ФИЗИКО-ХИМИЧЕСКИЕ ОСНОВЫ НАНОТЕХНОЛОГИИ

Профессор Н.Г. Рамбиди

7. Нанотрубки

Структура нанотрубок

Bonds in atoms and molecules

- **Ionic bonds** — **Coloumb interaction between oppositely charged ions**

  $NaCl$

- **Covalent bonds** — **Shared valence electrons (strength depends on distance)**

  H - C = C - H
  H   H

- **Metallic Bonds** — **Delocalised electrons spreading over the entire crystal**

  See HB notes

- **Van der Waals bond** — **Dipole-dipole attraction (fluctuating dipoles, 1/1000 strength of covalent bonds)**

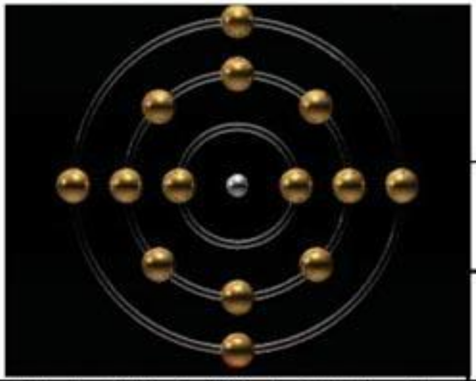
  $N_2 - N_2$

Periodic Table

Peter Bøggild, MIC 2003

Key:

element name atomic number **symbol** atomic weight (mean relative mass)



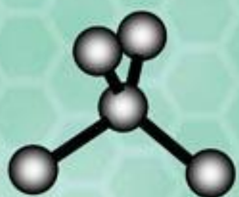
1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

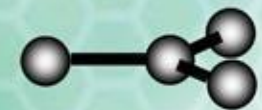
*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

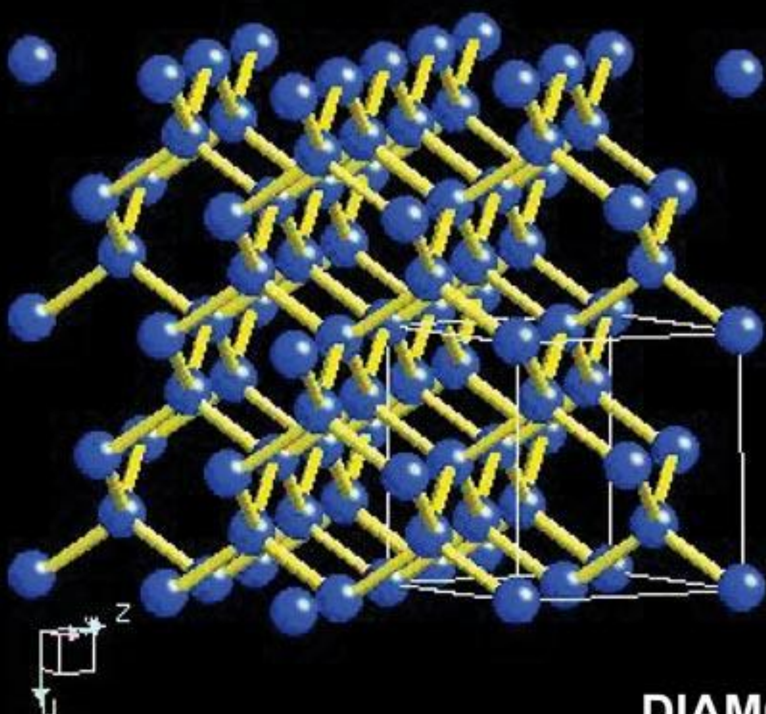
Link: www.webelements.com

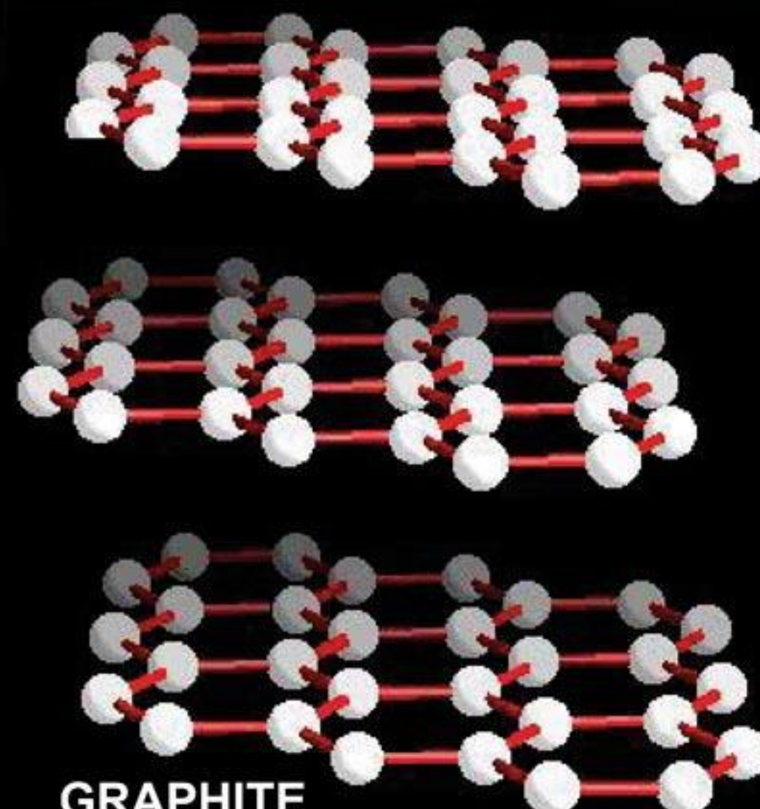
Diamond and graphite

Bond length 1.4 nm
Stacking distance 3.4 nm



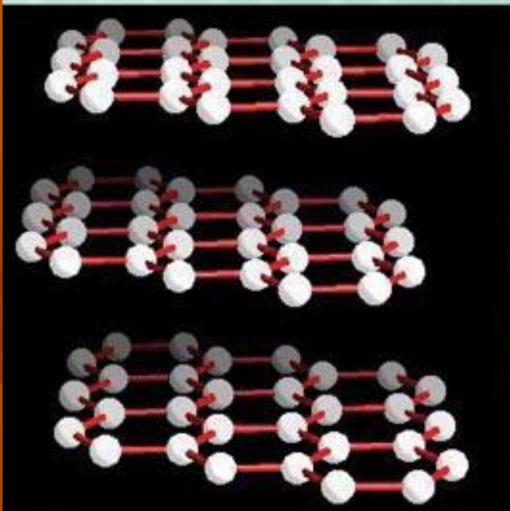




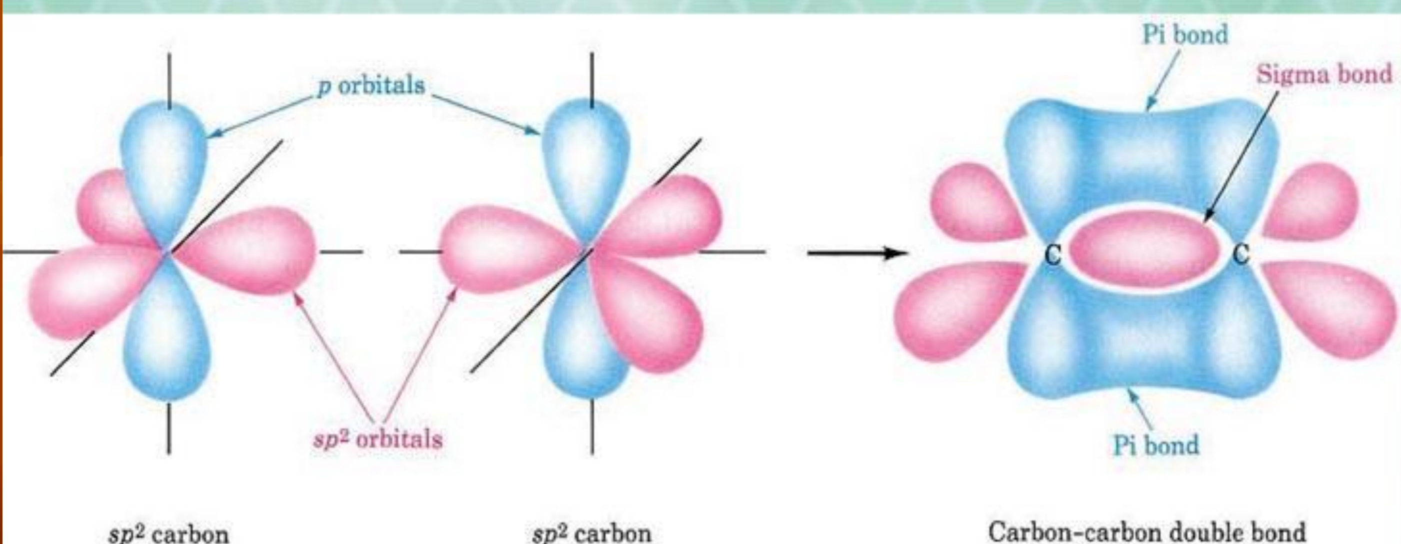


DIAMOND GRAPHITE

sp^2 hybridisation



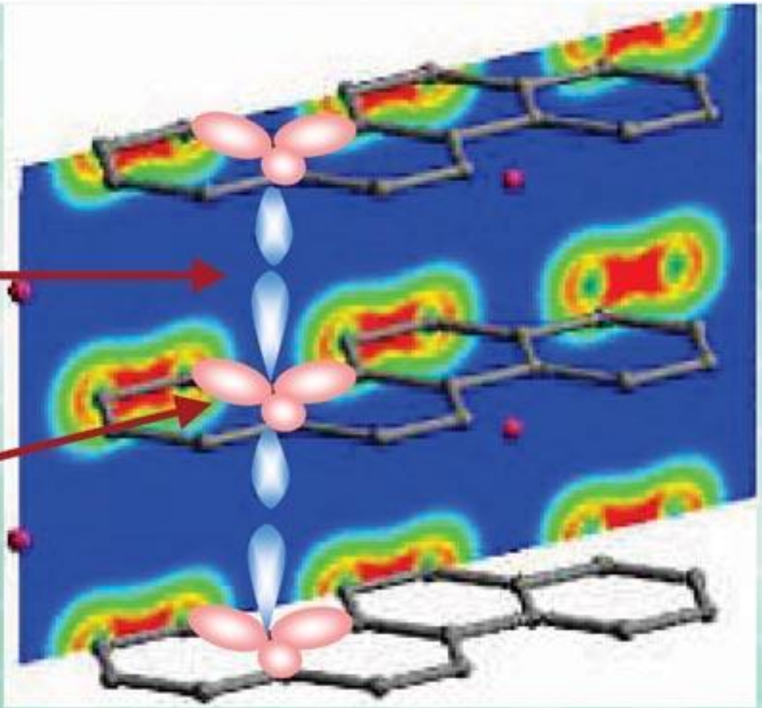
- Graphite is a stack of single ”graphene” sheets
- In graphene the electron bonds *hybridize*; they form three identical ”sigma” orbitals at 120 degrees to each other.
- Each bond originates from one s and two p orbitals (sp^2). The remaining p orbital is perpendicular to the plane, called a π-bond (pi).
- The strength of the π bond (van der Waals bond) is much weaker than the σ bond (covalent)
- Electrons are delocalized in pi-bonds – current can flow in the graphene layer

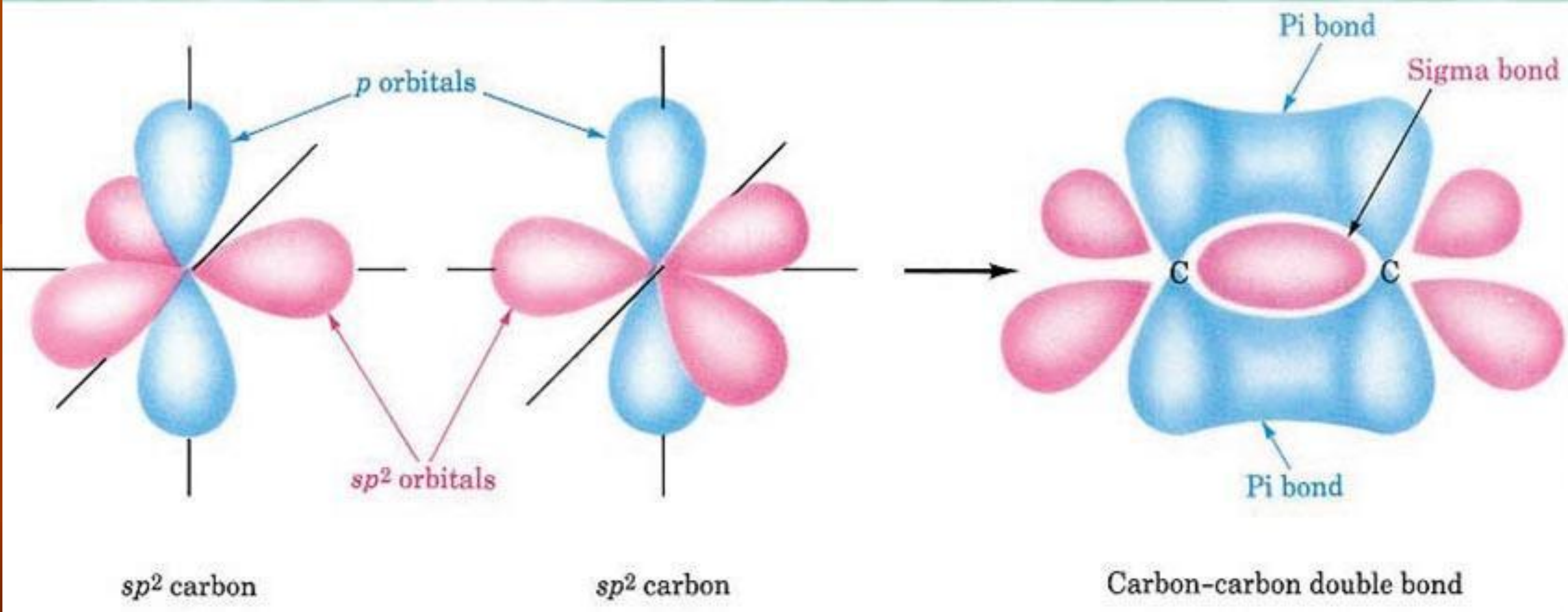


σ and π-bonds

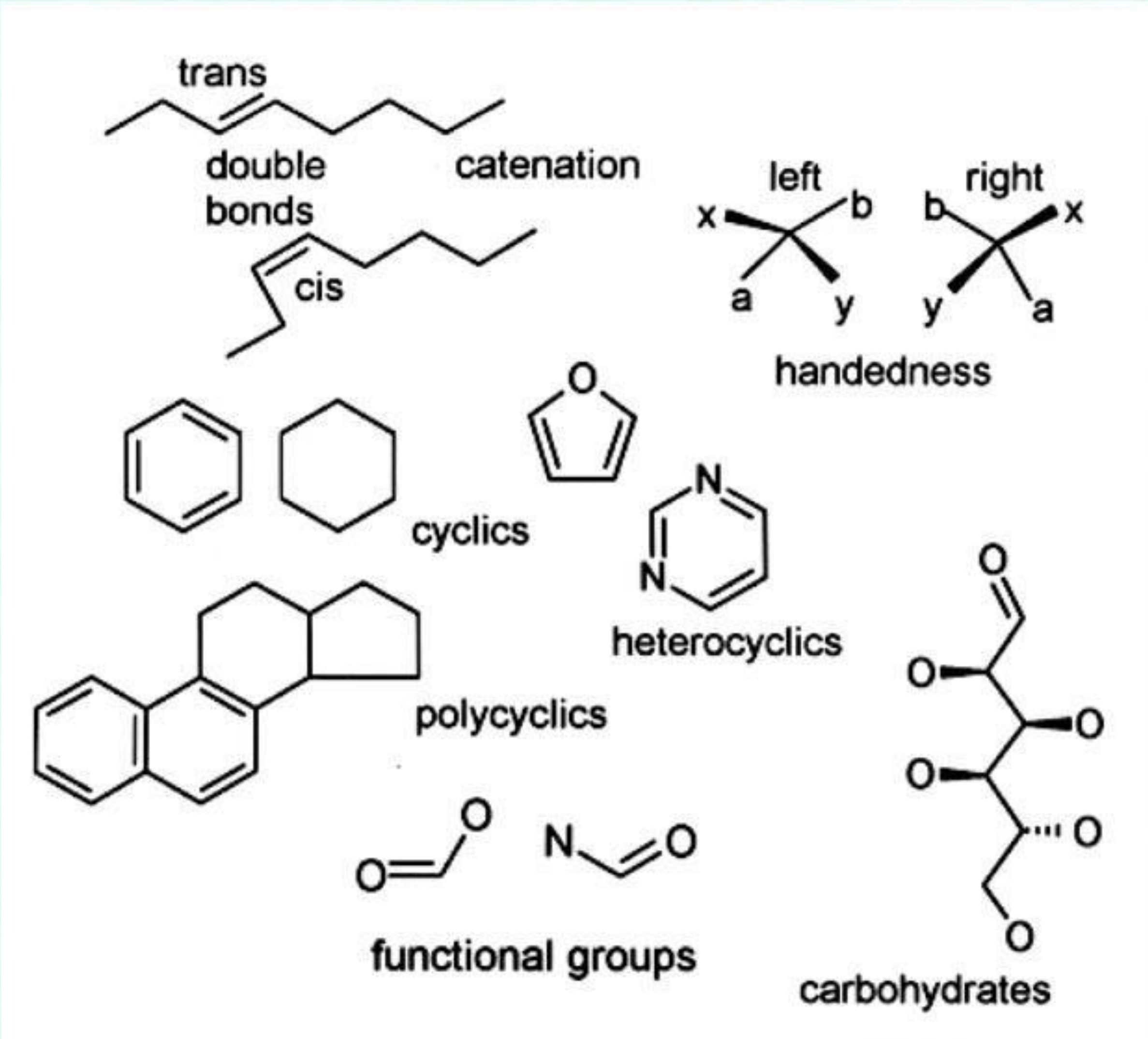
π bonds (weak)

sp² hybridised bonds (strong)





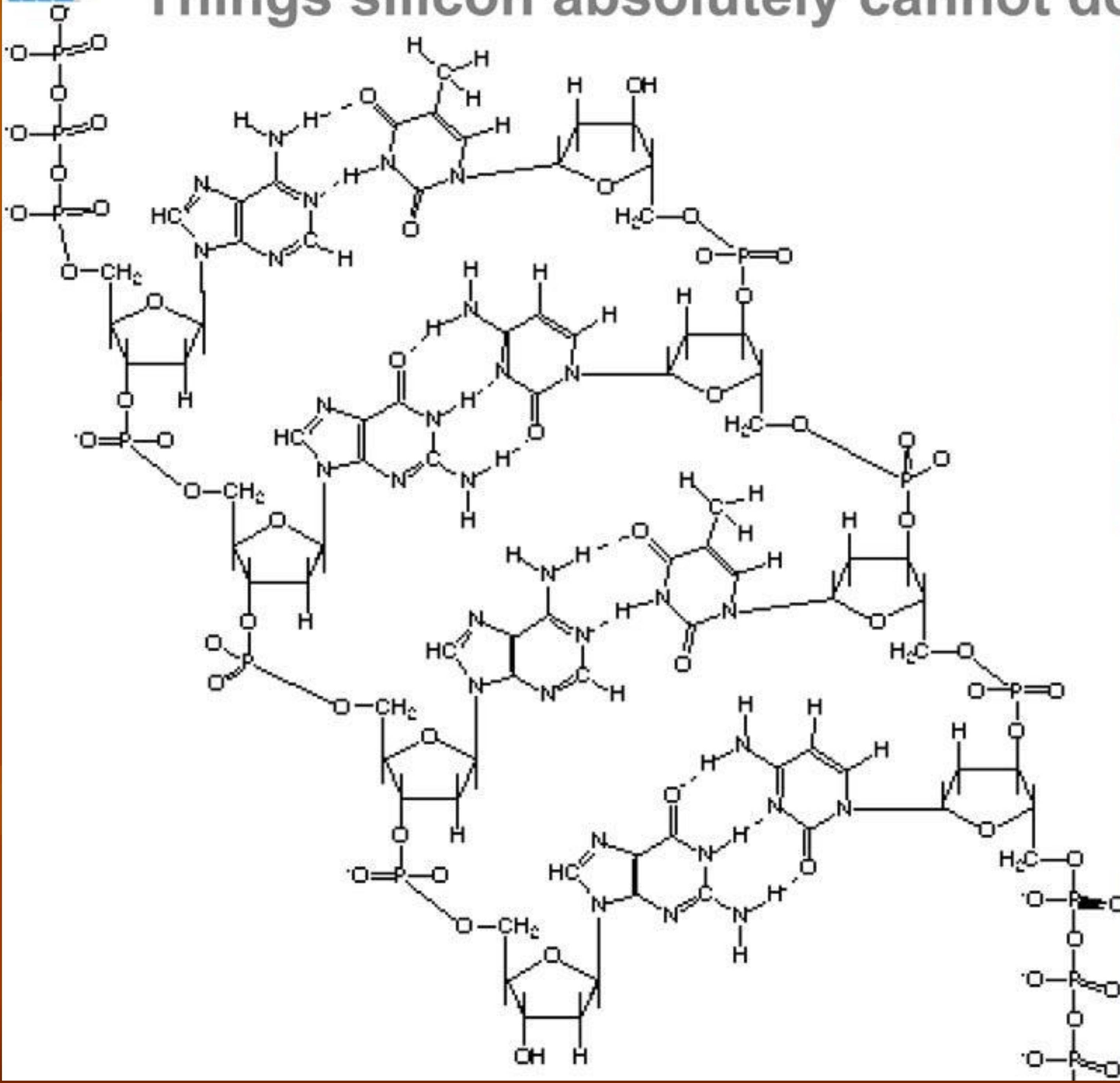
Things silicon cannot do!

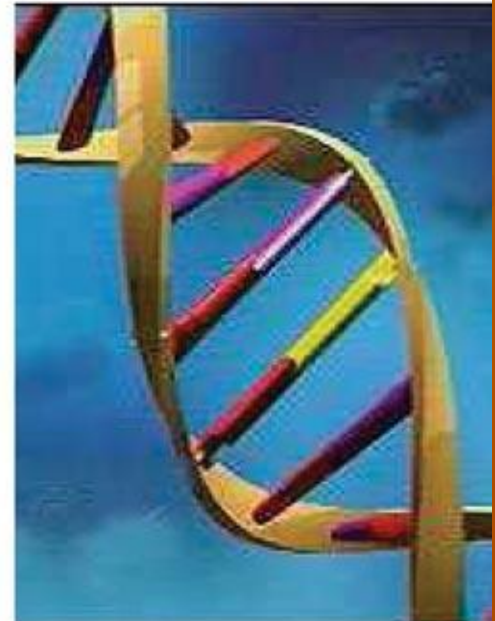


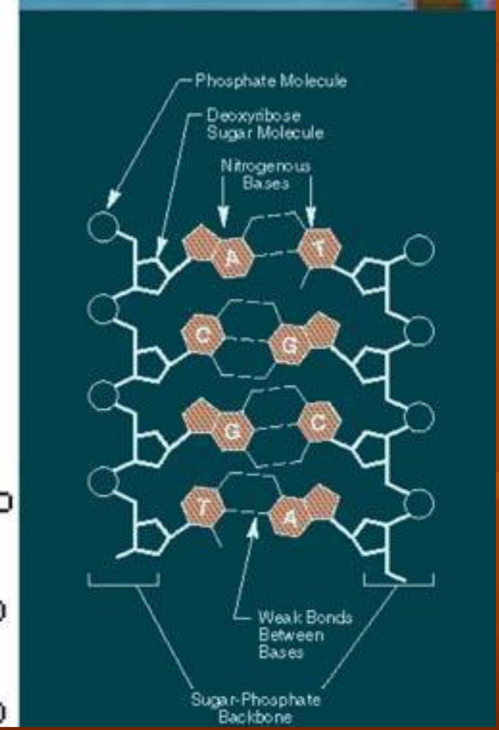
WHAT IS SPECIAL ABOUT C

- **C** can form chains with itself
- **C** forms stable compounds with many elements (N, O, H) but preferrably itself
- **C** does not bind too strongly to O - does not oxidise, like silicon and many other solids
- ...on the other hand it forms strong bonds with hydrogen (important for terminating "loose ends")

Things silicon absolutely cannot do!

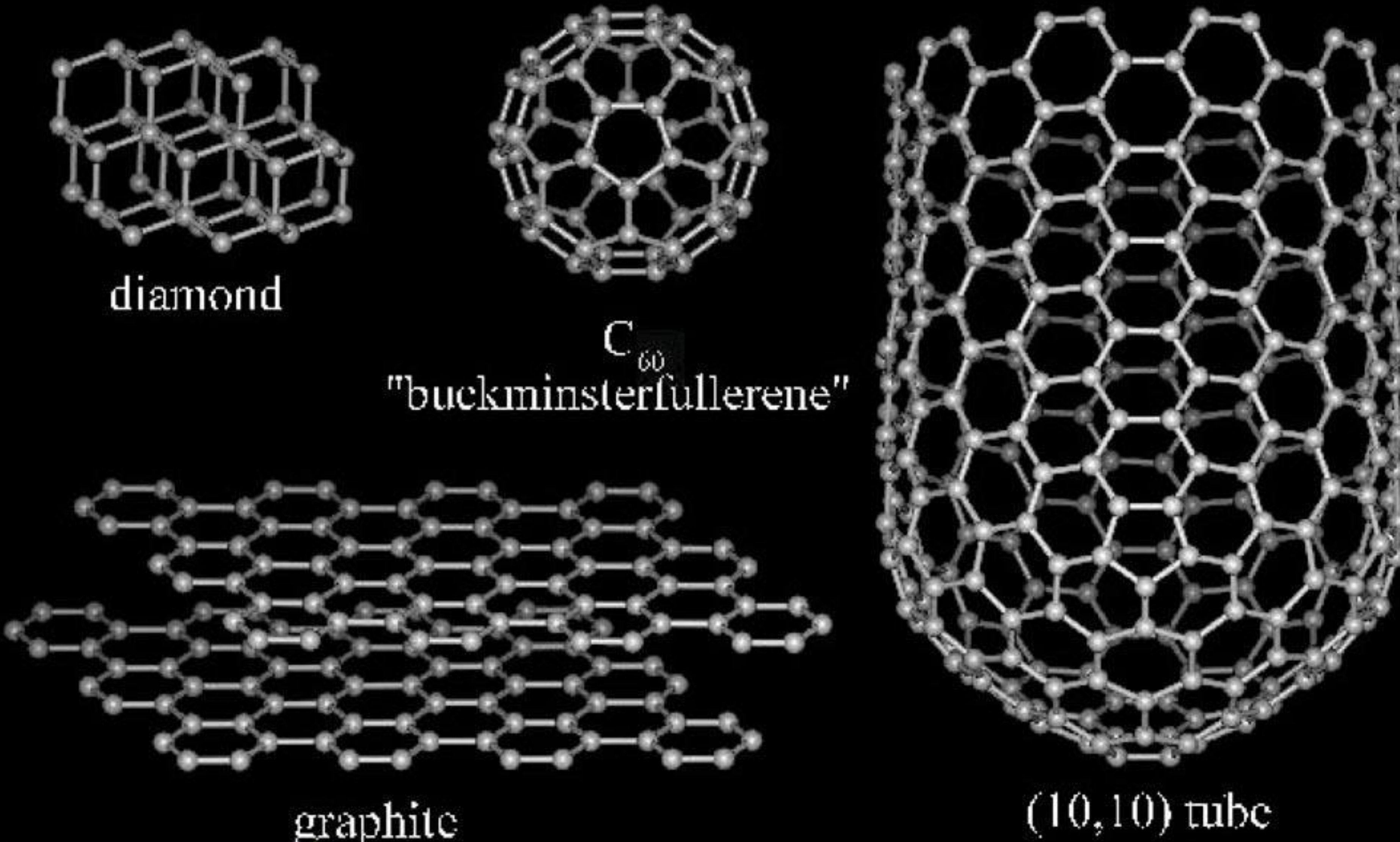






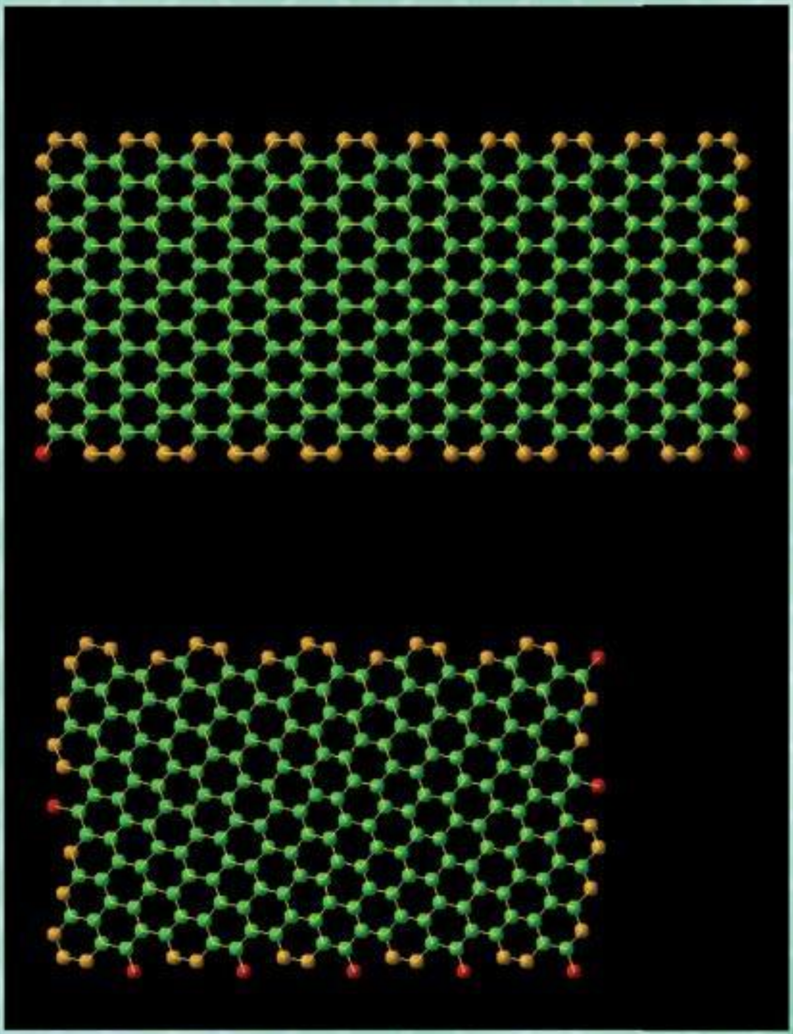
Carbon sooth...?

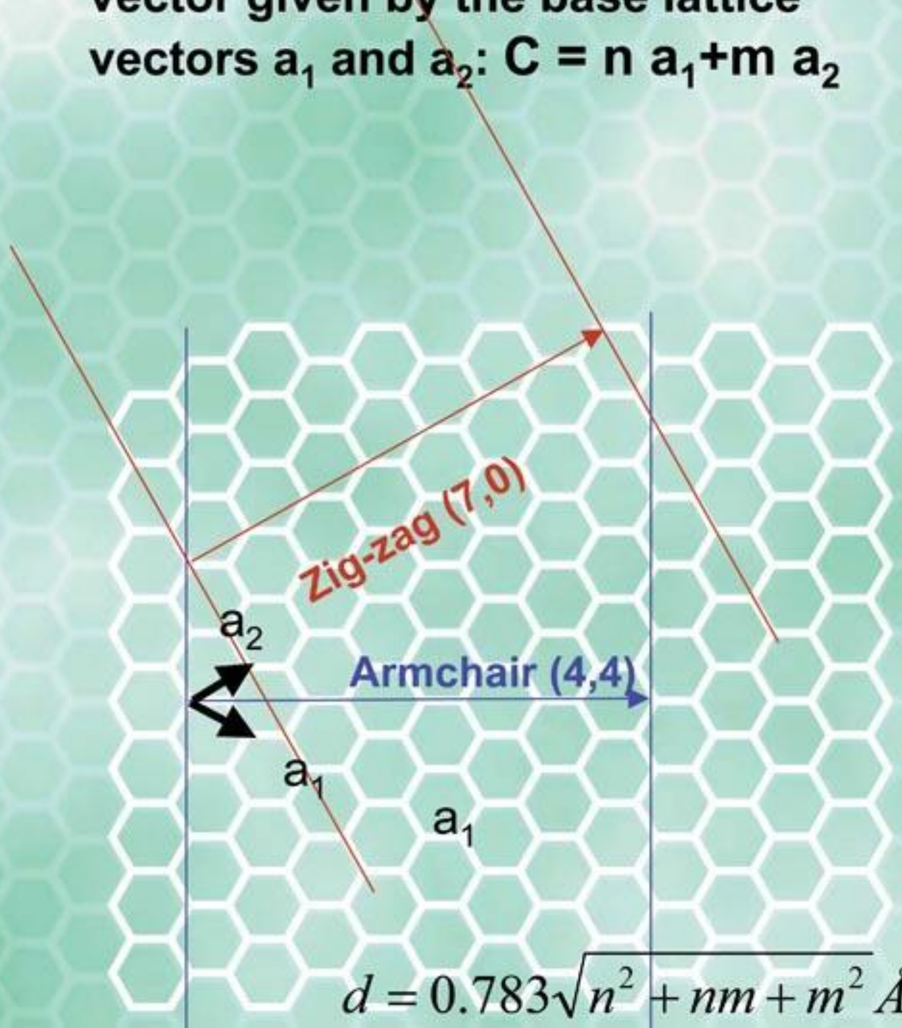
Carbon's allotropic forms



Rolling a sheet of graphene

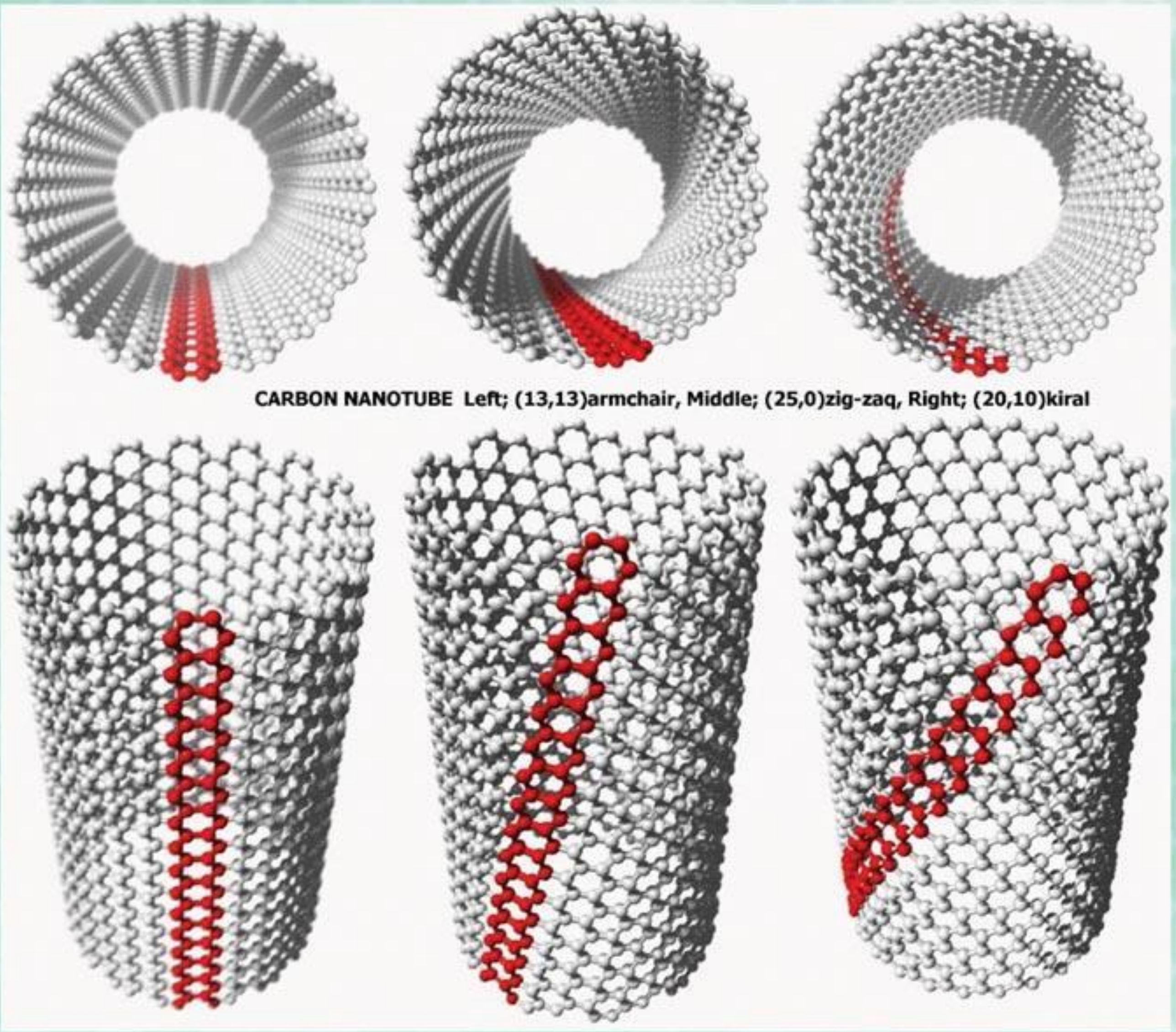
- Nanotubes can be rolled in different angles between 0 and 30 degrees.
- They are classified by the chirality vector given by the base lattice vectors a_1 and a_2: $C = n\, a_1 + m\, a_2$



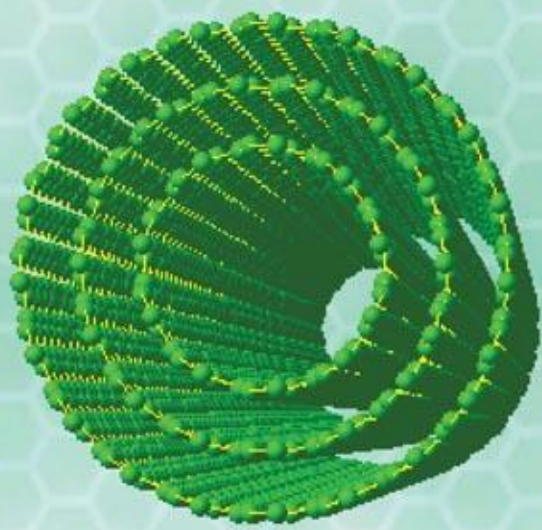


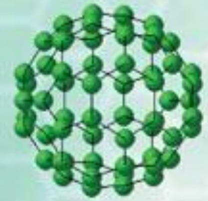
$$d = 0.783\sqrt{n^2 + nm + m^2}\ \text{Å}$$

Simulation Gallery

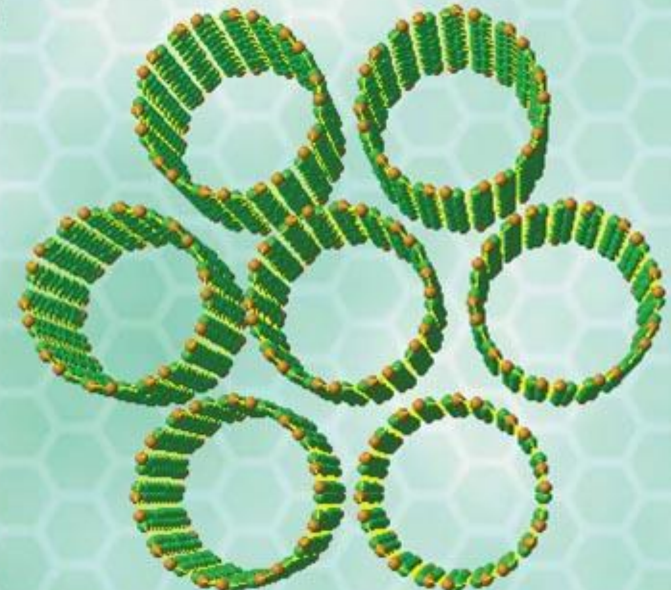

CARBON NANOTUBE Left; (13,13)armchair, Middle; (25,0)zig-zaq, Right; (20,10)kiral

Other types of nanotubes





C60



Multi-walled nanotube (MWNT)

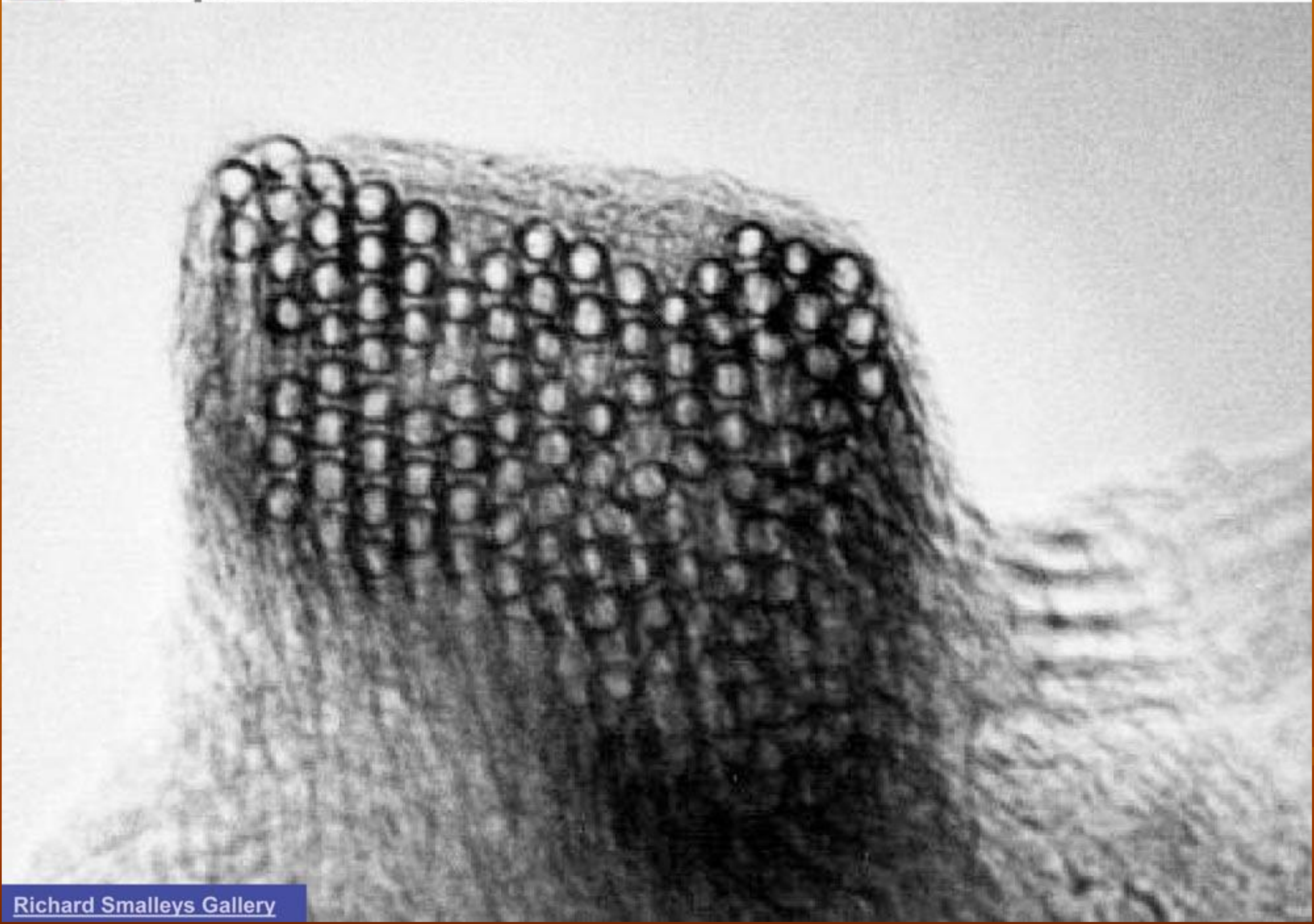
•5-50 walls interspacing: 3.5 nm (like graphite)
•diameters normally around 10-50 nm
(can be up to 200 nm)
•Can be very long, several 100 μm
•Walls slide easily inside each other (like graphite)
•The layers have independent chiralities
(one may be armchair, the next zig-zag)

Nanotube rope

•Like graphite, the layers slide easily on each other
•Stick together by van der Waals forces

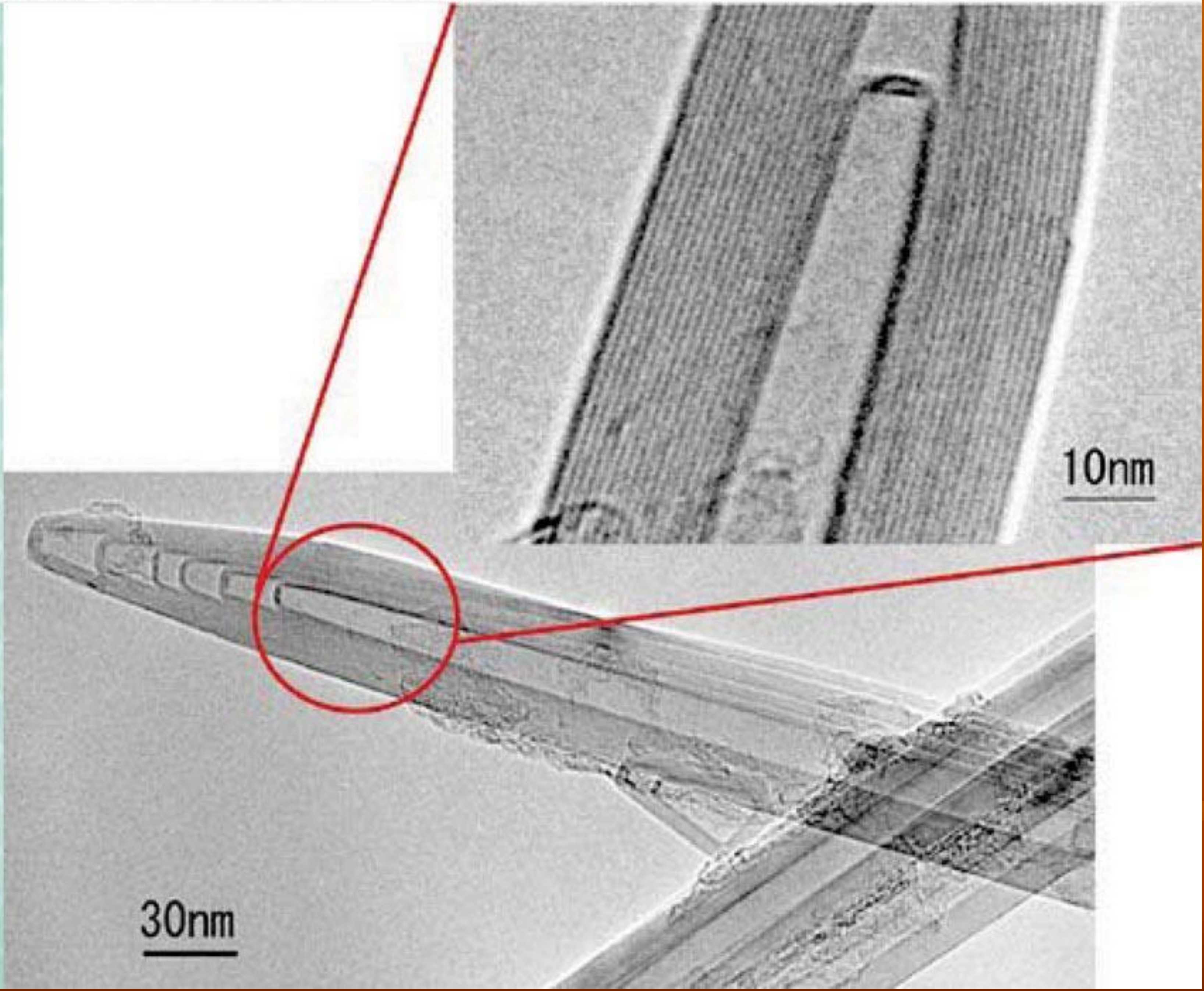
Simulation Gallery

Rope of nanotube



Richard Smalleys Gallery

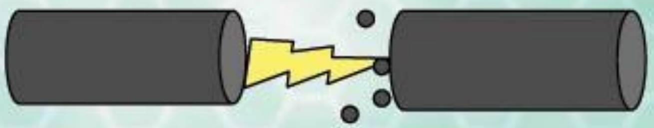
Multiwalled nanotubes



Saito Lab

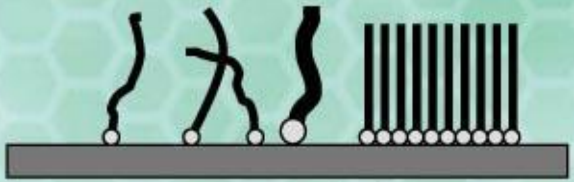
Методы формирования

Methods for fabrication of nanotubes



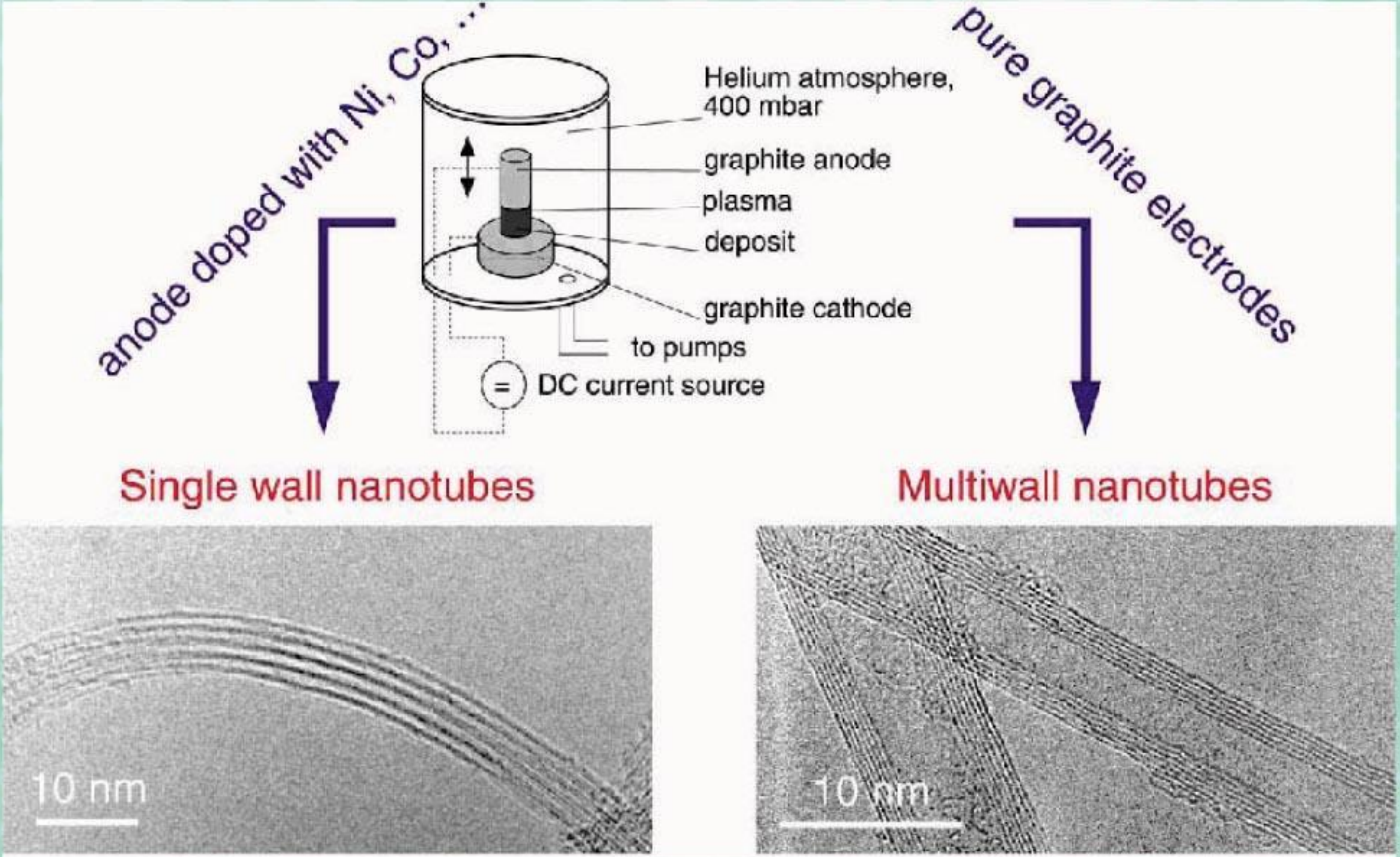
- **Arc discharge**
  - Carbon is evaporated by a plasma of Helium . This is ignited by a high current passing through a graphite anode and cathode

- **Laser evaporation**
  - Direct laser vaporization of transitional metal (e.g. Co-Ni,1%) graphite composite electrode targets is done in helium atmosphere at high temperatures (1200^{o}C).



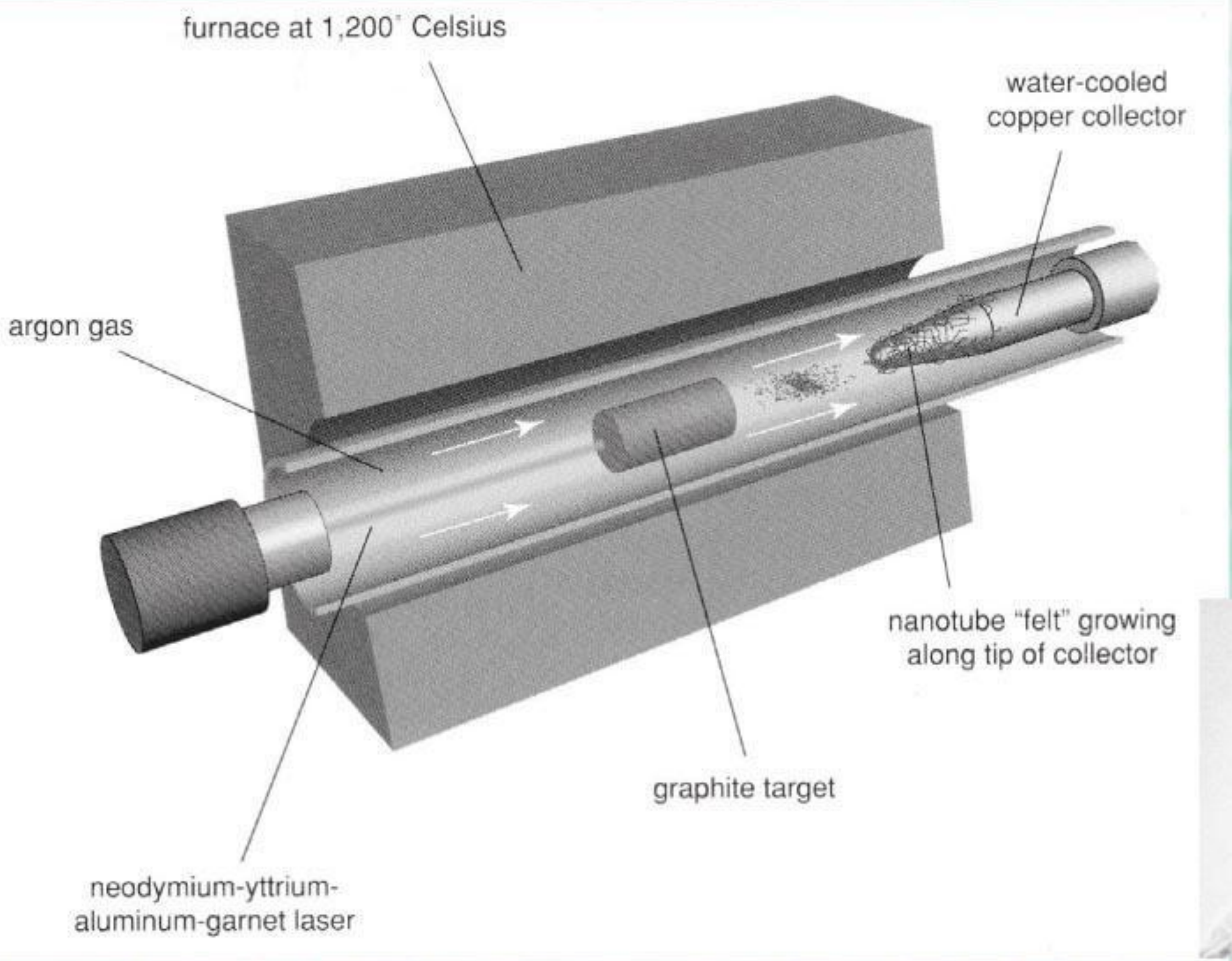
- **Chemical vapor deposition**
  - Organic gas is decomposed (e.g. Methane) in an oven containing catalyst particles, at 600-800C. The diameter and type of catalyst particles determine the nanotube diameter and properties.

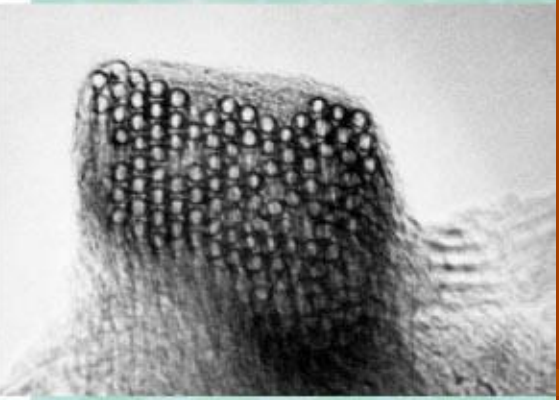
Arc discharge



Result: Pure SWNT and MWNT of high quality

Laser ablation

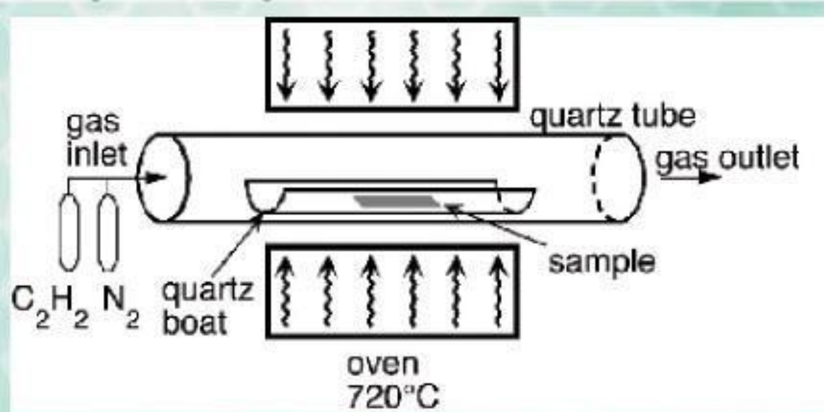


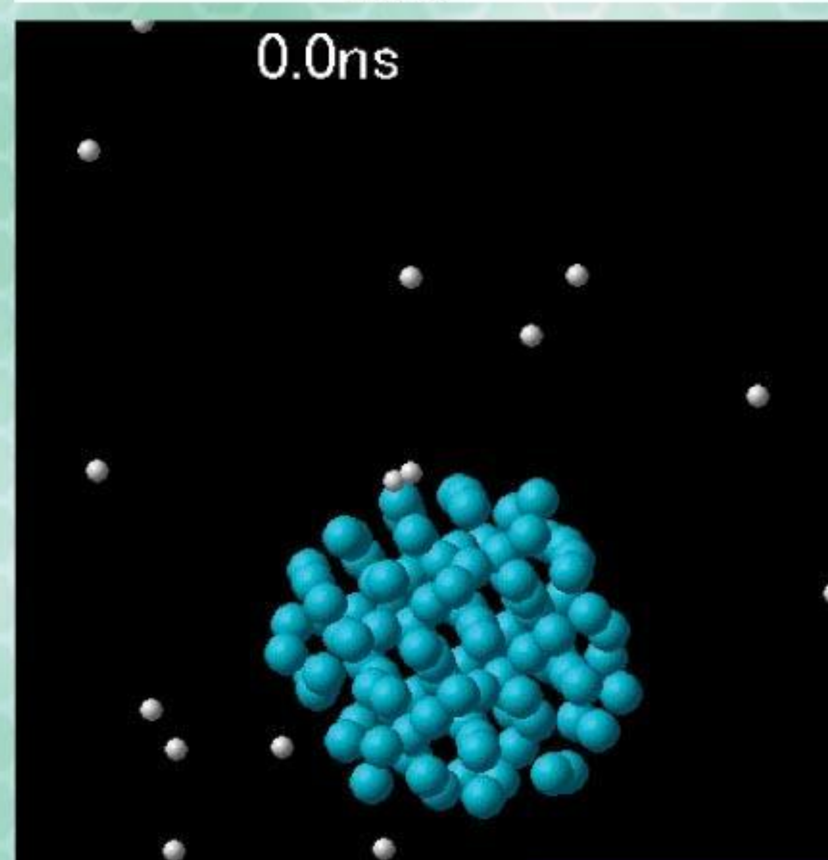


Result: Pure SWNT and ropes of high quality

Chemical vapor deposition (CVD)

- **CVD**
  - A hydrocarbon gas is decomposed at a high temperature
  - Carbon diffuses into catalyst particle Ni, Fe and is expelled in form of a nanotube
- **MWNT:**
  - Acetylene, 600 – 800°C.
- **SWNT**
  - Carbon monooxide, 900 – 1200°C (SWNT have higher formation energy)
- **Result:**
  - SWNT and MWNT of moderate quality
  - Many impurities and defects
  - large quantities, can be lithographically positioned

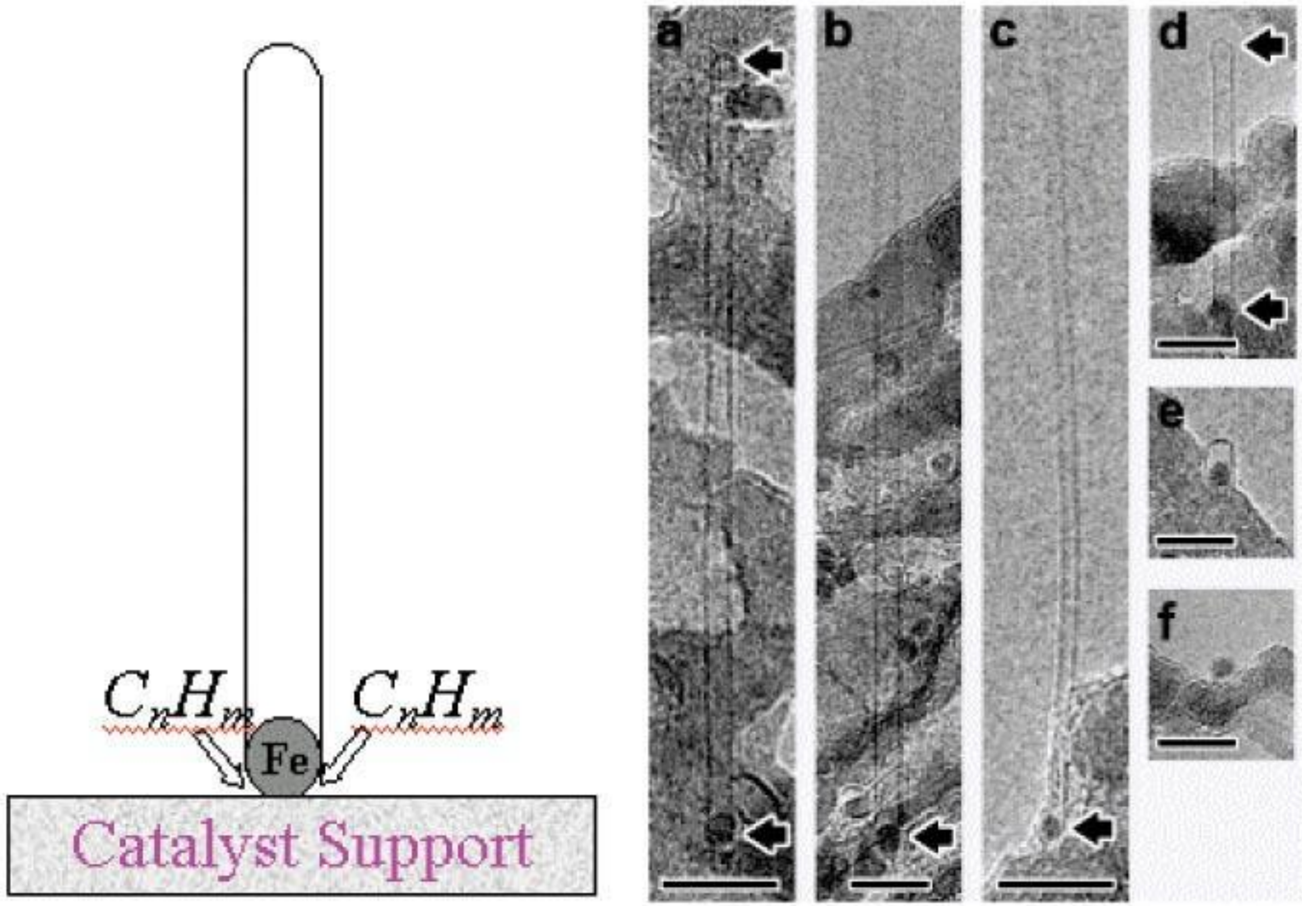




Introduction to carbon nanotube growth

Simulation Gallery

Chemical vapor deposition



'Base' Growth Model

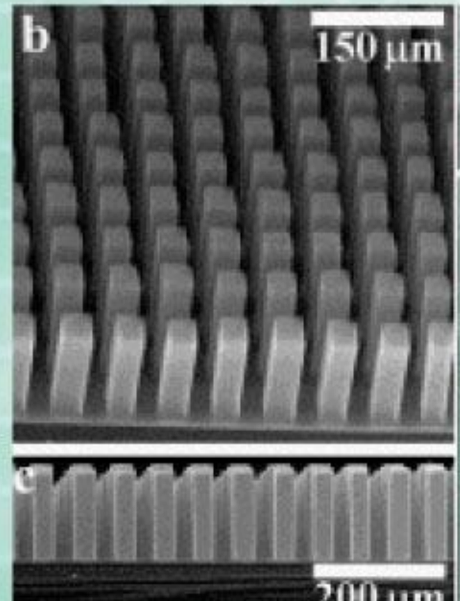
TEM data showing particle-tube relation

The catalyst particles grow from the base, and keep growing as long as the process continues and the catalyst is not encapsulated by carbon soot

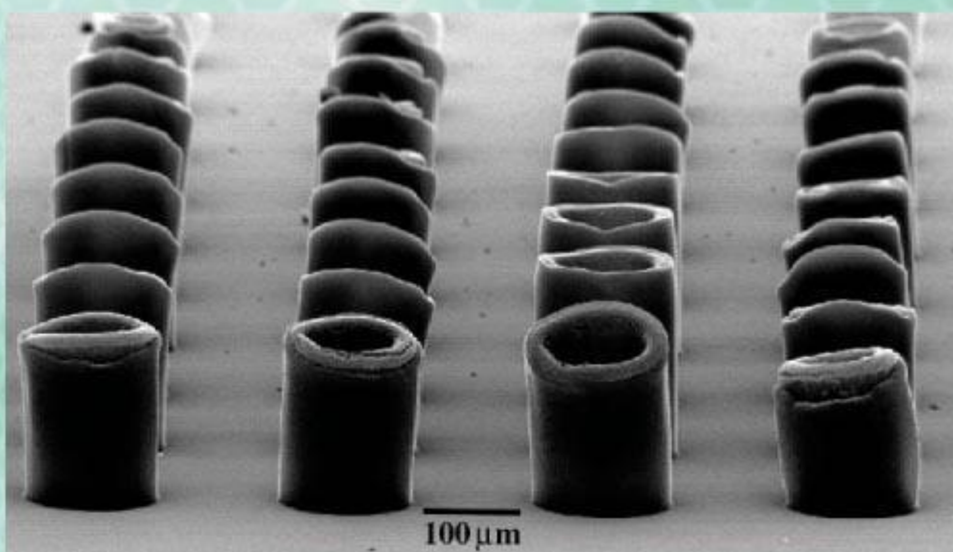
CVD tubes (Stanford)

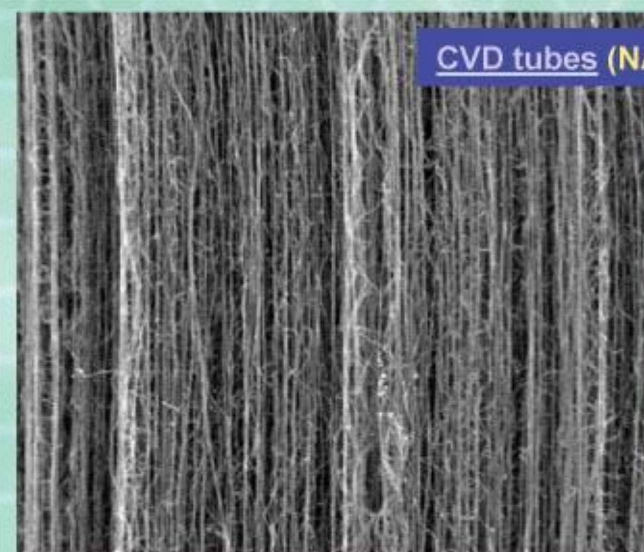
Chemical vapor deposition

- **Catalyst printing**
  - Catalyst material is lithographically deposited on a surface. The nanotubes grow straight up in thick ropes matching the footprint of the catalyst
  - Applications> field emission displays .



CVD tubes (Stanford)



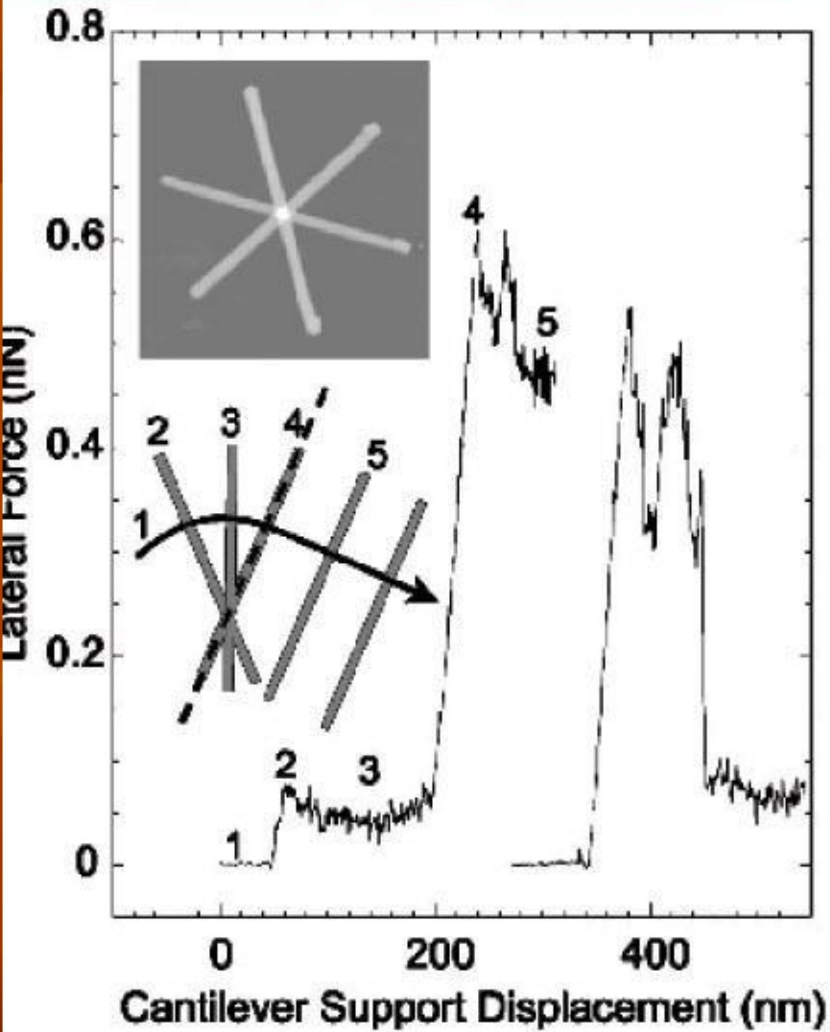


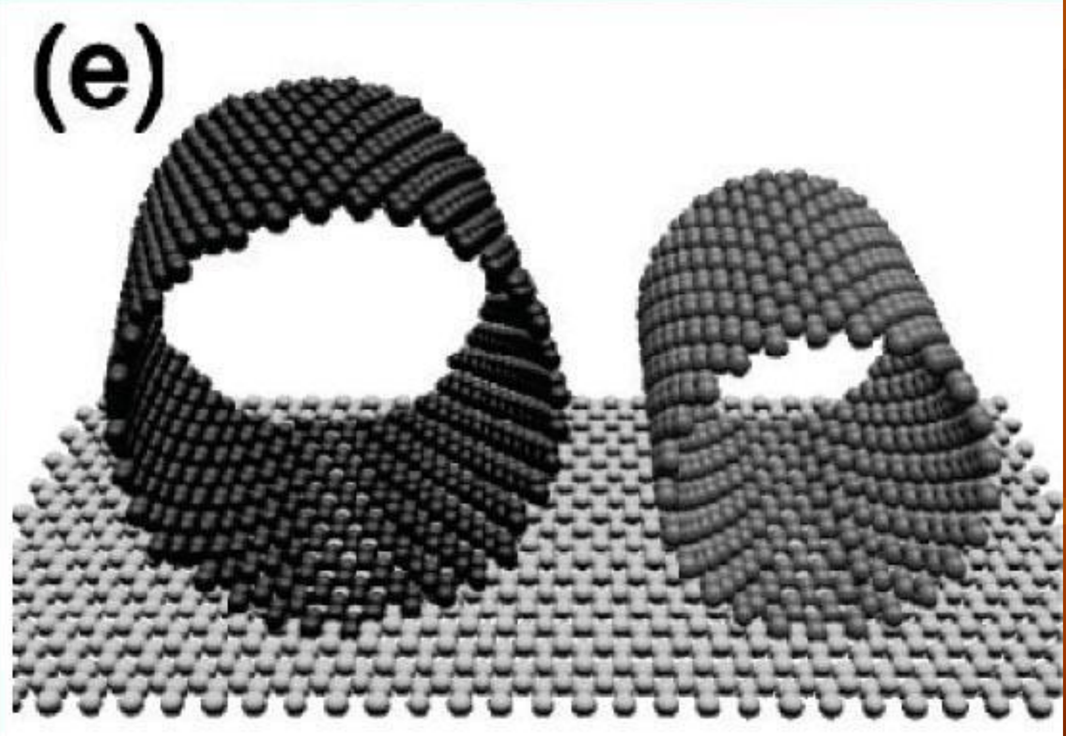
CVD tubes (NASA)

Свойства нанотрубок

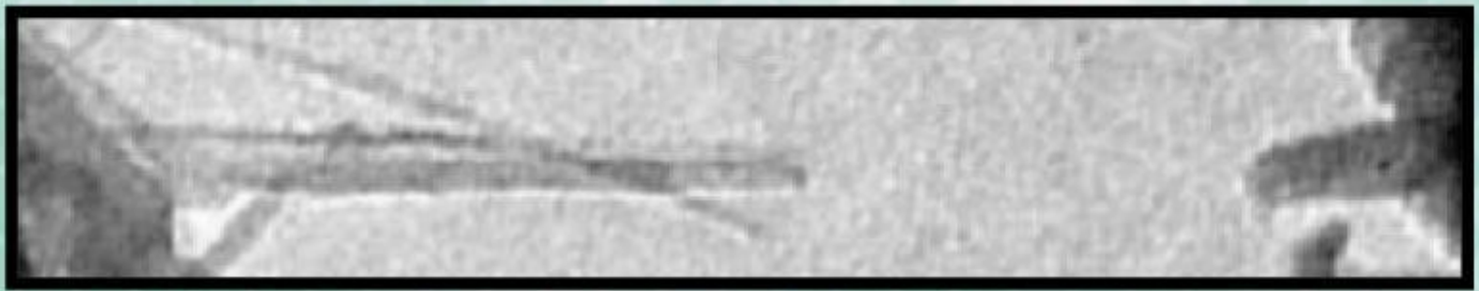
Friction

- The nanotubes were pushed on a graphite surface with an AFM tip.
- Whenever the tubes aligned with the graphite lattice, the friction coeffcient went orders of magnitude up...
- Friction due to lattice lock-in
- FRICTION IS DIFFERENT AT NANOSCALE



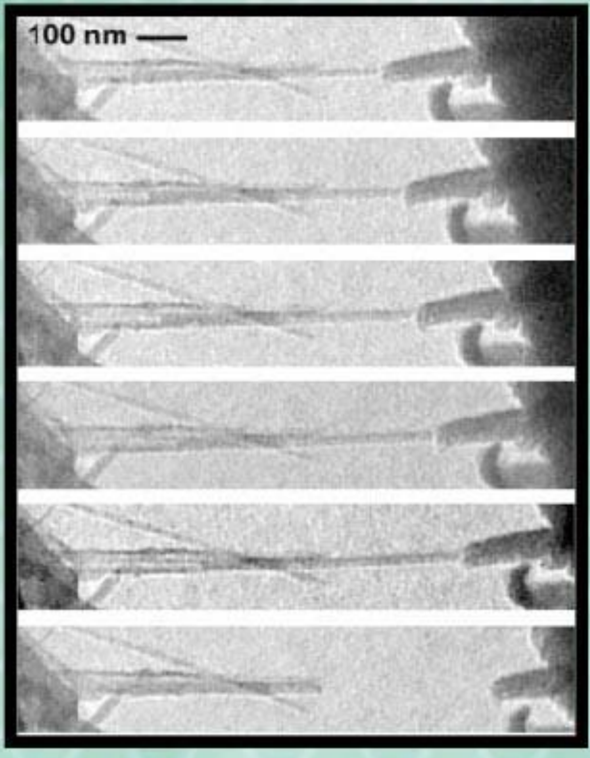


Mechanical properties: tensile strength



J. Cumings and A. Zettl, Science 289, 602 (2000).

- **Pulling a multiwalled nanotube**
  - The inner tube is dragged out of the outer shell – like a **telescope**
  - When the tube breaks, the remainder snaps back into its shell
  - Difficult to measure tensile strength
- **Defects degrade the strength**
  - CVD MWNT much weaker due to high defect densities

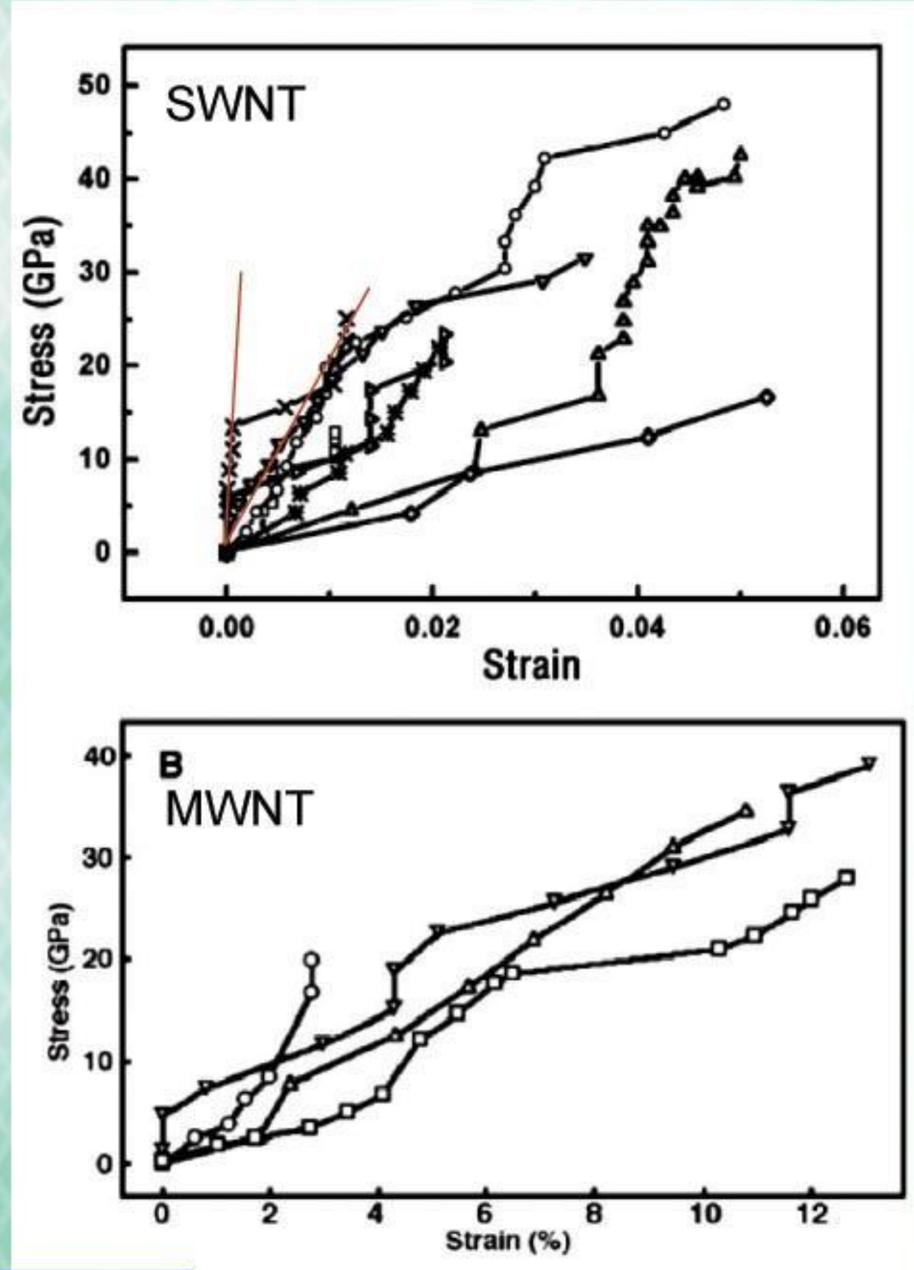


Mechanics of carbon nanotubes (Qian, Northwestern University)

Tensile strength

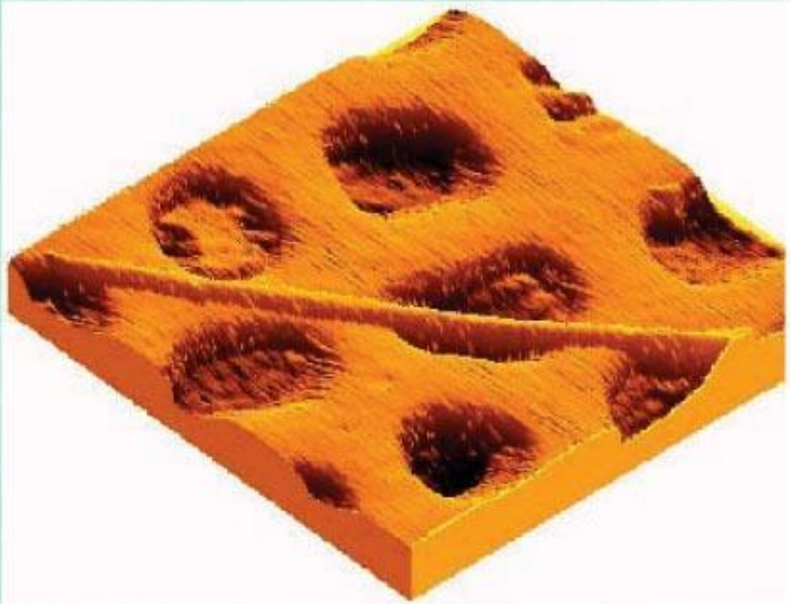
Youngs modulus
- SWNT: 1.3 TPa
- MWNT: 1 Tpa

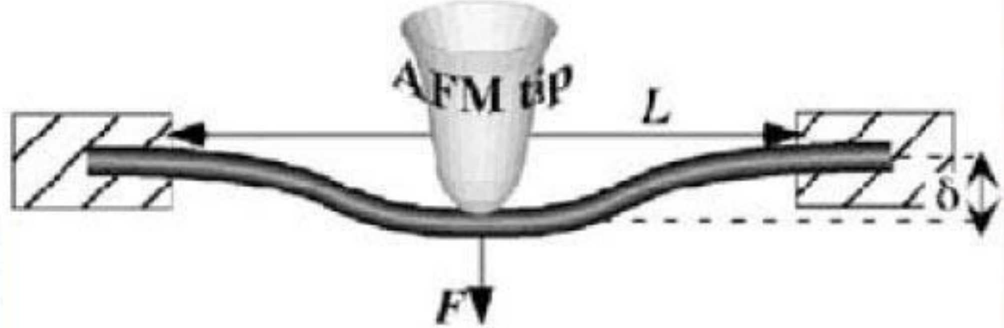
Tensile strength
- 30-60 GPa
- Theory: 200 GPa

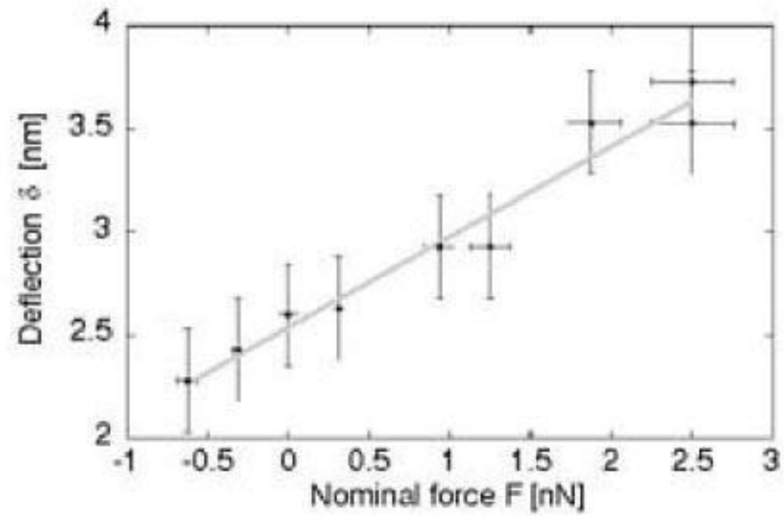


Mechanical properties

- **Youngs modulus: 1 TPa (MWNT, SWNT)**



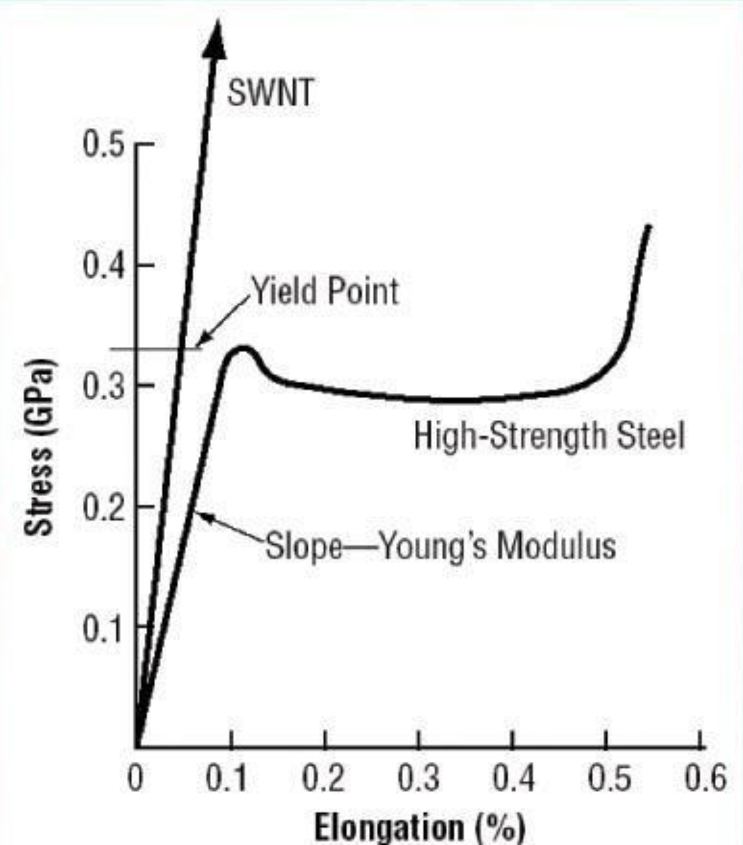




Mechanical properties

Material	Youngs modulus (Gpa)	Tensile Strength (Gpa)	Density (g/cm3)
Silicon	**47**	**1 (brittle!)**	**2.3**
Steel	**208**	**0.4 (ductile)**	**7.8**
Carbon Nanotubes	**1000 (MWNT), 1300 (SWNT)**	**30-60* Theory: 150-200**	**1.3**

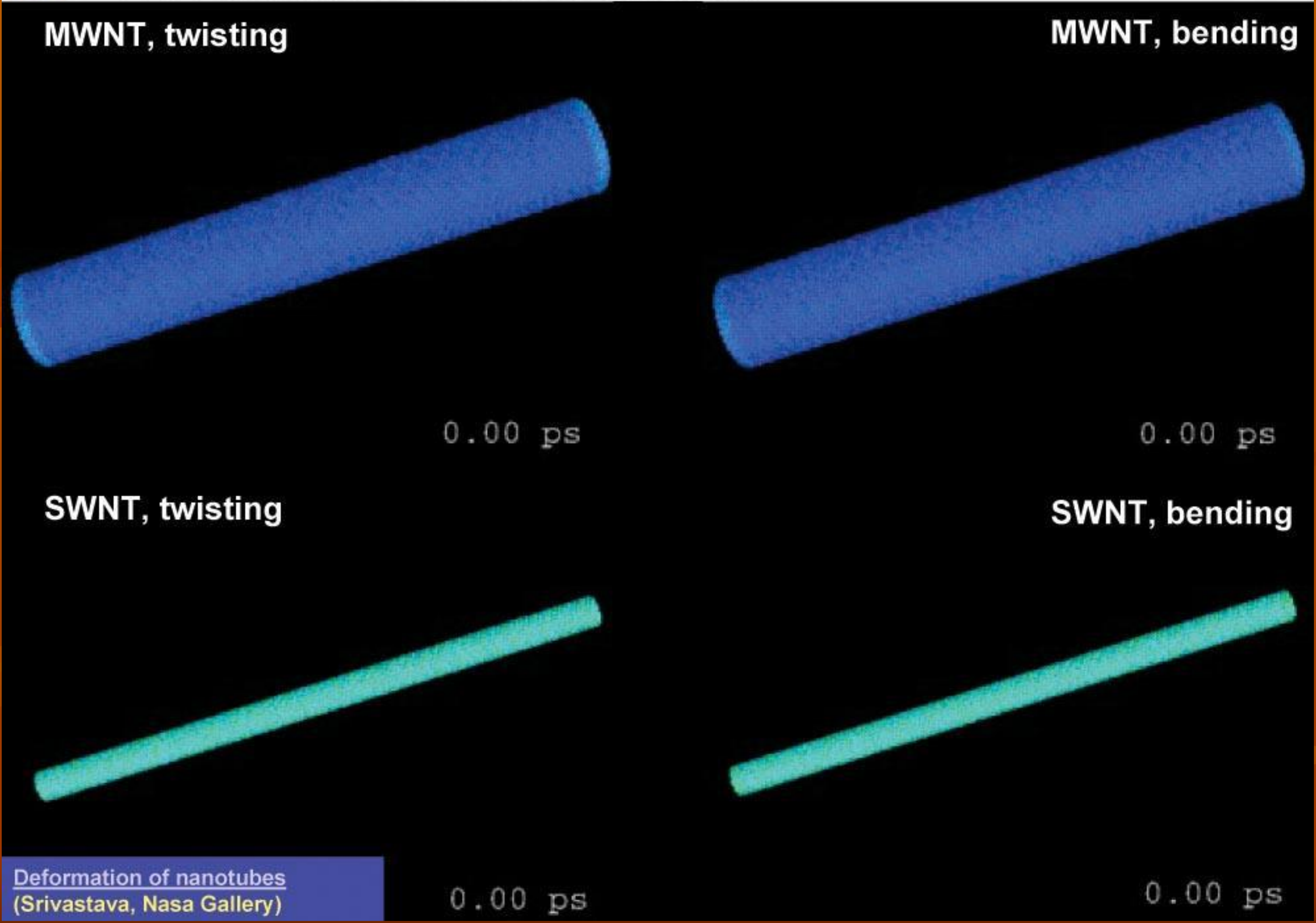
*(brittle at low temp, ductile at high, depend on chirality)



- **Nanotubes 100 times stronger than steel and 6 times lighter**
- **Nanotubes can sustain a large tensile strain:**
  - **5% (SWNT)**
  - **10% (MWNT)**

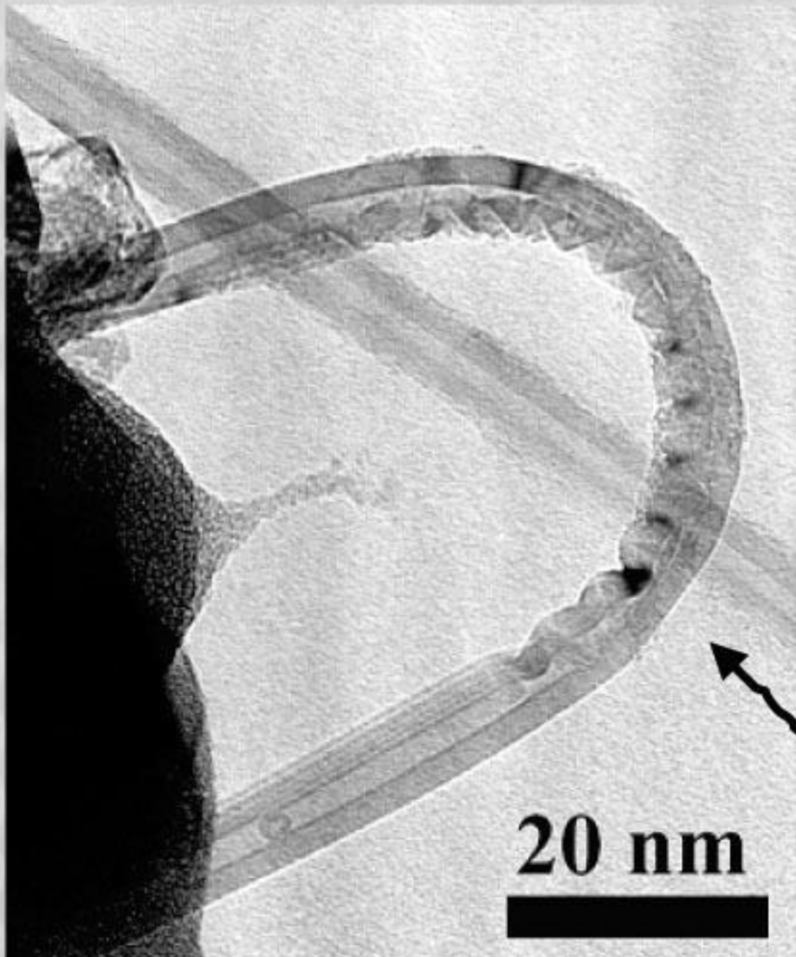
Brittle and ductile behavior of nanotubes **(Nardelli, PRL, 1998)**

Deformation of nanotubes

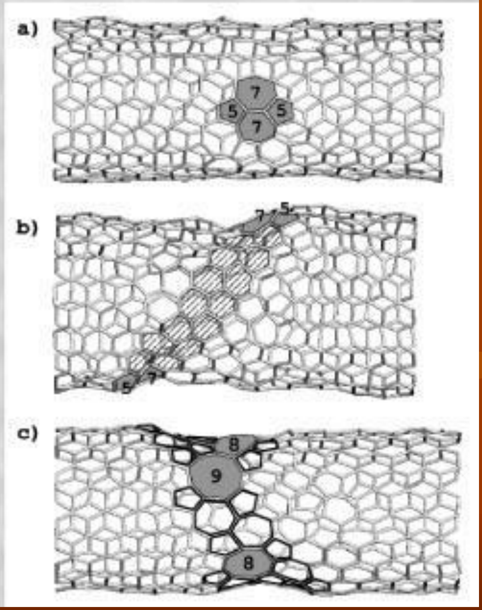


Deformation of nanotubes
(Srivastava, Nasa Gallery)

Deformation of nanotubes



- **Nanotubes can be deform plastically - reversibly**
  - Do not break by bending
  - Deform with little fracturing: stress is compensated by rearrangement of carbon atoms
  - Full recovery upon release



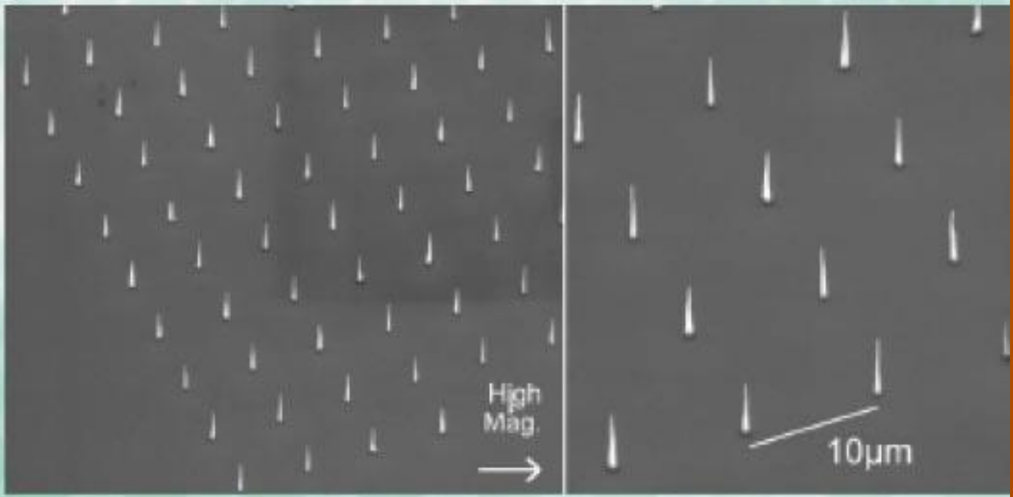
By the way: what happens to the electrical transport???

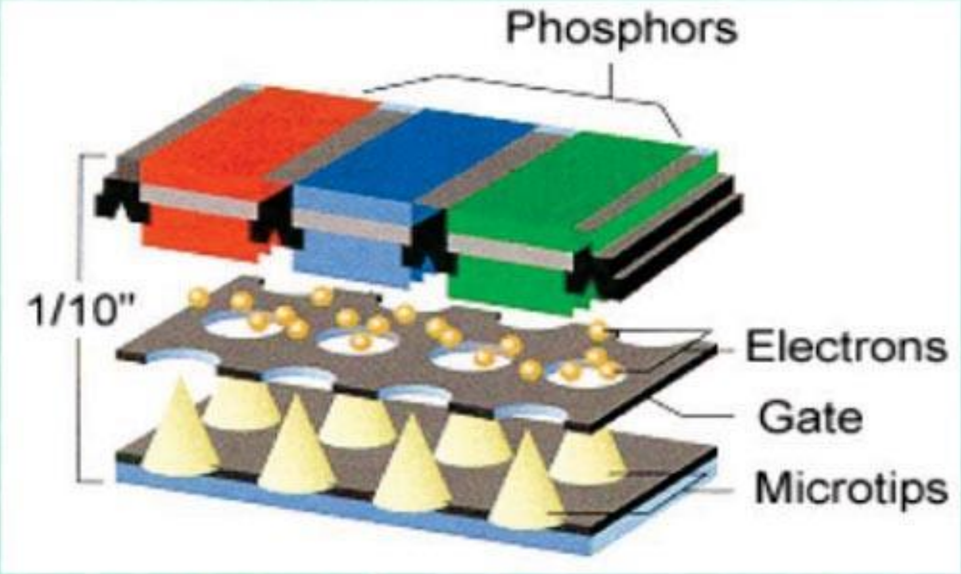
Области применения

Nanotube display

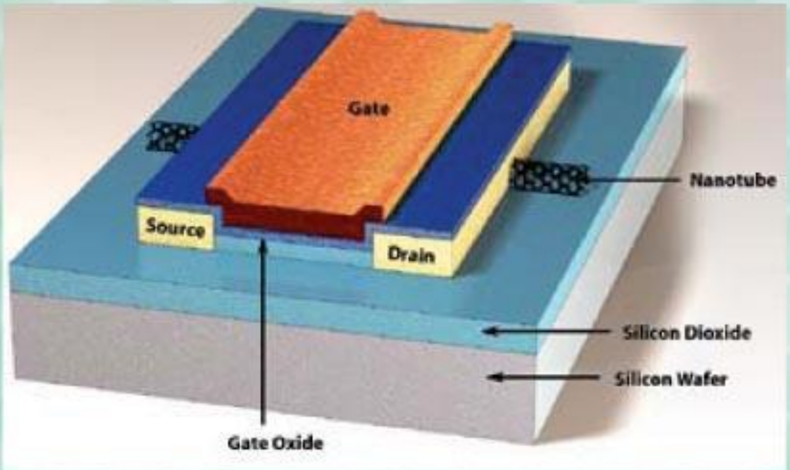
Carbon nanotube arrays

- Nanotubes can conduct very high current densities
- NT are very sharp (field intensity depends on tip sharpness)
- Ideal properties for field emitters
- Prototypes already made (5 inch color and 14 inch grayscale)





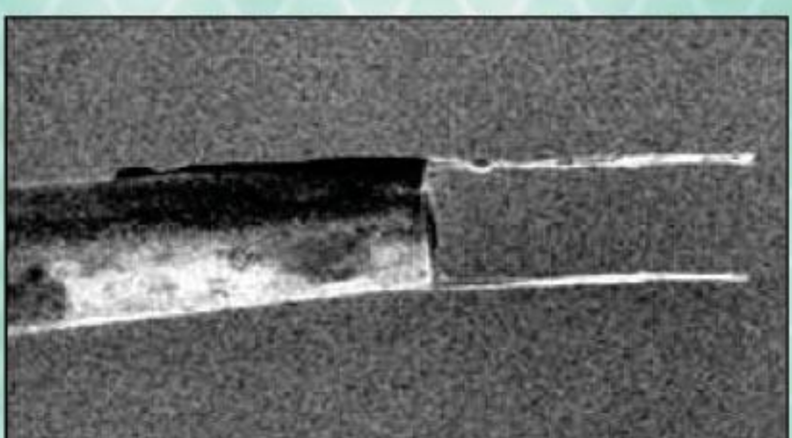
Nanotube transistor



FIELD EFFECT TRANSISTORS

Nanotubes for Electronics (Collins and Avouris, Scientific american)

Nanotube transistor (IBM)



NANO TWEEZERS

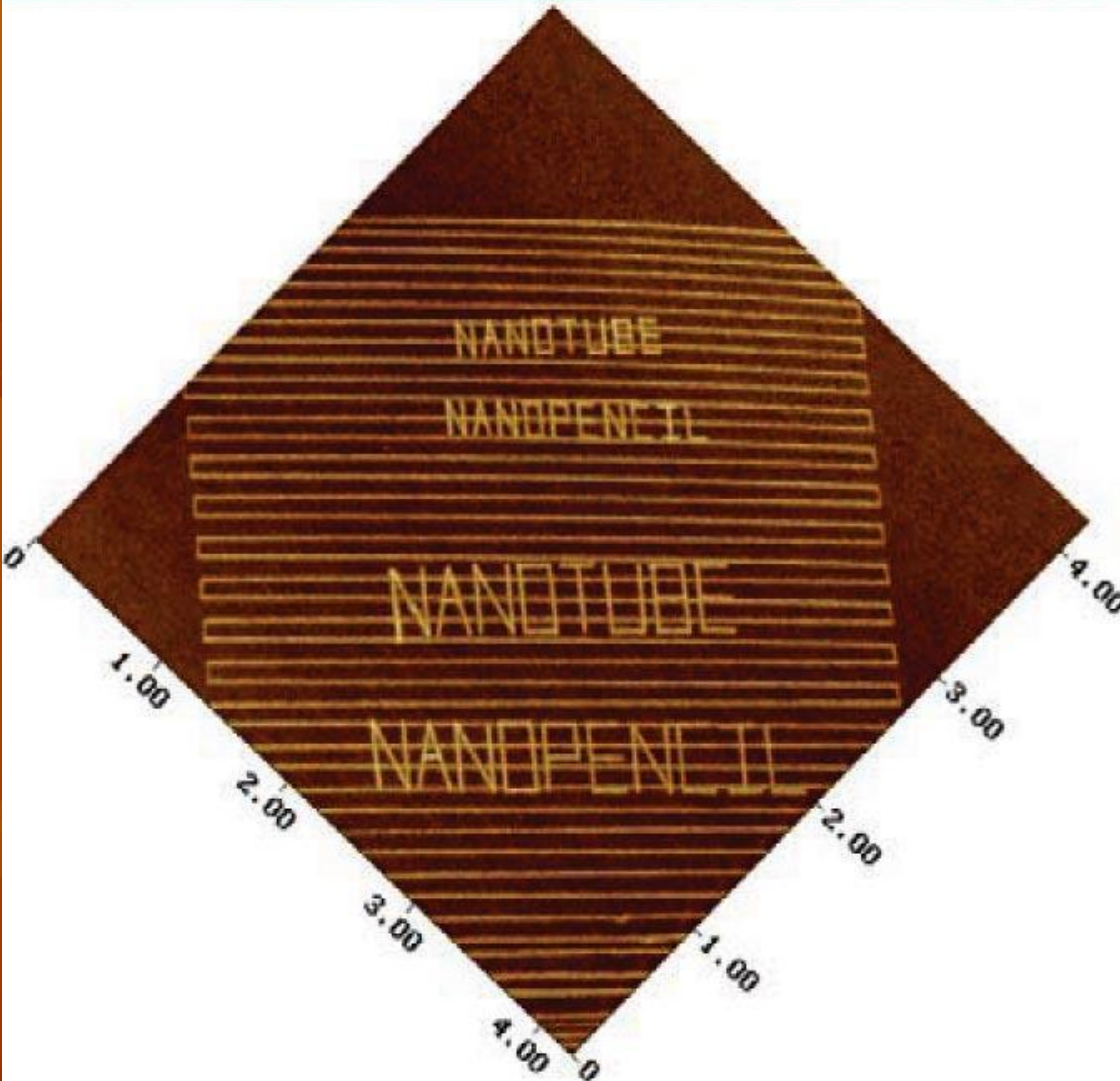
Nanotube Nanotweezers", P. Kim and CM Lieber, Science 286, 2148 - 2150 (1999).

More on this in lecture 4

Nanotube Nanotweezers (BBC News article)

Nanotweezers grabbing DNA (Research paper)

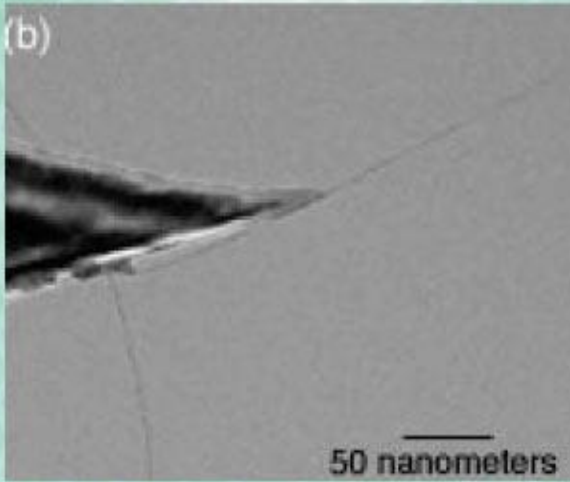
A real nanotube stiftblyant



Appl. Phys. Lett., 73, 1508 (1998).

A nanotube at the end of an AFM:

- High aspect ratio
- Nanolithography
- Conducting AFM/STM

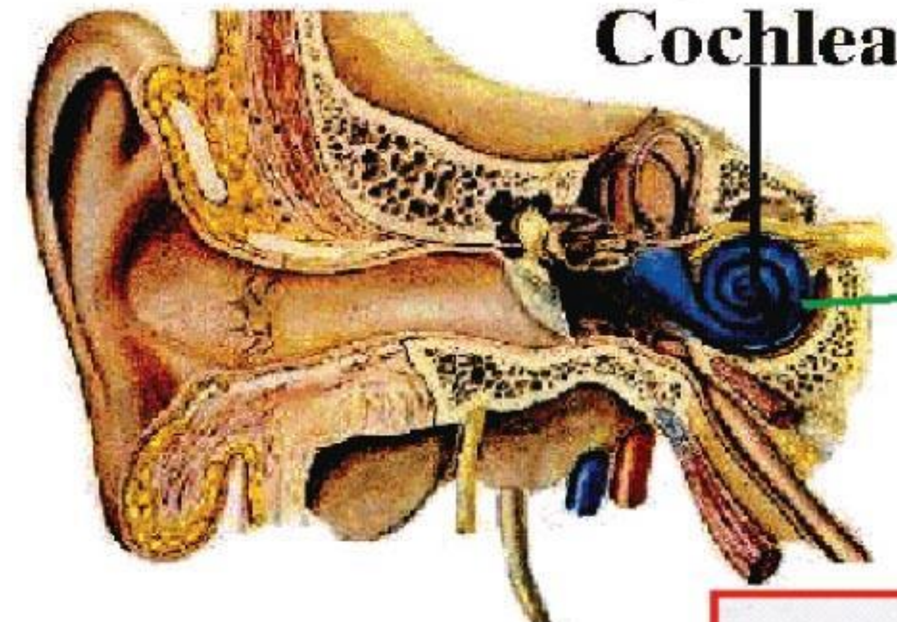


Nanotube AFM (Popular article)

Nanotube AFM (Lieber, Harvard)

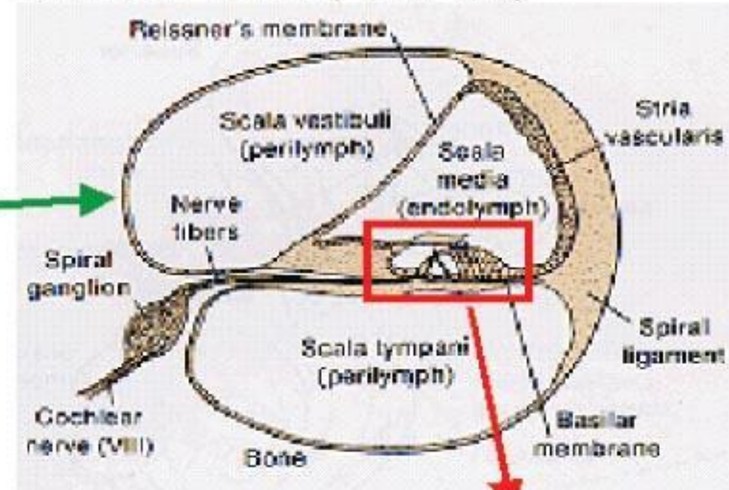
Nanotube pencil (Dai, Stanford)

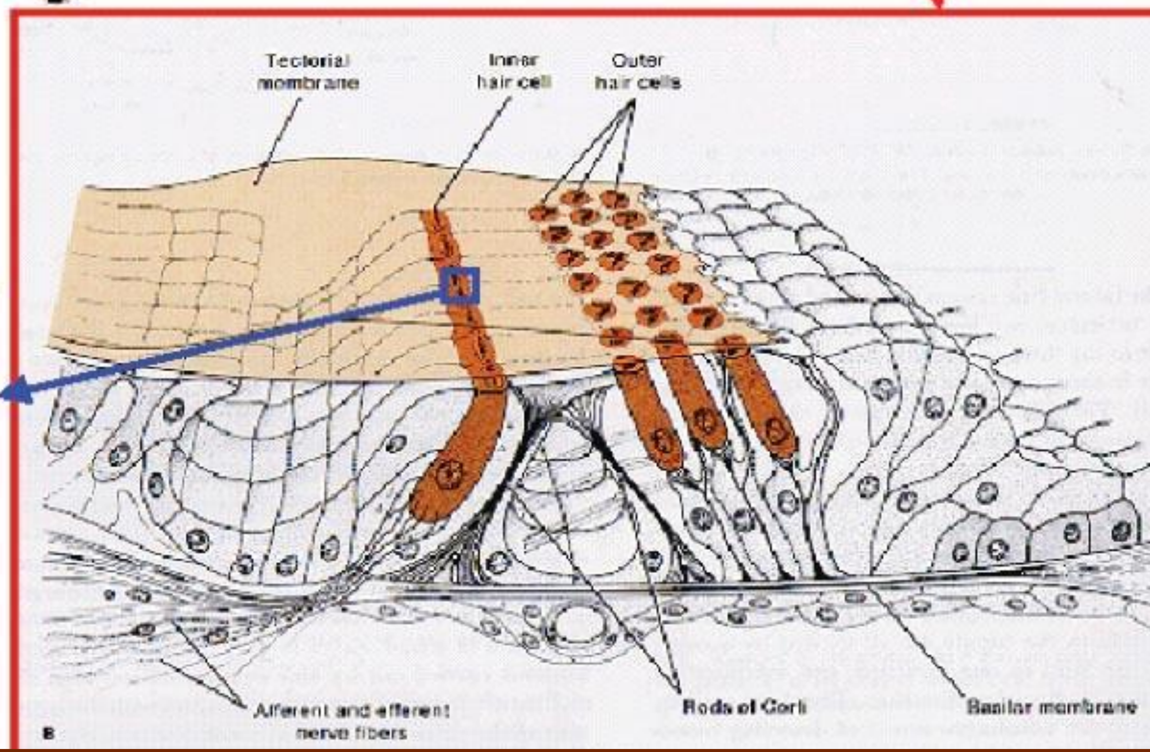
Nanotube hearing aid



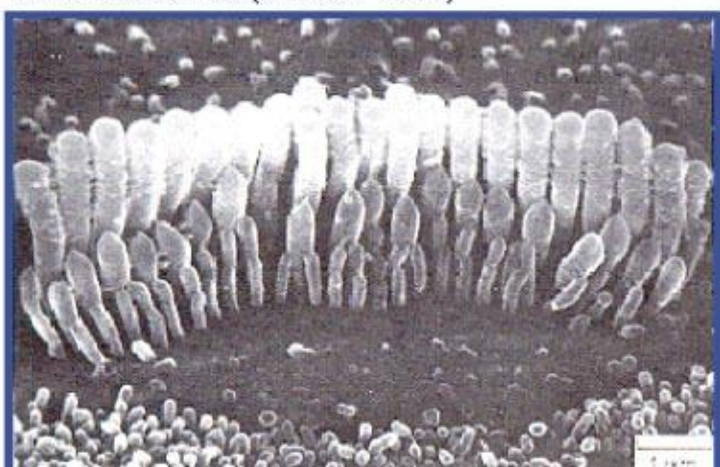
(Alec N. Salt, Washington University)

Cross-section through cochlear canal (Eckert 1988)

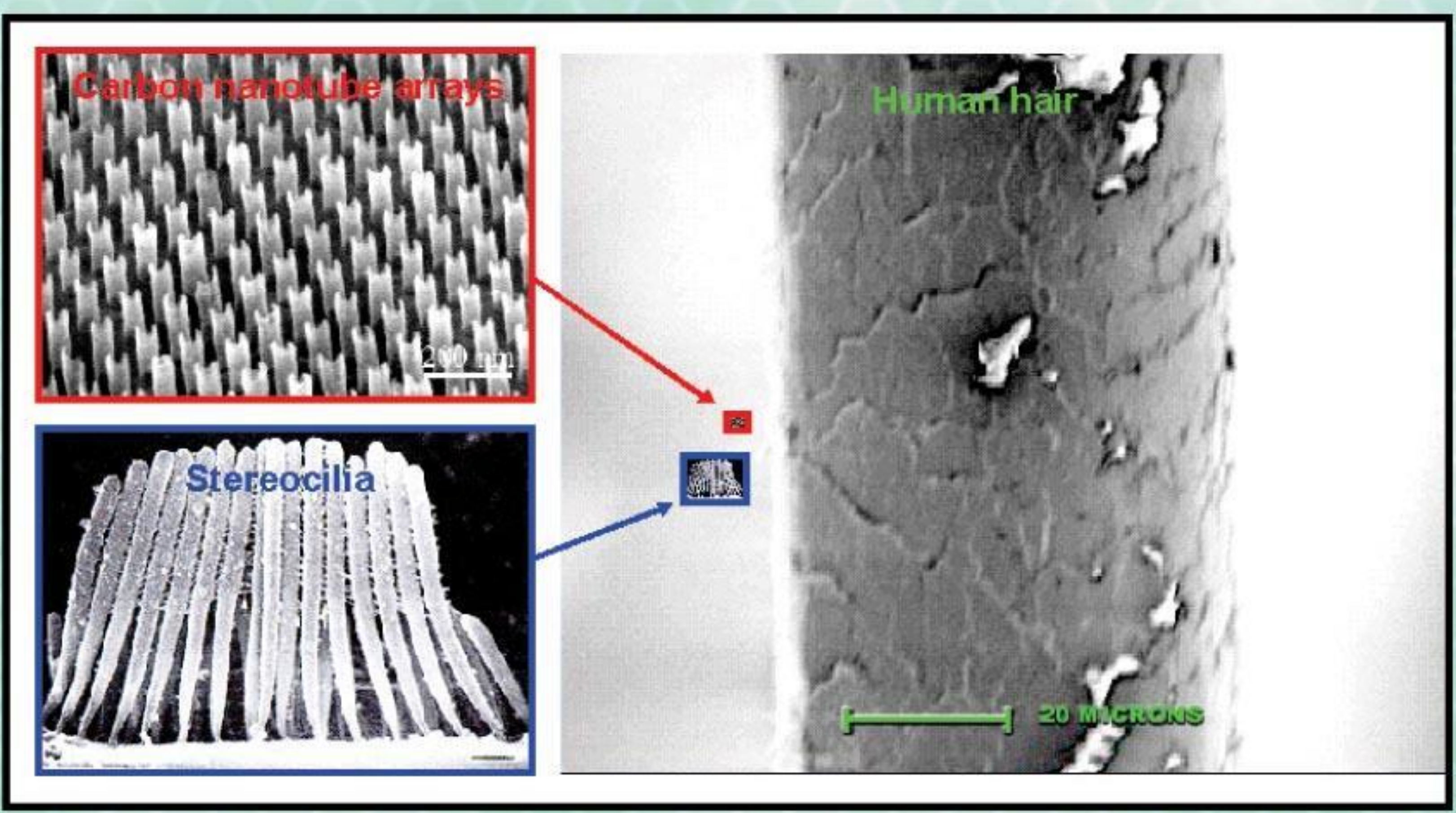




Stereocilia (Pickles 1988)



Nanotube hearing aid



- **Highly ordered arrays of parallel carbon nanotubes grown by CVD**
- **Claimed to be sensitive enough to pick up activity level of living cells (how does a cancer cell sound?)**

Nanoscale Ears (NASA) Nano hearing aid (DARPA)

Nanoscale materials: space elevator

A space shuttle uses 1.8 million kg rocket fuel

A space elavator uses none

What is needed

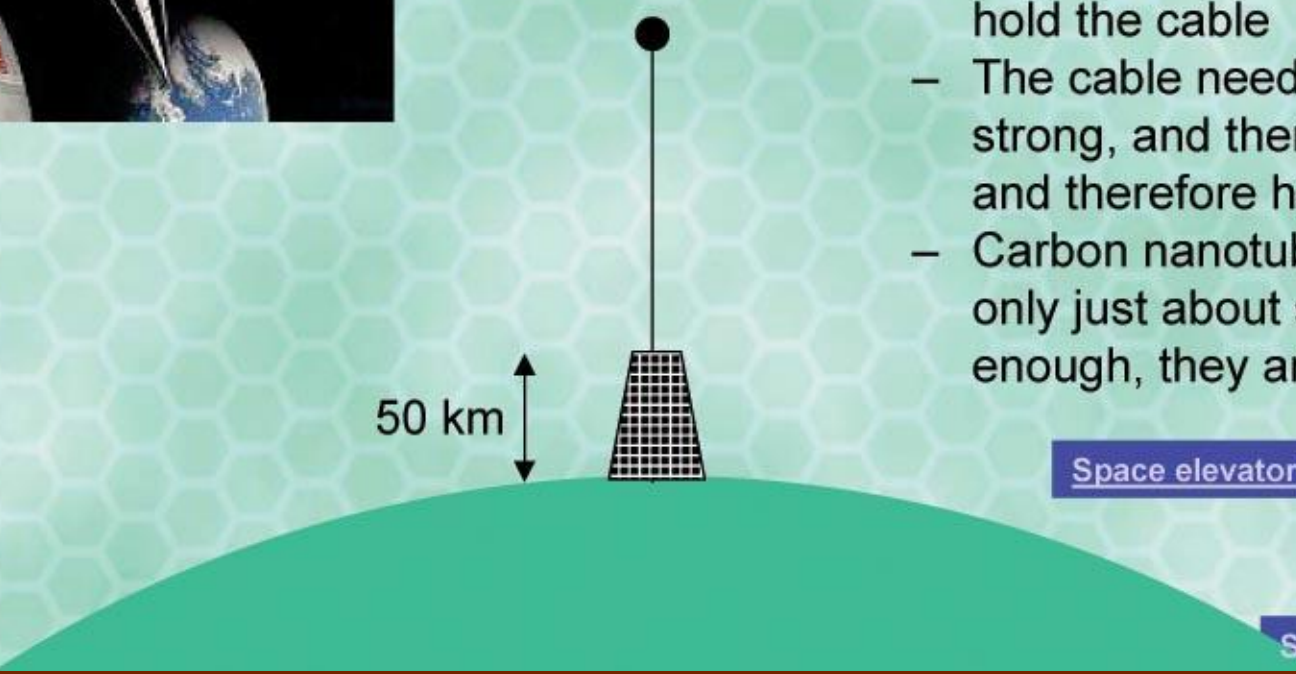
- An extremely tall base tower on Earth
- A heavy weight orbiting the Earth
- A cable that connects the tower to the weight
- A spacecraft that can ride the cable into orbit

Space elevator

Nanoscale materials: space elevator

NASA REPORT

- **Cable length**: 144000 km
- **Cable material**: 60 GPa tensile strength
- **Base tower** (anchor): 50 km
  - The tower is necessary to hold the cable
  - The cable needs to be strong, and therefore thick, and therefore heavy itself
  - Carbon nanotubes are not only just about strong enough, they are also light!



Space elevator report (NASA)

Space elevator