



Introduction to Nanotechnology and Nanoscience – Class#6

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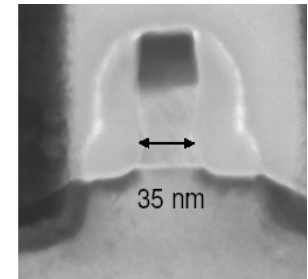
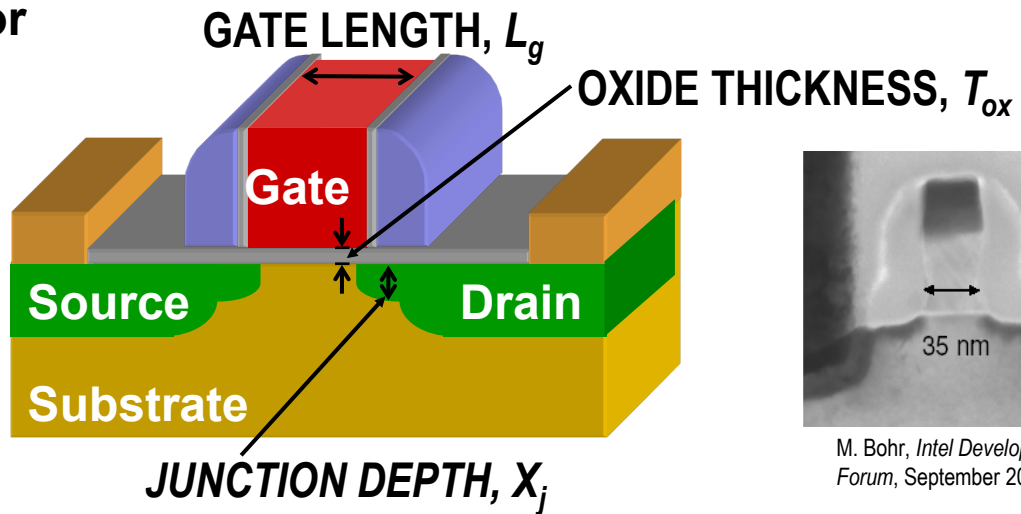
Outline

- Recap
- Top-down – MEMS
- HW #2
- CNT – paper #1 & 1-1 revisit



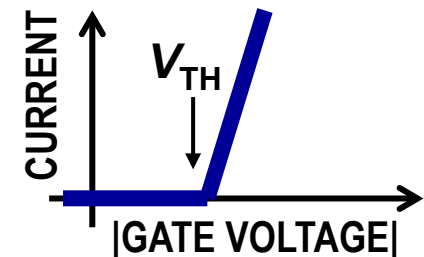
The MOSFET

Metal-Oxide-Semiconductor
Field-Effect Transistor:



M. Bohr, Intel Developer Forum, September 2004

- Current flowing through the **channel** between the **source** and **drain** is controlled by the **gate** voltage.
- “N-channel” & “P-channel” MOSFETs operate in a complementary manner
“CMOS” = Complementary MOS

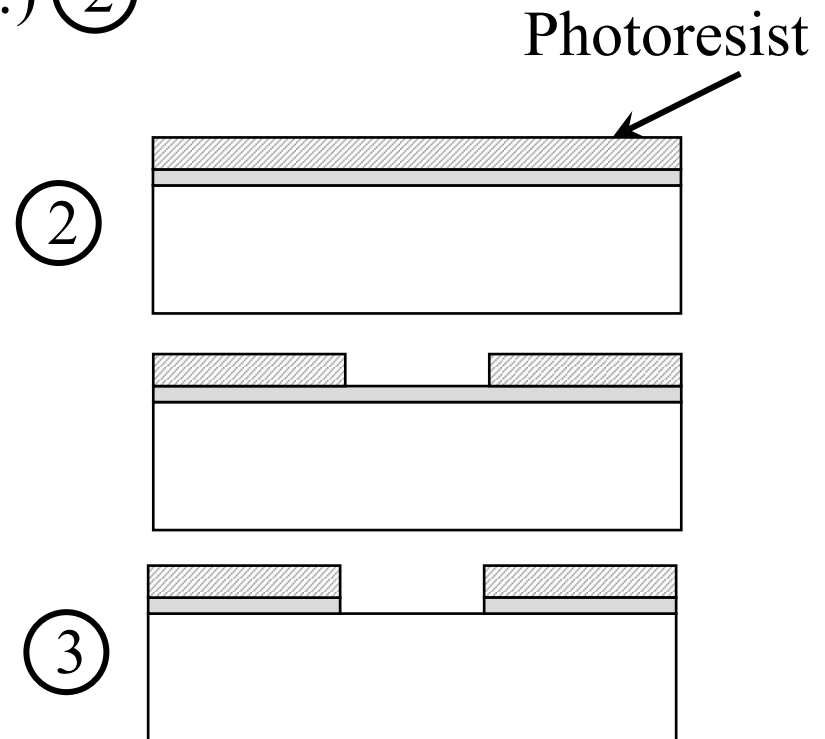
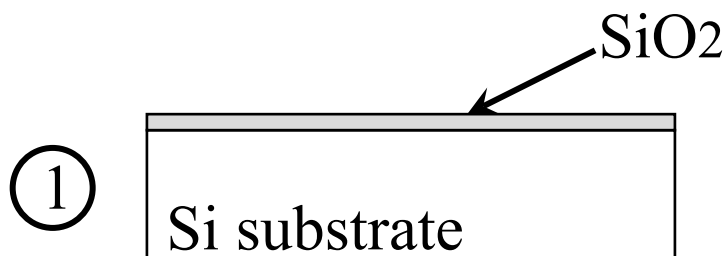




IC Process

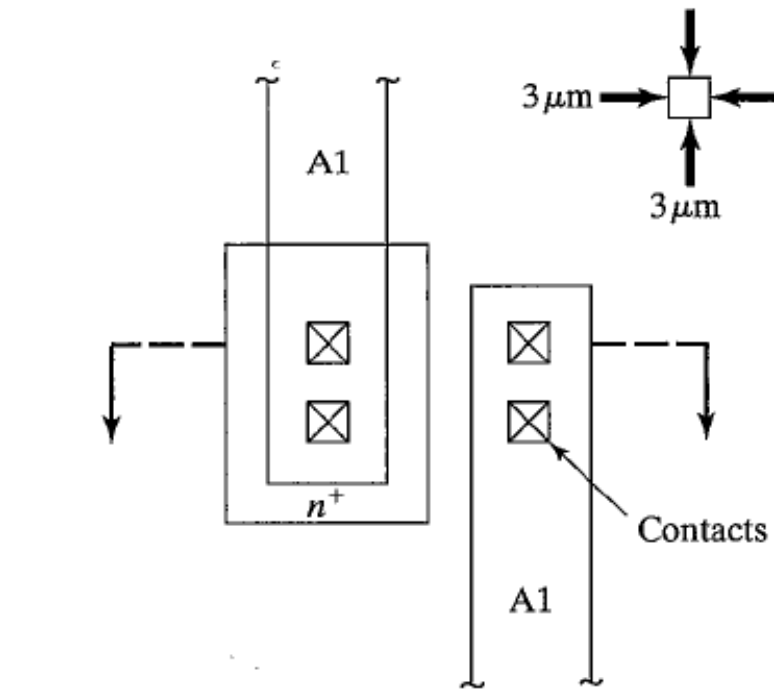
□ General fabrication flow

- Wafer clean
- Thin film deposition (SiO_2 , Si_3N_4 , metal ...) ①
- Lithography (mask#1, #2, ...) ②
- Etching ③

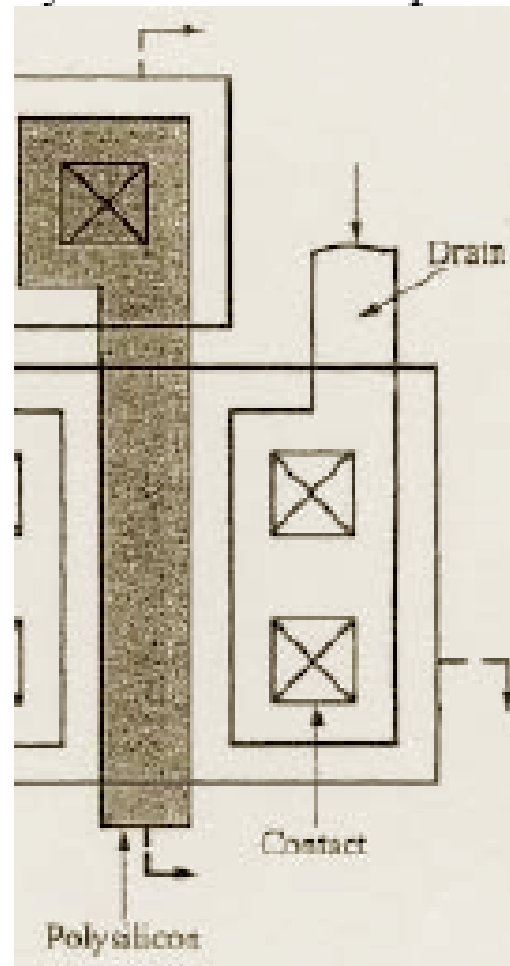
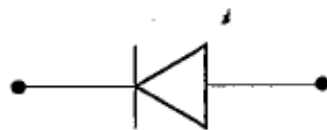
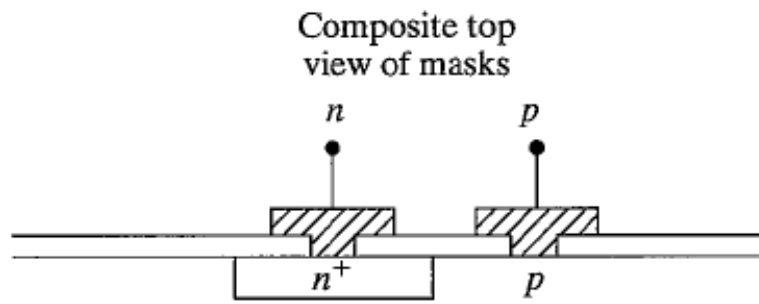




HW#1 – Problem 4



Draw the cross-sectional view diagram in the areas at the drawing in scale and the minimum feature size my MOSFET can be placed in an area of 1"x1"





MOSFET Regions of Operation (NMOS)

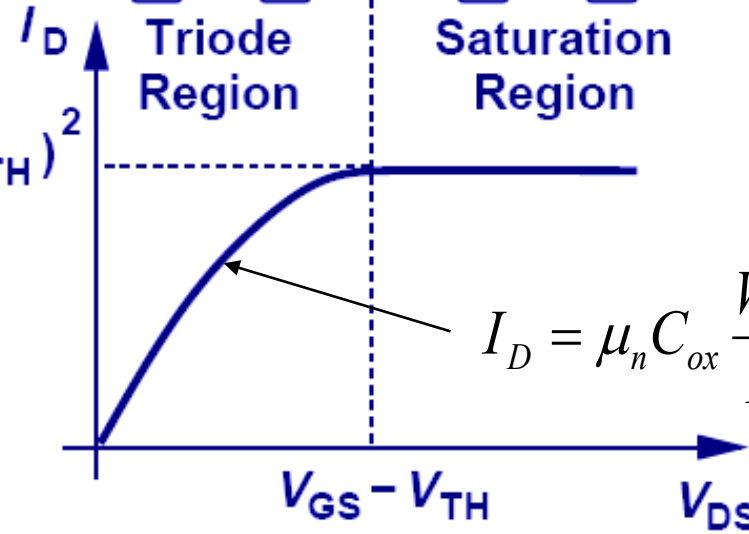
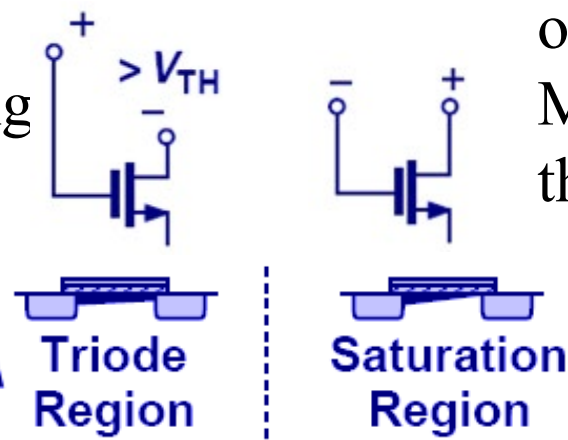
- When the potential difference between the gate and drain is greater than V_{TH} , the MOSFET is operating in the *triode region*.

- When the potential difference between the gate and drain is equal to or less than V_{TH} , the MOSFET is operating in the *saturation region*.

Gate capacitance

$$\frac{1}{2} \mu_n C_{ox} \frac{W}{L} (V_{GS} - V_{TH})^2$$

Electron mobility



$$I_D = \mu_n C_{ox} \frac{W}{L} \left[(V_{GS} - V_{TH}) - \frac{V_{DS}}{2} \right] V_{DS}$$



Water Analogy

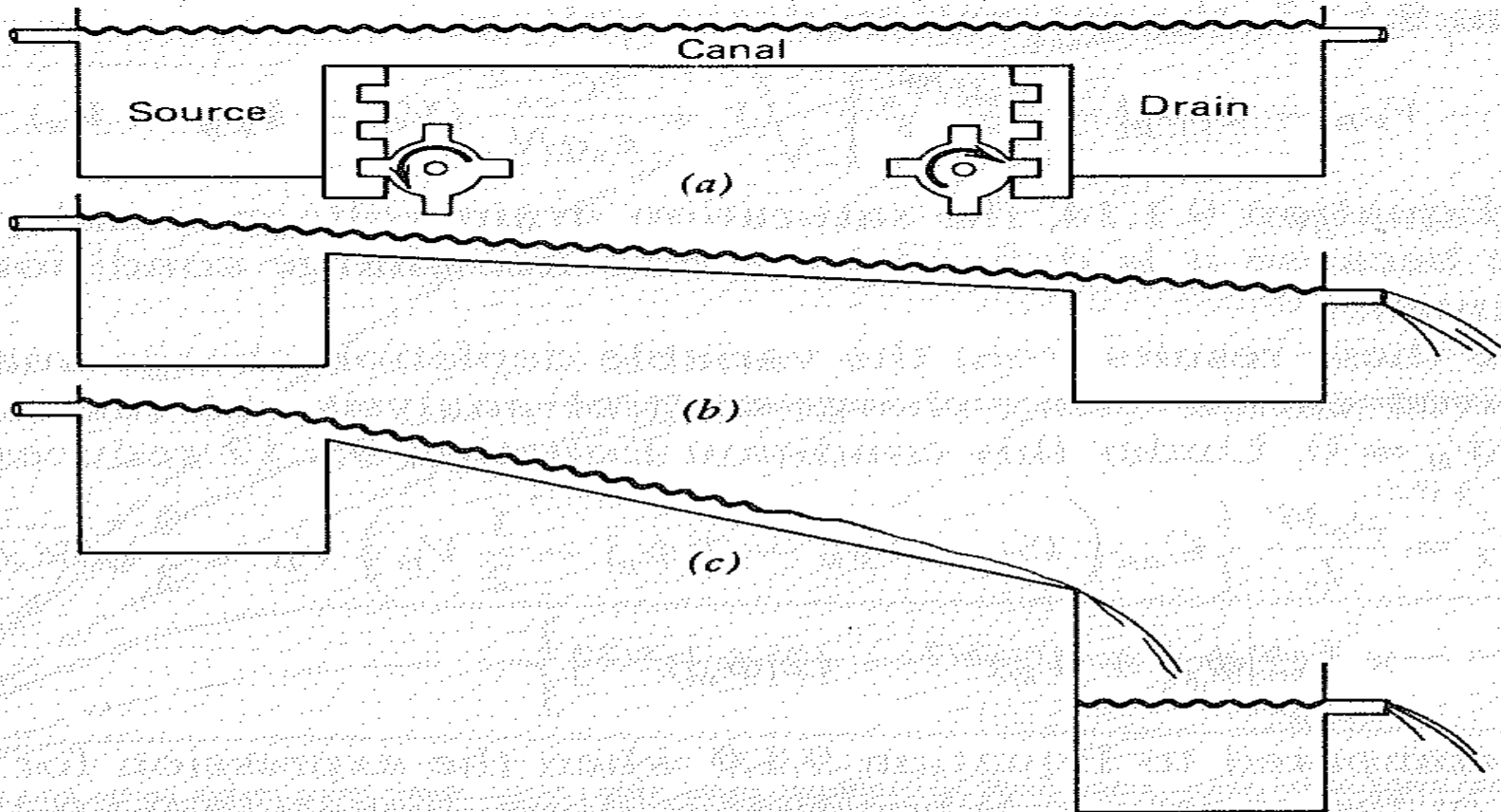
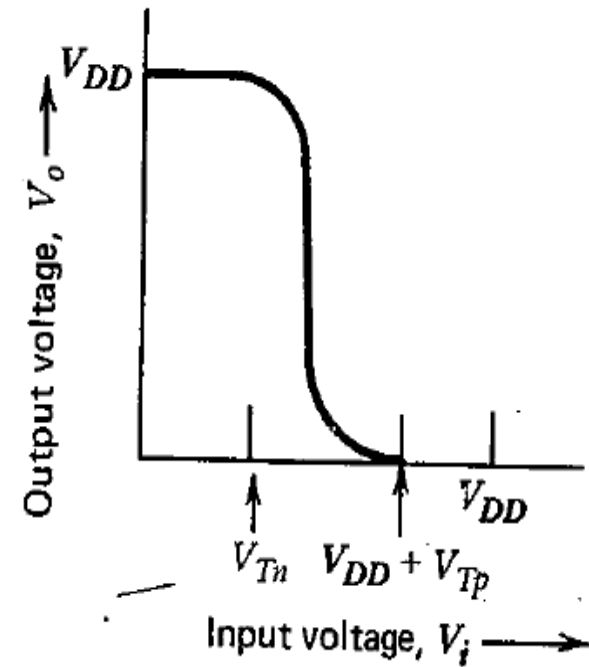
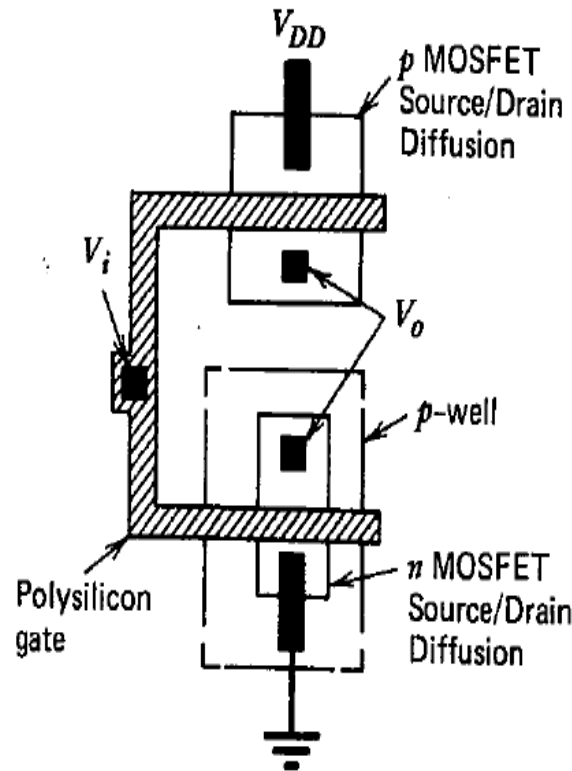
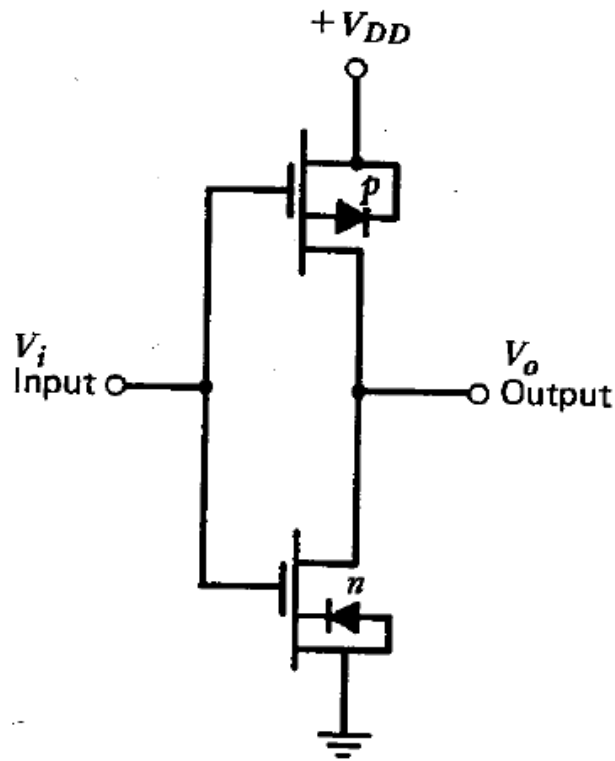


Figure 9.6 Water analogy for a MOSFET. (a) When the source and drain are level, there is no flow ($V_{DS} = 0$). The water depth in the canal can be varied by the gear and track (V_{GS}). (b) When the drain is lower than the source, water flows along the canal. (c) The flow is limited by the channel capacity; lowering the drain further only increases the height of the waterfall at its edge.



CMOS Inverter



- One or the other MOSFET is always cut off such that there is no DC path to carry current from the supply (except the leakage current). Power dissipation only happens during switching → low power consumption as compared to NMOS or PMOS



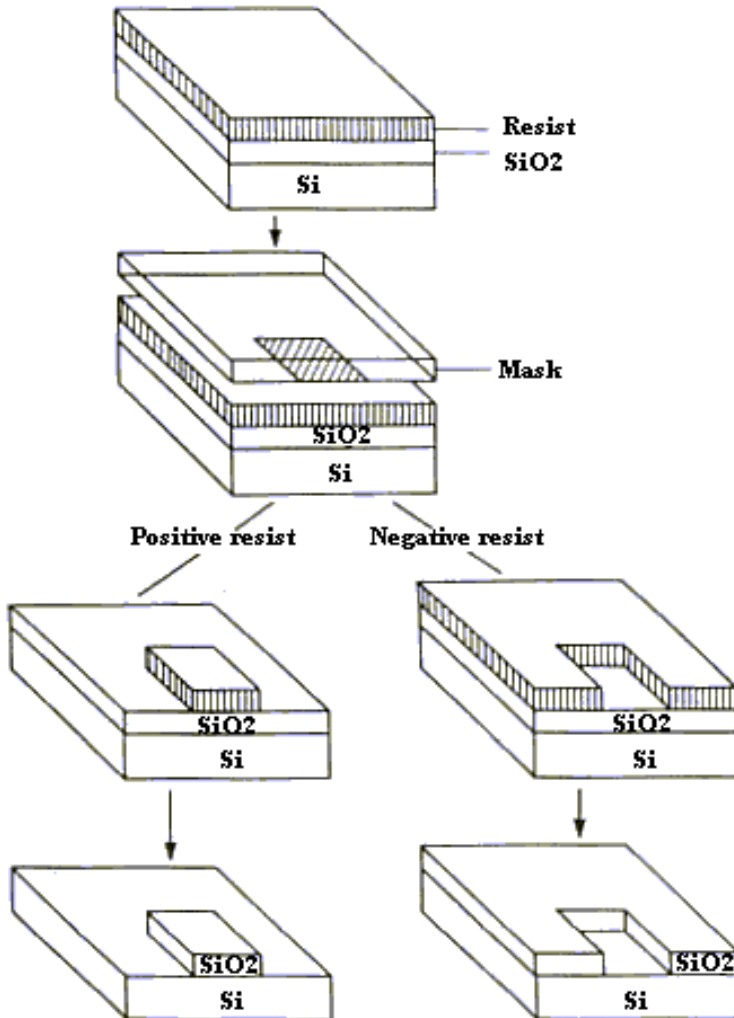
Top-Down: Photolithography

Step 1: Spin photoresist (a UV-sensitive polymer) and bake to cross link polymer

Step 2: UV expose to a mask—UV light will break cross-linked bonds

Step 3: Develop with developer

Step 4: Can then wet or dry etch





MEMS

□ MEMS (Micro Electro Mechanical Systems)

- Device scale --- 10^{-3} to 10^{-6} meter
- Fabrication capability --- 10^{-6} to 10^{-7} meter
- Material --- silicon, metals
- Market --- 14 billion at 2000*

□ MEMS and IC (Integrated Circuit)

- Process and Equipment --- same, modified
- Devices --- micro mechanical structures for MEMS

□ MEMS Technologies

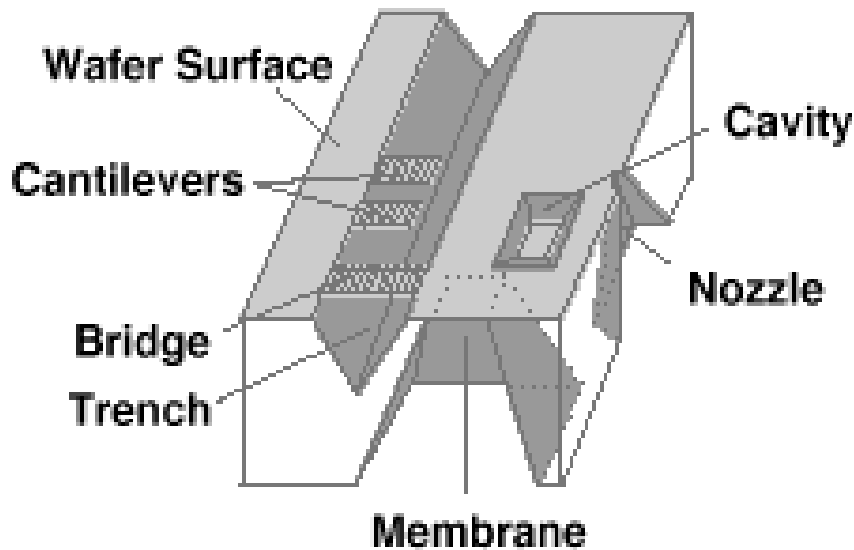
- Japan → Micromachines
- Europe → Microsystem Technologies
- Products → Sensors and Actuators



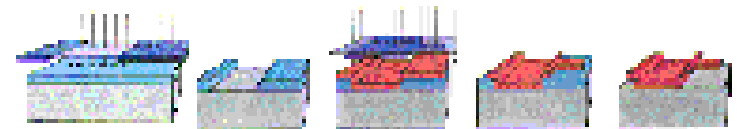
MEMS Fabrication

- MEMS collocate sensing, computing and actuating to change and control physical world

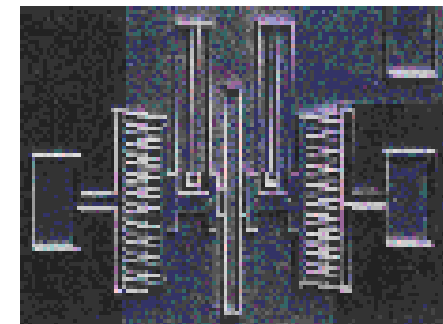
Common MEMS Fabrication Processes



Bulk Micromachining



Surface Micromachining





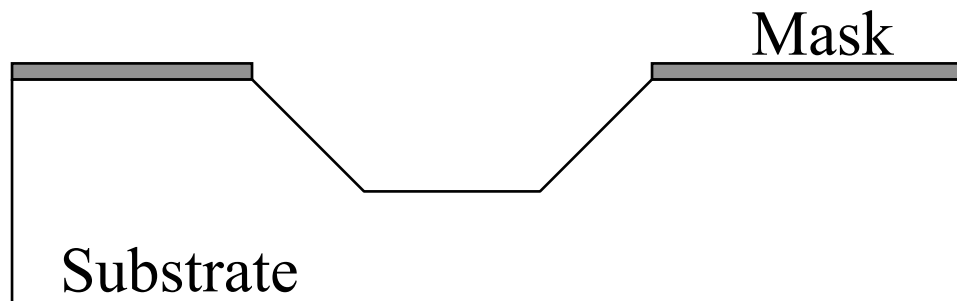
Bulk Micromachining History

- Silicon anisotropic etching < 1950
- Piezoresistive effect in silicon = 1953
- Semiconductor strain gauge = 1957
- Silicon pressure sensor > 1960
- National semiconductor catalog = 1974
- Microactuator > 1980
- Microaccelerometer > 1980



Bulk Micromachining

- Micro mechanical structures are formed by etching of substrate (silicon wafer)
 - Anisotropic etchants: KOH, EDP, TMAH ...
 - Isotropic etchants: HF+HNO₃+CH₃COOH ...
 - Etching Stops: P⁺silicon, p-n junction ...
 - Etch masks: SiO₂, Si₃N₄ ...



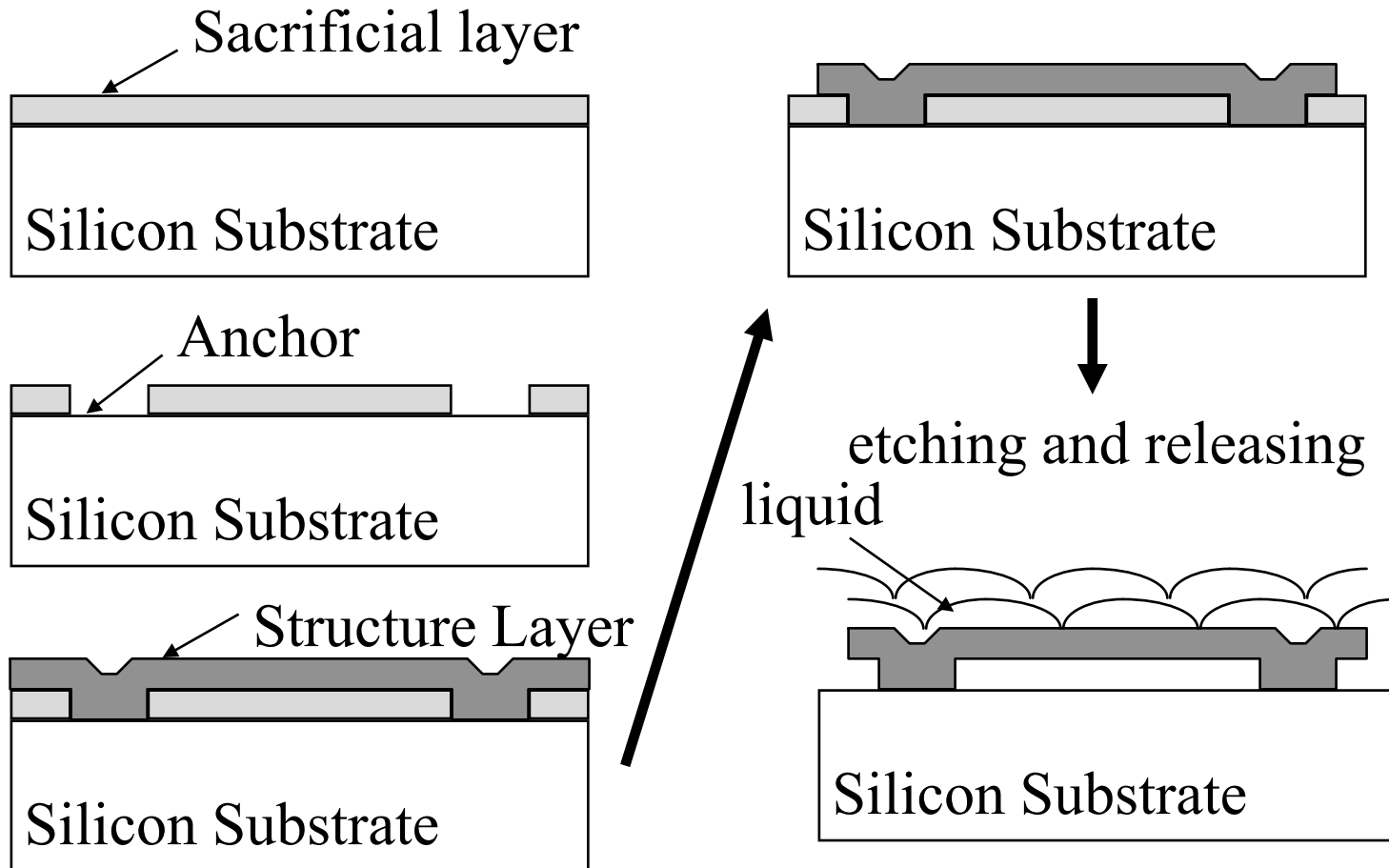


Surface Micromachining History

- Surface microstructures are fabricated by selective etching of multiple layers of deposited and patterned thin film (“surface micromachining was coined by P.W. Barth in 1985 in contrast to “bulk” micromachining)
- “Beam lead” process at Bell Labs in the late 1950s
- “Resonant Gate Transistors” in the mid-1960s in Westinghouse Research Labs.



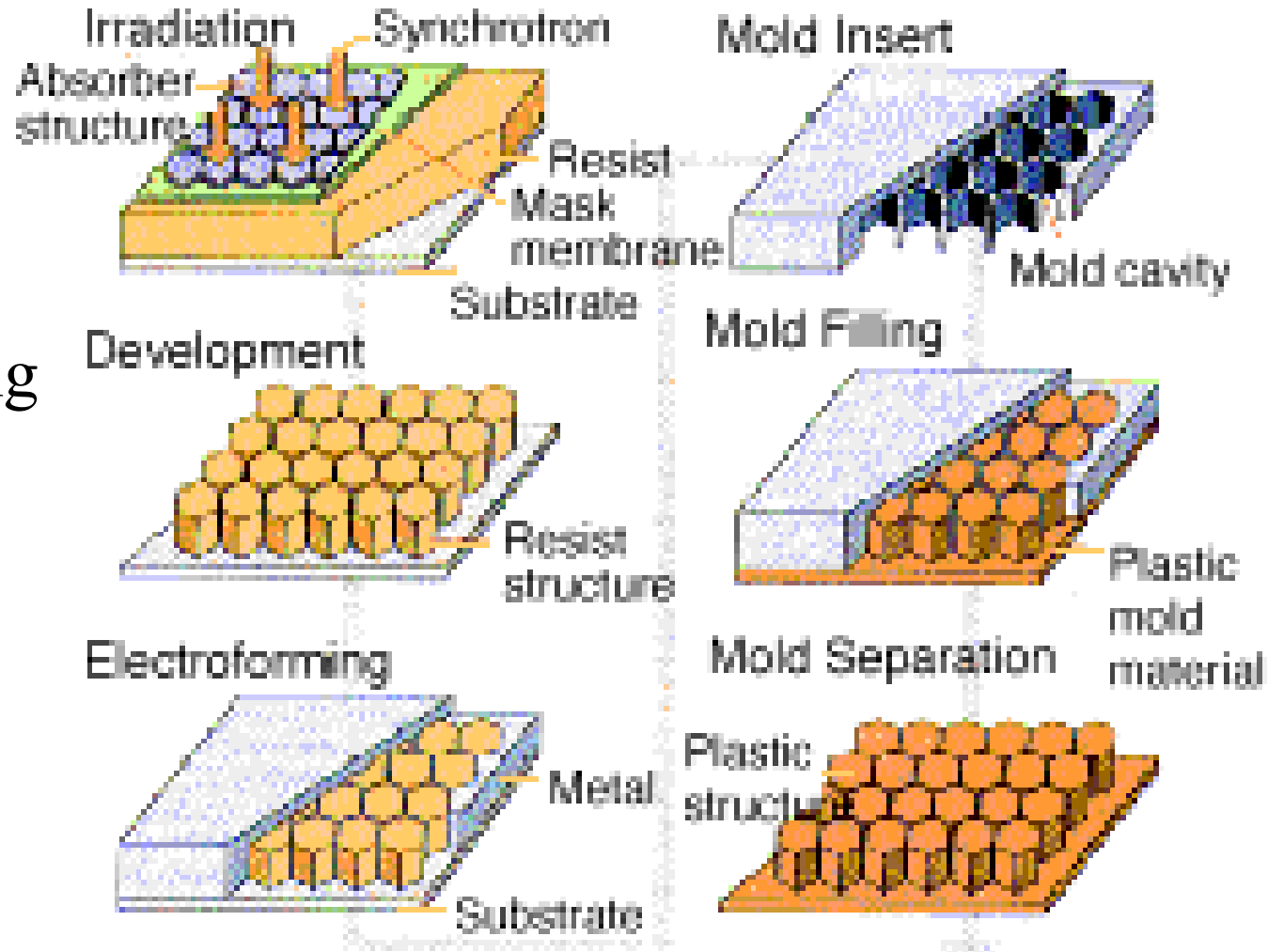
Surface Micromachining





LIGA/Deep UV Processes

- Lithographie
- Galvanoformung
- Abformung





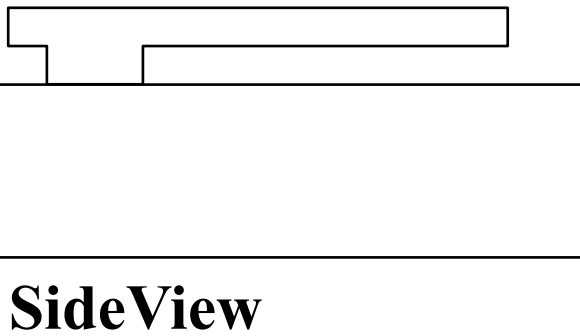
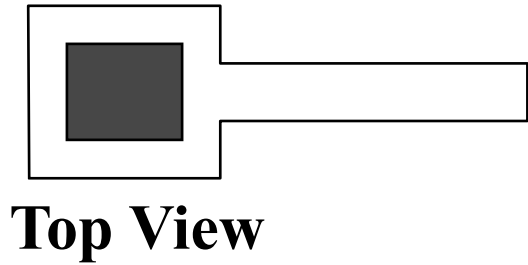
Mask

□ How to make a mask?

- CAD system →
- Tape →
- Pattern generator →
- 10x reticules →
- Flash lamps (to expose series of rectangular)



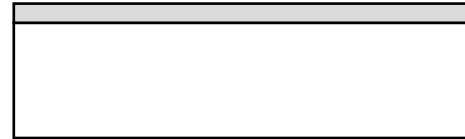
How to Make Cantilever?



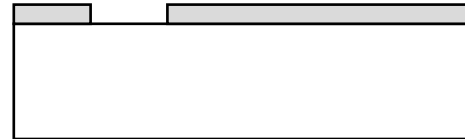
Start



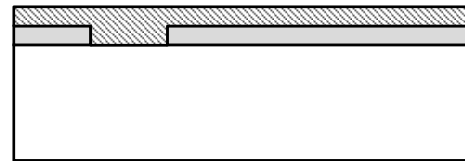
SiO₂



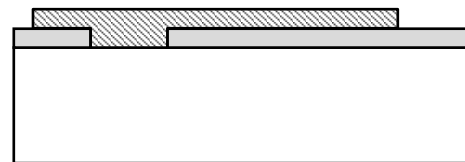
Mask#1



Polysilicon

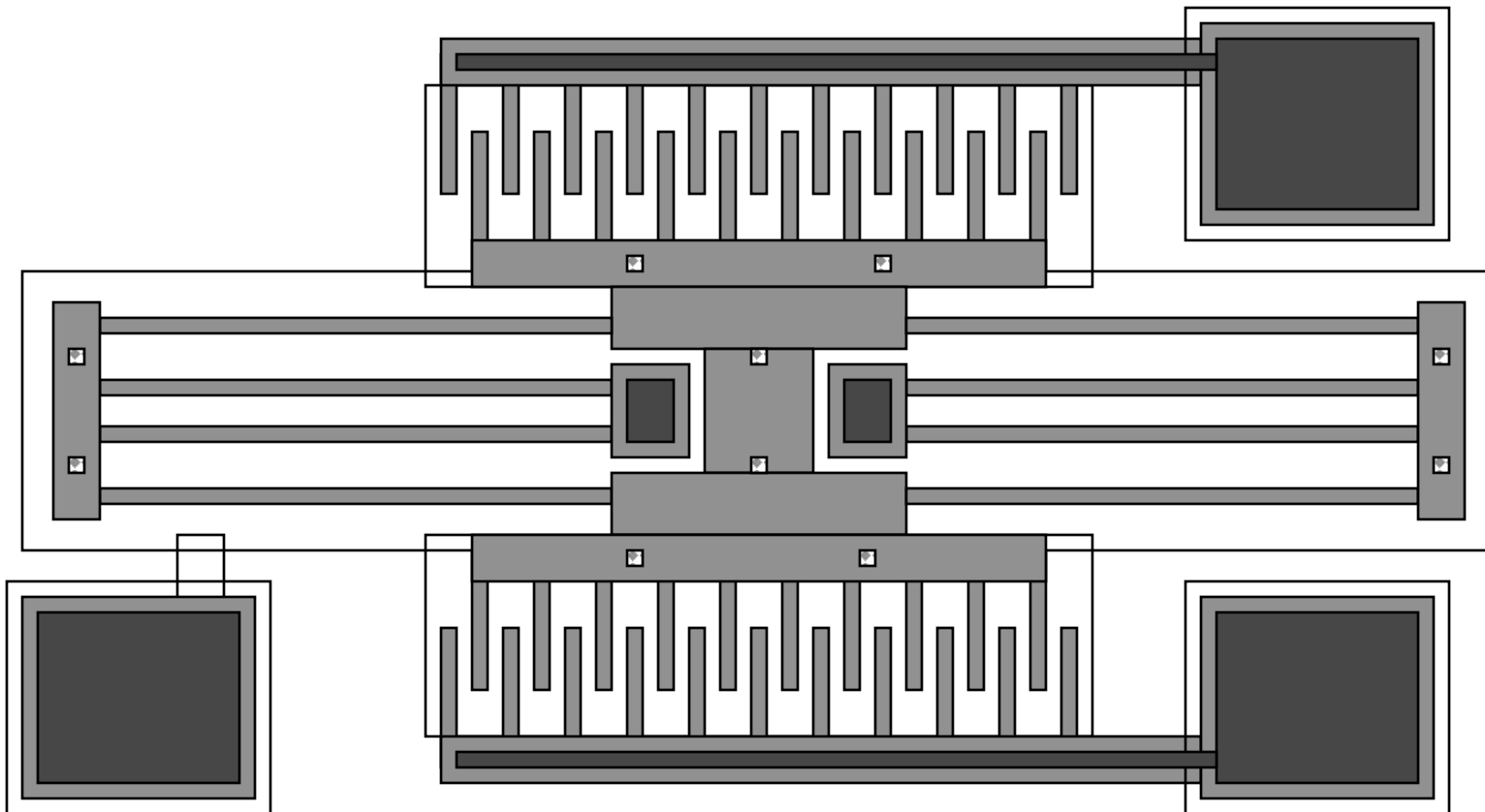


Mask#2



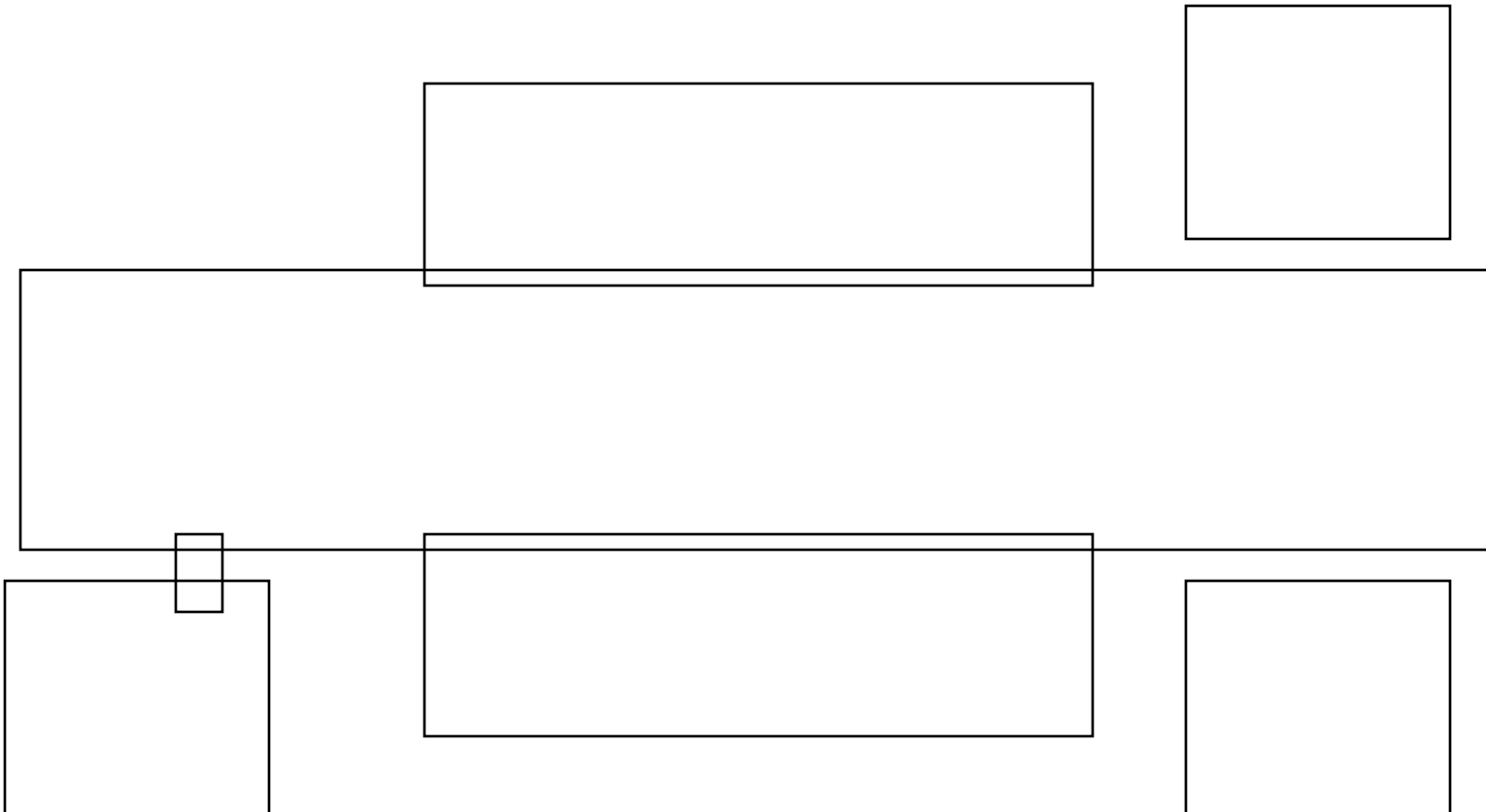


Device Example - Comb Drive



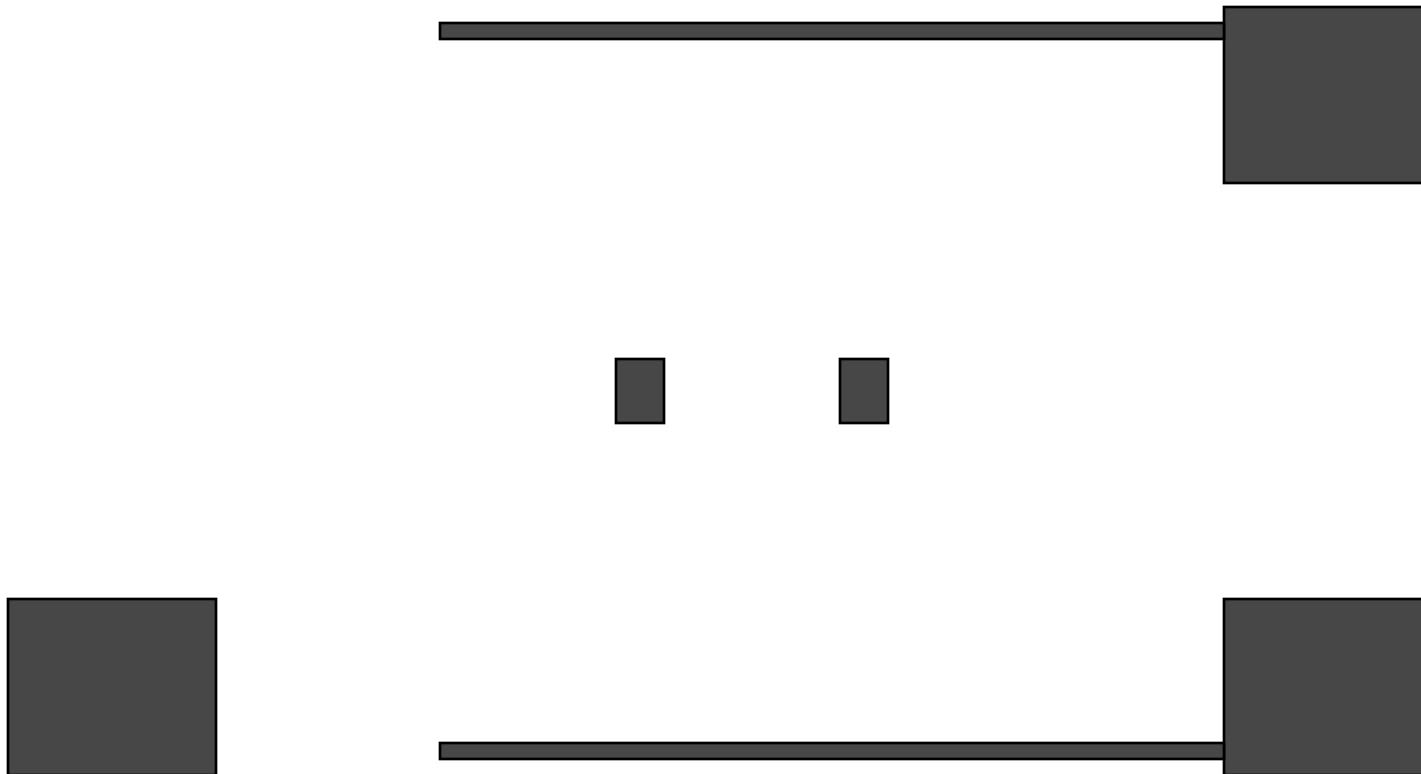


Device Example - Poly0



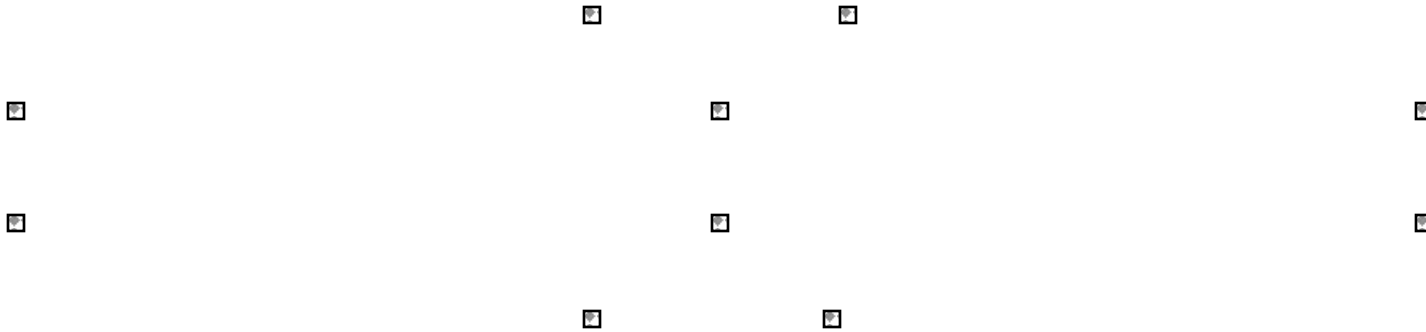


Device Example - Anchor1



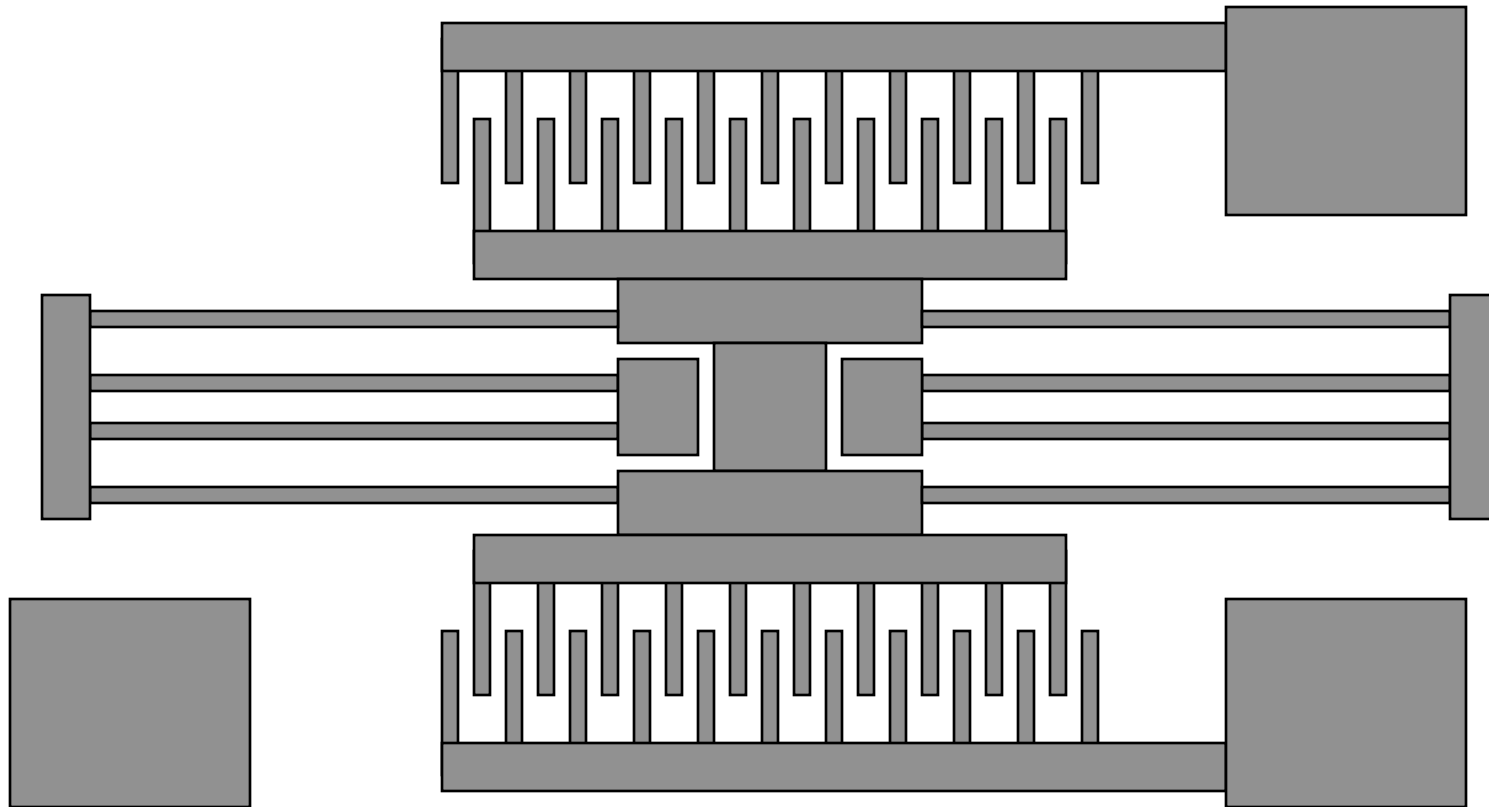


Device Example - Dimple





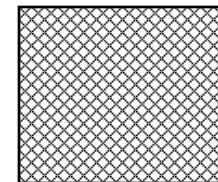
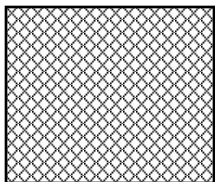
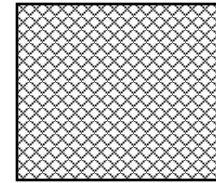
Device Example - Poly1





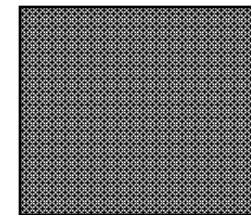
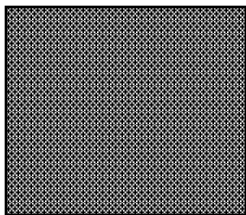
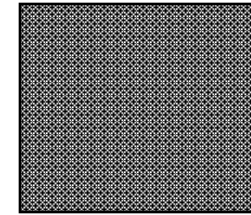
Device Example - Poly1_Poly2_Via

Microsystems Laboratory
UC-Berkeley, ME Dept.





Device Example - Poly2





Device Example - Metal





HW#2

University of California at Berkeley
College of Engineering
Mechanical Engineering Department

ME118/ME218N, Spring 2024

Liwei Lin

Problem Set #2
Due Feb. 8 (Thursday)

Problem 1 (MOSFET)

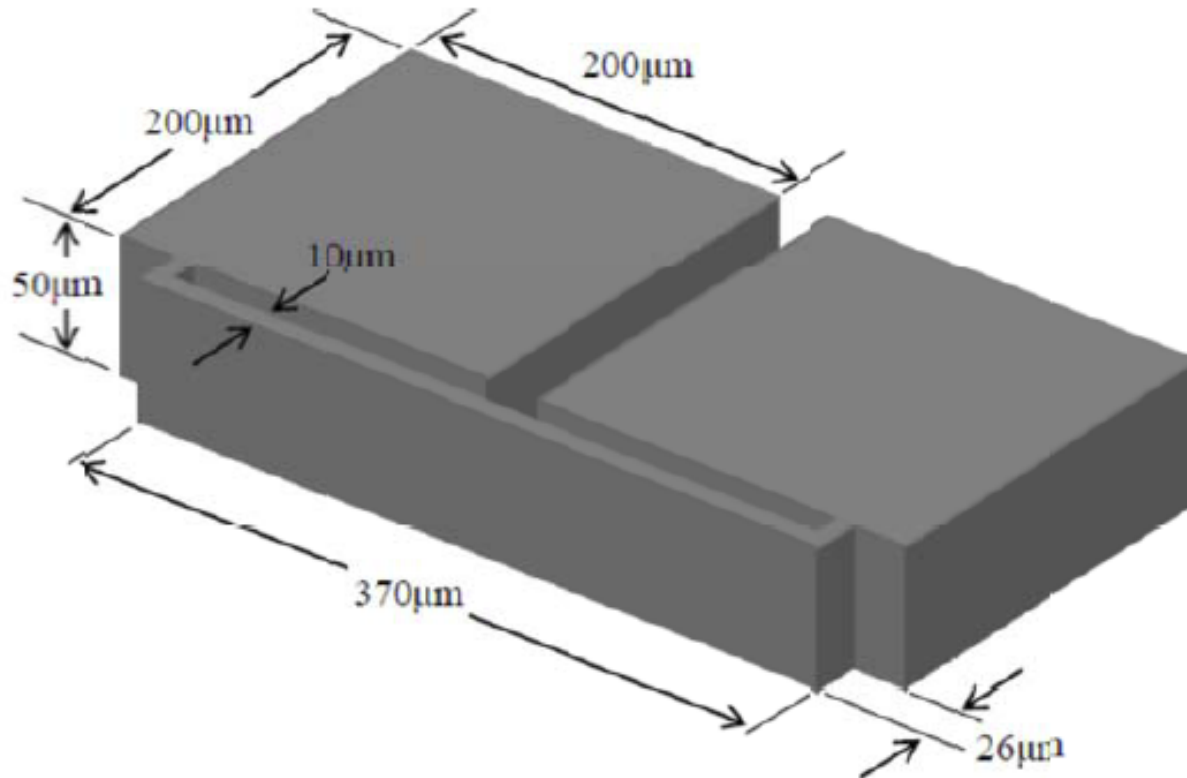
- a. Sketch the 3D view model of an n-channel MOSFET (can be the same as the one we have discussed in class and the same figure). Please clearly mark all regions such as n and p doped regions, terminals ...
- b. Explain the principal operation of the n-channel MOSFET. Is the charge through the channel transported by holes or electrons?
- c. Explain modes of operation of a MOSFET, including graphic illustrations.



Problem #2

Problem 2 (Top-Down Process – MEMS)

The figure shows an old experimental sample we used in previous ME 118 class for laboratory. The structure is made from the SOI (Silicon on Insulator) substrate using the top silicon layer as the structural layer. Please design a process flow chart to make this device – cross sectional view figures on the left and concise process explanations on the right. Please also draw the “mask(s)” to make the device.

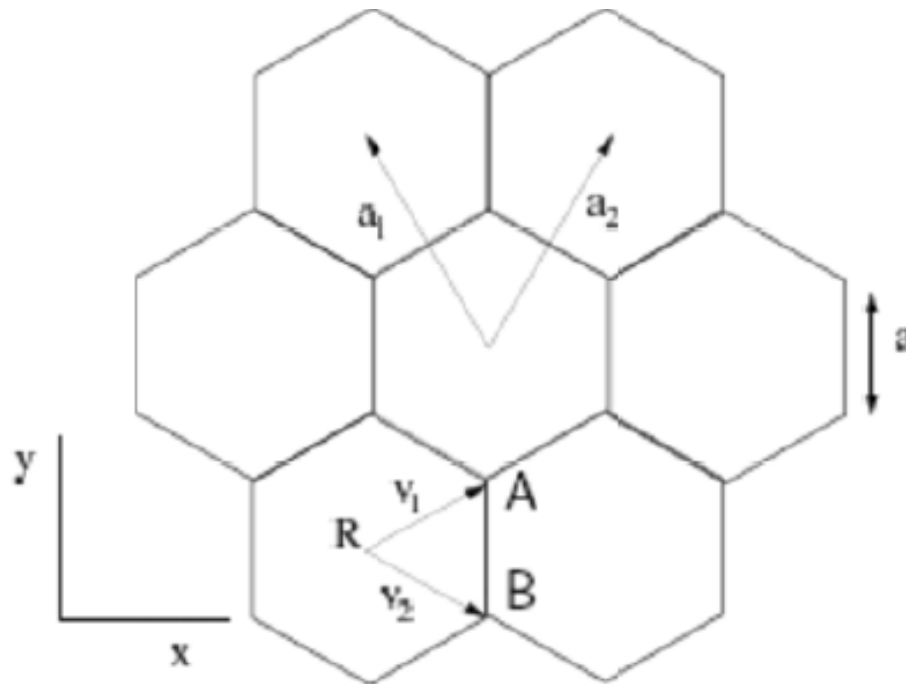




Problem #3

Problem 3 (Graphene & CNT)

A graphene sheet is a honeycomb lattice of carbon atoms (see figure). Let the distance between carbon atoms be a . A good model for graphene is to consider a single plane in which there is one valence electron per carbon atom. We will use the tight-binding approximation, in which this electron can occupy a single p_z orbital at each carbon site. Let \mathbf{R} denote the centers of the hexagons in the honeycomb: these form the underlying hexagonal Bravais lattice. Please notice that the latter is indeed a Bravais lattice differently from the graphene honeycomb lattice. The unit cell spanned by \mathbf{a}_1 and \mathbf{a}_2 contains two carbon atoms conventionally labeled as A and B atom, located at $\mathbf{R} + \mathbf{v}_A$, $\mathbf{R} + \mathbf{v}_B$, as shown in the figure.





Problem #3

Carbon nanotubes are made up of a section of the graphene lattice that has been wrapped up into a cylinder. You can specify the way the lattice is wound up by identifying the winding vector \mathbf{W} . The winding vector must be a Bravais lattice vector, and so can be specified by two integers:

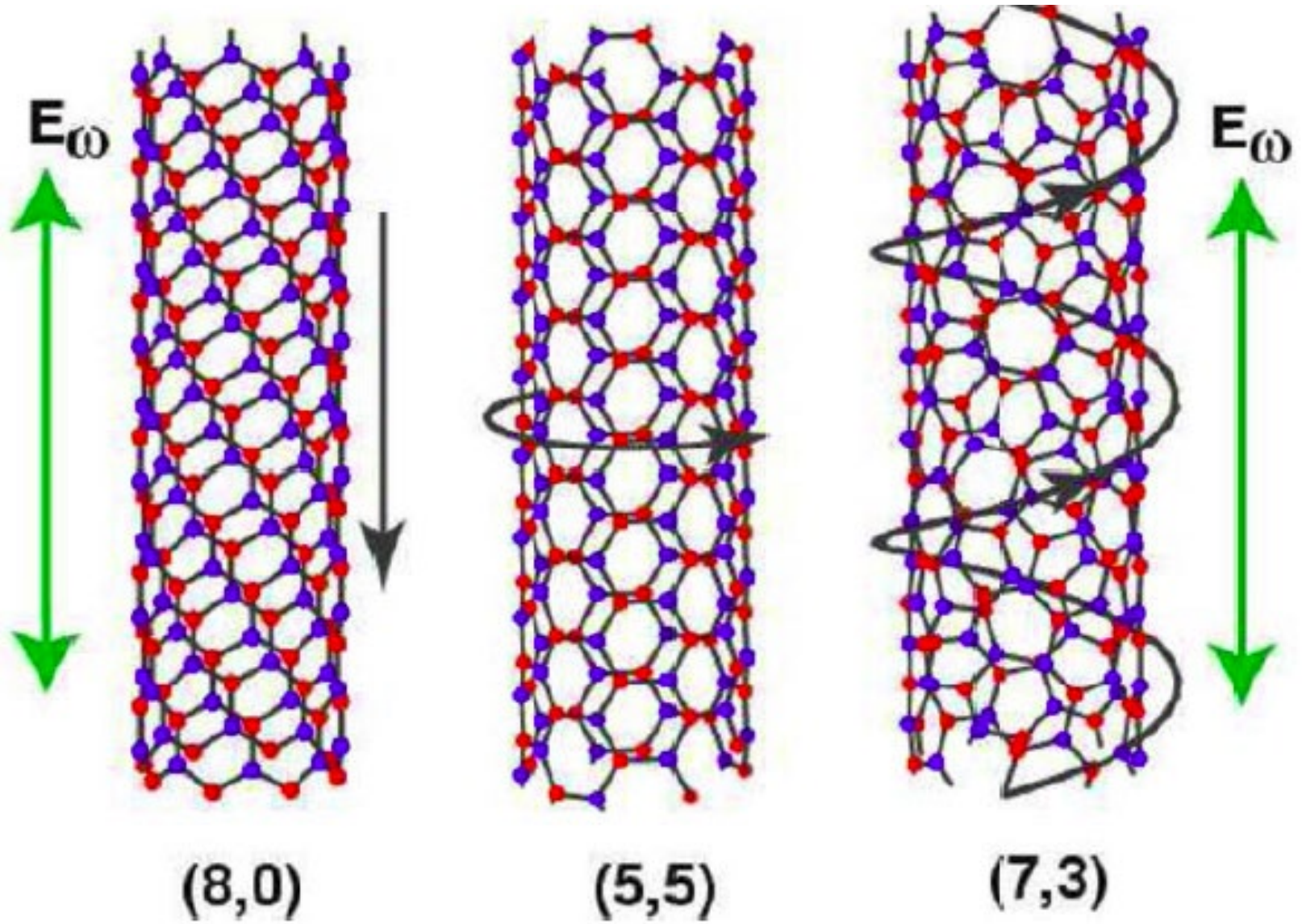
$$\mathbf{W} = n \mathbf{a}_1 + m \mathbf{a}_2;$$

where n and m are integers. To construct a nanotube, take a graphene lattice and mark one atom (either A type or B type) as the origin. Shift the origin of the vector \mathbf{W} on the chosen atom. The new vector \mathbf{W}_n will point to another atom of the same type. Roll up the sheet perpendicular to \mathbf{W}_n so that the second atom sits exactly on top of the first. You have constructed a $(n;m)$ nanotube! Nomenclature: we can specify some special tubes said **achiral**: they are $(n; n)$ tubes which are called **armchair tubes**, and $(n; 0)$ **zig-zag tubes**. All other tubes are said **chiral**.

- Build a $(5; 5)$ armchair tube (i.e. with scissors and adhesive tape!) by making use of transparencies - You can download this sheet from course homepage and print it out. The easy way to submit your homework is to take and print out a photo with finished structure on a white paper with you name on the paper as the evidence.
- Construct a $(8; 0)$ zig-zag tube.
- Build a chiral $(7; 3)$ tube.
- Create and name a new tube of your own.

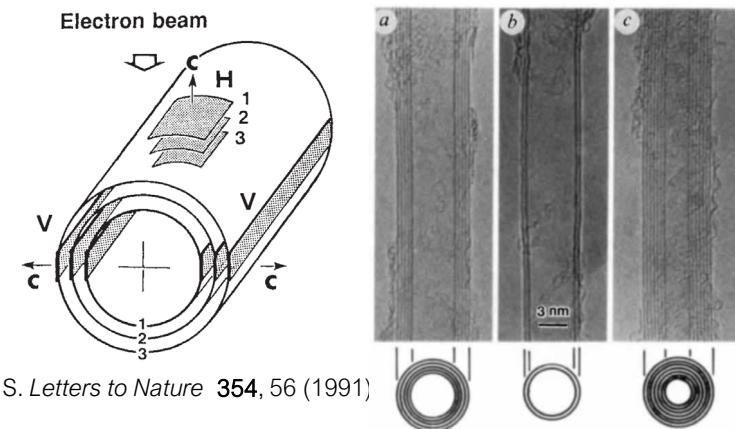
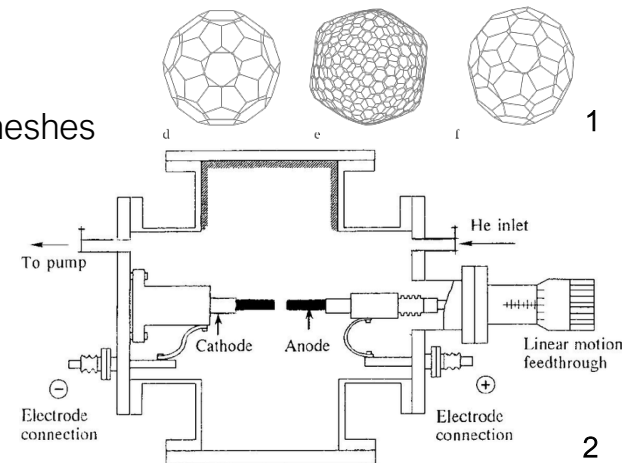


Problem #3



Helical Microtubules of Graphitic Carbon

- Carbon is known to maintain various allotropes (e.g., diamond, graphite, etc.)
 - Fullerenes consist of single/double sp^2 hybridized C bonds to form closed meshes (rings 5-7 atoms)
- Synthesis via d.c. arc-discharge evaporation
 - Carbon electrode (Ar 100 torr)
 - Electrode-site specific growth, most likely due to low-energy nucleation (defects etc.)
 - Polyhedral particles with shell structures (5-20 nm in diameter)
- Electron micrographs display $\{002\}$ lattice images
 - Tubular-helical structure (2-50 sheets)
 - Sheet separation ~ 0.34 nm matching bulk graphite
- Smallest tube ~ 2.2 nm diameter (ring of 30 C hexagons)
 - Neighboring hexagons on ring meet at 6° (C_{60} rings meet at 42°)
 - C_{60} bond angle energy < graphite

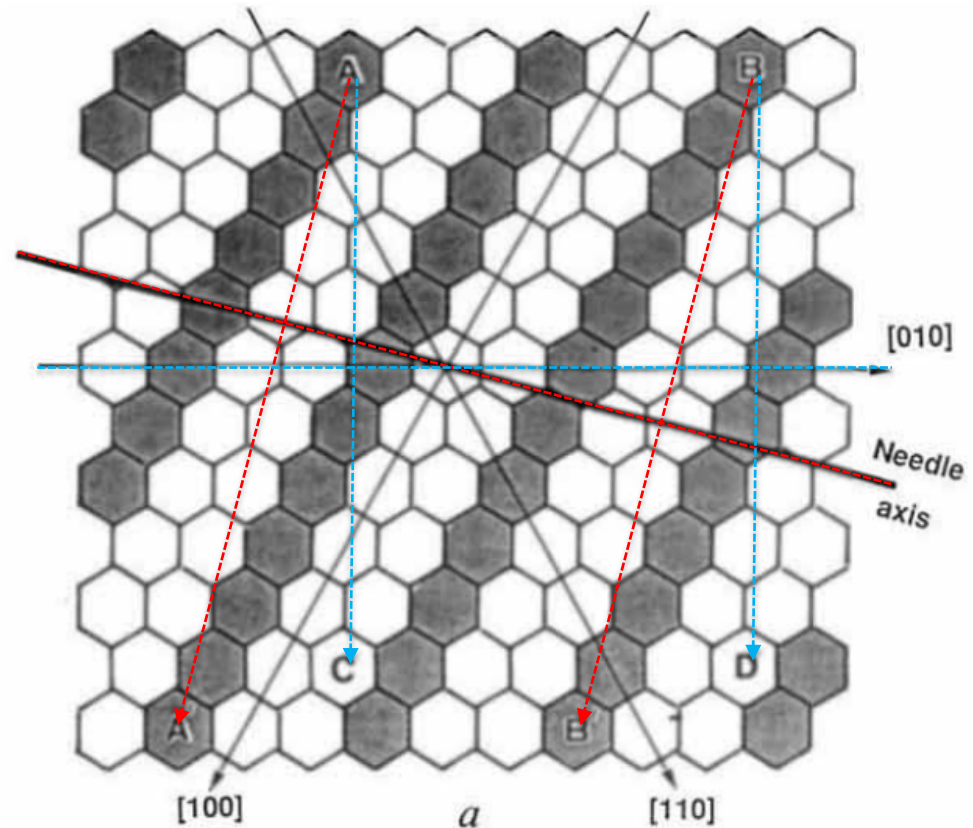


Lijima, S. *Letters to Nature* **354**, 56 (1991)

1. https://en.wikipedia.org/wiki/File:Eight_Allotropes_of_Carbon.svg 2. Harris P.J.F. *Carbon Nanotube Science: Synthesis, Properties and Applications*. 2nd ed. Cambridge University Press; 2011.

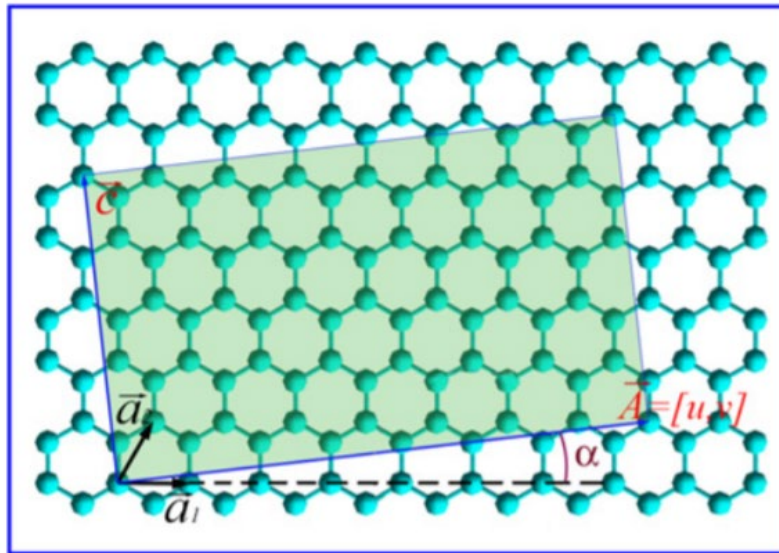
Helical Arrangement

- **Red** - helical arrangement (→ lead to the mirror symmetry);
- **Blue** – not helical arrangement (rarely been observed).

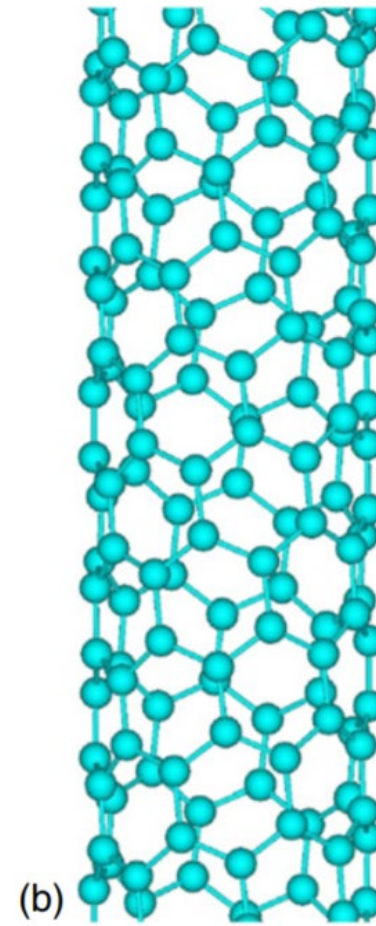


Helical Arrangement

- An example of (7, 1) carbon nanotube.

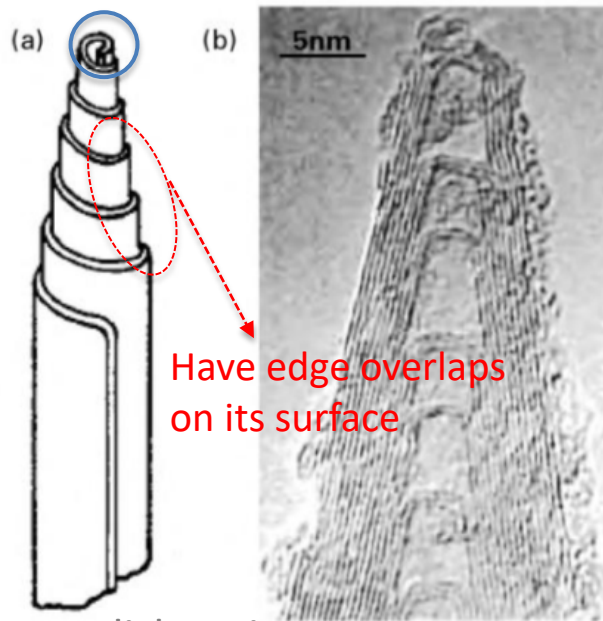


(a) “7” in a_1 direction; “1” in a_2 direction



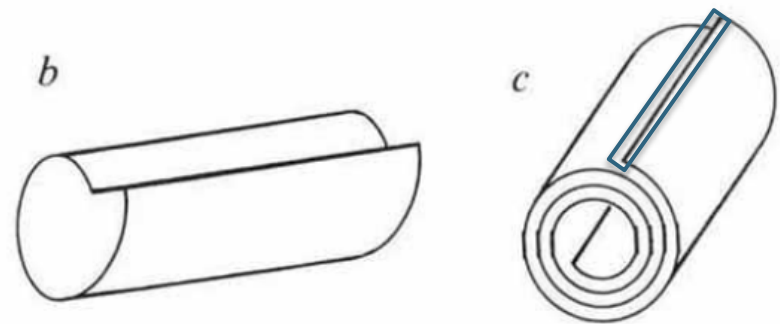
Brief Growth Model

Scroll model by Roger Bacon



Like screw dislocation
model

An example of carbon nanofiber



- Have spiral growth steps at the tube ends.



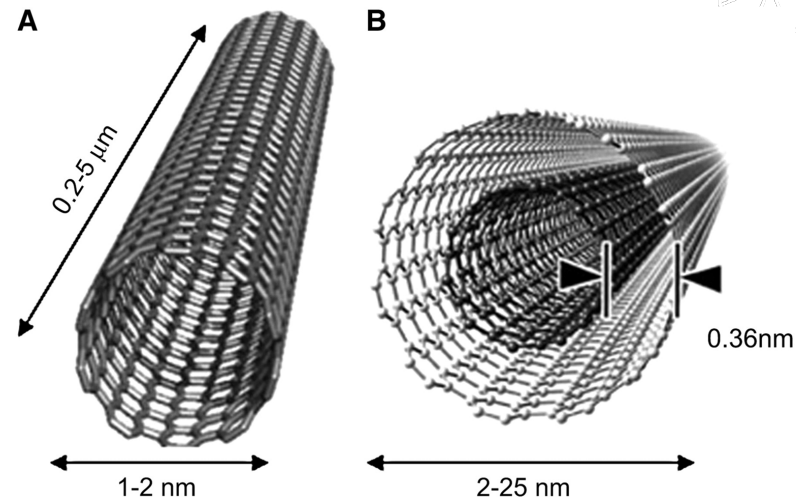
Single-shell Carbon Nanotubes of 1-nm Diameter

Sumio Iijima & Toshinari Ichihashi

ME 118/218 Paper 1+: Andrew Cheng, Michael Celebrado, Navin Jeyaselvan

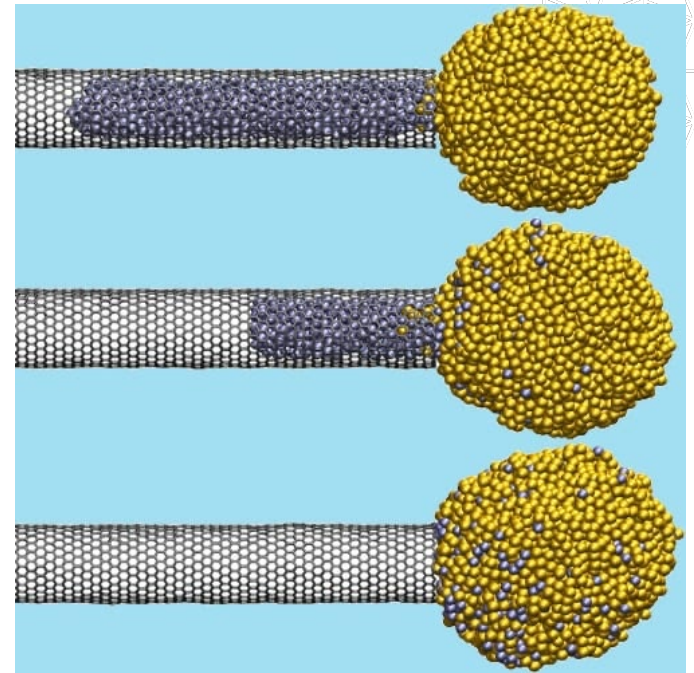
Overview

- Two years since Iijima first published discovery of carbon nanotubes (CNTs)
- Property calculations use single-shell CNTs but carbon-arc synthesis makes multi-shell CNTs
- Knowing the dimension and helical arrangement are important in proving and quantifying properties
- Key takeaways:
 - 1nm single-shell tubes form in the gas phase of a modified carbon-arc setup
 - the helical arrangement can be found with electron diffraction



Capillarity

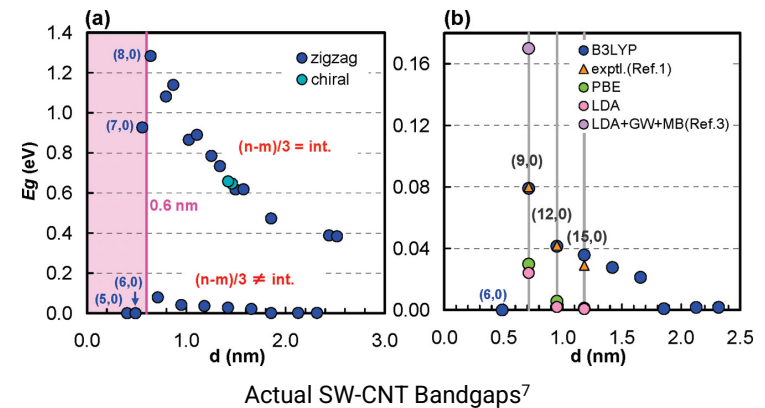
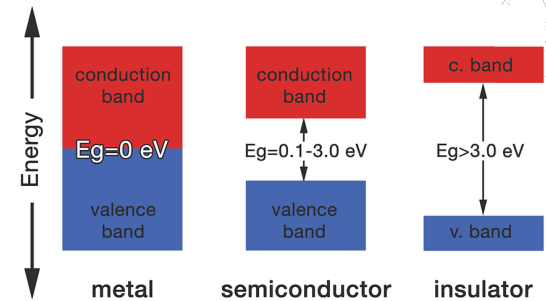
- Proven with liquid lead¹
- Nanocomposite fibers
- Heating in CO₂ can partially or completely destroy the tube caps and strip outer layers²
- Characterized as highly polarizable molecular straws capable of ingesting dipolar molecules³



Nanotube Being Used as a Pipette⁴

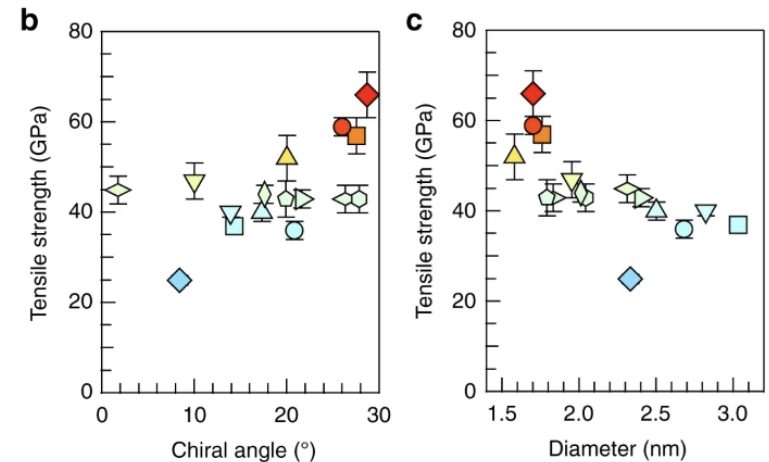
Electronic Properties

- All predictions and calculations
- Band Structure: Band gaps are metallic to semiconducting depending on diameter and helical arrangement⁵
- Carrier density similar to metal and zero band gap at room temperature
- $\frac{1}{3}$ are 1-D metals, $\frac{2}{3}$ are 1-D semiconductors⁶



Mechanical Properties

- All predictions and calculations⁸
- Strain energy / Carbon atom
 - Varies with $1/R^2$
 - Smaller in symmetric fullerene clusters with similar radii
- Continuum elastic theory relationships can apply here
- Elastic constants dependent on
 - Radius
 - Helical conformation

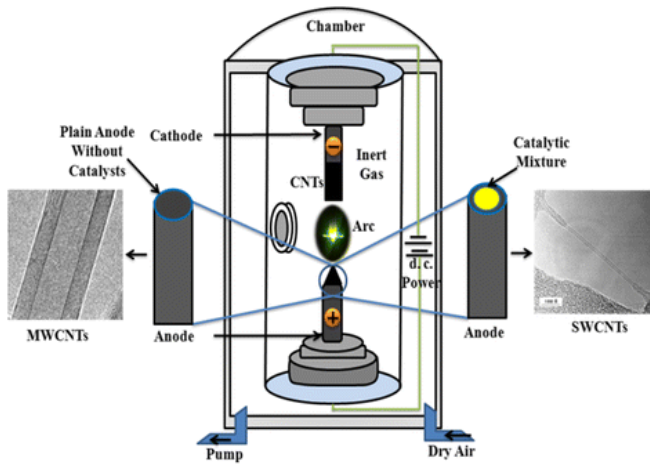


Tensile strength findings of CNTs⁹

Discussion

- Important step in:
 - Deliberate synthesis of single-walled CNTs
 - Further research for empirical evidence of properties
- Limitations
 - Difficult to control the diameter, length, and helical conformation

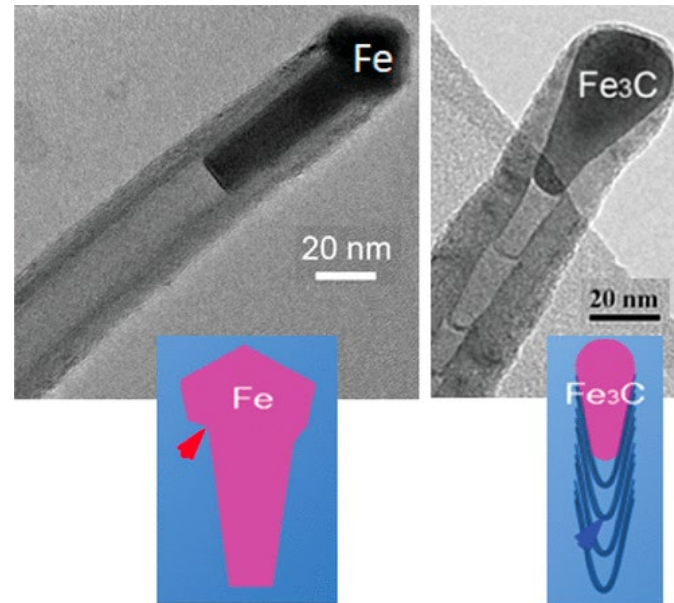
Nanotube Fabrication



- Carbon-arc chamber
 - Two vertical electrodes
 - Anode (Upper): 10 mm graphitic carbon rod
 - Cathode (Lower): 20 mm carbon rod
 - 10 torr methane, 40 torr argon
 - DC current of 200A at 20V
- Iron fillings vaporized
 - Droplet -> Vapor -> Condensation
 - Iron carbide above cathode

Nanotube Fabrication

- Iron has a catalytic role
 - Iron acts as heterogeneous deposition centers in vapor phase
 - Particles found on fiber tips
 - Atomic iron particles as homogeneous catalyst
 - Assists in formation of single-shell tubules
- No tubules in absence of argon, iron or methane



Electron Microscopy

- Transmission Electron Microscope (Topcon 002B)
 - 120 kV/200 kV accelerating voltage
- Performed in ultra-high-vacuum (JEM 200FXV)

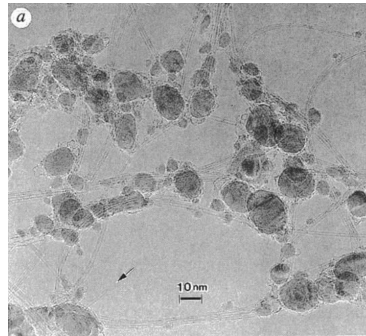


Figure 1a.
Bundles of single-shell carbon nanotubes with cementite particles



Figure 1b.
Individual single-shell nanotubes

Nanotube Diameters

- Figure 1b shows tubules bridging two cementite particle aggregates
- Micrographs recorded at optimum forces
 - Two dark lines of tubules corresponds to side portion of cylinders

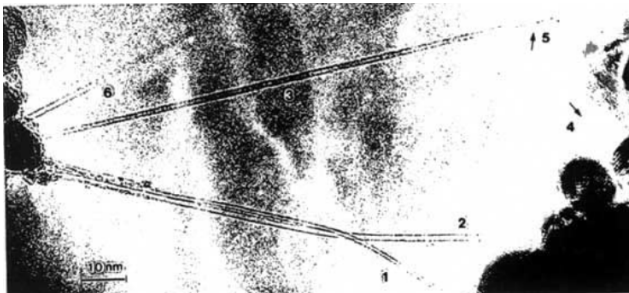


Figure 1b.
Individual single-shell nanotubes

- Thinnest tube (1) with diameter of 0.75nm
 - Attached to thicker, 13nm tube (2)
- Tubules 1,2 curved, tubule 3 (0.92nm) straight across 140 nm opening
- Longest tubule- 700nm long, 0.9nm diameter
- Short, terminated tubules (4, 5)
 - Entangled with cementite particles
- Figure 2- Histogram of diameters of 60 tubules from 0.7nm to 1.6nm
 - Two peaks at 0.8nm and 1.05nm

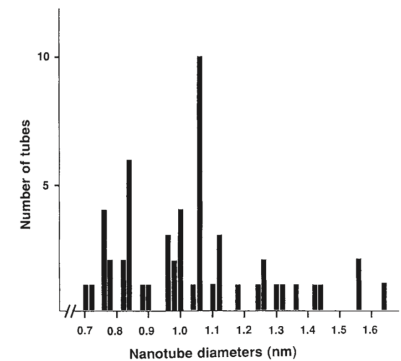


Figure 2
Frequency of single-shell carbon nanotube diameters



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How do we Study the Structure of Carbon nanotubes ?

Electron Micrograph	Electron Diffraction
An image obtained by bombarding the specimen with a finely focused (<10 nm diameter) electron beam with an acceleration voltage under vacuum, and detecting the transmitted, secondary, backscattered and diffracted electrons, and characteristic X-rays emitted.	Electron diffraction is a technique that allows determination of the crystal structure of materials. When the electron beam is projected onto a specimen, its crystal lattice acts as a diffraction grating, scattering the electrons in a predictable manner, and resulting in a diffraction pattern.
Source : Royal Society of Chemistry 2024	Source : Science Direct Electron Diffraction - An Overview

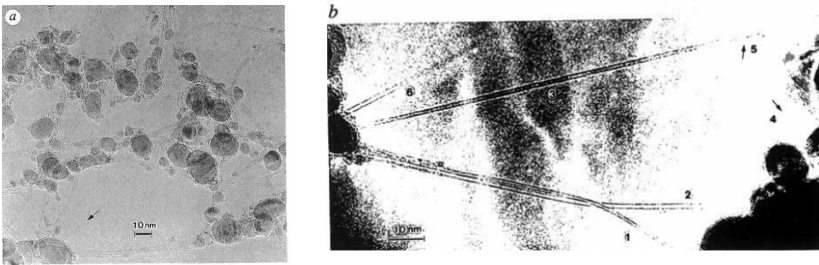


Figure 1 : Electron micrograph showing bundles of single-shell carbon nanotubes which are curved and entangled.

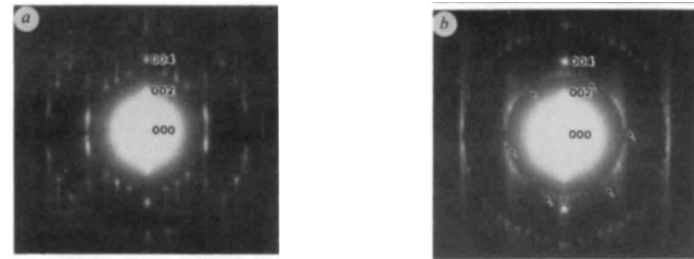


Figure 2 : Electron diffraction patterns from individual microtubules of graphitic carbon.

Source: Iijima, Sumio, and Toshinari Ichihashi. "Single-shell carbon nanotubes of 1-nm diameter." Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan.

Structure of Carbon nanotubes

- Electron Microscopy reveals
 - Coaxial tubes of graphitic sheets
 - Ranging in number from 2 up to about 50
- Diameter of the Needle Ranges from 4 to 30nm and up to 1 micrometre in length
- High Resolution Micrographs of typical Needles Shows that its Seamless and Tubular Structure (Same number of Lattice Fringes from both the sides of the needle)
- The tip of the Needles are usually closed by caps that are curved , polygonal or cone shaped
- The last of these have specific opening angles of about 19 degrees or 40 Degrees

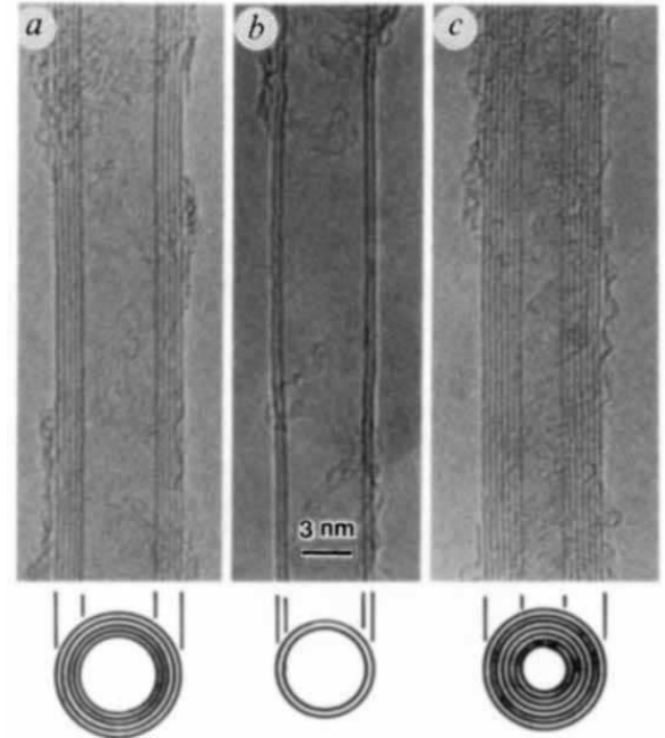


Figure 3 : Electron Micrographs of Microtubules of Graphitic Carbon

Source: Iijima, Sumio, and Toshinari Ichihashi. "Single-shell carbon nanotubes of 1-nm diameter." Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan.

Fraunhofer Diffraction

Fraunhofer diffraction deals with the limiting cases where the source of light and the screen on which the pattern is observed are effectively at infinite distances from the aperture causing the diffraction.

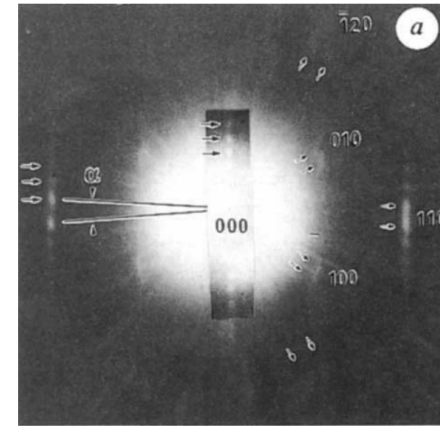
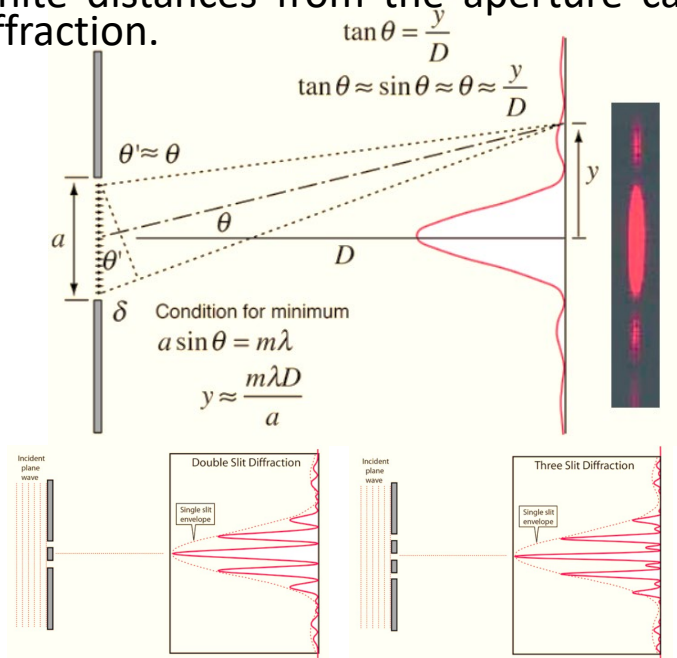


Figure 1 : Electron Diffraction Pattern from a Single Shell Nano Tubule

Fraunhofer Diffraction from the two portion of the tubules Conveys

- Each streaked spot has intensity maxima appearing with a period of 0.73 nm⁻¹.
- The value corresponds to the diameter measured on the tubule (1.37 nm).
- Alpha Measured = 7 Degrees

Source: Iijima, Sumio, and Toshinari Ichihashi. "Single-shell carbon nanotubes of 1-nm diameter." Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan.

Structure Of Carbon Nanotubes

Electron Beam of 20 nm Diameter was focused on to the Single Tubule so that the area comprised about 2000 Carbon Atom

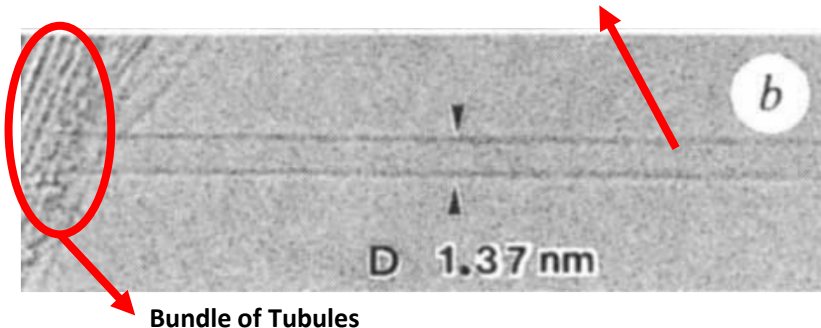
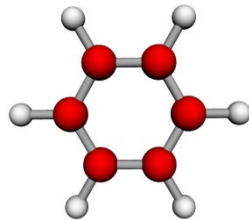


Figure 4 : Electron Micrograph of Single-Shell nanotubule

Reason for the Extremely weak and Diffused Diffraction

- Small Scattering Volume
- Cylindrical Structure

Carbon Atom Hexagons are arranged in Helical Fashion

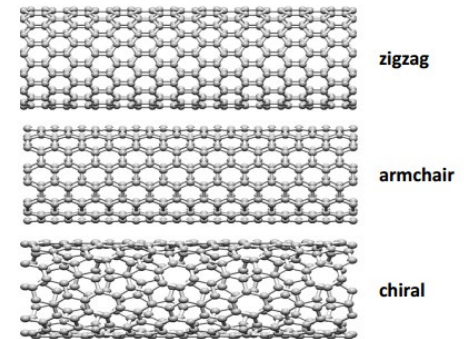


Two hexagonal diffraction pattern Confirms Helicity

There are two hexagonal (hk0) diffraction patterns rotated $\pm a/2$ from perfect alignment along the tube axis, and these patterns show mirror symmetry both along and perpendicular to the tube axis. The mirror symmetry confirms helicity in the single-shell tubule structure

Helical Pitch Varies from Needle to Needle and tube to tube Within Single Needle

Other Arrangements of Carbon Atom Hexagons



Source: Iijima, Sumio, and Toshinari Ichihashi. "Single-shell carbon nanotubes of 1-nm diameter." Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan. Online Open-Source Images

What Makes Each Carbon Nanotubes Unique ?

- Tubule Diameter (D)
- Pitch Angle (Alpha) With Respect to the Fibre Axis
- Helicity

Author's Speculation

- Single Shell Tubules Might be the Embryo for the Multi Shell Tubules
- In the Proposed Model
 - Tubule Ends are Open → Dangling Bonds → Carbon Atoms are Captured**
- In Single Shell Tubes , Author assumes that axial growth dominates over layer growth
- Iron present in the vapour Phase act as a Homogeneous Catalyst

Source: Iijima, Sumio, and Toshinari Ichihashi. "Single-shell carbon nanotubes of 1-nm diameter." Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan.