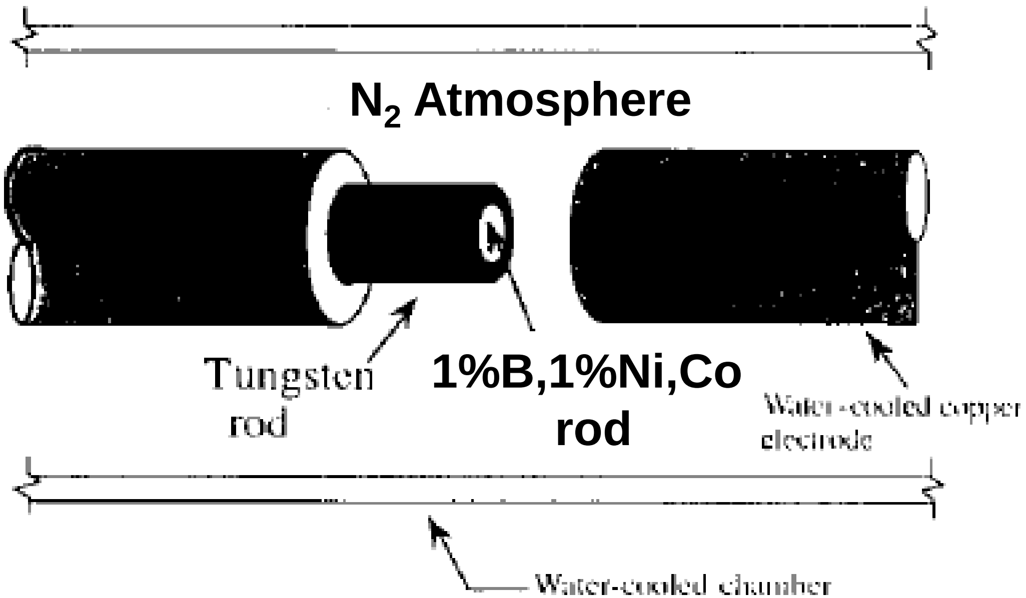
III.Structure Imaging of BN Nanotubes

- Nanotube Growth:
  - Arc (60A, 30-45VDC) synthesis in "dynamically stabilized" N_2 atm (380 T)
    - (Chem. Phys. Lett. 316 211 (2000))
- Nanotube HRTEM Characterization
  - Philips CM300 FEG (300 kV)
    - – 0.17 nm point resolution

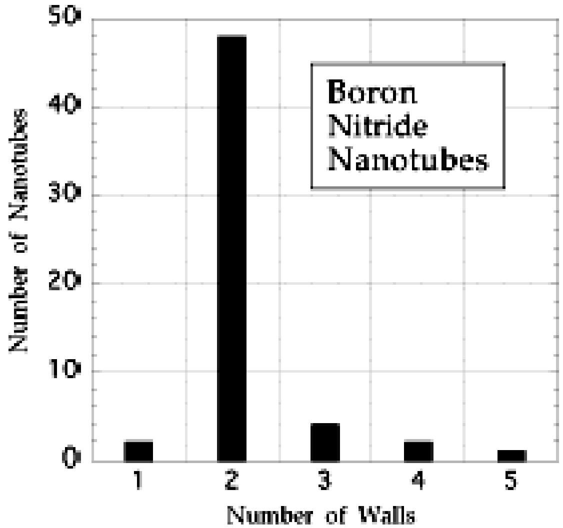
Motivation

- Two (different size)atom tube structure
- Two walled (predominantly) nanotubes

BN Nanotube Growth

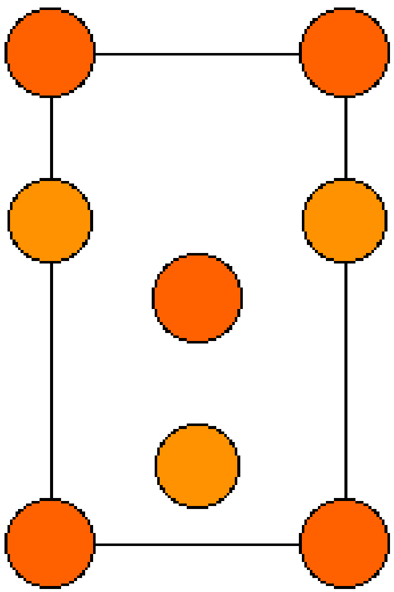


adapted from
"Fullerines: Chemistry, Physics and Technology",Ch. 17 (2000).

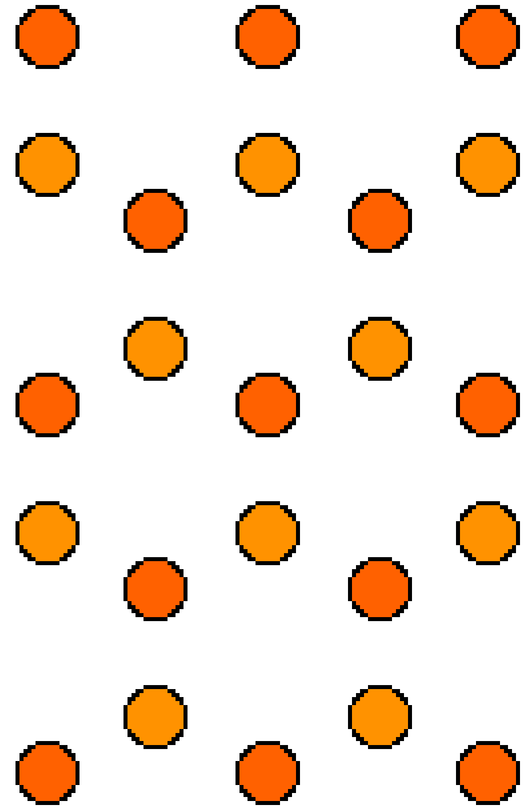


Chem. Phys. Lett. 382 133 (2003).

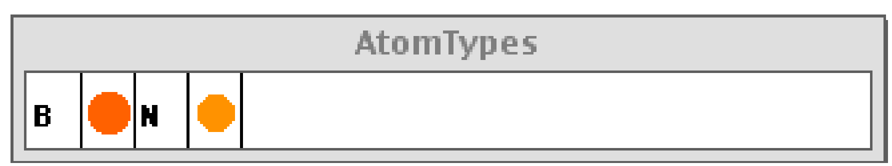
BN Structure



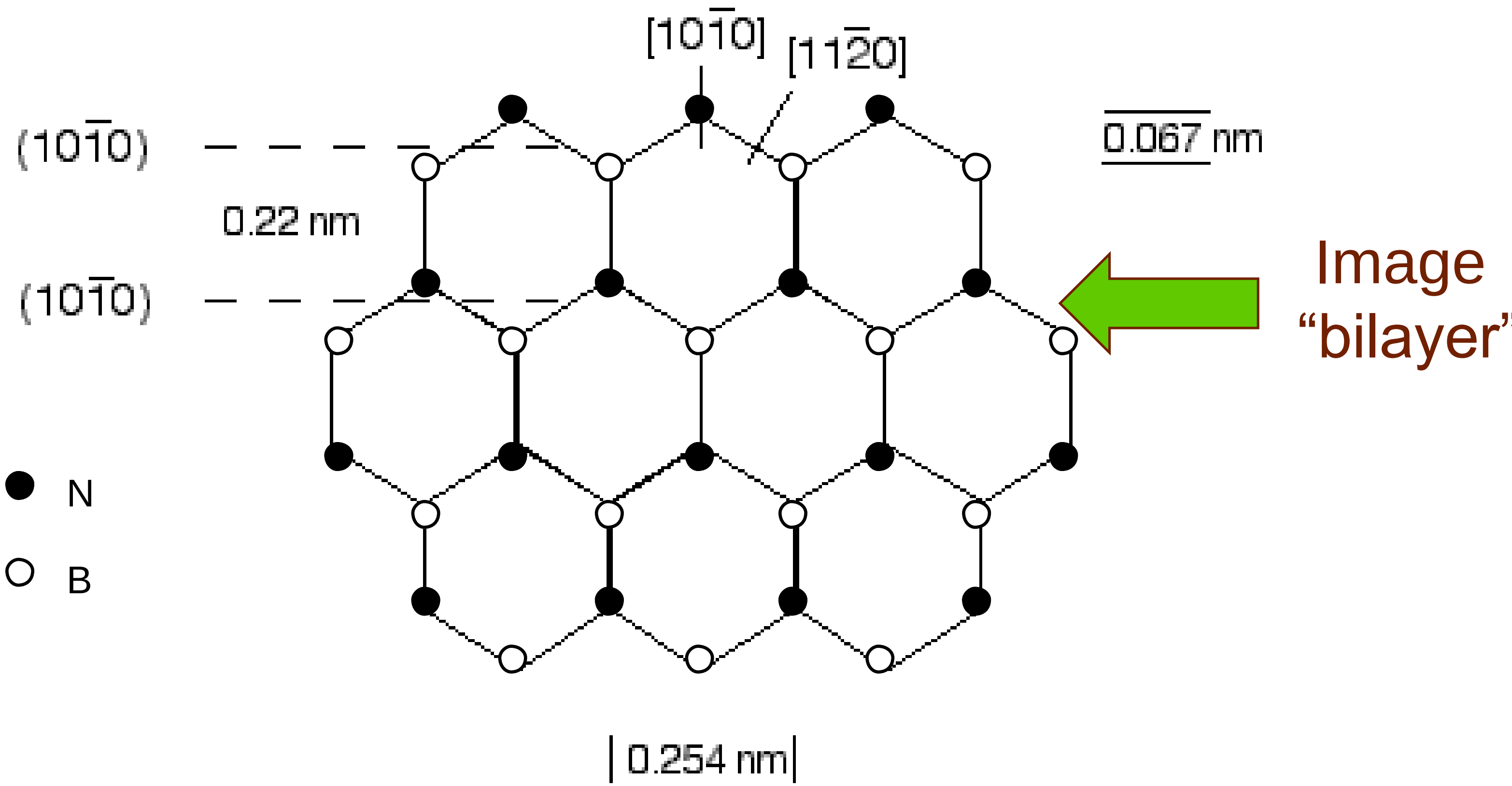
a = 0.246 nm
c=0.669 nm



Atomic Basis:
B:(0,0,0) & (.5,.5,0)
N:(.5, .1588,0) & (0,.6588,0)

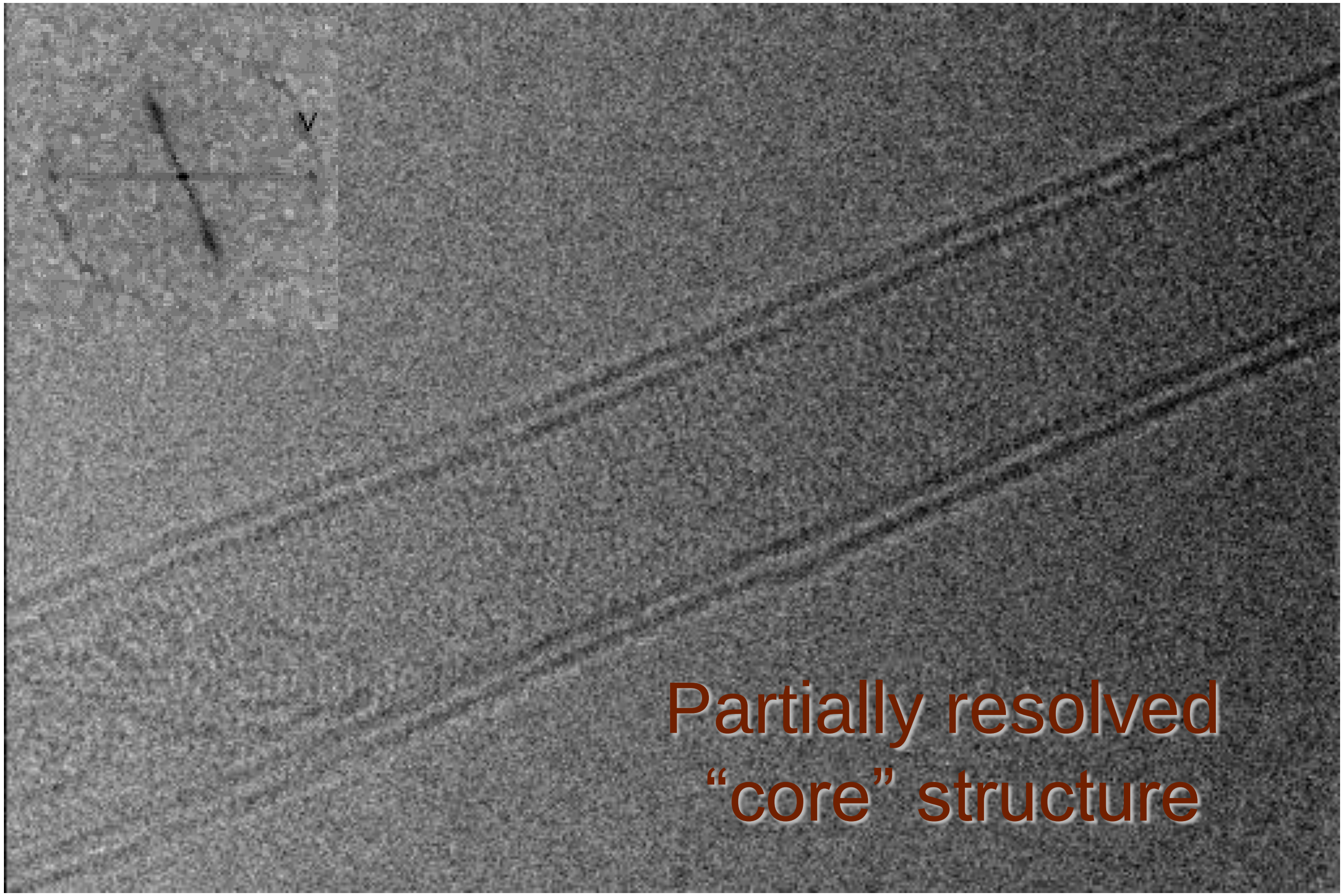


BN Basal Plane



Schematic sketch of boron nitride basal plane, showing the {1 0. 0} **bilayers**.

Two Wall BN Tube

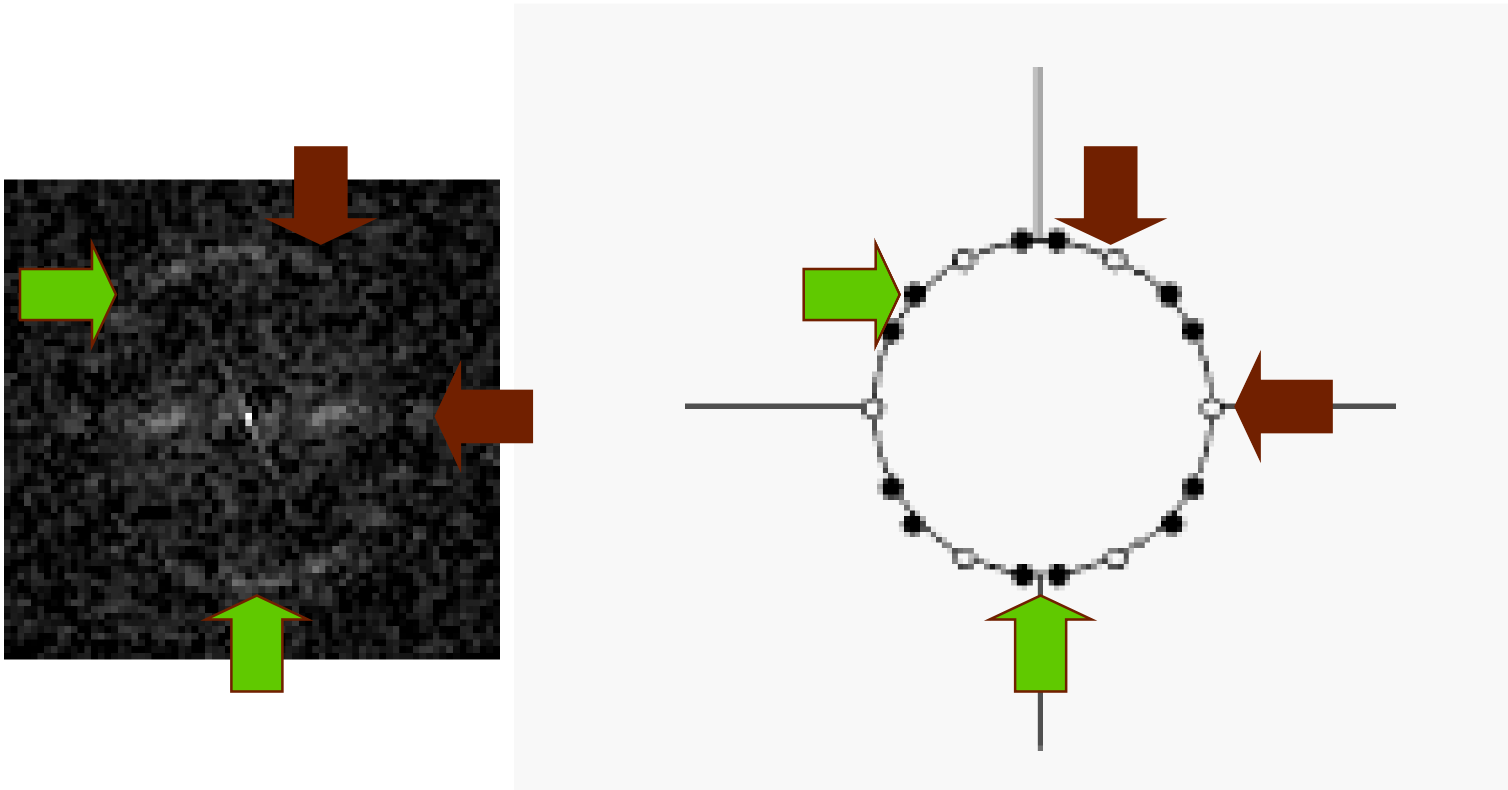


Results - 2 Wall BN Tube

“bilayer” = 0.22 nm
“sidewall” = 0.37 nm
(bulk = 0.34 nm)

- Tube 1
  - $< _{(00.2),(11.0)} = 83^{o}$
  - Maxima at 37^{o} and 19^{o}
    - <10.0> (zig-zag) tube axis
      - $\sim 7^{o}$ chirality
- Tube 2
  - $< _{(00.2),(01.0)} = 64^{o}$; $< _{(00.2),(11.0)} = 57^{o}$
  - Maxima at $\pm 4^{o}$
    - <11.0> (armchair) tube axis
      - $\sim 4^{o}$ chirality

Deconvolution of 2W BN FHT Pattern



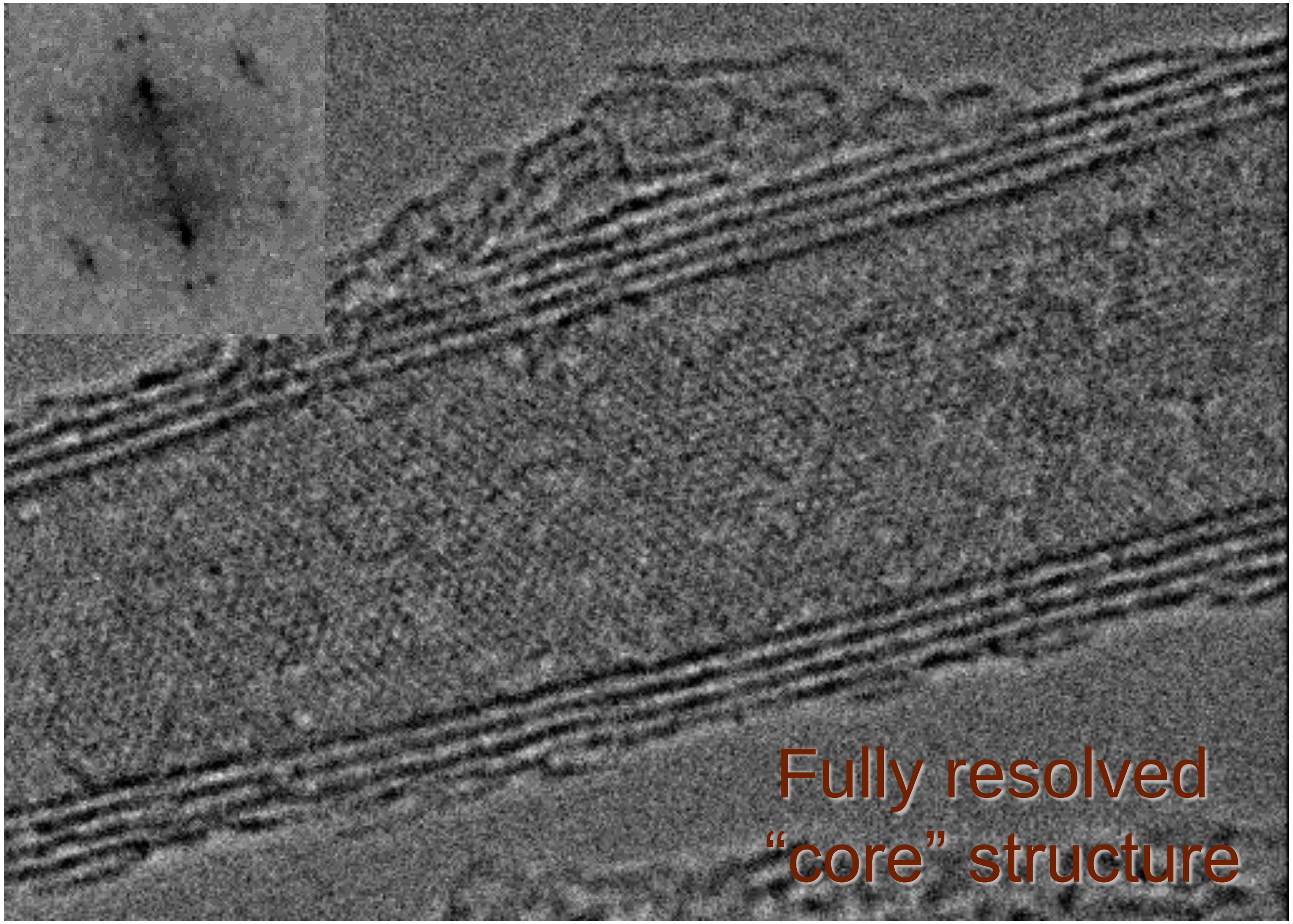
10.0 tube

11.0 tube

Geometrical Arguments

- for axis along <10.0> (zig-zag)
  - Unit cell "width" = a (= 0.254 nm);
  - Wall spacing = c (= 0.34 nm)
    - Circumference/width = $2\pi c/a$ = **8.4** (**high strain**)
    - get defect regions leading to polygonization
  - But if **c = 0.37**,
    - Circumference/width = $2\pi c/a$ = **9.15** (**low strain**)
    - less defects
- for axis along <11.0> (armchair)
  - Unit cell "width" = $\sqrt{3}$ a
    - Circumference/w = $2\pi c/a\sqrt{3}$ = 4.15 (**low strain**)

BN Four Wall Tube

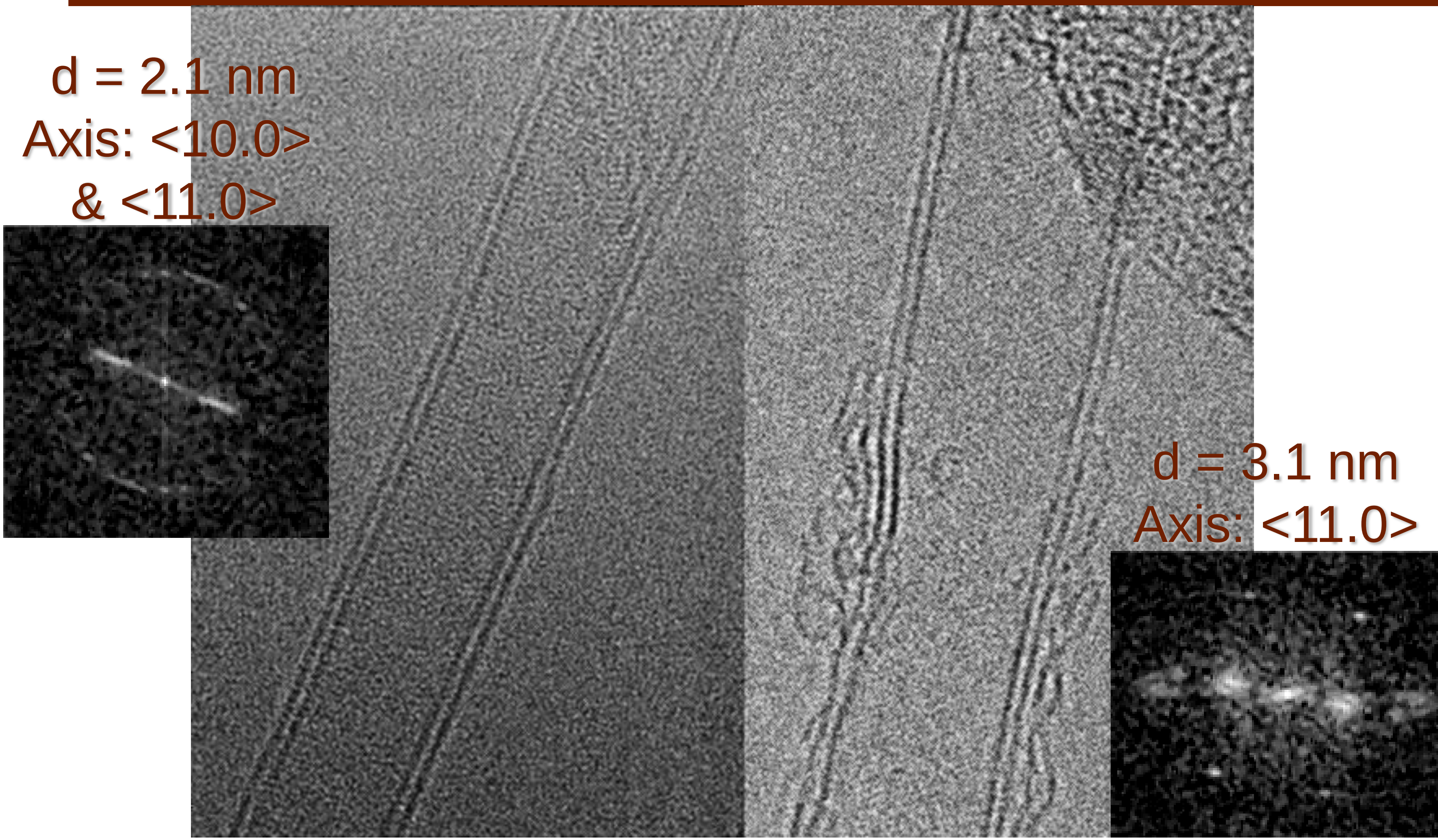


Results-4 Wall BN Tube

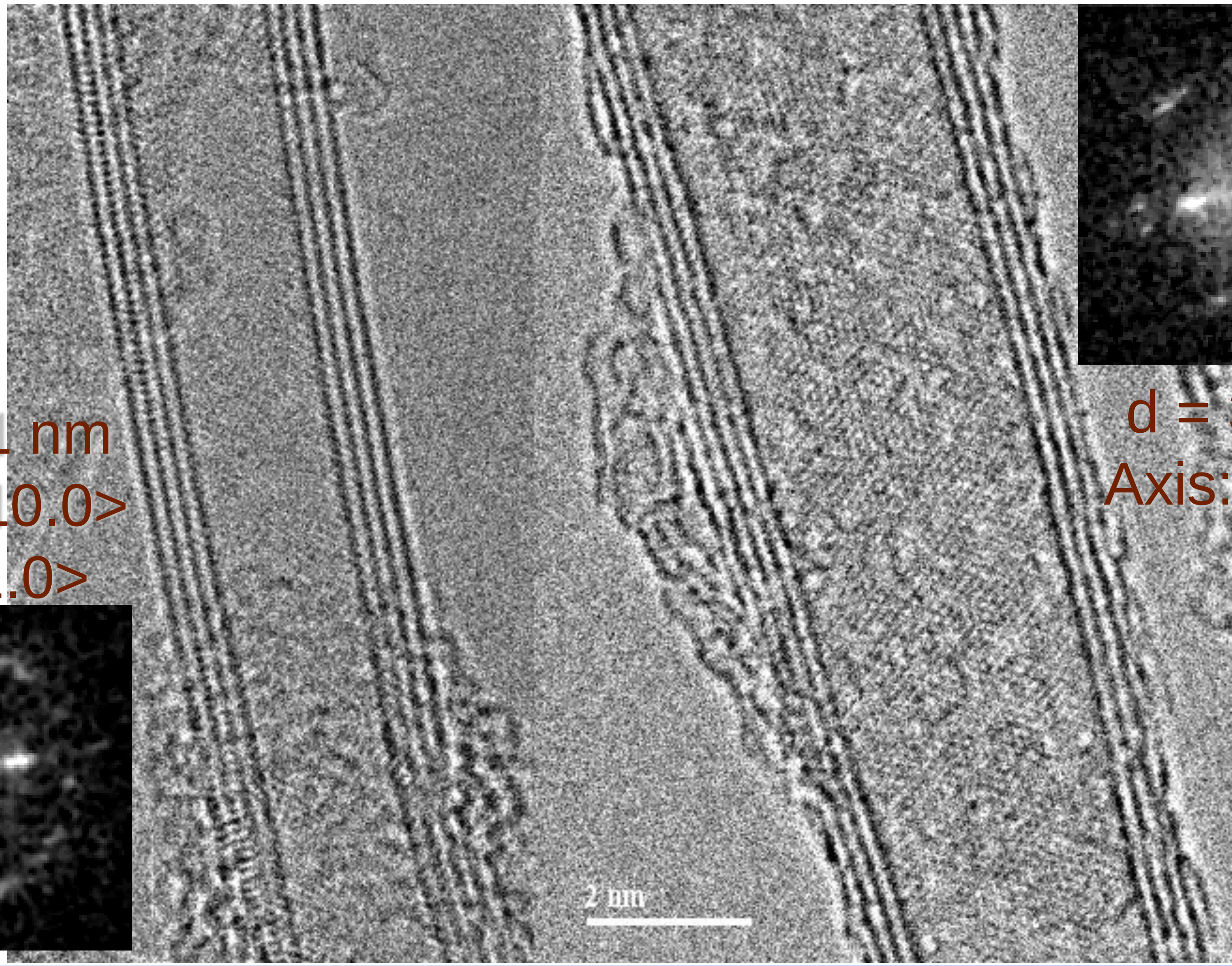
"bilayer" = 0.22 nm
"sidewall" = 0.34 nm

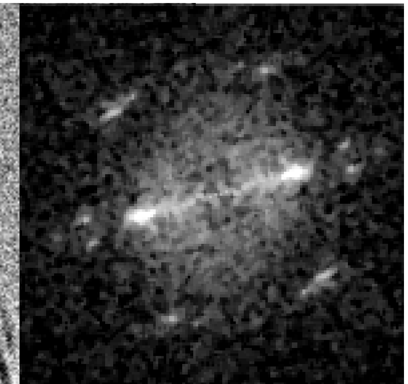
- all tubes
  - no orthogonal reflections
    - tube axis <11.0> (armchair)
  - small spot splitting
    - ~ 4º chirality

Core Diameter Effects - 2W



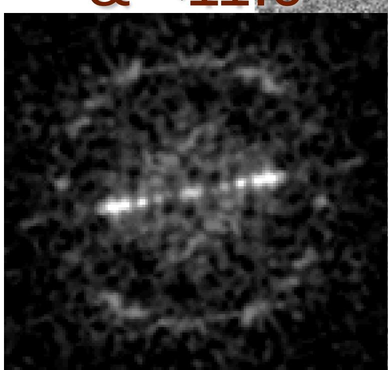
Core Diameter Effects - 4W





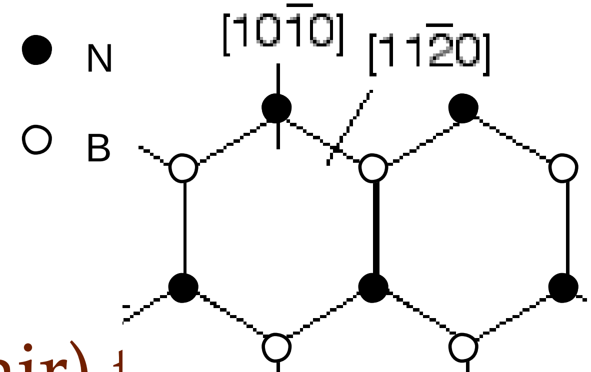
d = 3.9 nm
Axis: <11.0>

d = 2.1 nm
Axis: <10.0>
& <11.0>



BN NT Growth (d~ 2 nm)

- First tube
  - <10.0> (zig-zag) due to lower energy of N-terminated planes
- Subsequent tubes
  - Readjust to give c>0.34 nm
  - Align along <11.0> (armchair) to minimize tube closure strain



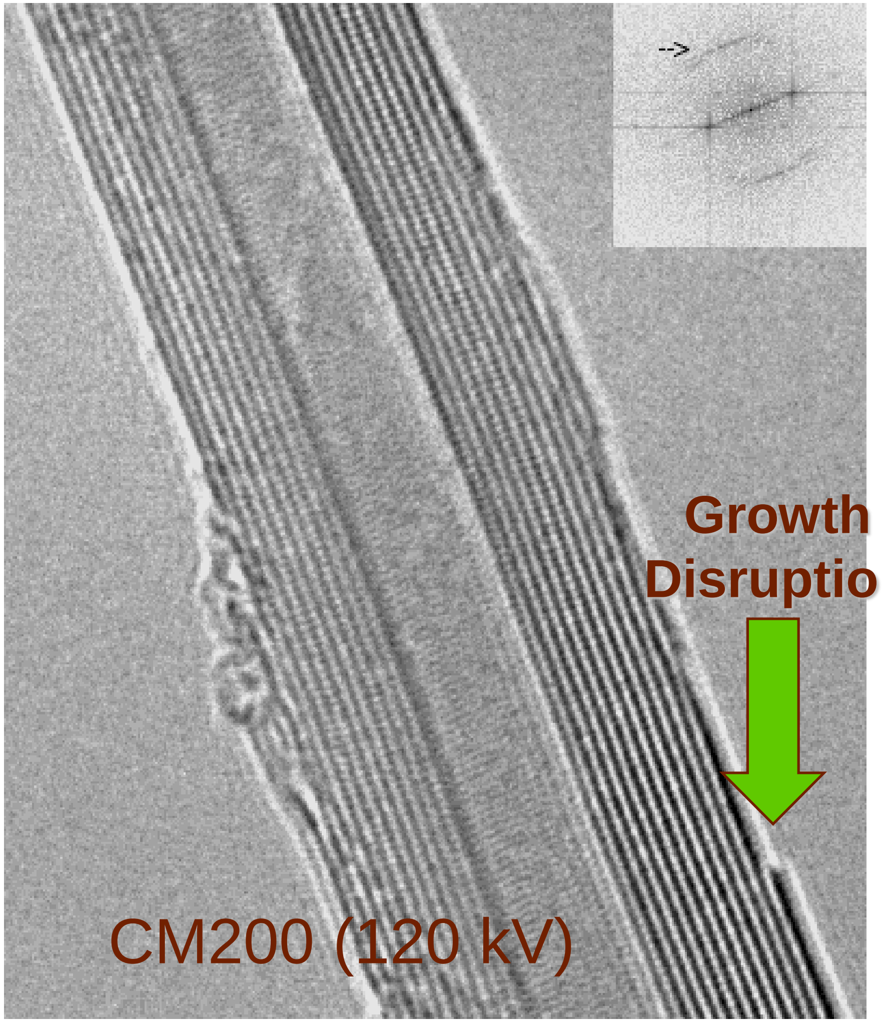
CNT-no energetic preference

BN NT Growth (d~ 3 nm)

- Alignment along <11.0> (armchair) to minimize tube closure strain

- Tubes (2W & 4W) nearly defect-free
  - near predicted mechanical properties possible

Multiwall BN Tubes

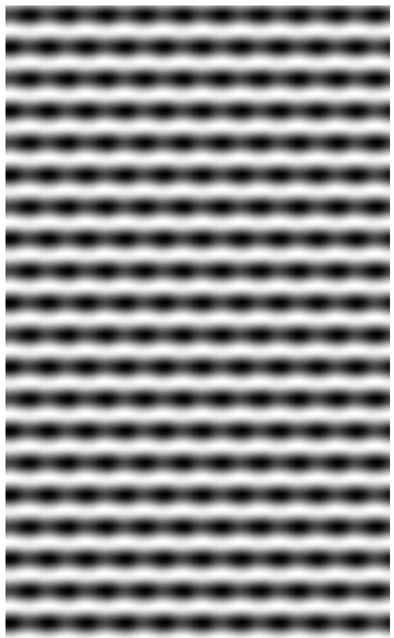


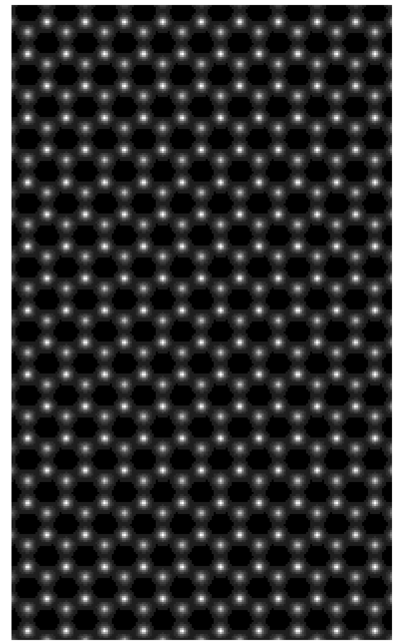
Results-Multiwall BN Tubes

"bilayer" = 0.22 nm
"sidewall" = 0.34 nm

- tube axis <11.0>
- tilt & chirality evident from FHT
- growth termination in outer walls

6W BN Image Simulation

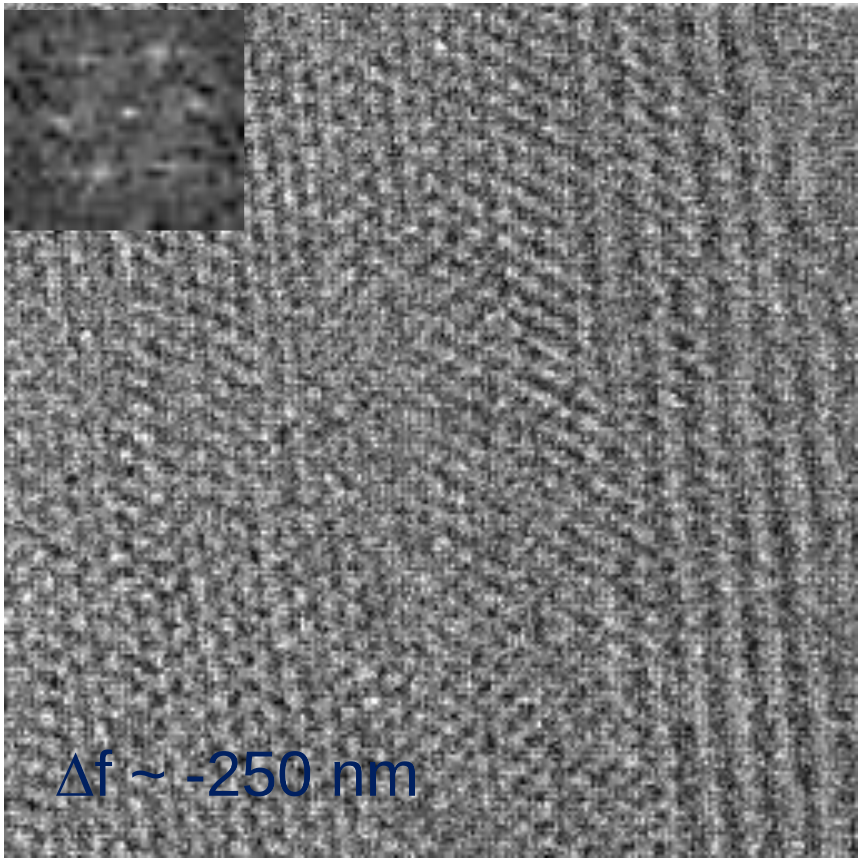




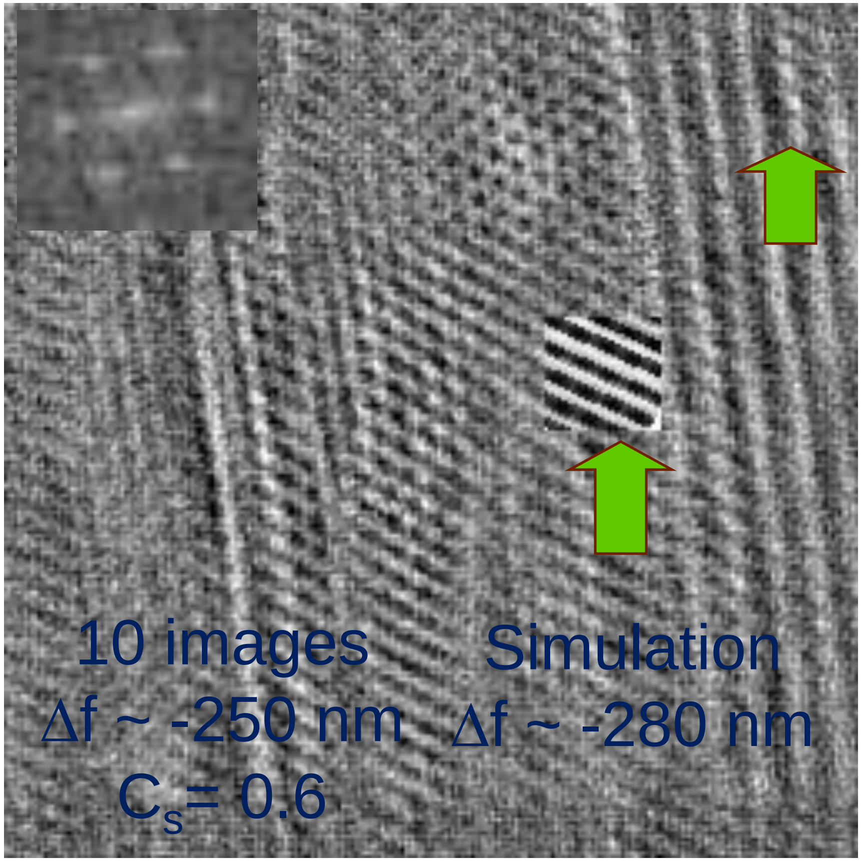
Simulated Image
Δf = -280 nm

Projected Potential

6W BN Reconstructed Image

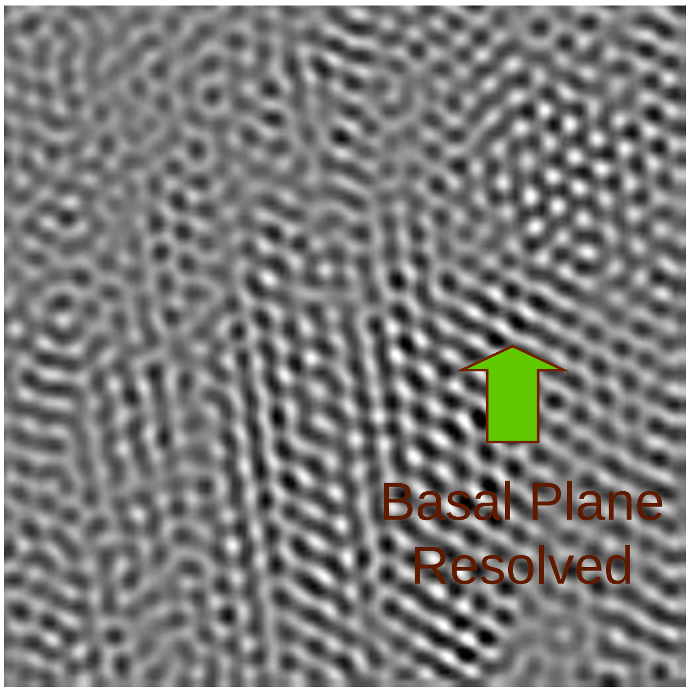


Single Image

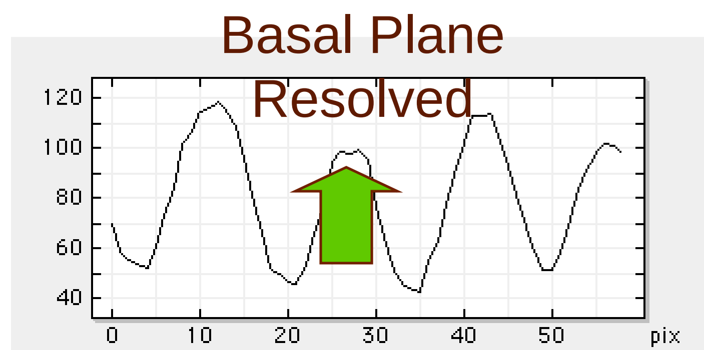


Reconstructed Image

6W BN Image Reconstruction



Reconstructed Image



Line Intensity Scan
(along basal plane)

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