Chapter 4-1. Design of Nanomaterials based on Vapor Processing

1. Introduction

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- 1.2. Classification of Vapor Processing Techniques

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- 3.1. Process Principle
- 3.2. Advantages & Disadvantages
- 3.3. Atomic Layer Deposition

Reference:
Handbook of nanostructured materials and nanotechnology, volume 1, Chapter 4, Academic press (2000)

1.1. Nanophase Processing Technique

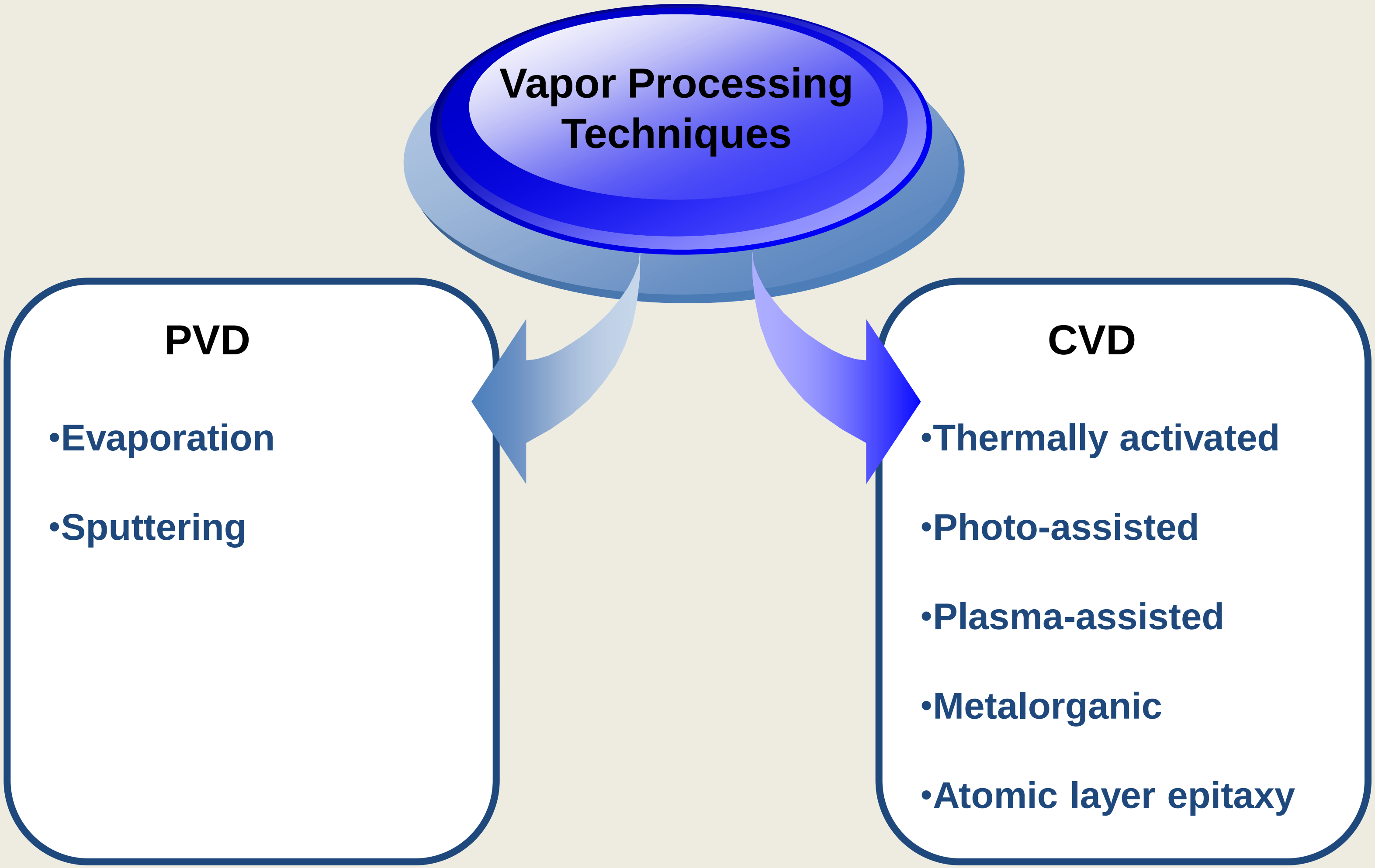
Processing route	Processing methods	Product materials
Solid-liquid	Mechanical milling	Powder
Liquid	Sol-gel Sonochemistry Hydrothermal Electrodeposition Gas atomization Laser beam melting Melt spinning	Powder/film Powder Powder Powder/film Powder Film Continuous ribbon
Vapor	Chemical vapor deposition Physical vapor deposition Aerosol processes Flame-assisted deposition	Powder/film Powder/film Powder/film Powder

1.1. Nanophase Processing Technique

Processing route	Processing methods	Disadvantages
Solid-liquid	Mechanical milling	• Tedious and time consuming process (Mixing, frinding, calcination, sintering, etc) • Prone to contamination from milling media • Suffering from chemical and phase inhomogeneities • Expensive and limited to the processing of ultrafine powder
Liquid	Sol-gel Sonochemistry Hydrothermal Electrodeposition Gas atomization Laser beam melting Melt spinning	• Require a high number of processing steps (Pretreatment, mixing, chemical reactions, filtration, purification, drying, etc) • Tedious ad can cause contamination • Waste treatment is difficult

1. Introduction

1.2. Classification of Vapor Processing Techniques



Vapor Processing Techniques

PVD

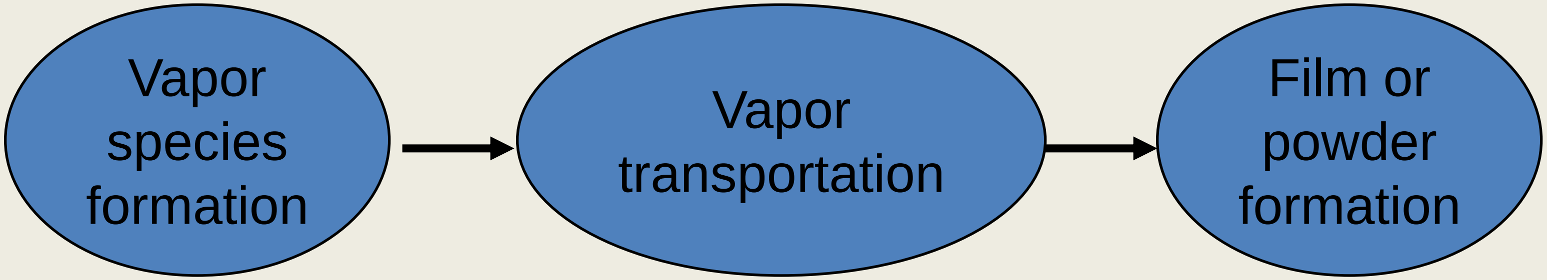
- Evaporation
- Sputtering

CVD

- Thermally activated
- Photo-assisted
- Plasma-assisted
- Metalorganic
- Atomic layer epitaxy

2. Physical Vapor Deposition

2.1. Process Principle



Vapor species formation

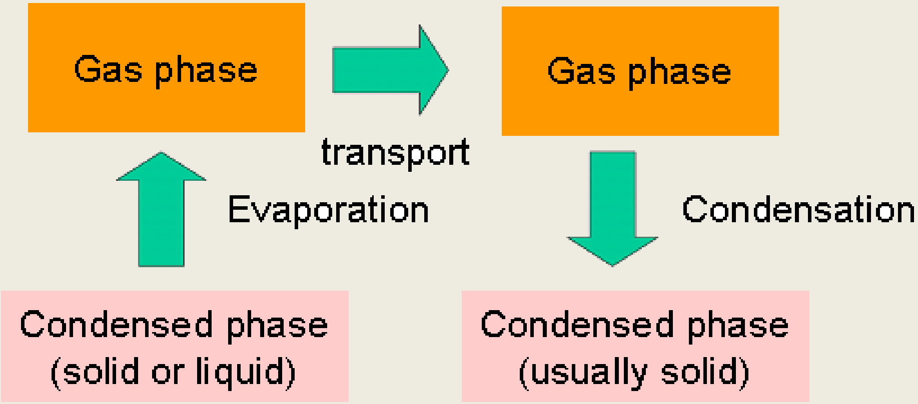
Vapor transportation

Film or powder formation

- evaporation
- sputtering (Ar+)
- ion plating (high v)

- collision
- ionization

- condensation
- nucleation
- growth
- ion bombardment



2.1. Process Principle

Evaporation rates

- Heinrich Hertz equation (empirical eqn.)

*P** is the equilibrium vapor pressure of the evaporant at T.
P is the ambient hydrostatic pressure acting upon the evaporant in the condensed phase.

Experimentally, that the evaporation rate was proportional to (*P** - *P*)
– Also, the evaporation rate could not be increased by supplying more heat unless the equilibrium vapor pressure was also increased by this action.
– maximum evaporation rate when is only achieved in a vacuum, where *P* = 0.

The net evaporation flux is the difference
between the collision rates for the two fluxes

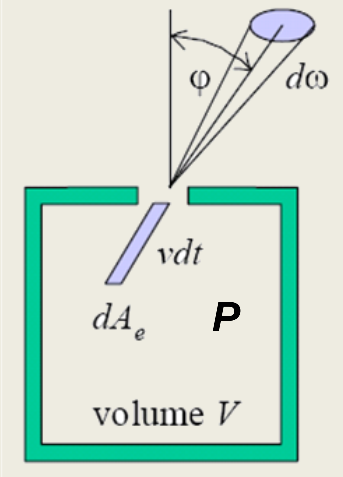
$$\frac{dN_e}{A_e dt} = (2\pi m k_B T)^{-1/2}(P^* - P)$$

2.1. Process Principle

Evaporation rates

- Solid angle $d\omega = \dfrac{dA}{r^2}$, $\text{Max.}\,\omega = \dfrac{4\pi r^2}{r^2} = 4\pi$

➢ Knudsen Cell



The evaporant flux into a solid angle of dw from a source area of dA_e

$$d^4 N_e = N \underline{\frac{v\,dt \cos\varphi\, dA_e}{V}}\, \underline{\frac{d\omega}{4\pi}}\, \Phi(v^2)\, dv$$

Maxwell distribution of velocity

Fraction of molecules within striking distance in time dt

Fraction of molecules entering the solid angle dw is dw/4π

$$\frac{d\omega}{4\pi} = \frac{\text{Target solid angle, dw}}{\text{Maximum solid angle}}$$

After simple mathematical operation,
Total impingement rate is

$$\frac{d^2 N_e}{dA_e\, dt} = (2\pi m k_B T)^{-1/2} P$$

Mass evaporation rate through the orifice and the total mass of evaporated material are,

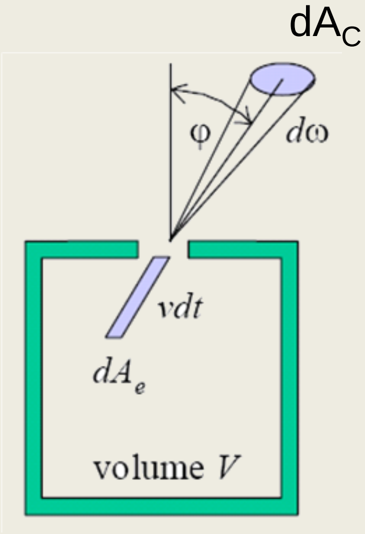
$$\Gamma = m \frac{d^2 N_e}{dA_e dt} = \left(\frac{m}{2\pi\, k_B T} \right)^{1/2} P \qquad M_e = \int_0^t \int_0^{A_e} \Gamma\, dA_e\, dt$$

2. Physical Vapor Deposition

2.1. Process Principle

Condensation

The deposited evaporant mass per unit area of condensation surface is



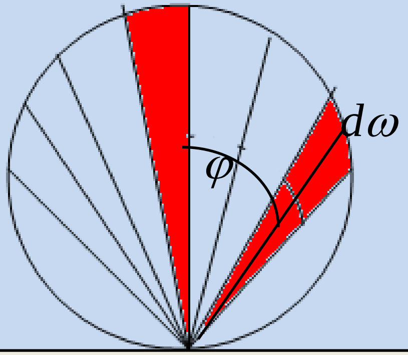
Solid angle, dw, is

$$d\omega = \frac{dA_c \times \cos\psi}{r^2} \quad , \quad dA_c = \frac{r^2 d\omega}{\cos\psi}$$

$$dM_c = M_e \cos\varphi \frac{d\omega}{\pi} \leftarrow \left(\int \cos\varphi d\omega = \int_0^{2\pi} \int_0^{\pi/2} \cos\varphi \sin\varphi \mathrm{d}\varphi \mathrm{d}\phi = \pi \right)$$

By Lambert’s cosine law

$$\rightarrow \frac{dM_c}{dA_c} = \frac{M_e}{\pi r^2} \cos\varphi \cos\psi$$



- Lambert’s cosine law

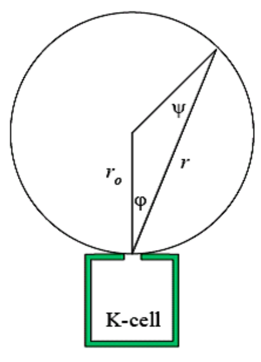
the radiant intensity observed from a "Lambertian" surface is directly proportional to the cosine of the angle

2. Physical Vapor Deposition

2.1. Process Principle

Condensation

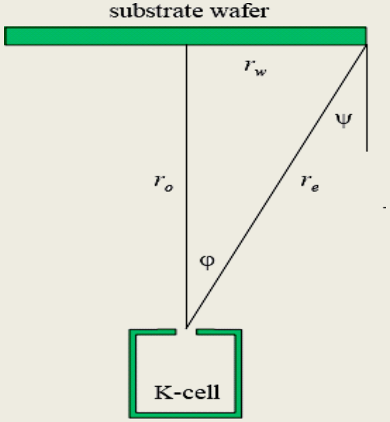
Uniform coating
on sphere



$$\cos\varphi = \cos\psi = \frac{r}{2r_o}, \qquad \frac{dM_c}{dA_c} = \frac{M_e}{4\pi r^2}$$

Uniform coating

Uniformity of an evaporated film across a flat surface



Reduction factor for edge thickness:

$$\frac{d_{edge}}{d_{center}} = \frac{r_0^2}{r_0^2 + r_w^2}\cos\varphi\cos\psi = \left[\frac{r_0^2}{r_0^2 + r_w^2}\right]^2$$

Ex) for a 3-inch diameter wafer suspended 18 inches above a Knudsen cell:
d_{edge}/d_{center} = 0.986, or a non-uniformity of 1.4 %

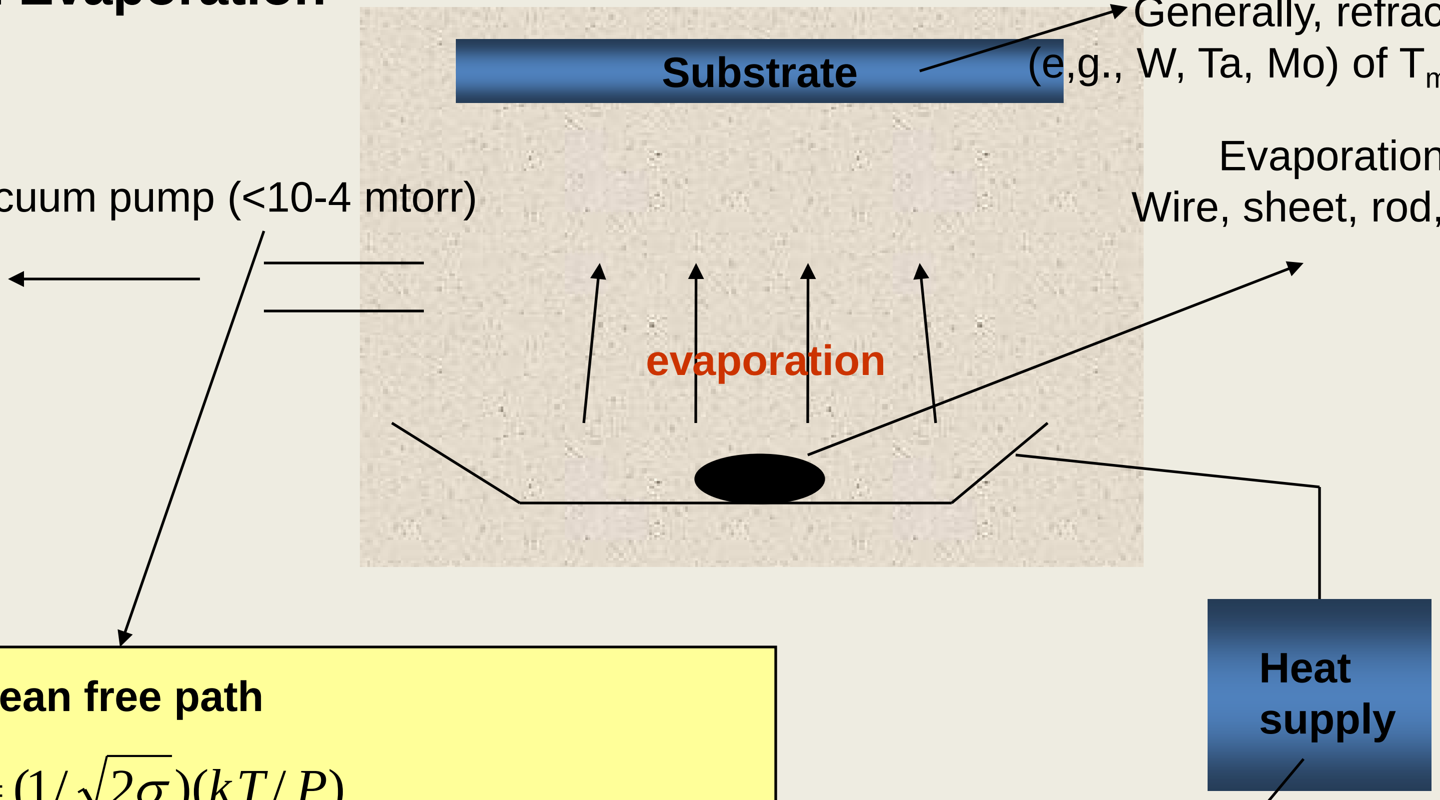
2.2. Advantages & Disadvantages

Advantages	Disadvantages
• ultrapure, fine film or powder can be produced • good structure control by care monitoring of the processing conditions • as-deposited materials are already nanocrystalline in nature and do not require any further work to reduce the particle size or heat treatment to burn out the precursor complexes	• deposition process needs to operate in the low vapor pressure range • the synthesis of multi-component materials is difficult, except for the laser ablation method • Line of sight deposition process, which causes difficulty in producing nanocrystalline films on complex-shaped components, and has poor surface coverage

2. Physical Vapor Deposition

CNDL

2.3. Evaporation



Generally, refractory metal (e,g., W, Ta, Mo) of $T_m > 1539^{o}C = T_{m,\,Fe}$

Vacuum pump (<10-4 mtorr)

Evaporation sources
Wire, sheet, rod, powder form

Mean free path

$$\lambda = (1/\sqrt{2\sigma})(kT/P)$$

$$\{\sigma : \text{the collision cross section of the gas}\}$$

Pressure, Cross section $\downarrow$

Temperature $\uparrow$

$\longrightarrow$ Large λ

- Resistance : Joule heating evaporation
- Induction
- Arc : Cathodic-arc deposition
- E-Beam : E-Beam evaporation
- Laser : laser ablation

2.3. Evaporation

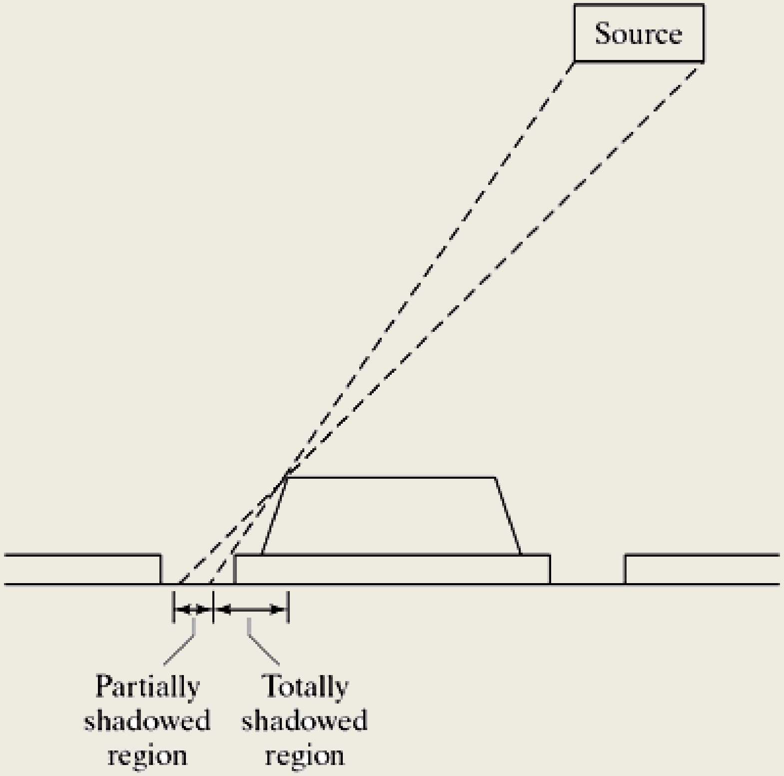
Feature of Evaporation Method

- The material to be vaporized can be in any form and purity
- The residual gases and vapors in the vacuum environment are easily monitored
- The rate of vaporization is high
- The line-of-sight trajectories and point sources allow the use of deposition onto defined areas
- The cost of thermally vaporizing a given quantity of material is much less than that of sputtering the same amount of material

- However, limitations of utilization of material, non-stoichiometric deposits

2.3. Evaporation

Shadowing or step coverage



- Shadowing and Step Coverage Problems Can Occur in Low Pressure Vacuum Deposition in which the Mean Free Path is Large
- When evaporation is performed in poor vacuum or close to atmospheric pressure, the resulting deposition is generally non-uniform and tends not to be a continuous or smooth film. Rather, the deposition will appear fuzzy or cloudy.

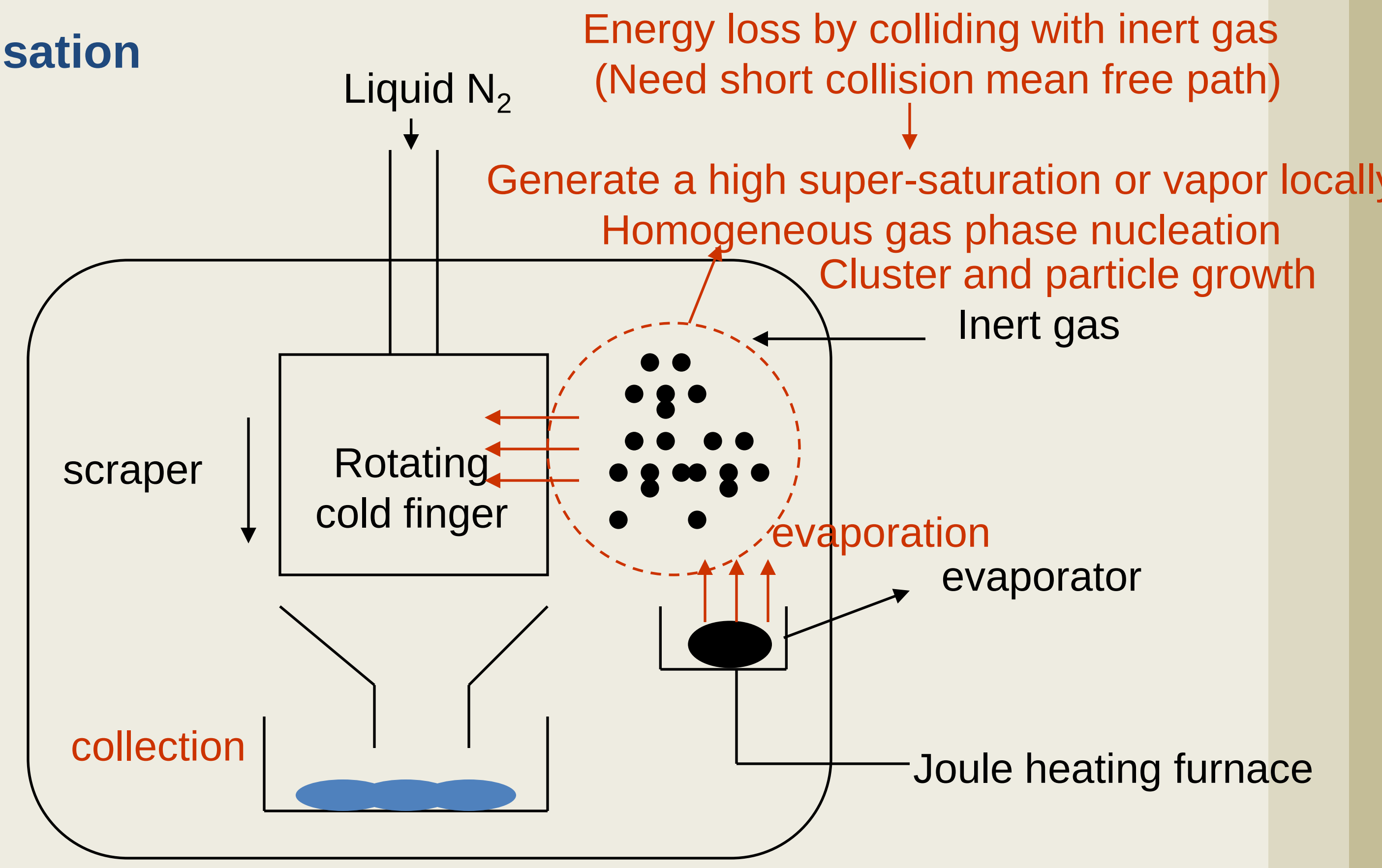
2. Physical Vapor Deposition

2.3. Evaporation

Inert-Gas Condensation

Transportation via natural gas convection

For small particle size, higher evaporation rate is required



Energy loss by colliding with inert gas (Need short collision mean free path)

Generate a high super-saturation or vapor locall

Homogeneous gas phase nucleation

Cluster and particle growth

Liquid N_2

Inert gas

scraper

Rotating cold finger

evaporation

evaporator

collection

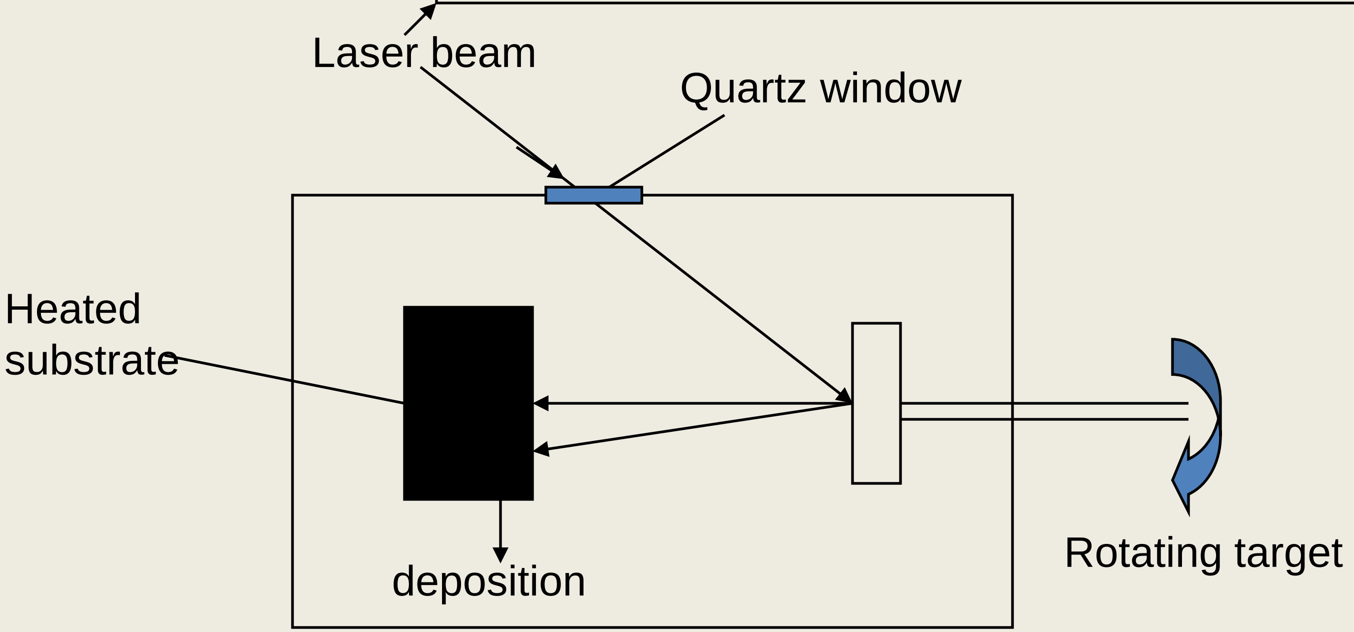
Joule heating furnace

2. Physical Vapor Deposition

2.3. Evaporation

Laser Ablation

Excimer : mostly used 193nm(ArF), small pulse width(6-12ns)
Nd:YAG laser, ruby laser, CO_2 laser



- Producing multi-component materials
  with well-controlled stoichiometry by accurate transfer of the target composition to the coating
- High production cost

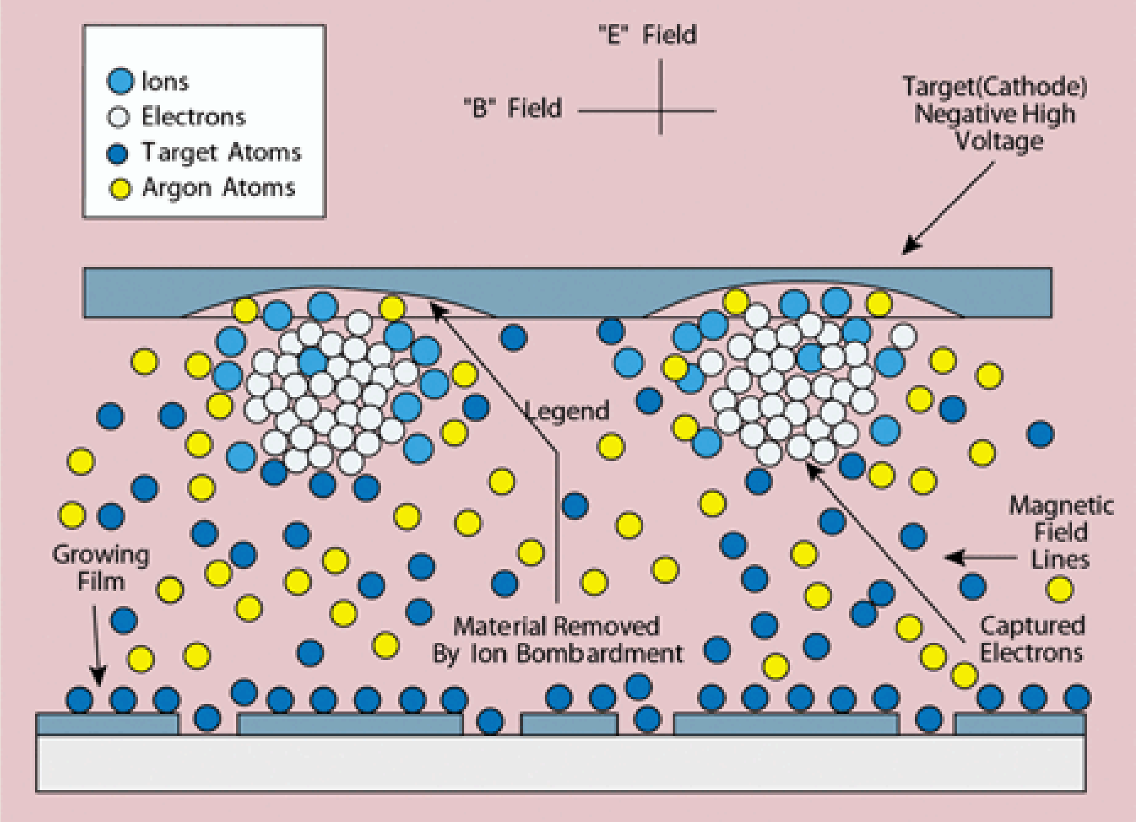
2.4. Sputtering

- Sputtering is a term used to describe the mechanism in which atoms are ejected from the surface of a material when that surface is struck by sufficiency energetic particles.
- Alternative to evaporation.
- First discovered in 1852, and developed as a thin film deposition technique by Langmuir in 1920.
- Metallic films: Al-alloys, Ti, TiW, TiN, Tantalum, Nickel, Cobalt, Gold, etc.

Advantages

- Use large-area-targets which gives uniform thickness over the wafer.
- Control the thickness by Dep. time and other parameters.
- Control film properties such as step coverage (negative bias), grain structure (wafer temp), etc.
- Sputter-cleaned the surface in vacuum prior to deposition.

2.4. Sputtering



Ref. www.vacgen.com/catalogue/section-16/intro.htm

Glow discharge to produce energetic particles (ions)

↓

Momentum transfer from an indirect energetic projectile to a solid or molten target,

↓

resulting in the ejection of surface atoms or molecules to produce the sputtered species

2.4. Sputtering

Application of Sputtering

- Thin film deposition:
  - Microelectronics
  - Decorative coating
  - Protective coating

- Etching of targets:
  - Microelectronics patterning
  - Depth profiling microanalysis

- Surface treatment:
  - Hardening
  - Corrosion treatment

2.4. Sputtering

Parameters influencing to sputtering yield

- The ejected atoms have much more energy and velocity than atoms that have been thermally evaporated

- Sputtering yield , **S**
  - The number of atoms ejected per incident particle (ion)

•Energy of the incident particle
- threshold exists
- E↑→S↑

•Target temperature, T
- insensitive at below 600°C

Momentum transfer

$$W = \frac{kV}{P_T d}$$

•Mass of incident particle, M
- M↑→S↑ : more collisions will occur

•Angle of incidence,
angle↑→S↑

$$S \propto \frac{1}{\cos\theta}$$

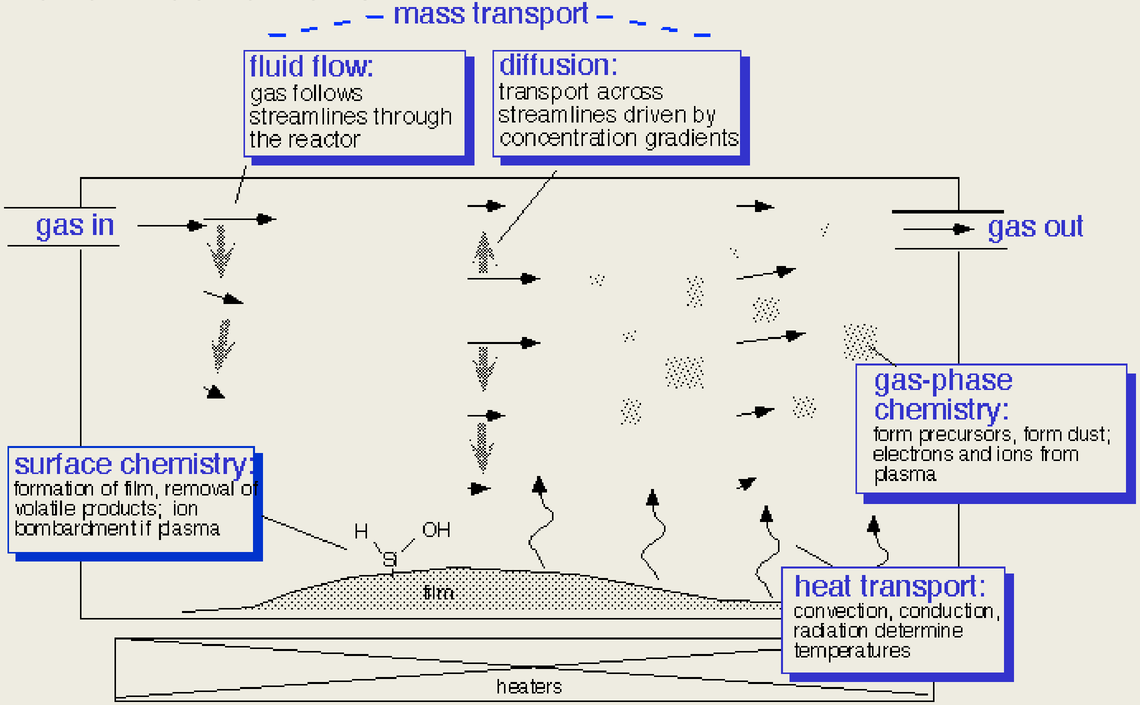
V: working voltage
i :discharge current
d: anode-cathode distance
P_T: gas pressure
k :proportionality constant

•Heat of vaporization, H, of target materials
- H↓ →S↑

•Target crystallinity
- densely packed crystallographic place →S↑

3. Chemical Vapor Deposition

- CVD is a more complex method than PVD
- Involves mass transport, heat transfer, and chemical reactions under non-equilibrium conditions



mass transport

fluid flow: gas follows streamlines through the reactor

diffusion: transport across streamlines driven by concentration gradients

gas-phase chemistry: form precursors, form dust; electrons and ions from plasma

surface chemistry: formation of film, removal of volatile products; ion bombardment if plasma

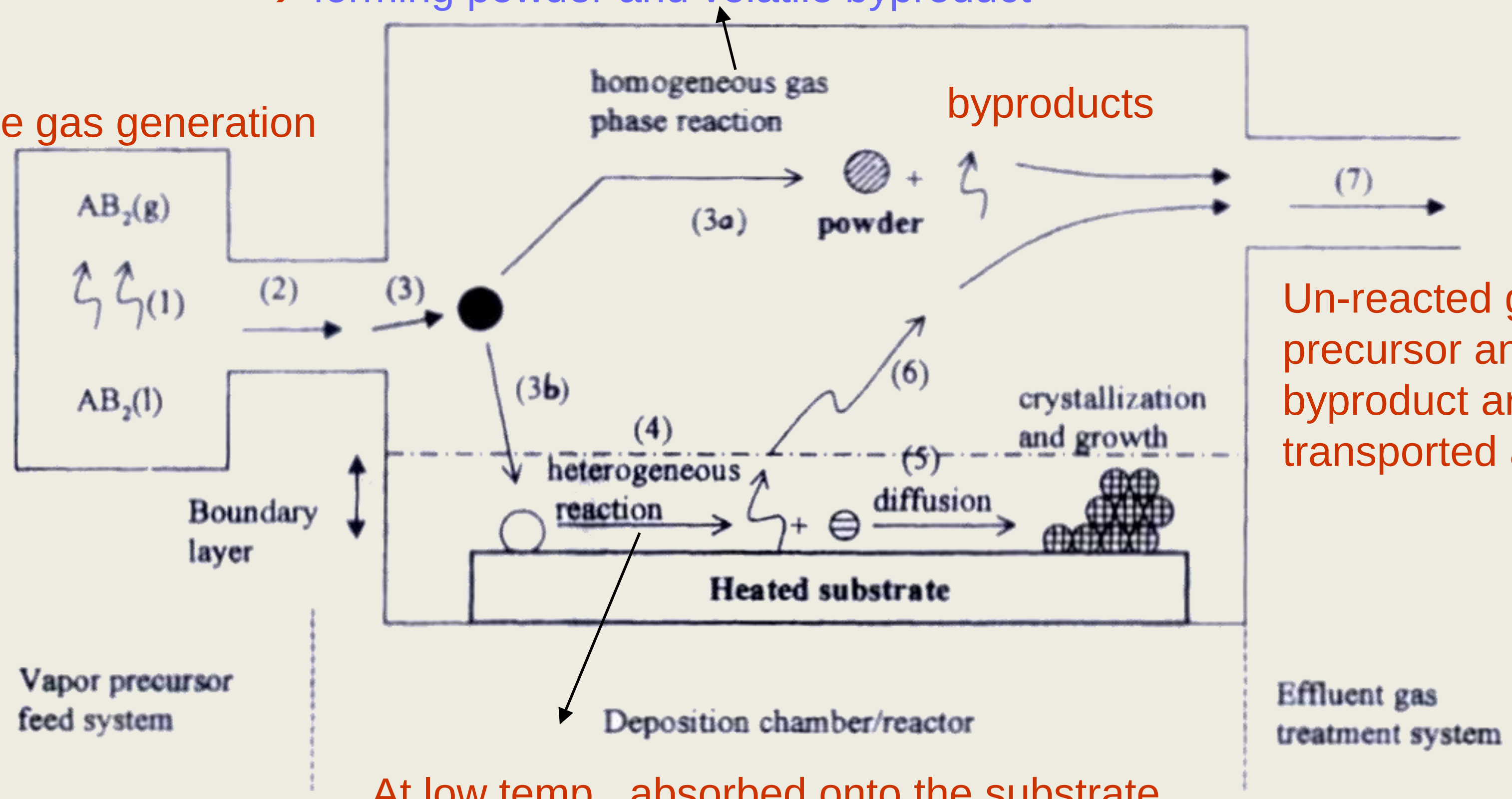
heat transport: convection, conduction, radiation determine temperatures

•However, the process modeling or simulation is mostly based on thermodynamic database, thermo-chemical equilibrium modeling and transport phenomena modeling, which assumed the CVD system is in equilibrium

3. Chemical Vapor Deposition

3.1. Process Principle

At high temp., decomposition and homogeneous gas phase reaction intermediate species → decomposition and/or chemical reaction→ → forming powder and volatile byproduct



Active gas generation

byproducts

Un-reacted gas precursor and byproduct are transported away

At low temp., absorbed onto the substrate, heterogeneous reactions occur at the gas-solid interface
→ forming thin layer (films) and byproduct

3. Chemical Vapor Deposition

3.1. Process Principle

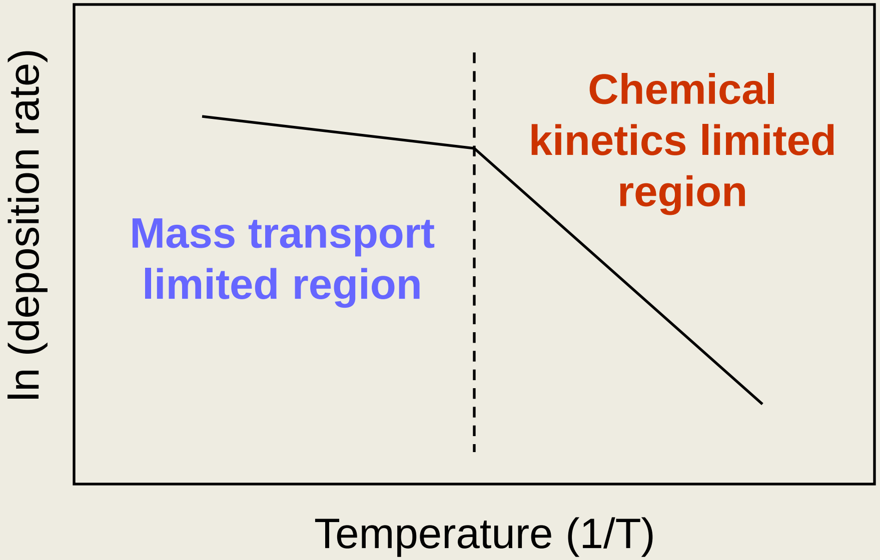
The effect of the temperature on the deposition rate

- Main CVD parameters : T, P, input gas ratio, and flow rate [temp. is the dominant parameter]

Mass transport limited region

-depend on the rate of diffusion of active gases due to enough high temperature

- so, efficient at low pressure condition



Chemical kinetics limited region

-depend on temperature

- The deposition increases rapidly in the chemical kinetics limited regions as temperature increase

Temp ↑

- **thermally activated reactions ↑**

↓

- growth rate ↑
- surface mobility of atomic species ↑
- surface diffusion ↑

3. Chemical Vapor Deposition

CNDL

3.1. Process Principle

Thermodynamic aspects I

$A + B = C_{solid} + D$

Where A and B are supplied gas, C is solid product (deposition)
Gas D diffuses away from the substrate during process

Molar Gibbs free energy change is $\Delta G_m = G_m^f - G_m^i$ $\quad \left(G_m = \sum X_n \mu_n\right)$

i is initial state

f is final equilibrium state

$$G_m^i = X_A^i \mu_A^i + X_B^i \mu_B^i, \quad G_m^i = X_A^f \mu_A^f + X_B^f \mu_B^f + X_C^f \mu_C^f + X_D^f \mu_D^f$$

$$\left(\mu_j = \mu_j^0 + RT \ln P_j\right)$$

As CVD reaction is proceed → P_C, P_D is increased → ΔG_m is increased → reaching equilibrium
P_A, P_B is decreased

Driving Force for Deposition in the CVD Process, Journal of Materials Science Letters, 13, 1437-1439 (1994)

3.1. Process Principle

Thermodynamic aspects I

A + B = C_{solid} + D

Where A and B are supplied gas, C is solid product (deposition)
Gas D diffuses away from the substrate during process

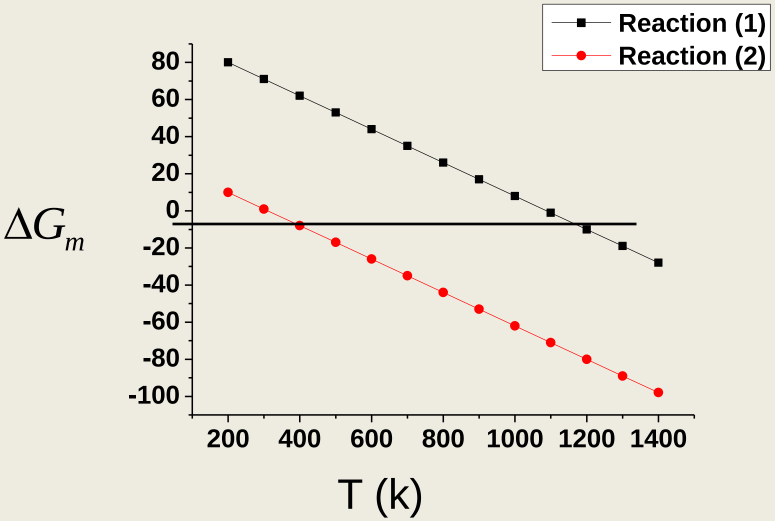
Molar Gibbs free energy change is $\Delta G_m = G_m^f - G_m^i$ $\left(G_m = \sum X_n \mu_n\right)$

i is initial state

f is final equilibrium state

Example

(1) $TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl$
(2) $TiCl_4 + B_2H_6 \rightarrow TiB_2 + 4HCl + H_2$



3. Chemical Vapor Deposition

3.1. Process Principle

Thermodynamic aspects II

A + B = C_{solid} + D

Where A and B are supplied gas, C is solid product (deposition)
Gas D diffuses away from the substrate during process

- In a point of view of product (C_{solid}) during CVD process,

Partial pressure of C in the gas phase

Equilibrium vapor pressure of solid C

Chemical potential of solid product

$$\mu_{C_{solid}} = \mu_C^0 + RT \ln P_C^{\mathrm{v.p}}, \qquad \mu_{C_{gas}} = \mu_C^0 + RT \ln P_C^{\mathrm{gas}}$$

Chemical potential of gaseous state

$$\Delta\mu_C = -RT \ln \frac{P_C^{\mathrm{gas}}}{P_C^{\mathrm{v.p}}}, \qquad \alpha = \frac{P_C^{\mathrm{gas}}}{P_C^{\mathrm{v.p}}}$$

saturation ratio

In order for deposition to be possible, $P_C^{\mathrm{gas}} > P_C^{\mathrm{v.p}}$
So, the gas phase reaction on the growing surface is sufficiently fast → CVD is proceeded

Driving Force for Deposition in the CVD Process, Journal of Materials Science Letters, 13, 1437-1439 (1994)

3. Chemical Vapor Deposition

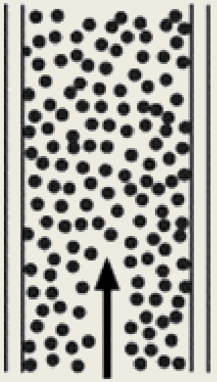
3.1. Process Principle

Efficient contact between the gas phase and the growing surface

- The simplest ones are **fixed bed and flat hearth**, whose particles do not move relative to each other

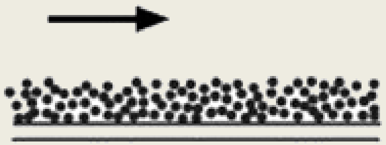
- If the gas flow rate is sufficiently low, the gas merely percolates through the void species between the stationary particles

- Often used for CVD processes devoted mainly to catalyst preparation and CNT synthesis



Fixed bed

Gas flows over powders



Flat hearth

Gas flows through powders

In both cases, particles do not move relative to each other

Principles and applications of CVD powder technology, Vahlas et al, Materials Science and Engineering R 53 (2006) 1–72

3. Chemical Vapor Deposition

3.1. Process Principle

Efficient contact between the gas phase and the growing surface

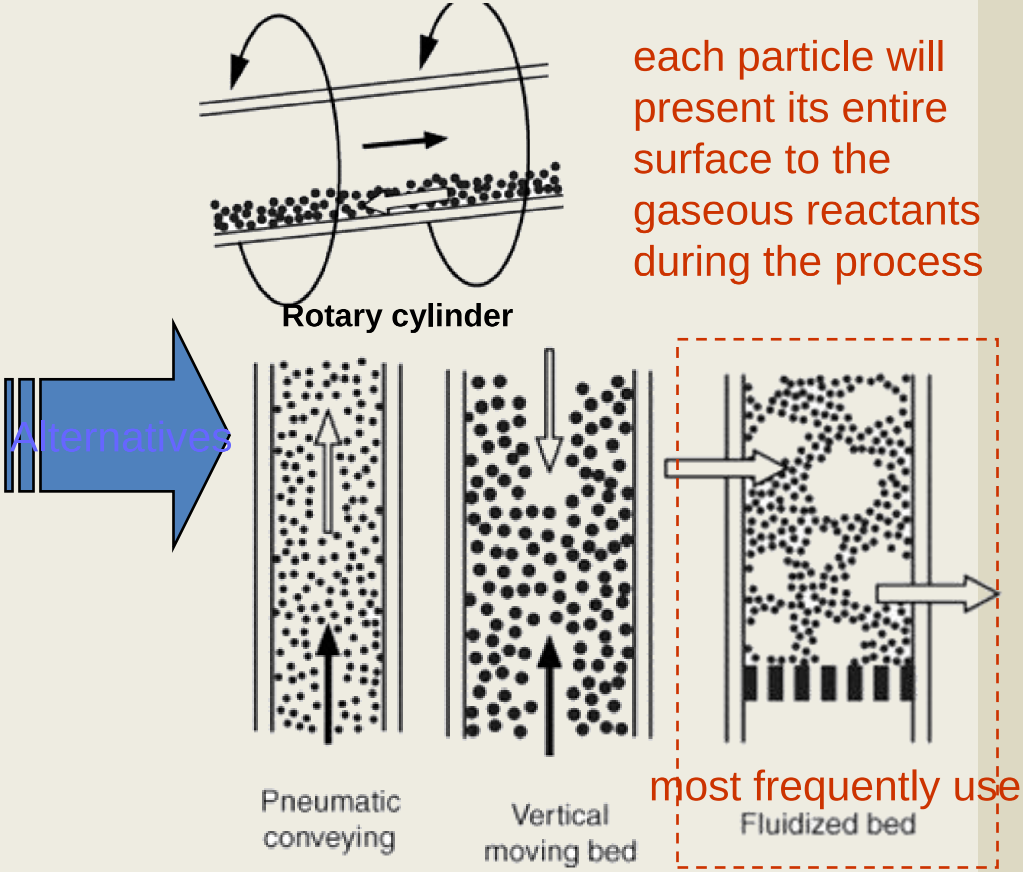
drawbacks of simple fixed bed and flat hearth

(i) - diffusion limitations in the case of chemical vapor infiltration
- inefficient contact between the gas reactants and the inner particles;

(ii) impossible to perform deposition on the entire surface of each particle due to contact points among them and with the reactor walls

(iii) when high growth rates and/or high thickness is aimed, clogging phenomena can occur;

(iv) due to all above drawbacks, the scale-up of these processes is problematic.



each particle will present its entire surface to the gaseous reactants during the process

most frequently used

Principles and applications of CVD powder technology, Vahlas et al, Materials Science and Engineering R 53 (2006) 1–72

3.2. Advantages & Disadvantages

Advantages	Disadvantages
• Capability of producing highly dense and pure materials • Non line-of-sight process. Can be used to coat complex-shaped components uniformly	• Include the chemical and safety hazards • Toxic, corrosive, flammable, and/or explosive precursor gases • Difficult to deposit multi-component materials with well-controlled stoichiometry because different precursors have different vaporization rates

3.3. Atomic Layer Deposition

Definition of ALD

- ALD is a method of applying thin films to various substrates with atomic scale precision.
- Similar in chemistry to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separated during the reaction.
- ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible.
- By keeping the precursors separated throughout the coating process, atomic layer thickness control of film grown can be obtained as fine as atomic/molecular scale per monolayer.
- Introduced in 1974 by Dr. Tuomo Suntola and co-workers in Finland to improve the quality of ZnS films used in electroluminescent displays.
- Recently, it turned out that ALD also produces outstanding dielectric layers and attracts semiconductor industries for making High-K dielectric materials.

Ref: "Atomic Layer Deposition," Wikipedia: The Free Encyclopedia, Wikimedia Foundation, 24 April 06.

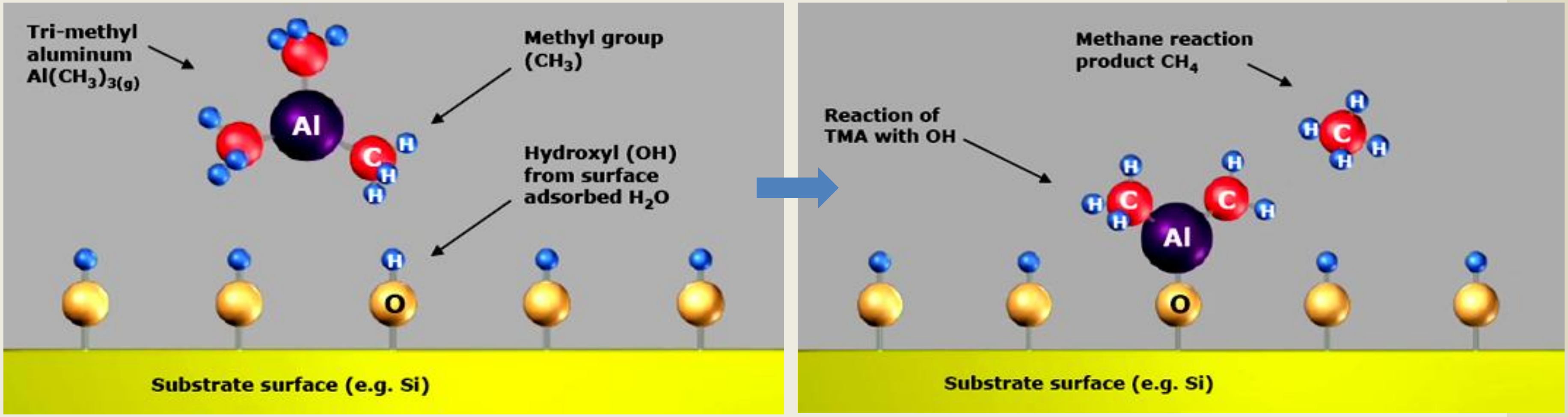
3.3. Atomic Layer Deposition

Definition of ALD

- Releases sequential precursor gas pulses to deposit a film one layer at a time on the substrate.
- The precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. A second precursor of gas is then introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface.
  Two fundamental mechanisms:
  - *Chemisorption saturation process*
  - *Sequential surface chemical reaction process*
- Example: ALD cycle for Al_2O_3 deposition
- Since each pair of gas pulses (one cycle) produces exactly one monolayer of film, the thickness of the resulting film may be precisely controlled by the number of deposition cycles.

3.3. Atomic Layer Deposition

Example: ALD cycle for Al_2O_3 deposition



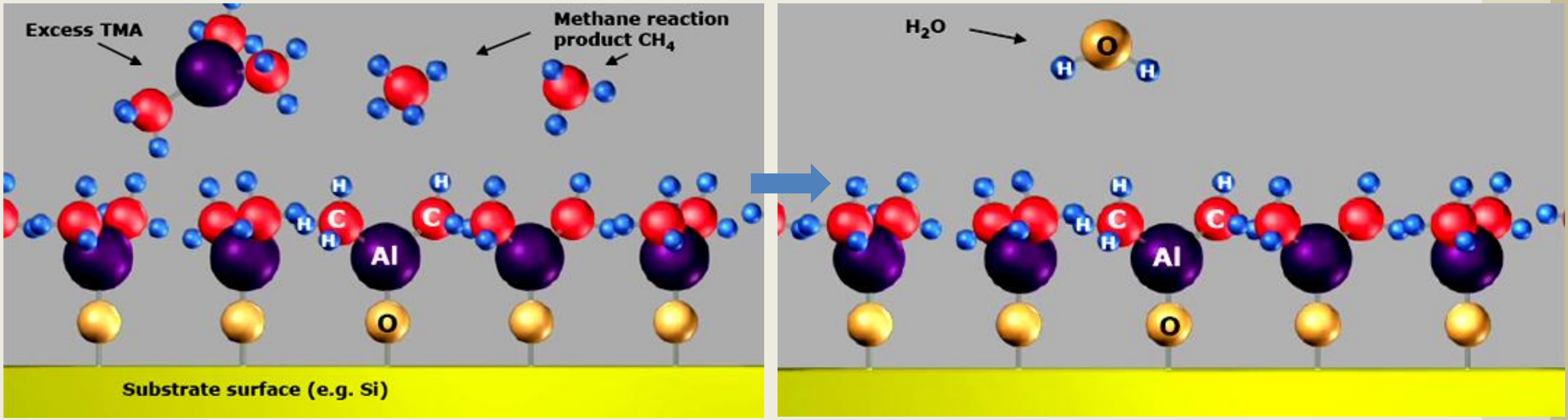
Trimethyl Aluminum (TMA) reacts with the adsorbed -OH groups, Producing methane

$Al(CH_3)_{3\ (g)} + :Si\text{-}O\text{-}H_{\ (s)} \rightarrow :Si\text{-}O\text{-}Al(CH_3)_{2\ (s)} + CH_4$

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

3.3. Atomic Layer Deposition

Example: ALD cycle for Al_2O_3 deposition



Trimethyl Aluminum (TMA) reacts with the adsorbed -OH groups, TMA does not react with itself, terminating the reaction to one later. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.

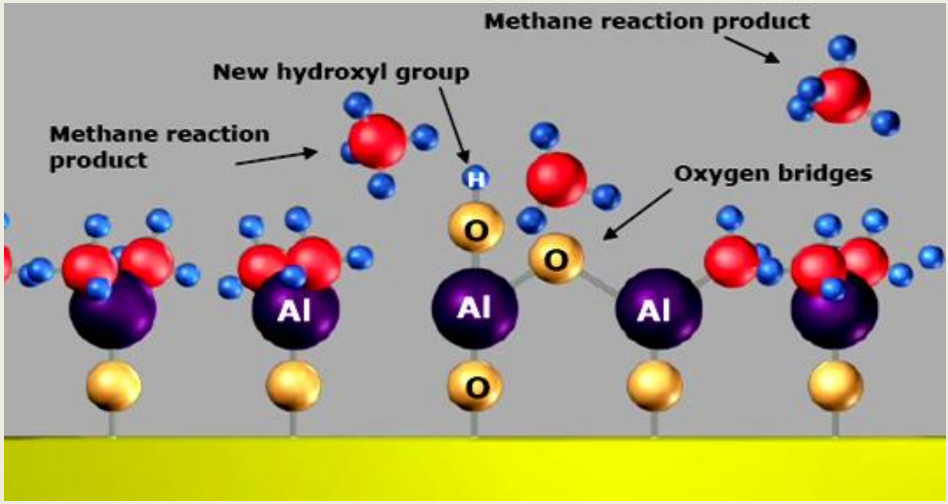
After the TMA and methane reaction product is pumped away, water vapor (H_2O) is pulsed into the reaction chamber.

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

3. Chemical Vapor Deposition

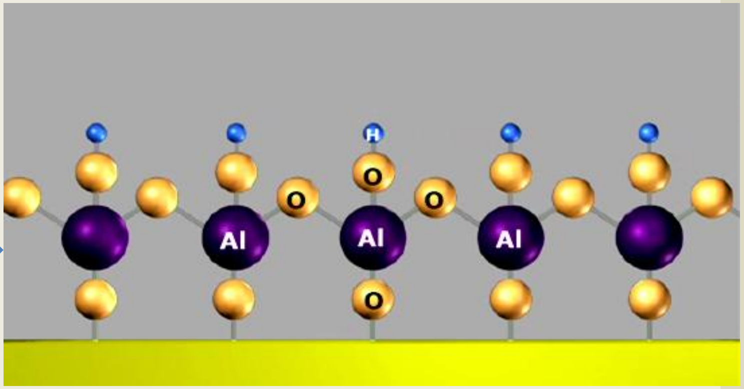
3.3. Atomic Layer Deposition

Example: ALD cycle for Al_2O_3 deposition

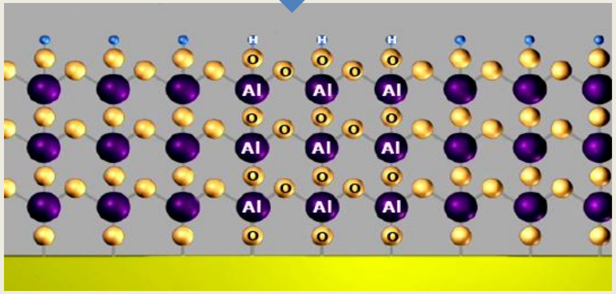


H_2O reacts with the dangling methyl groups on the new surface forming aluminum oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again methane is the reaction product

$2H_2O_{(g)} + :Si\text{-}O\text{-}Al(CH_3)_{2\,(s)} \rightarrow :Si\text{-}O\text{-}Al(OH)_{2\,(s)} + 2CH_4$



The reaction product methane is pumped away, Excess H_2O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer

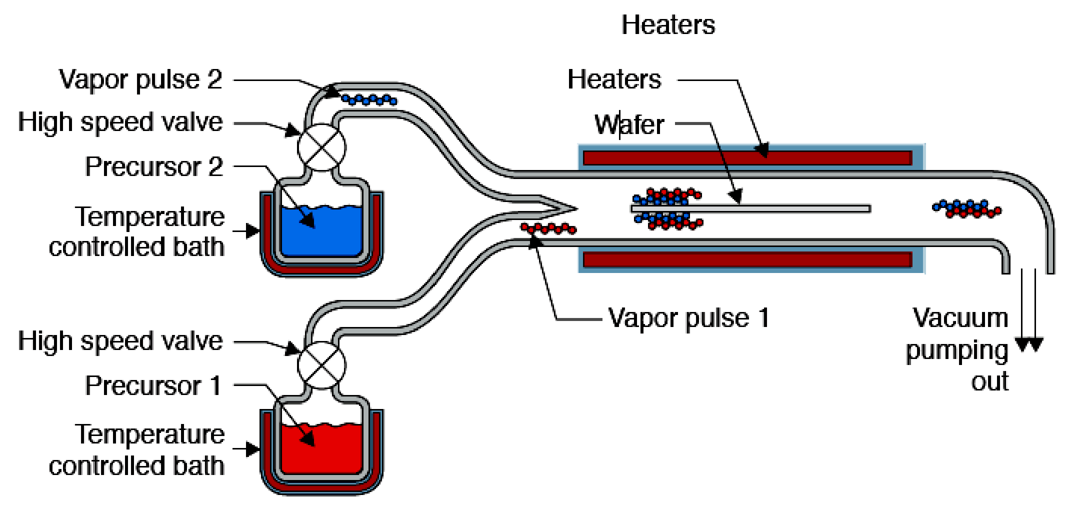


Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

3.3. Atomic Layer Deposition

ALD reactors

- **Closed system chambers** (most common)
  - The reaction chamber walls are designed to effect the transport of the precursors.



Schematic of a closed ALD system

Ref: "Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC, 24 April 06.

Chapter 4-2. Carbon Nanotubes

1. **Introduction**
    - 1.1. Carbon allotropes
    - 1.2. What are CNTs?
    - 1.3. Discovery of CNT: misunderstanding and truth
    - 1.4. Classification of CNT
2. **Structures of CNTs**

3. **Properties of CNTs**
    - 3.1. Electronic properties of CNTs
    - 3.2. Mechanical properties of CNTs
    - 3.3. Magnetic properties of CNTs

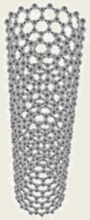
Chapter 4-2. Carbon Nanotubes

CNDL

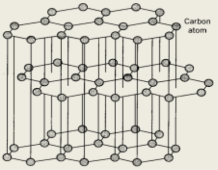
1.1. Carbon allotropes

Nobel Prize
2000

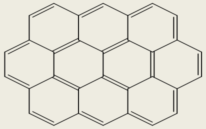
Carbon nanotube



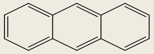
Graphite



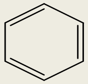
Graphene

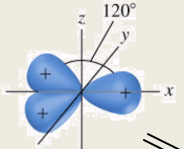


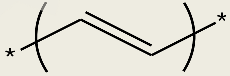
Anthracene



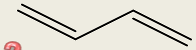
Benzene



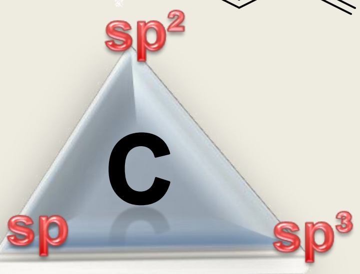


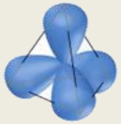


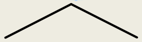
Polyacetylene



1,3-Butadiene

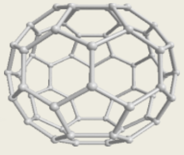




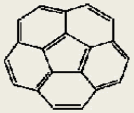


Propane

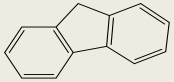
Nobel Prize
1996



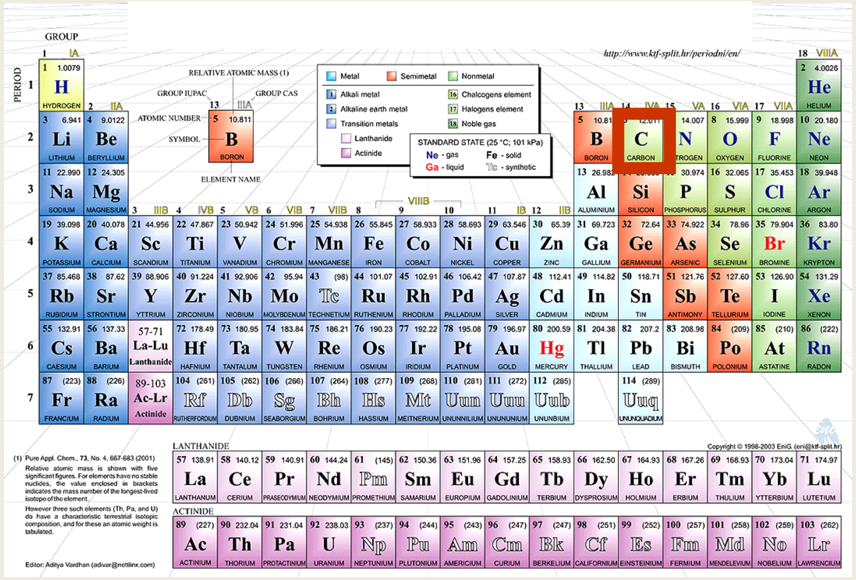
Fullerene



Corannulene



Fluorene



GROUP

RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
13 IIIA
5 10.811
B
BORON

▨ Metal	▨ Semimetal	▨ Nonmetal
1 Alkali metal		16 Chalcogens element
2 Alkaline earth metal		17 Halogens element
Transition metals		18 Noble gas
Lanthanide		
Actinide		

STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic

http://www.ktf-split.hr/periodni/en/

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.81 B BORON	6 12.011 C CARBON	14.007 N TROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	Si SILICON	30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

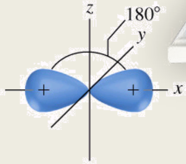
57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., **73**, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

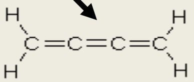
Editor: Aditya Vardhan (adivar@netlinx.com)



Butadiyne

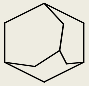
$H-C\equiv C-C\equiv C-C\equiv C-H$

Polyyne

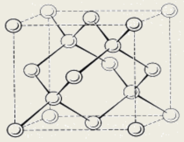


Cumulene

Carbyne



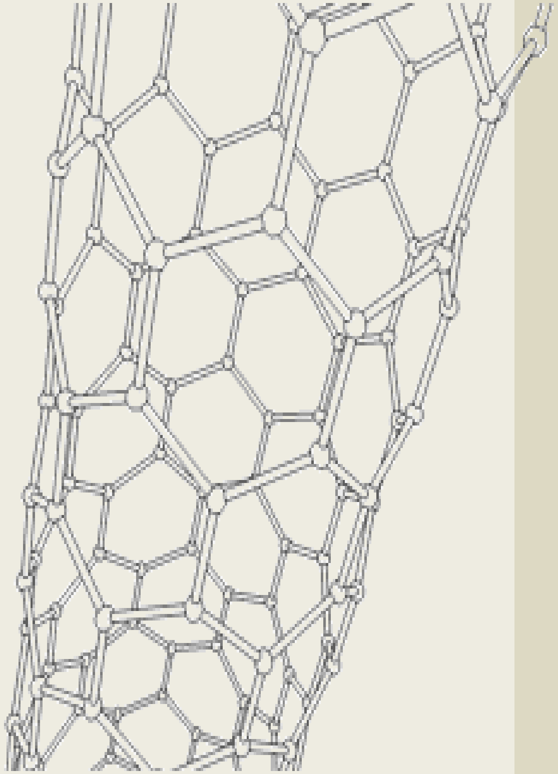
Adamantane



diamond

1.2. What are CNTs?

- Carbon nanotube (CNT) is a new form of carbon, configurationally equivalent to two dimensional graphene sheet rolled into a tube.
- Molecular-scale tubes of graphitic carbon with outstanding properties
- They are among the stiffest and strongest fibers known, and have remarkable electronic properties and many other unique characteristics.
- For these reasons they have attracted huge academic and industrial interest, with thousands of papers on nanotubes being published every year.
- Commercial applications have been rather slow to develop, however, primarily because of the high production costs of the best quality nanotubes.

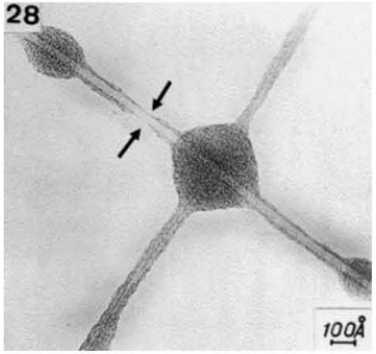


1.3. Discovery of CNT: misunderstanding and truth

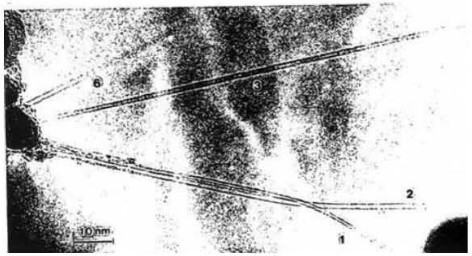
Single-Walled Carbon Nanotubes (SWCNTs)의 발견

1976년 일본의 Endo 그룹에 의해 최초로 발견. Ref: M. Endo *et al*, *J Cryst Growth* **32** (1976) 335–349.

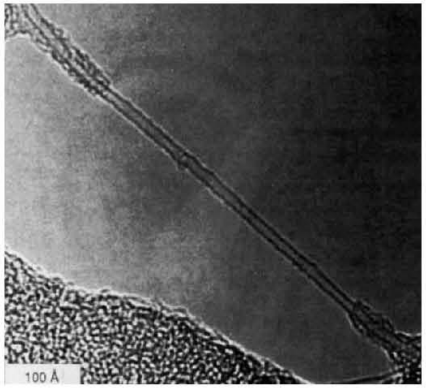
1993년 2편이 동시에 발표 (nature 지 6월 17번째 이슈). Submitting 날짜 : 일본 NEC연구소의 Iijima group (4월 23일), 미국 IBM 연구소의 Bethune group (5월 24일) Ref: S. Iijima *et al.*, *Nature* **363** (1993) 603–605. , D.S. Bethune *et al.*, *Nature* **363** (1993) 605–607.



J Cryst Growth **32** (1976) 335–349



Nature **363** (1993) 603–605



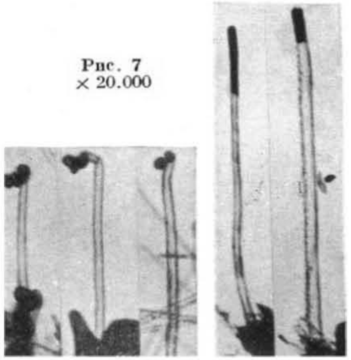
Nature **363** (1993) 605-607

Multi-Walled Carbon Nanotubes (MWCNTs)의 발견

1952년 러시아의 Radushkevich 그룹에 의해 MWCNTs와 흡사한 carbon filament가 발견됨. Ref: L.V. Radushkevich et al., *Zurn Fisic Chim* **26** (1952) 88–95.

1973년 독일의 Boehm과 영국의 Baker 그룹에 의해 여러가지 금속촉매를 이용한 carbon filament 제조에 관한 논문이 발표 되었음. Ref: H.P. Boehm, *Carbon* **11** (1973), pp. 583–590., R.T.K. Baker *et al.*, *J Catal* **30** (1973) 86–95.

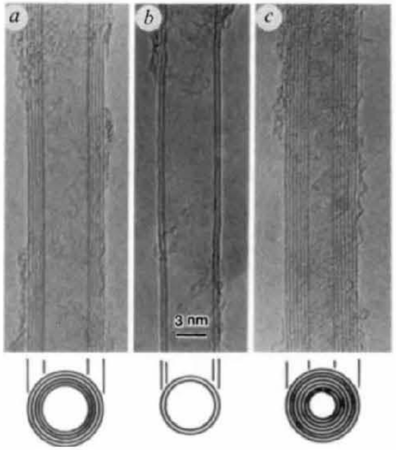
1991년 일본의 Iijima에 의해 MWCNTs에 대한 논문 발표됨. Ref: S. Iijima, *Nature* **354** (1991) 56–58.



Zurn Fisic Chim **26** (1952) 88–95.

J Catal **30** (1973) 86–95.

Carbon **11** (1973) 583–590.

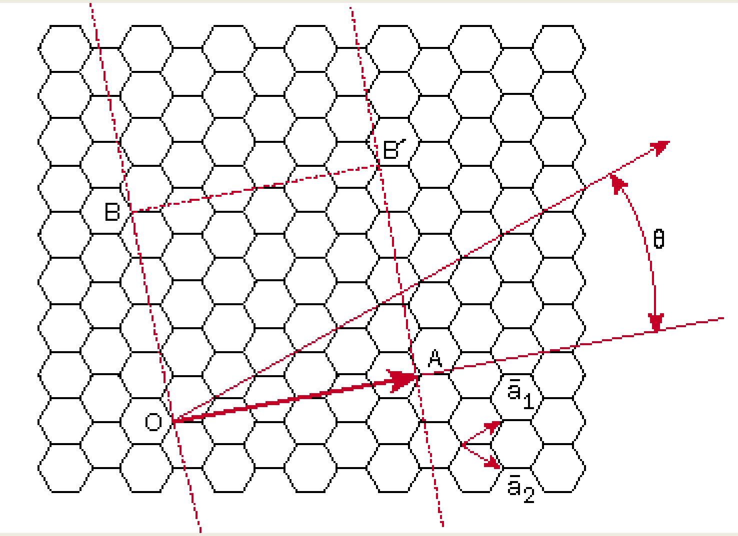


Nature **354** (1991) 56–58.

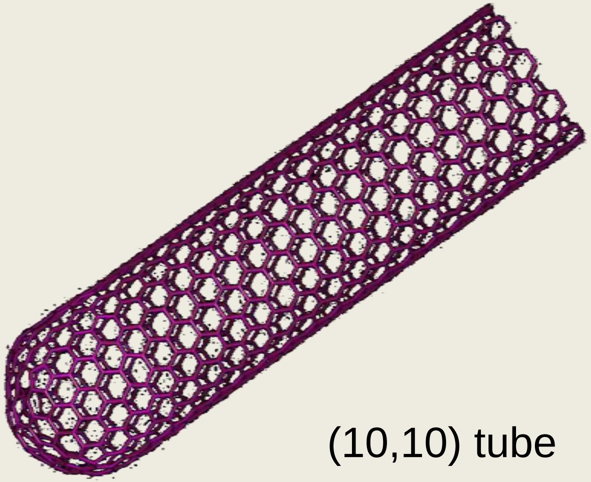
1. Introduction

1.4. Classification of CNT

- Single-wall Carbon nanotubes (SWCNTs)
  - one graphite sheet seamlessly wrapped-up to form a cylinder
  - typical radius 1nm, length up to mm



(From Dresselhaus et al., Physics World 1998)

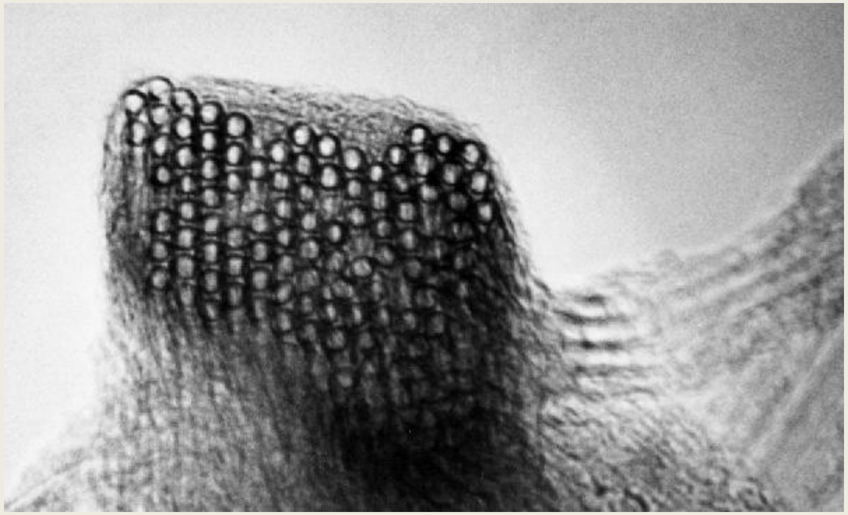


(10,10) tube

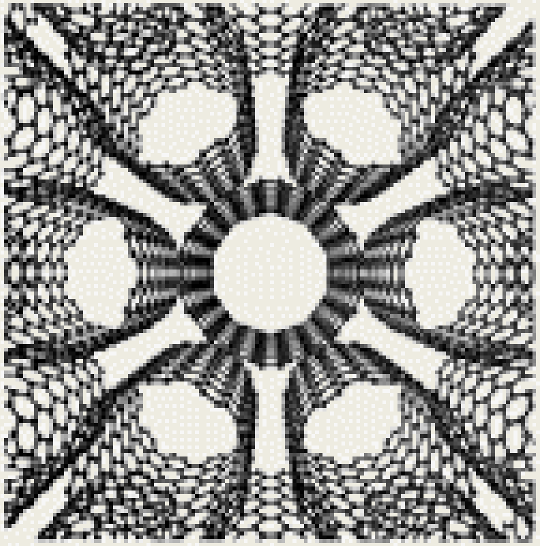
(From R. Smalley´s web image gallery)

1.4. Classification of CNT

- Ropes: bundles of SWNTs
  - triangular array of individual SWNTs
  - ten to several hundreds tubes
  - typically, in a rope tubes of different diameters and chiralities



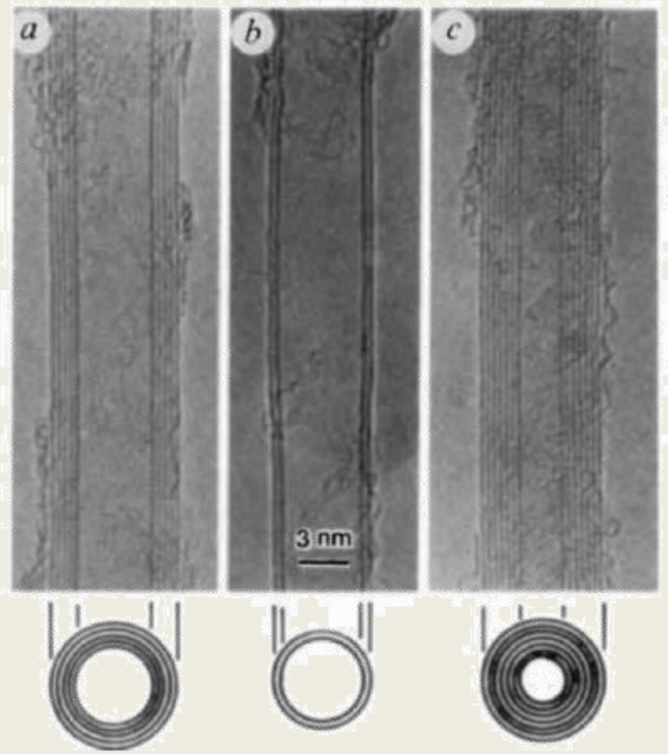
(From R. Smalley´s web image gallery)



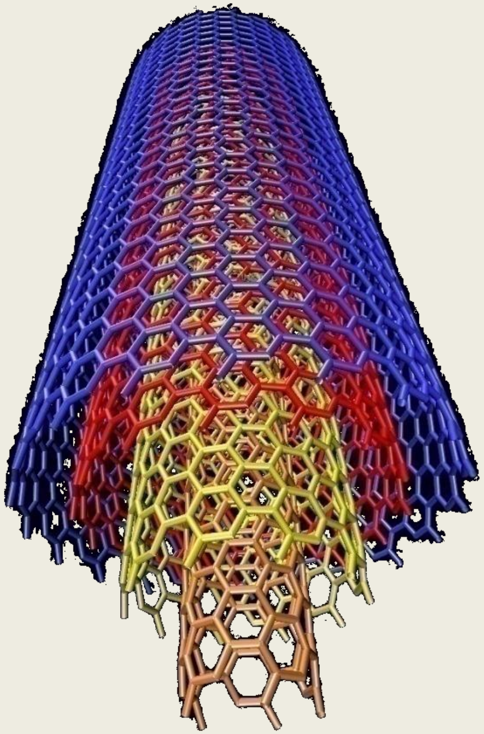
(From Delaney et al., Science 1998)

1.4. Classification of CNT

- Multiwall nanotubes (MWCNTs)
  - russian doll structure, several inner shells
  - typical radius of outermost shell > 10 nm



(From Iijima, Nature 1991)

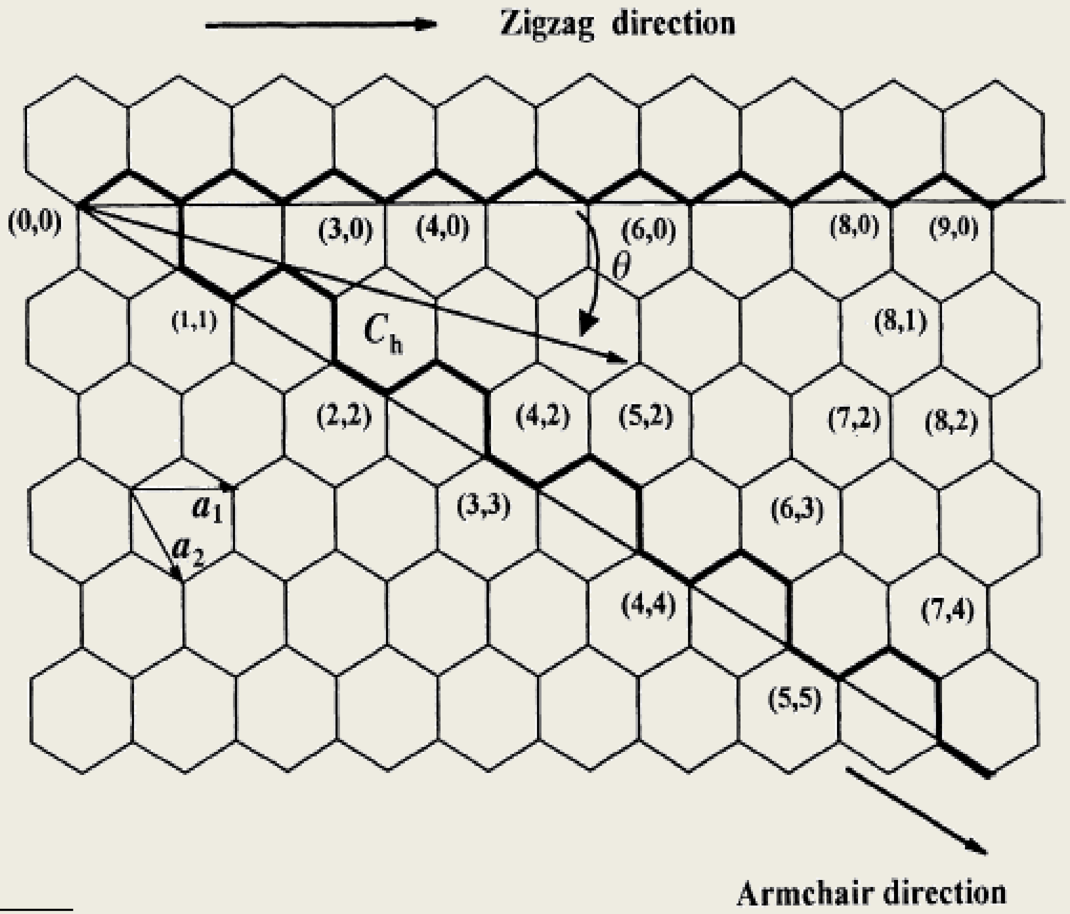


(Copyright: A. Rochefort, Nano-CERCA, Univ. Montreal)

2. Structures of CNTs

Chiral Vector, C_h

$$\boxed{C_h = n\,a_1 + m\,a_2}$$



Diameter

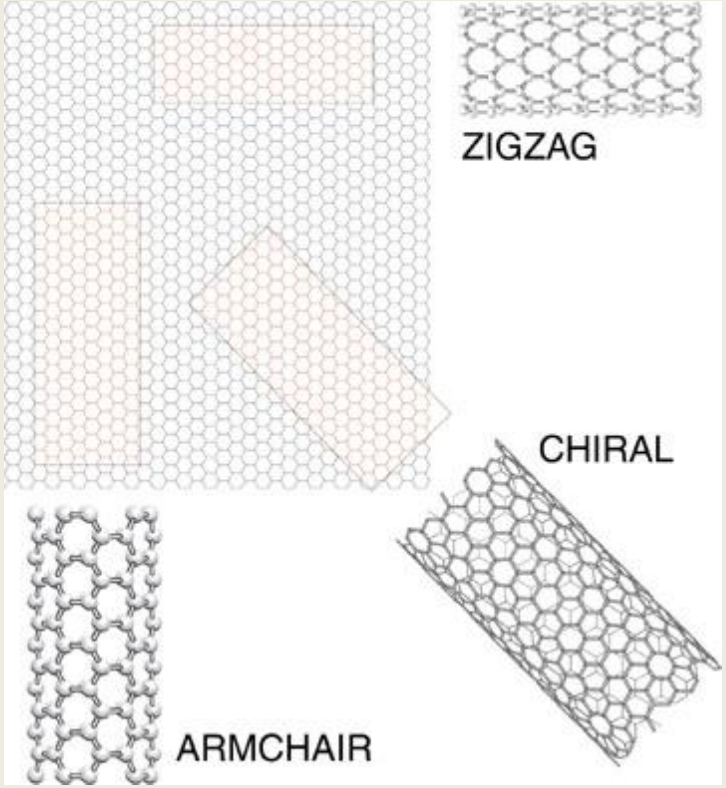
$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi}$$

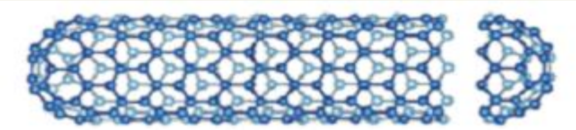
Chiral angle

$$\theta = \arccos\frac{2n+m}{2\sqrt{n^2 + nm + m^2}}$$

2. Structures of CNTs

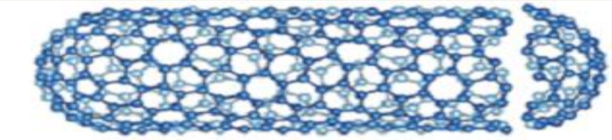
Three Types of Nanotubes





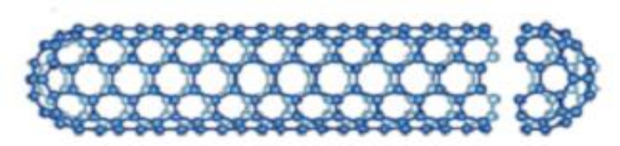
zigzag nanotube (n,0) $\theta=0^{o}$

- ❖ all others are semiconductors with a band gap that inversely depends on the diameter



chiral nanotube (n,m) $0^{o}<\theta<30^{o}$

- ❖ n-m=3k , semiconductors with a tiny band gap



armchair nanotube (n,n) $\theta=30^{o}$ ❖ metallic

S. G. Louie, Top. *Appl. Phys*., **80** (2001) 113

2. Structures of CNTs

Structural Properties of CNTs

Symbol	Description	Formula
a	length of unit vectors	$a=\sqrt{3}a_{C-C}=2.49\text{Å}$ $a_{C-C}=1.42\text{Å}$
a_1 a_2	unit vectors	$\left(\frac{\sqrt{3}}{2},\frac{1}{2}\right)a,\ \left(\frac{\sqrt{3}}{2},-\frac{1}{2}\right)a$
b_1 b_2	reciprocal lattice vectors	$\left(\frac{1}{\sqrt{3}},1\right)\frac{2\pi}{a},\ \left(\frac{1}{\sqrt{3}},-1\right)\frac{2\pi}{a}$
C_h	chiral vector	$C_h=na_1+ma_2\equiv(n,m)$ $(0\le\lvert m\rvert\le n)$
L	length of C_h	$L=\lvert C_h\rvert=a\sqrt{n^2+m^2+nm}$
d_{CNT}	diameter	$d_{CNT}=\frac{L}{\pi}$

Symbol	Description	Formula
θ	chiral angle	$\tan(\theta)=\frac{\sqrt{3}}{2n+m}$
d	gcd (n,m)	
d_R	gcd (2n+m,2m+n)	
T	translational vector	$\mathrm{T}=t_1a_1+t_2a_2\equiv(t_1,t_2)$ $t_1=\frac{2m+n}{d_R},t_2=-\frac{2n+m}{d_R}$
T	length of **T**	$T=\lvert\mathrm{T}\rvert=\frac{\sqrt{3}L}{d_R}$
N	number of hexagons in the unit-cell	$N=\frac{2(n^2+m^2+mn)}{d_R}$

R. Saito, G. Dresselhaus, and M. Dresselhaus, “*Physical Properties of Carbon Nanotubes*.” London: Imperial College Press, 1998

3.1. Electronic properties of CNTs

The electronic properties of nanotubes derived from the dispersion relation of a graphite sheet with the wave vectors (k_x, k_y)

$$E(k_x, k_y) = \pm\gamma\{1 + 4\cos(\frac{\sqrt{3}k_x a}{2})\cos(\frac{k_y a}{2}) + 4\cos^2(\frac{k_y a}{2})\}^{1/2}$$

γ : the nearest neighbor-hopping parameter, 2.5 – 3.2 eV
a: lattice constant, 0.246nm

One third of the tubes are metallic and two thirds are semiconducting. The band gap for a semiconducting tube is give by

$$E_g = 2d_{cc}\gamma / D$$

ex) 1 nm wide semiconducting tube → 0.7 - 0.9 eV

The curvature effect of $\sigma - \pi$ rehydbridization has been investigated using *ab-initio* calculation.

→ $\sigma - \pi$ rehydbridization can open up a small band gap (~0.02 eV) for nonarmchair metallic tubes.
→ This effect is found to be very rapidlly disappearing with the tube diameter.

Intertube coupling (SNWT rope, MWNT)

→ The intertube coupling induces a small band gap for certain metallic tubes but a reduced band gap by 40 % for semiconducting tubes in SWNT
→ In case of MWNT, the intertube coupling is relatively smaller because of bigger diameter.
→ All semi-conducting tubes in a MWNT tend to be semi-metallic just like graphite

3.1. Electronic properties of CNTs

A Single SWNT, a SWNT rope, or MWNT behave like a quantum wire

→ The confinement effect on the tube circumference
→ The conductance for a SWNT, a SWNT rope, or MWNT is given by

$$G = G_0 M = (2e^2/h)M$$

G_0= $(2e^2/h)$ = (12.9 kΩ)$^{-1}$, quantized conductance
M: an apparent number of conducting channels
ex) perfect SWNT, M=2

→ M is determined not only by the intrinsic properties of a nanotube itself, but also by the intertube coupling and the scatters such as defects, impurities, structural disotortions, coupling with substrate, and contacts.

Resistivity & Conductivity

→ The resistivity of graphite varies remarkably depending on sample quality.
→ The highest quality graphite ; At RT in-plane resistivity is 0.4 μΩm.
SWNT ropes and MWNTs ; The resistivity if found to decrease with temperature,
and the RT value are much higher than 0.4 μΩm
because nanotubes are randomly oriented in the sample.
→ The π electron is more delocalized in a defect-free nanotube and thus should give rise to higher conductivity than that of graphite.

3.1. Electronic properties of CNTs

Electronic properties of heterogeneous nanotubes (bent and branched structures)

→ These structures are molecular mimics of 2- or 3-terminal heterojunctions that connect two or three different nanotubes in the form of A-B or A-B-C in which A, B, and C can be a metallic or semiconducting tube.

→ Localized states appear in the junction interface containing pentagons and heptagons, they also observed in capped SWNT and MWNT ends

→ The interface may or may not be conducting, depending on how tubes are connected.
ex) (9,0)-(6,3) tube junction is not conducting for symmetric match
but conducting for asymmetric match

The electronic properties have been correlated with mechanical , chemical, biological, thermal, and magnetic interactions with nanotubes, so the extended electromechanical, electrochemical, thermal electronic, and electromagnetic properties are associated with applications of CNTs in sensors, actuators, field emission, batteries, fuel cell, capacitors, and many others.

3.2. Mechanical properties of CNTs

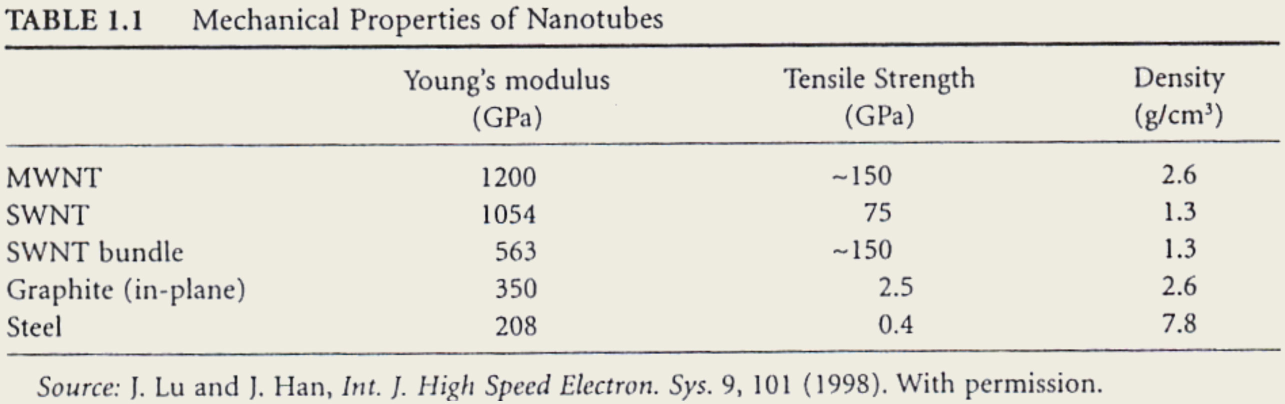


TABLE 1.1 Mechanical Properties of Nanotubes

	Young's modulus (GPa)	Tensile Strength (GPa)	Density (g/cm³)
MWNT	1200	~150	2.6
SWNT	1054	75	1.3
SWNT bundle	563	~150	1.3
Graphite (in-plane)	350	2.5	2.6
Steel	208	0.4	7.8

Source: J. Lu and J. Han, *Int. J. High Speed Electron. Sys.* 9, 101 (1998). With permission.

In general, various types of defect-free nanotubes are stronger than graphite.

→ The axial component of σ bonding is greatly increased when a graphite sheet is rolled over to form seamless cylinderical structure or a SWNT.

→ Young's modulus is independent of tube chirality, but dependent on tube diameter.

→ The Young's modulus for MWNT is higher than a SWNT, typically 1.1 to 1.3 TPa. (coaxial intertube coupling or van der Waals force)

→ Many SWNTs are held together in a bundle or a rope, the weak van der Waals force induces a strong shearing among the packed SWNTs. (decrease of Young's modulus)

The elastic response of a nanotube to deformation is also very remarkable.

→ CNTs can sustain up to 15 % tensile strain before fracture.

→ A high strain is attributed to an elastic buckling through which high stress is released. (Elastic buckling also exists in twisting and bending deformation)

→ A high elastic strain for several deformation mode is oriented from sp^2 rehybridization in nanotubes through which the high strain gets released.

3. Properties of CNTs

3.2. Mechanical properties of CNTs

sp^2 rehybridization will lead to change in electronic properties of a nanotube.

$$E_g = Eg_0 + \mathrm{sgn}(2P+1)3\gamma[(1+\upsilon)(\cos 3\theta)\varepsilon_l + (\sin g3\theta)\varepsilon_r]$$

→ E_g, zero strain band gap
θ , nanotube chiral angle
ε_l, tensile strain ε_r, torsion strain
υ, Poisson’s ratio
p = 0 (metallic tube), 1 (type I semiconductor),
-1 (type II semiconductor)

→ This equation predicts that all chiral or asymmetric tubes (0< θ <30º) will experience change in electronic properties for either tensile or torsional strain whereas symmetric armchair or zigzag tubes may or may not change their electronic change in electronic properties.

→ In asymmetric tubes, either strain will cause asymmetric σ-π rehybridization and therefore change in electronic properties.

→ Effect of strain on a symmetric tube is not so straightforward.

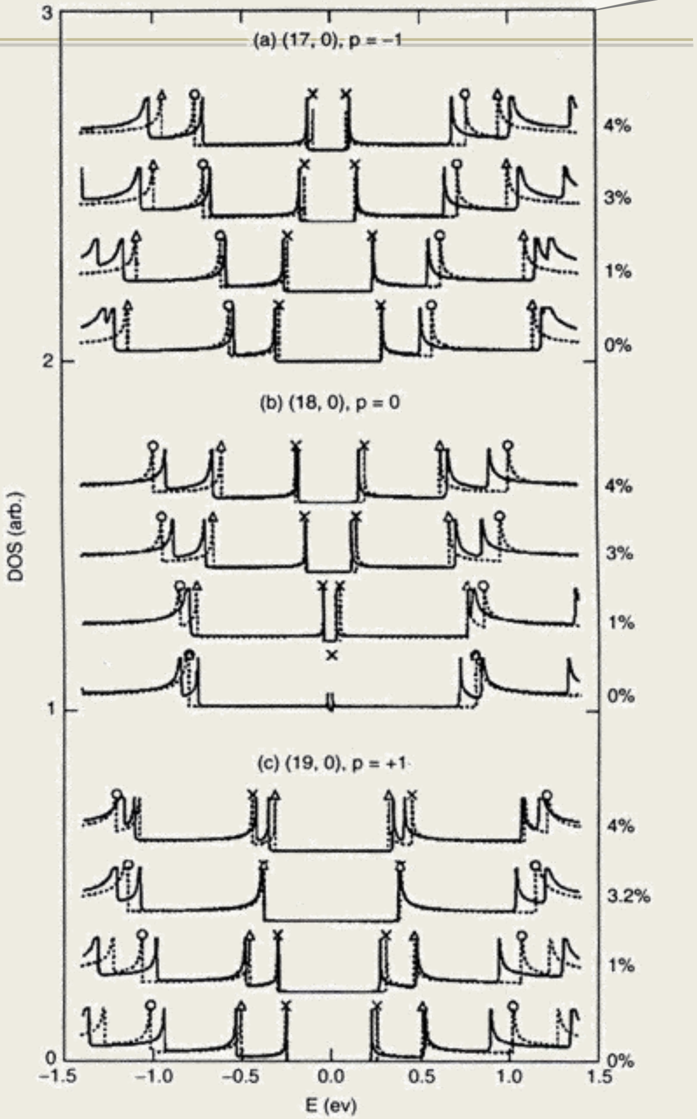


FIGURE 1.13 DOS with (dash line) and without (solid line) consideration of *s-p* rehybridization for three typical SWNTS. Values on the right side are stains. A small band gap of 0.02 eV at zero strain, caused by tube curvature or rehybridization, is seen for tube (18,0). Striking features of electromechanical properties include splitting and merging of VHS peaks including band gap opening and closing [65].

3.3. Magnetic properties of CNTs

Magnetic properties such as anisotropic g-factor and susceptibility of nanotubes are expected to be similar to those for graphite while some unusual properties may exist for nanotube.

→ The average observed g-value of 2.012 and spin susceptibility of 7 X 10^{-9} emu/g in MWNTs are only slightly lower than 2.018 and 2 X 10^{-8} emu/g in graphite.
→ The measured susceptibility gives the density of state at the Fermi level of 1.5 X 10^{-3} states/eV/atom, also comparable with that for in-plane graphite.

The band gap of nanotube under uniform magnetic filed parallel to the tube axis is given by:

(metallic nanotubes)

$E_g = E_{g0}\beta$, $0<\beta<3/2$

$E_g = E_{g0}|3-\beta|$, $3/2<\beta<3$

(semiconducting nanotubes)

$E_g = E_{g0}|1-\beta|$, $0<\beta<3/2$

$E_g = E_{g0}|2-\beta|$, $3/2<\beta<3$

→ A metal-insulator transition and band gap change for semiconductor tubes under magnetic field parallel to tube axis.
(similar to electrical response of nanotubes to mechanical deformation)

→ Driven by magnetic or strain field, the Fermi level will move away from the original position, and this results in the band gap change pattern in Fiqure 1.15.

→ Similar response can also be observed when magnetic field or strain field is perpendicular to tube axis.

3.3. Magnetic properties of CNTs

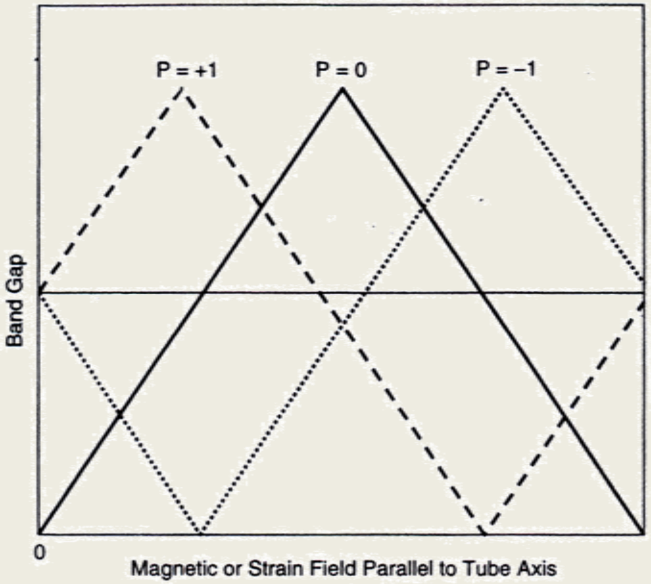


FIGURE 1.14 Band gap change pattern of three types of nanotubes (n,m) under either magnetic field or mechanical strain field. Integer $p = n - m - 3q = -1$, 0, and +1.

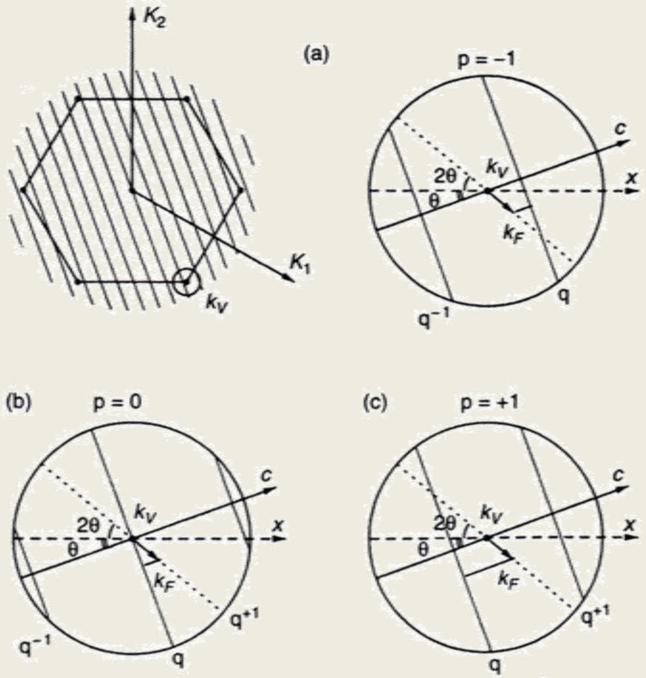
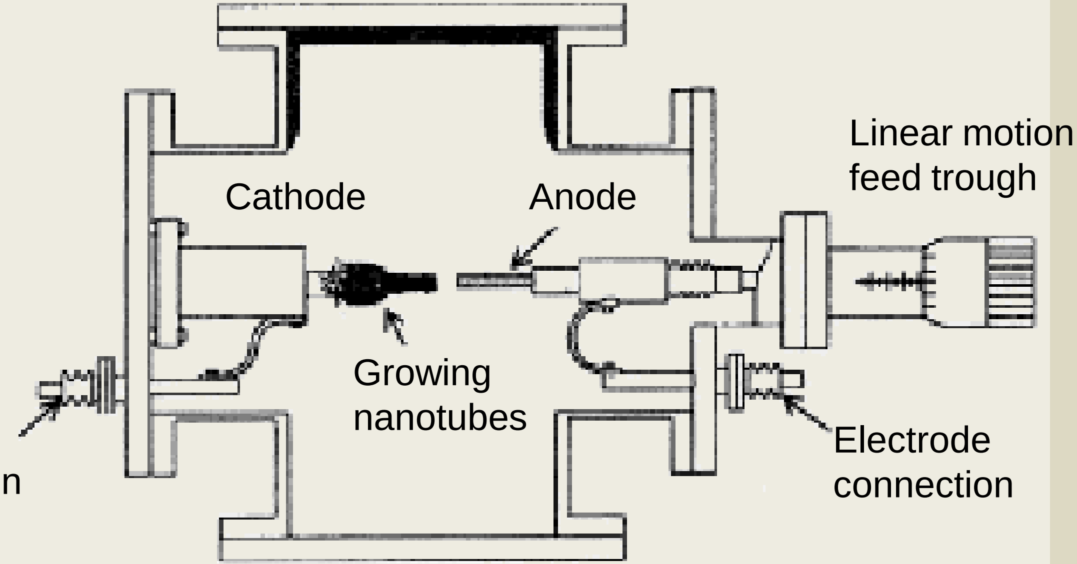


FIGURE 1.15 Driven by magnetic or strain field, the Fermi wave-vector K_F moves away from K_V at zero field, with the band gap measured by a distance between K_F and q line measure the bang gap. The band gap increases for $p = -1$ but increases for $p = 0$ and +1 tubes. The K_F move across q line for $p = -1$ but q+1 line to reach zero gap. This moving pattern results in the band gap change pattern shown in Figure 1.14 [65].

4. Synthesis of CNTs

4.1. Arc discharge



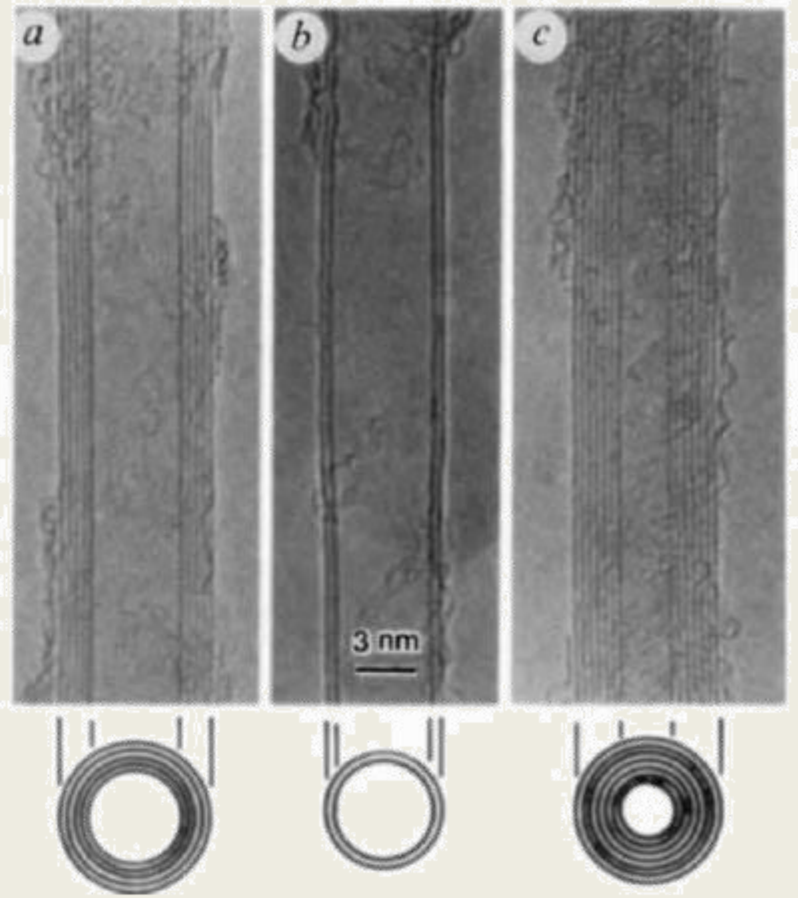
- First introduced by S. Iijima in NEC (*Nature* **354** (1991) 56)
- Further developed by Ebbesen and Ajayan in NEC (*Nature* **358** (1992) 220)
- Usually used in synthesis of carbon nanotubes in the early stage
- Carbon clusters from the anodic graphite rod caused by the collision are cooled to low temperature and condensed on the surface of the cathode
- Excellent Method for the production of both MWNT and SWNT
- CNTs are obtained by controlling growth conditions
- Low CNT purity and yield

  → For high purity: Higher chamber temperature, introduction of H_2 gas, sulfur compound

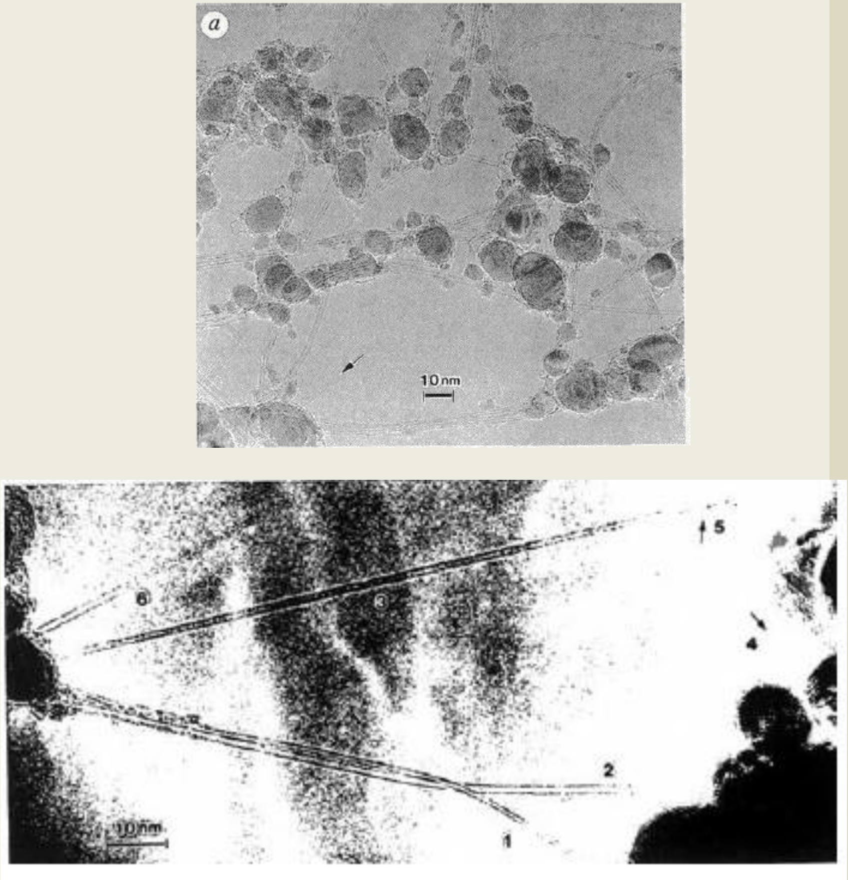
4. Synthesis of CNTs

4.1. Arc discharge

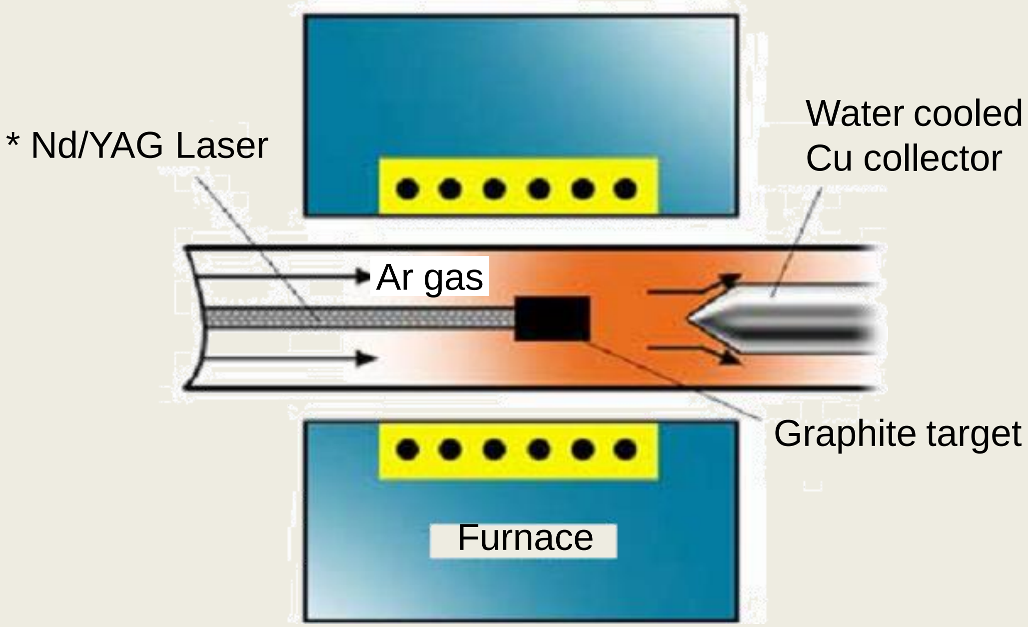
Helical microtubules of graphitic carbon
S. Iijima, *Nature* **354** (1991) 56



Single-shell carbon nanotubes of 1-nm diameter
S. Iijima, *Nature* **363** (1993) 603



4.2. Laser ablation

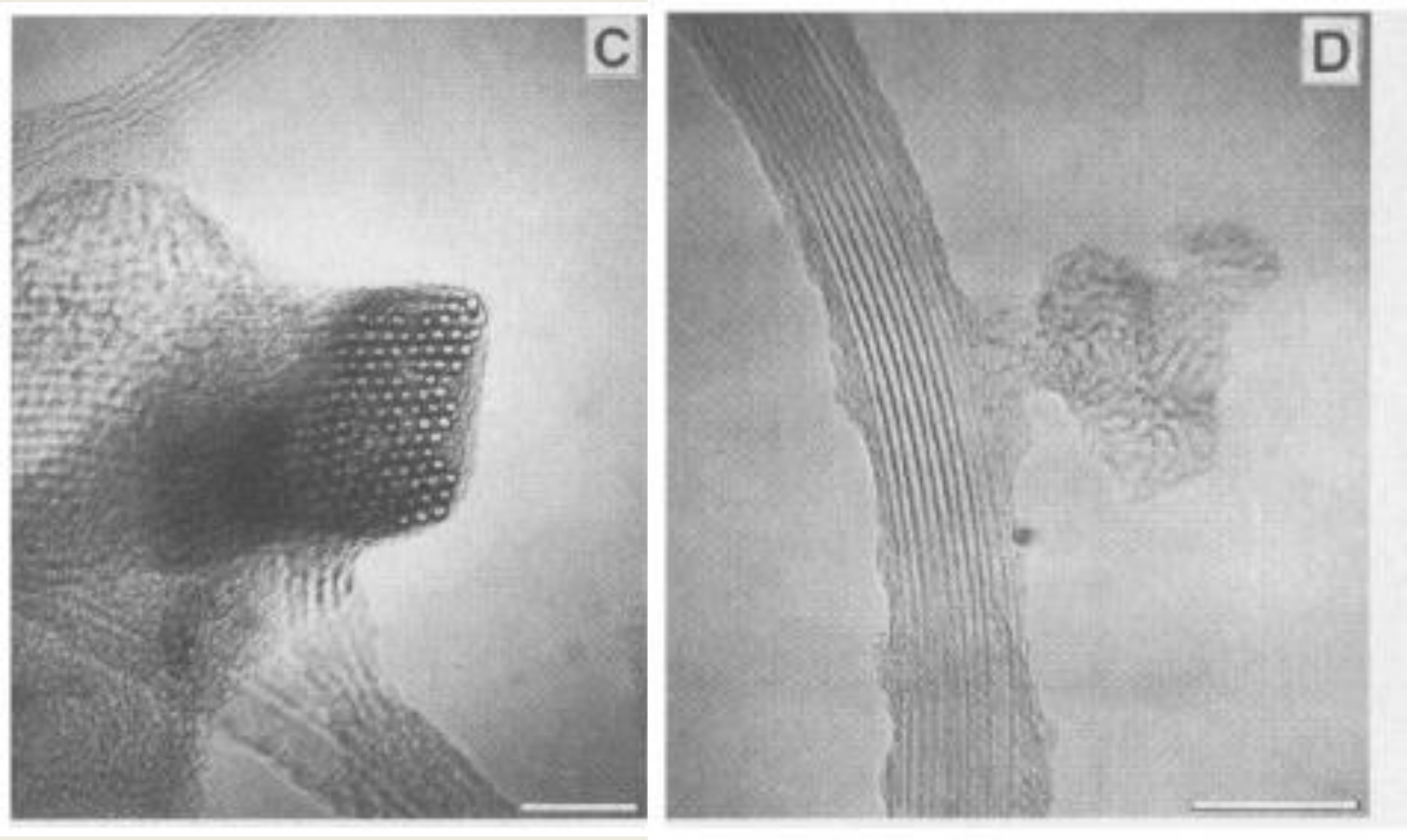


* Nd/YAG : neodymium-doped yttrium aluminium garnet (Nd:$Y_3Al_5O_{12}$)

- First introduced by R.E. Smalley in Rice University (*Science* **273** (1996) 483)
- Carbon clusters from the graphite target are cooled, adsorbed, and condensed on the Cu collector at a low temperature
- High quality SWCNT
- CNTs are obtained by controlling diameters
- High cost: requirement of specific equipments and large amount of energy consuming

4.2. Laser ablation

Crystalline ropes of metallic carbon nanotuebes
R.E. Smalley et.al., *Science* **273** (1996) 483



4.3. Chemical vapor deposition

- Involves heating a catalyst material to high temperatures in a tube furnace and flowing hydrocarbon gas through the tube reactor

- The materials are grown over the catalyst and are collected when the system is cooled to room temperature

- Key parameters are:
  Hydrocarbons - C_2H_2, C_2H_4, CH_4, …
  Substrate of catalysts - Ni, Co, Fe,…
  Growth Temperature

- CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, and the dissolution and saturation of carbon atoms in the metal nanoparticles

- Both MWNT and SWNT can be grown by CVD methods
  - MWNTs use acetylene gas for the carbon source and a growth temperature between 600 ~ 800°C
  - SWNTs use carbon monoxide or methane for a carbon source and a much higher growth temperature (900 ~ 1200°C)

4.3. Chemical vapor deposition

Kinds of CVD

- Supply method of activation energy
  - Thermal CVD
  - PECVD (plasma enhanced CVD)
  - PhCVD (photo assisted CVD)
  - LCVD (laser assisted CVD)

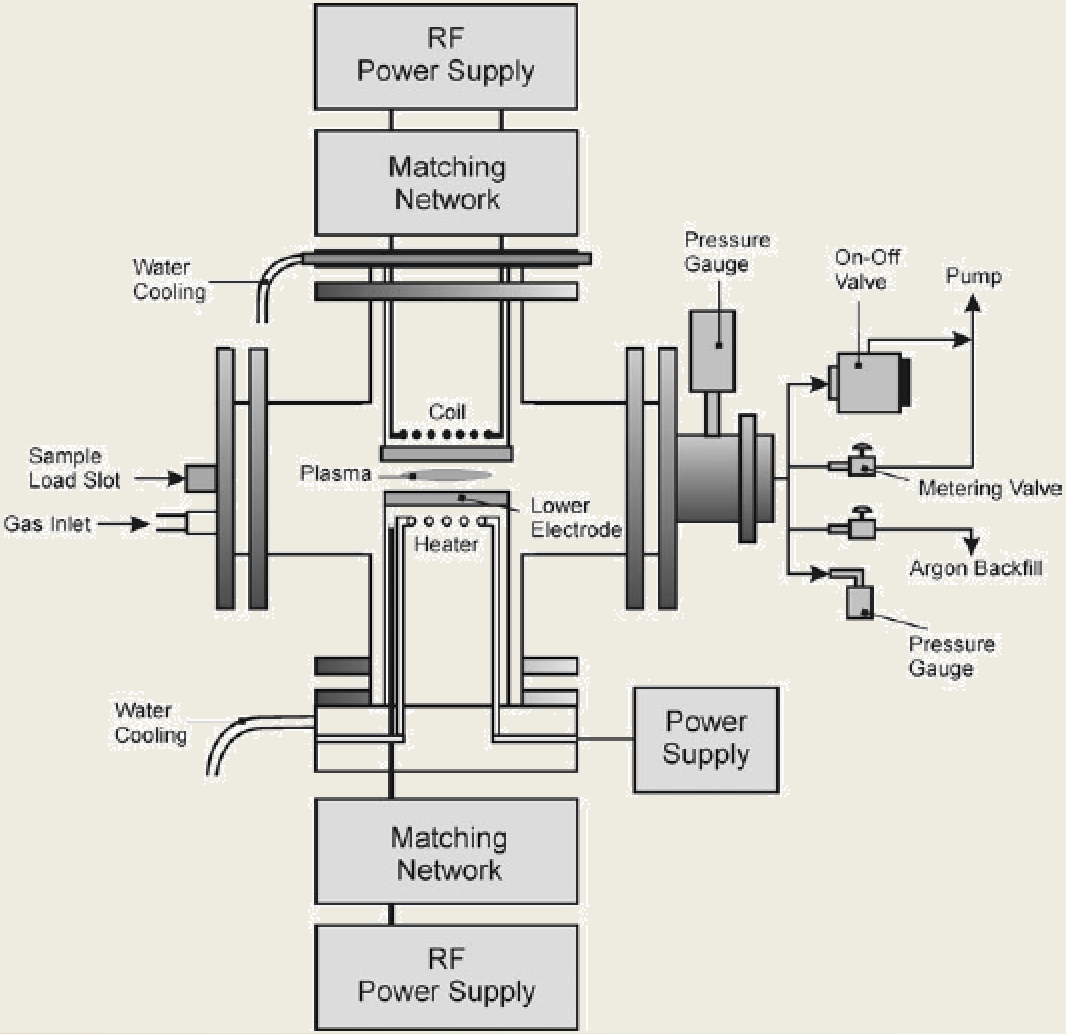
- Reaction temperature
  - High temperature CVD
  - Low temperature CVD

- Reaction gas
  - Conventional CVD : organic source
  - MOCVD (Metal organic CVD) : organometallic source

- Reaction pressure
  - LPCVD (Low pressure CVD) : several tens mTorr ~ several tens Torr
  - APCVD (Atmospheric Pressure CVD) : atmospheric

4.3. Chemical vapor deposition

Plasma enhanced CVD

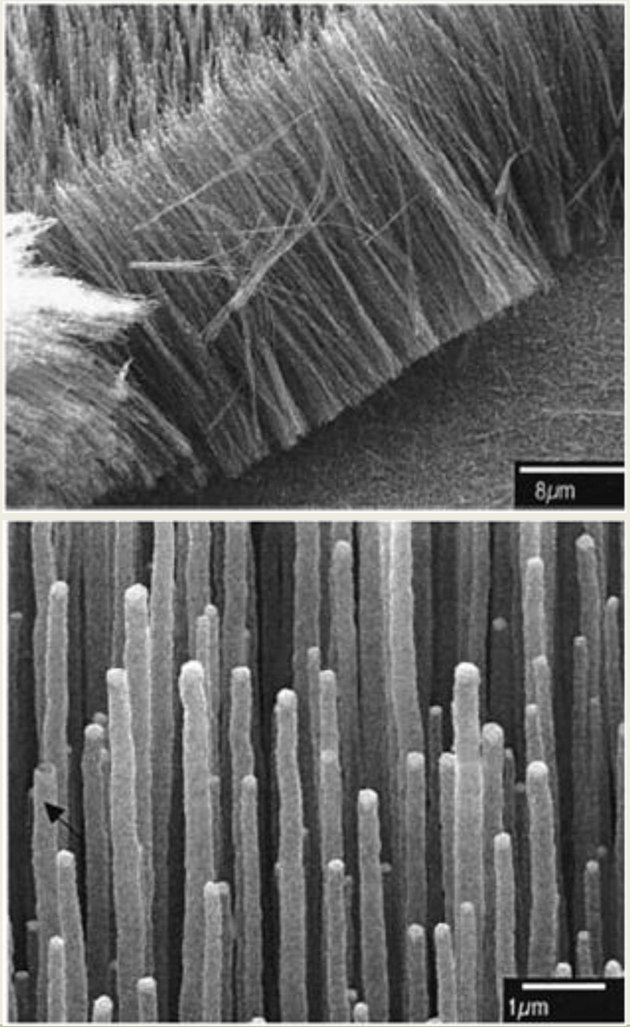


- The low temperature operation is possible (~ 500ºC) because the precursor dissociation is enabled by the high energy electrons in a plasma.
- High deposition rate
- Well aligned CNTs on the large area substrate
- Difficult to obtain the uniform products
- Low crystallinity

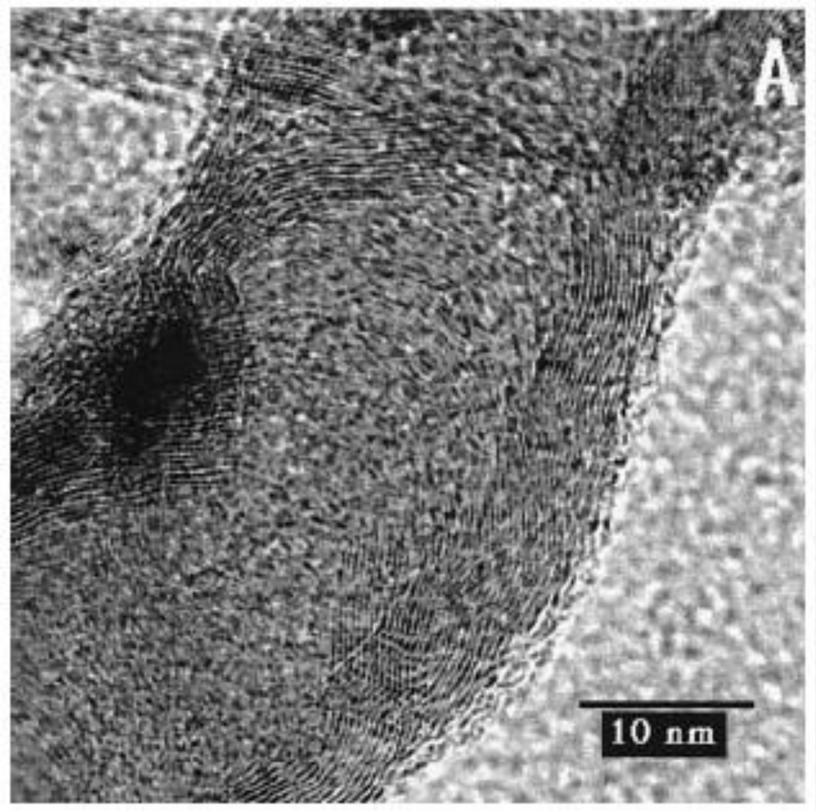
4. Synthesis of CNTs

4.3. Chemical vapor deposition

Plasma enhanced CVD



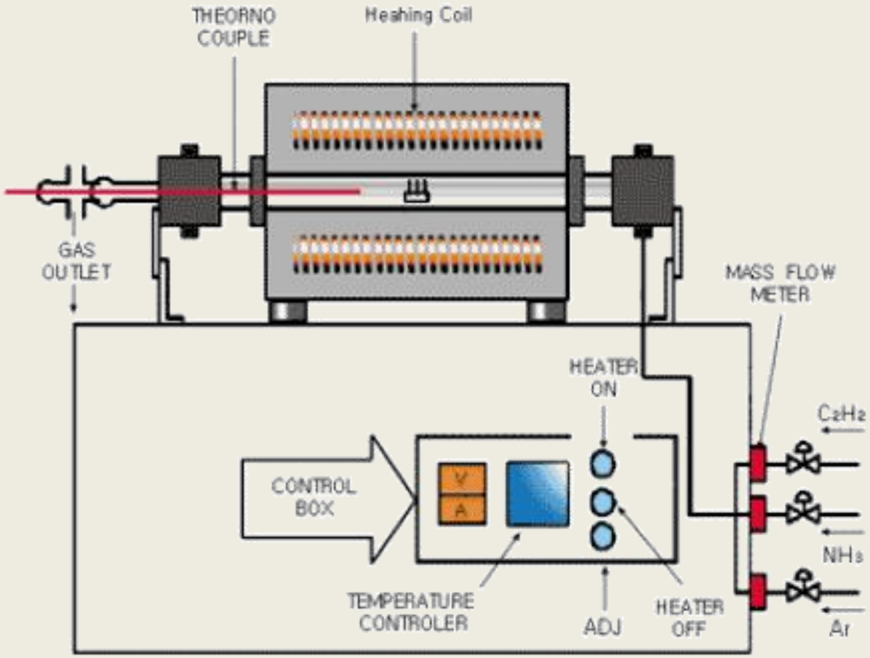
Synthesis of large arrays of well-aligned carbon nanotubes on glass
Z.F. Ren et.al., *Science* **282** (1998) 1105



4. Synthesis of CNTs

4.3. Chemical vapor deposition

Thermal CVD



Silicon oxide or Al substrates

↓

The substrate is covered by few nanometers metal film (Fe/Ni/Co)

700 ~ 950 ℃ ↓ NH_3 gas

Metal nanoparticle

↓ C_2H_2, CH_4, C_2H_4, CO

Carbon nanotube

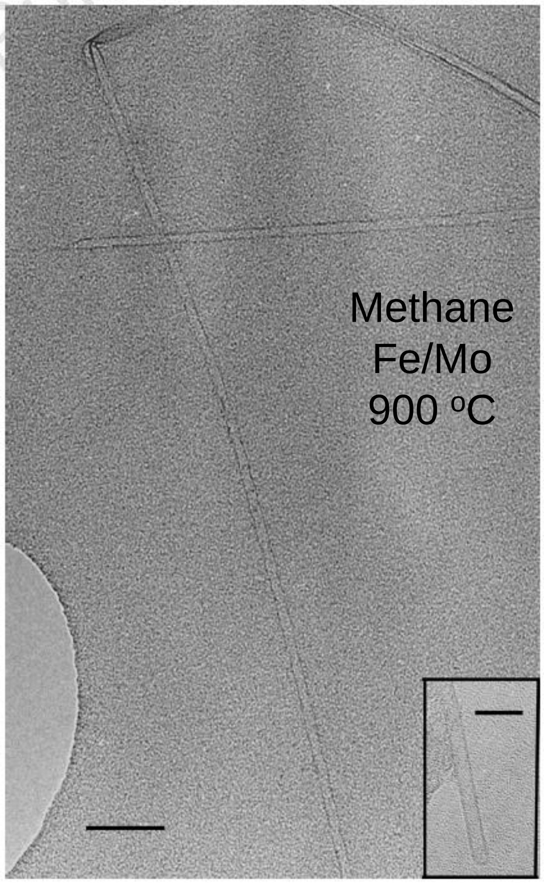
- Various sources can be used
- High purity CNT
- Controllability of microscopic structures
- Not good in homogeneity on substrate as change in the flow of the reaction gas leads to unstable gas supply

4. Synthesis of CNTs

4.3. Chemical vapor deposition

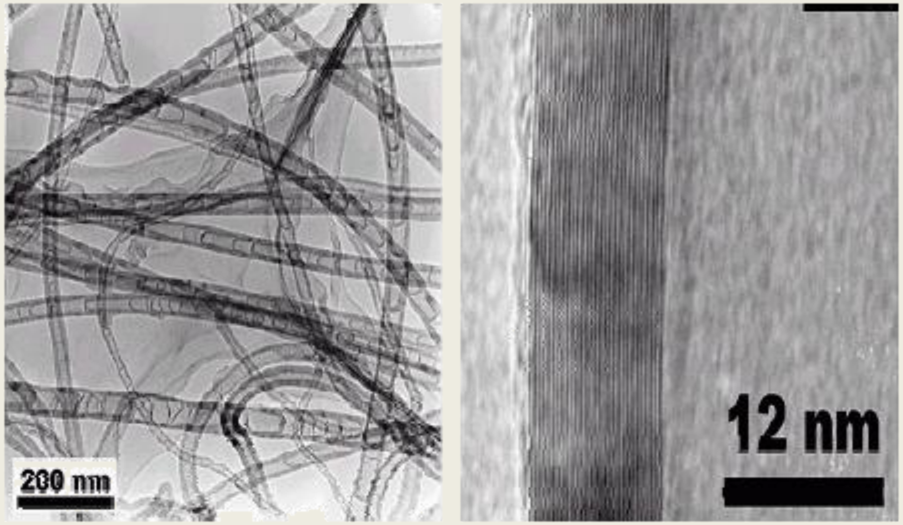
Thermal CVD

Synthesis of individual single walled carbon nanotubes on patterned silicon wafers
H. Dai et.al., *Nature* **395** (1998) 878



Methane
Fe/Mo
900 °C

Commercial MWCNT by IlJin Nanotech Co.

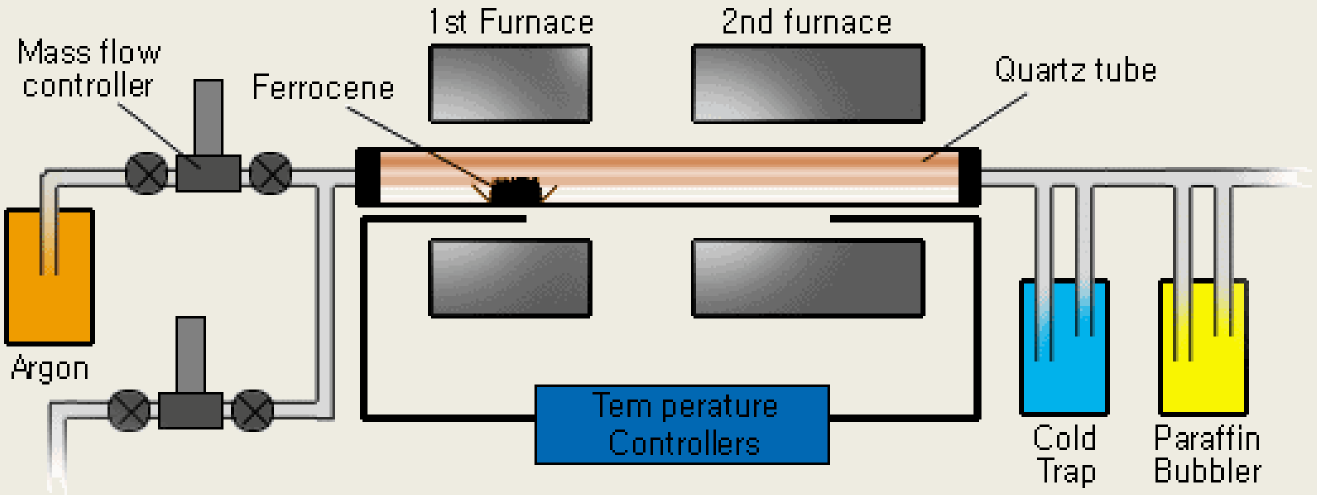


4. Synthesis of CNTs

4.4. Vapor phase growth

Low temp. region : vaporization and atomization of metal

High temp. region : growth of CNTs

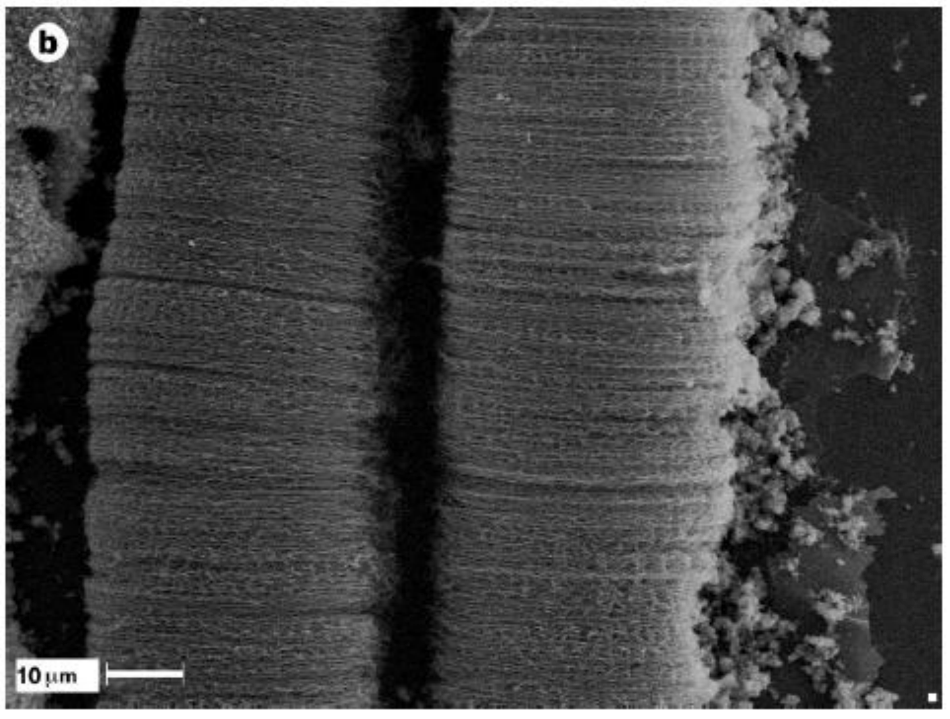


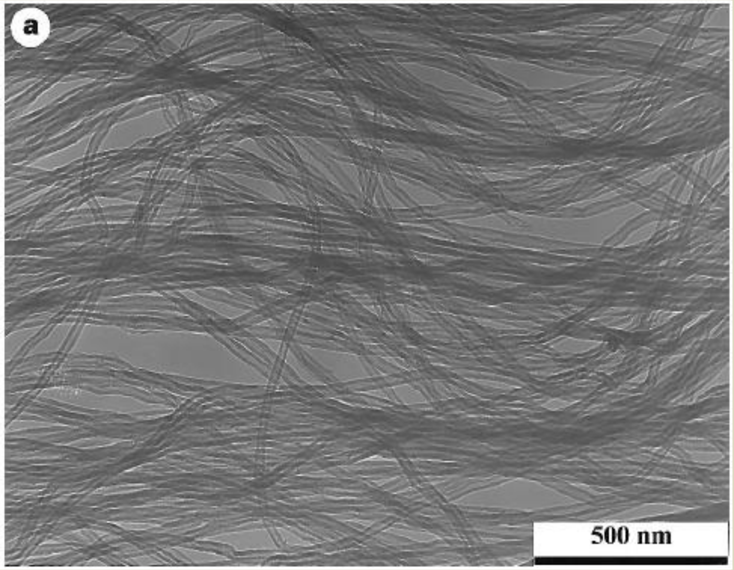
- Modified method of VGCF (Vapor Grown Carbon Fiber)
- VPG method does not use substrate, but makes reaction in the chamber supporting both reaction gas and metal catalyst in chamber
- Advantage of large scale CNT synthesizing
- Consuming the large amount of gas and low yield

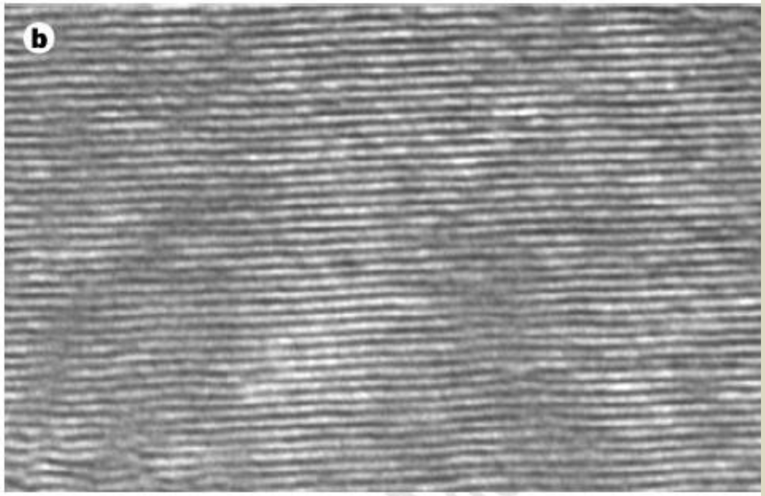
4. Synthesis of CNTs

4.4. Vapor phase growth

Controlled production of aligned-nanotube bundles
H.W. Kroto et.al., *Nature* **388** (1997) 52



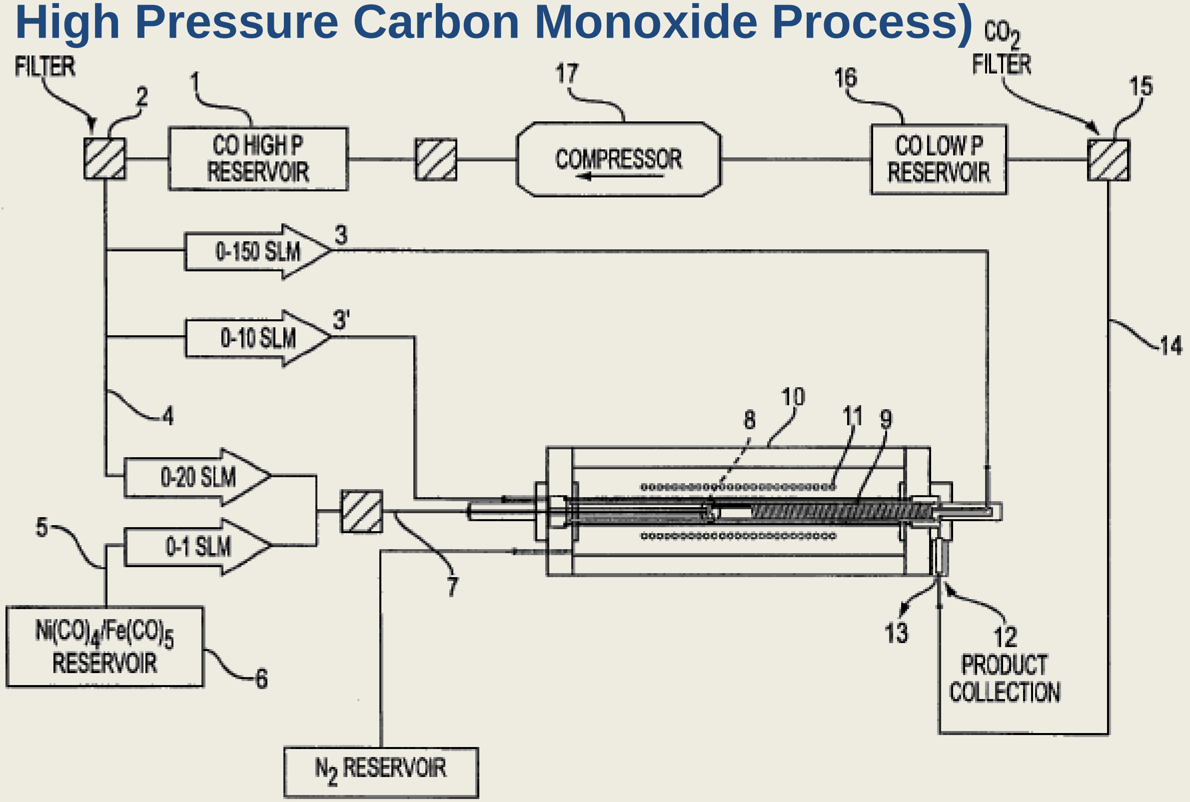




4. Synthesis of CNTs

4.5. Other methods

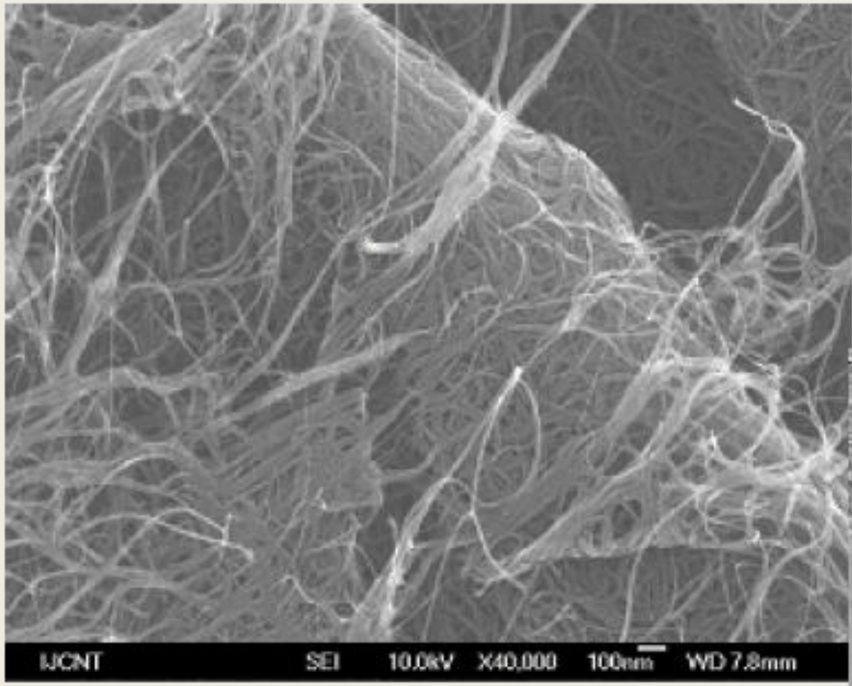
HiPCO (The High Pressure Carbon Monoxide Process)

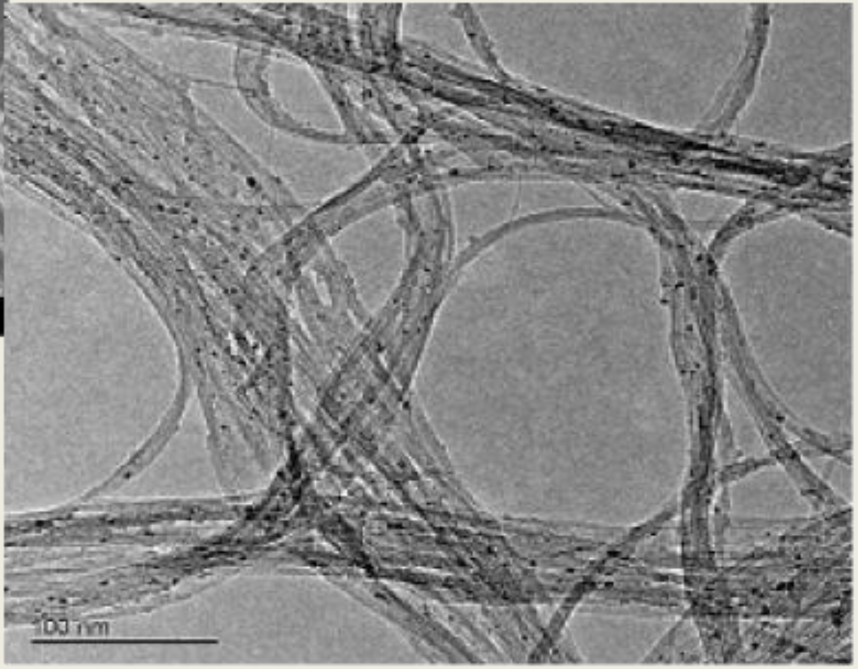


- Developed by R.E. Smalley in Rice University (1999)
- Preparation method of SWCNTs using high pressure CO as the carbon source
- The gas phase catalysts from a volatile organometallic precursor → decompose → forming metal clusters → CNT growth
- The only process that can make SWCNTs on a kilogram per day scale

4.5. Other methods

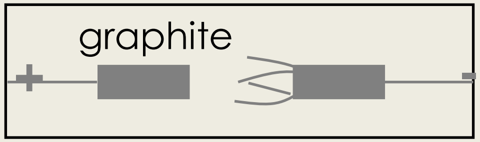
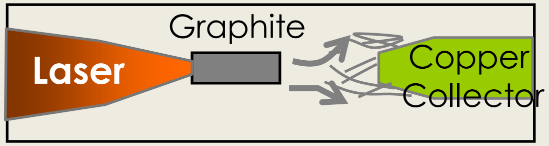
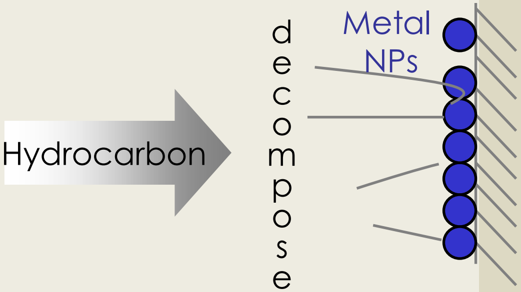
HiPCO (The High Pressure Carbon Monoxide Process)



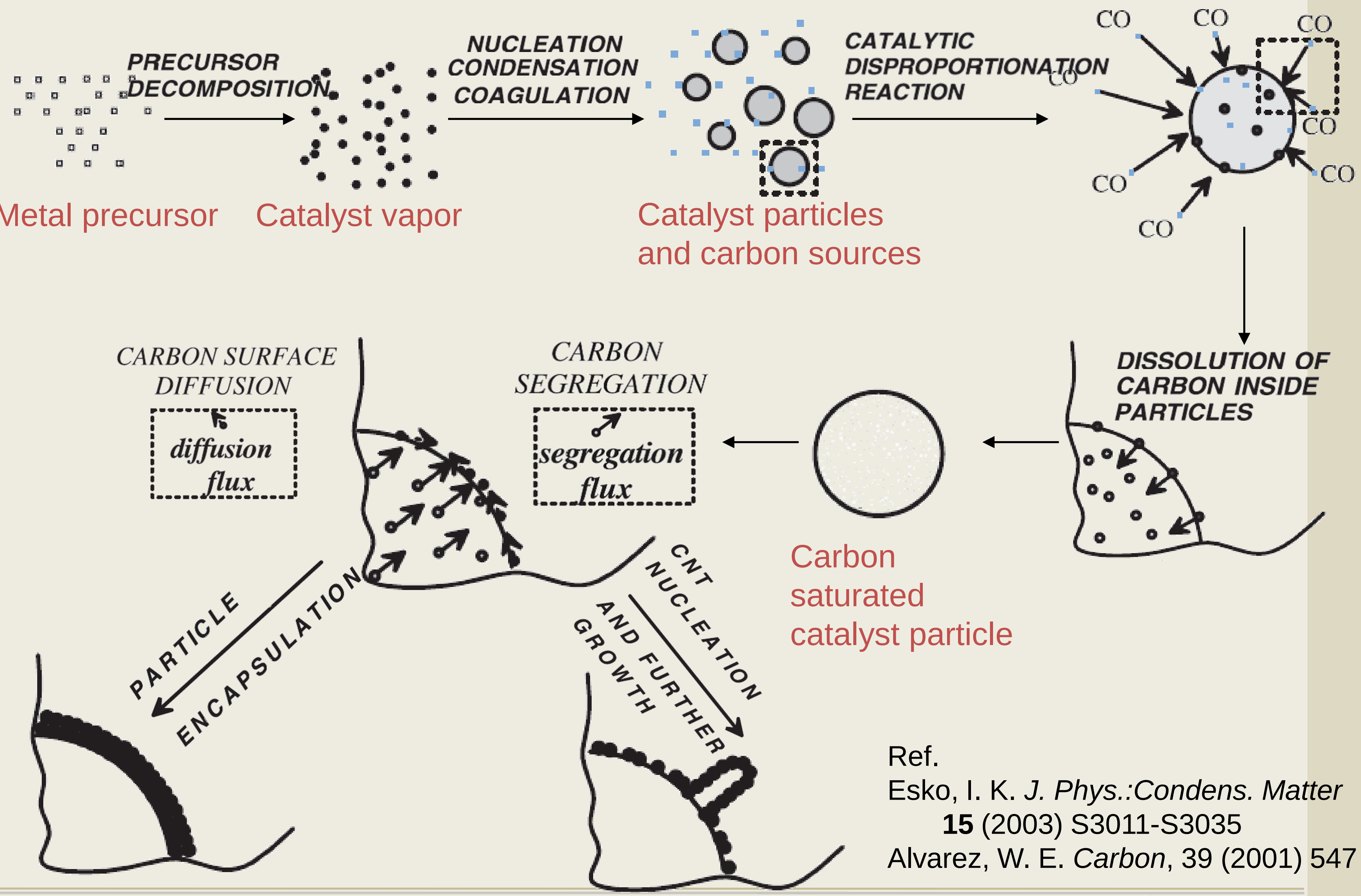


Commercial SWCNTs by CNI

4. Synthesis of CNTs

Method	Arc-discharge	Laser ablation	CVD
Who	Iijima, Ebbesen, Ajayan, NEC, Japan	Smalley, Rice Univ. USA	Endo, Shinshu Univ. Japan
How			
Yield	30 – 90 %	Up to 70 %	20 – 100 %
SWNT	Short tubes with diameter of 0.6-1.4 nm	Long bundles of tubes (5 – 20 μm) with diameter of 1 – 2 nm	Long tubes with diameters of 0.6 – 4 nm
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of 10 nm	Not very much interest Too expensive	Long tubes with diameters of 10 – 240 nm
Pro	Can easily produce Few structural defects W/O catalyst, cheap, open air synthesis	Good diameter control and few defects Quite pure	Easiest to scale up to industrial production Long length, simple process Diameter controllable, pure
Con	Short tubes with random sizes and directions Need a lot of purification	Costly technique due to lasers and high power	Usually MWNTs Are riddled with defects

Growth Mechanism of CNTs



Metal precursor

Catalyst vapor

Catalyst particles
and carbon sources

Carbon
saturated
catalyst particle

Ref.
Esko, I. K. *J. Phys.:Condens. Matter* **15** (2003) S3011-S3035
Alvarez, W. E. *Carbon*, 39 (2001) 547

4.6. Issues in the synthesis

- Low cost mass production
- High quality and high purity
- Chirality control
- Investigation of growth mechanism

5. Applications of CNTs

Potential applications and limitations

- The last couple of decades of work in fullerenes and nanotubes promised an amazing range of applications. (in electronics, energy, composites, sensors and biologies)

- However, these new concepts and ideas for applications of carbon nanomaterials have had a limited success in the marketplace, mainly due to issues in processing, scale-up and due to the inability to properly assess the time frame that is needed to take new products to market.

- There are a few applications of nanotubes that are indeed commercialized today.

- The success of the potential applications of CNTs depends on the large-scale synthesis and the stable supply of CNTs

5.1. Electronic devices

FET (Field-effect transistors)

- In hot pursuit of Moore’s law, semiconductor giants like Intel, IBM and AMD are commercially manufacturing silicon-based transistors at the 65-nm technology node (Q1, 2007). Intel intends to commercialize transistors at the 45-nm technology node.

- By an evolutionary process, a conservative estimate for the smallest conceivable silicon transistor at this point is 16 nm, expected to hit markets not prior to 2018. A revolutionary speedup of this process can be realistically envisioned only if nanotechnology can be controlled on a large scale.

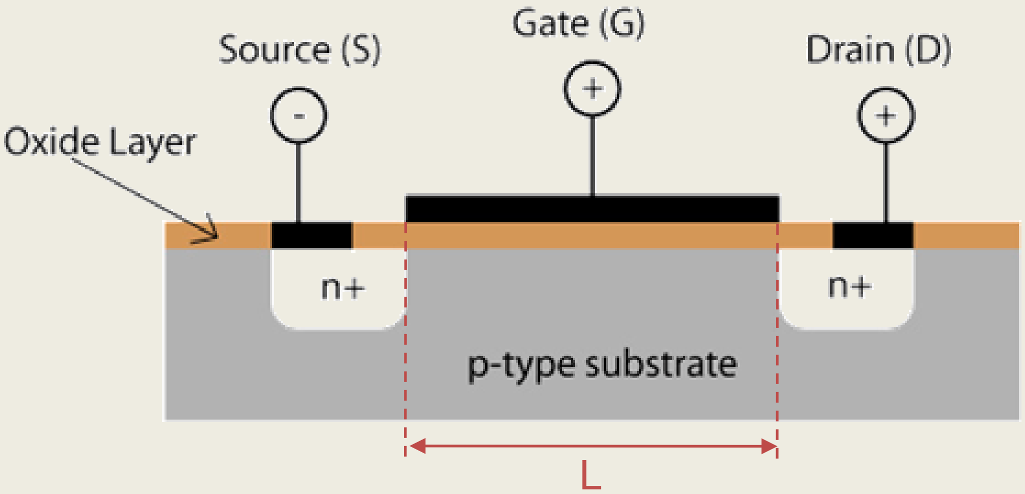
- SWCNTs have been demonstrated to operate as field-effect transistors almost a decade ago, and since then, the FETs have steadily grown in versatility and promise for future nanometer-scale electronics.
  (The earliest works on room-temperature CNT transistors: C.Dekker, *Nature* **393** (1998) 49)
  → very similar performance to a MOSFET (metal-oxide-semiconductor FET)

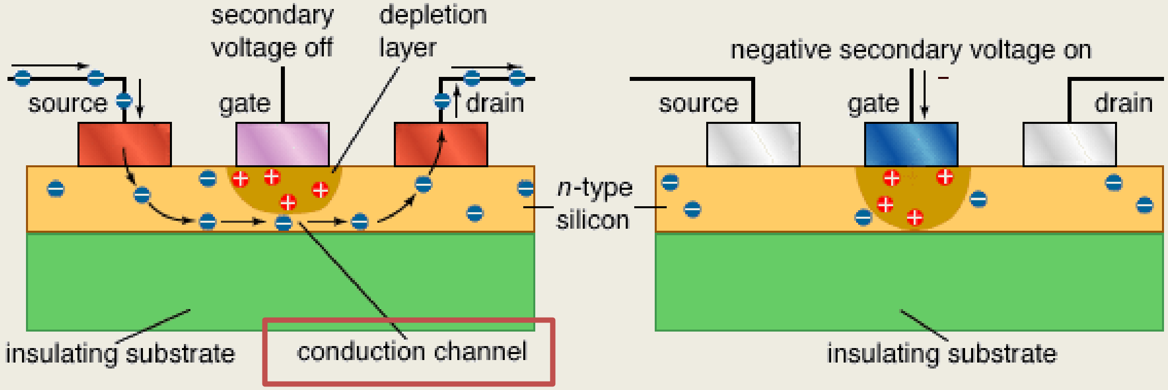
5. Applications of CNTs

5.1. Electronic devices

FET (Field-effect transistors): MOSFET

Structure of MOSFET



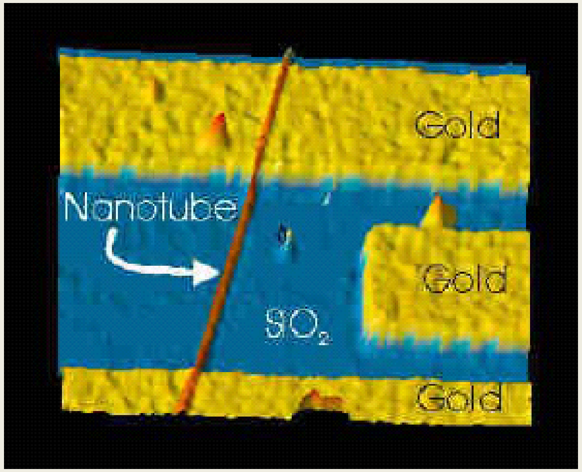


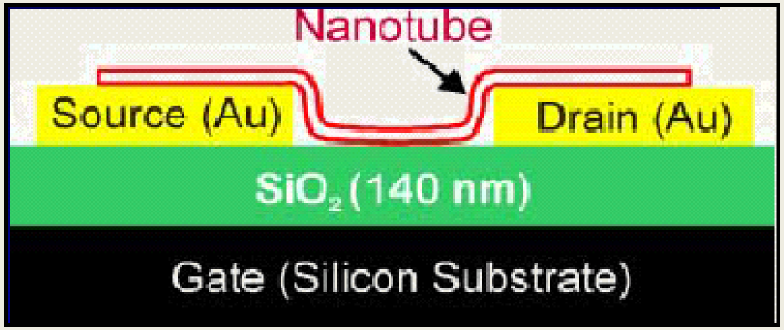
Ref. DoITPoMS, Department of Materials Science and Metallurgy, University of Cambridge

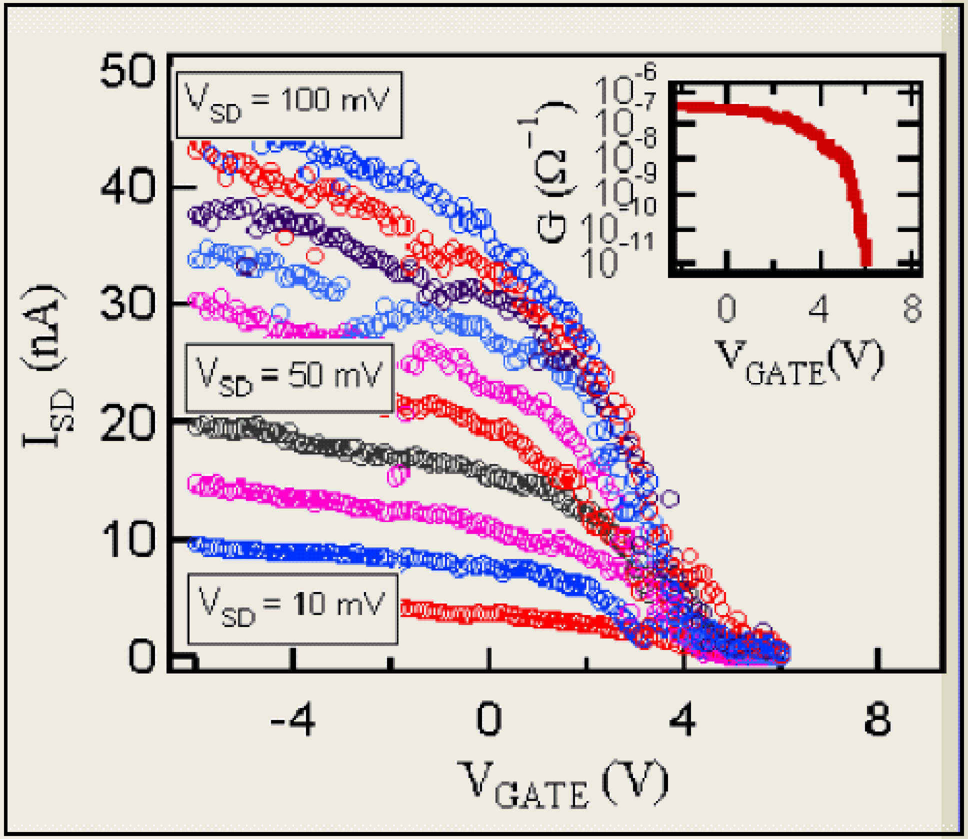
5. Applications of CNTs

5.1. Electronic devices

FET (Field-effect transistors): CNT-FET







Ref. IBM Research

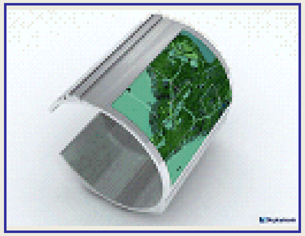
- CNTs as the conduction channel
- Advantages
  : 200 times more current-handling capability and 1000 times faster clock rate

5. Applications of CNTs

5.1. Electronic devices

TFT (Thin film transistors) for flexible display

Roadmap of the flexible display

1st Gen.	2nd Gen.	3rd Gen.	4th Gen.
"Durable Display"	"Bendable Display"	"Flexible Display"	"Disposable Display"
			
- Thin & Light - Rugged → Mobile Display	- Bendable - Conformable → Wearable Display	- Rollable - Folderble → Flexible Display	- Roll-to-Roll Process - Easy Printing → Paper-like Display

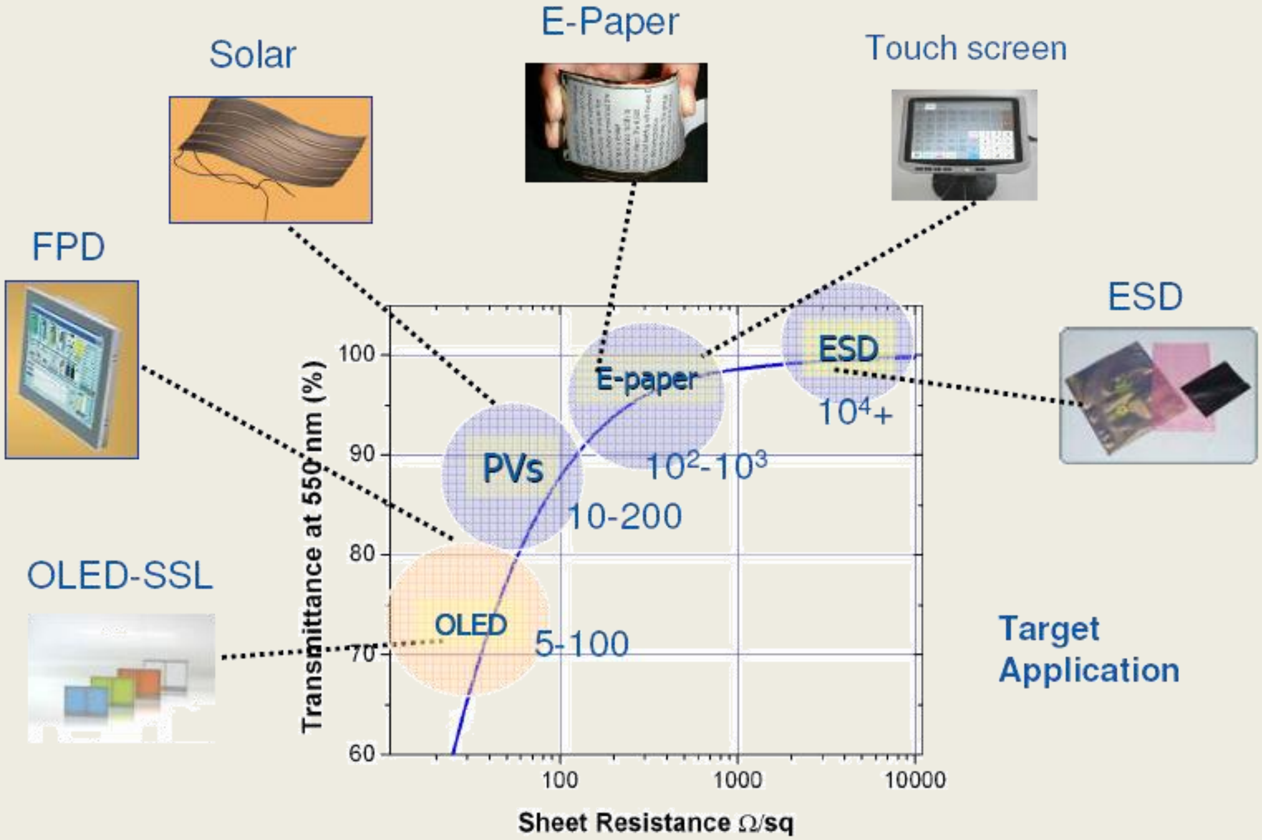
Ref. Flexible Display Technology and Market (2007~2017), Displaybank Report (2007)

5. Applications of CNTs

5.1. Electronic devices

TFT (Thin film transistors) for flexible display

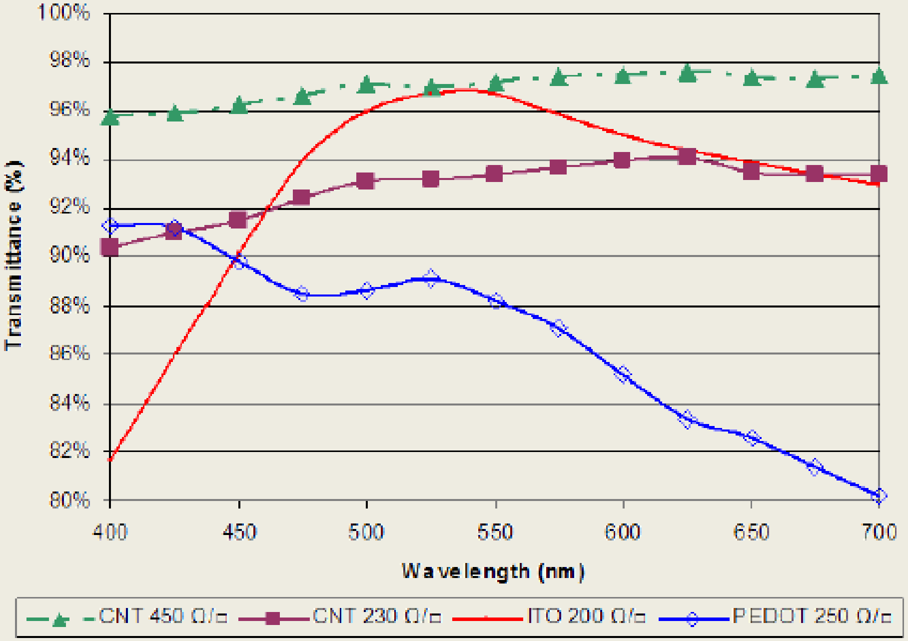
Target application areas



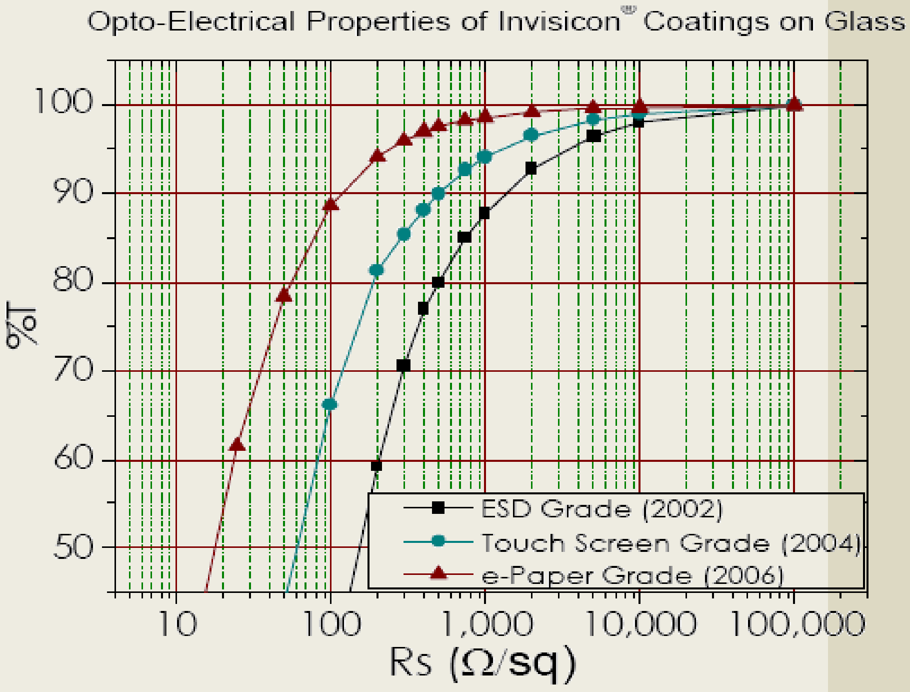
5.1. Electronic devices

TFT (Thin film transistors) for flexible display

Optical performance: visible transmittance of ITO, PEDOT and CNT film



Optical performance of CNT TFT



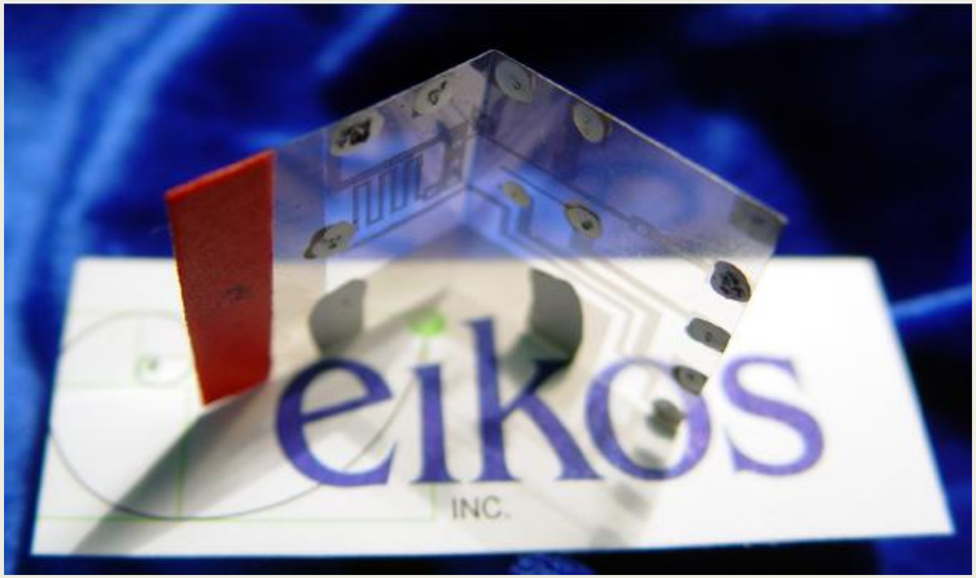
Ref. Veritas et Visus, “Touch Panel”, 1 (2006) 34

5. Applications of CNTs

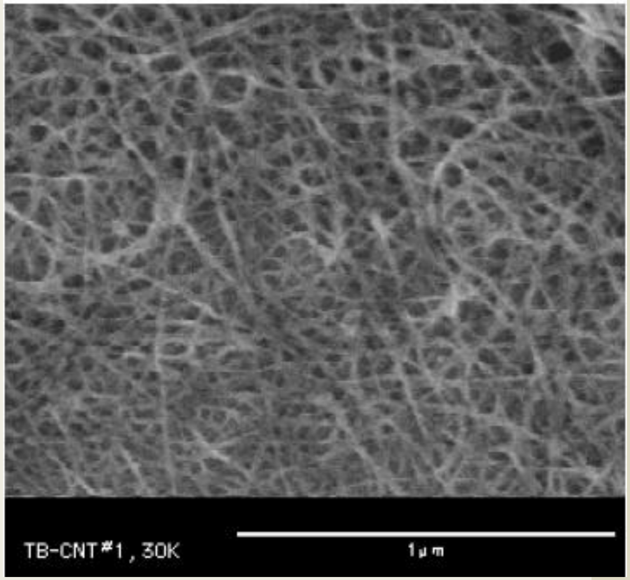
5.1. Electronic devices

TFT (Thin film transistors) for flexible display

Invisicon® Flexible, Transparent Circuits from Eikos



SEM Micrograph of CNT-TFT

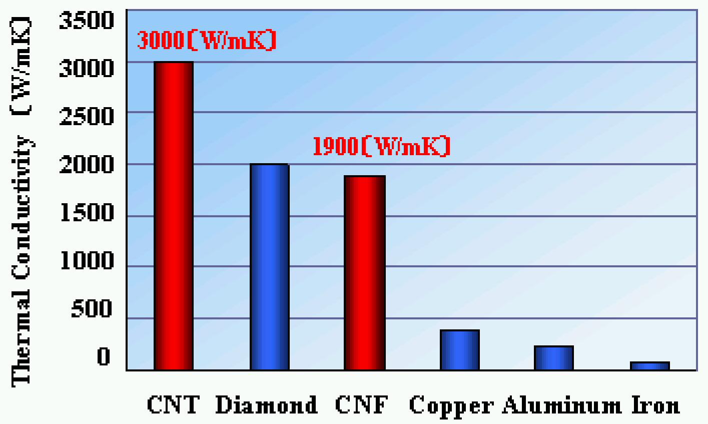


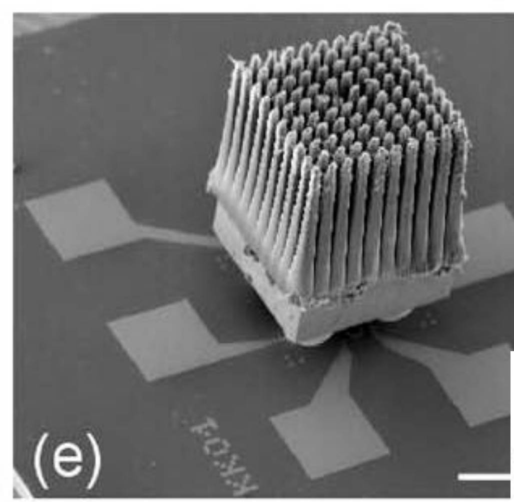
Ref. www.eikos.com

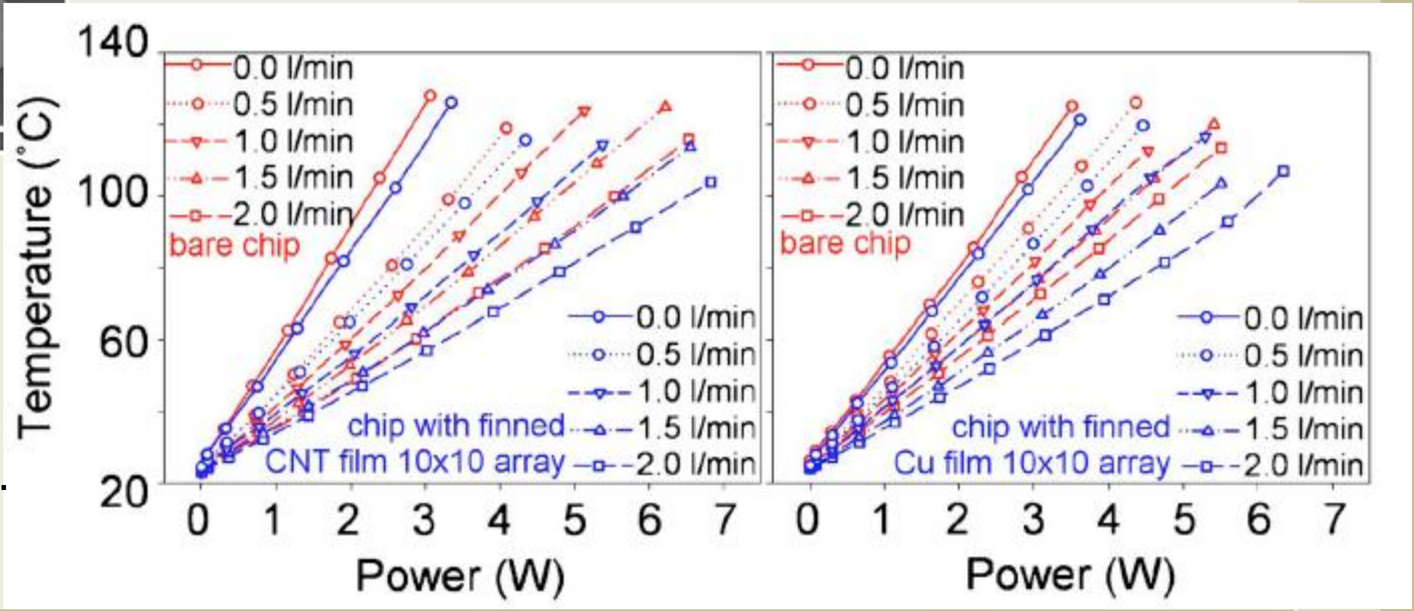
5.1. Electronic devices

Onchip thermal management

The comparison of the thermal conductivity of CNT with the best thermally conducting materials
(Ref. Web site from M. Endo group)





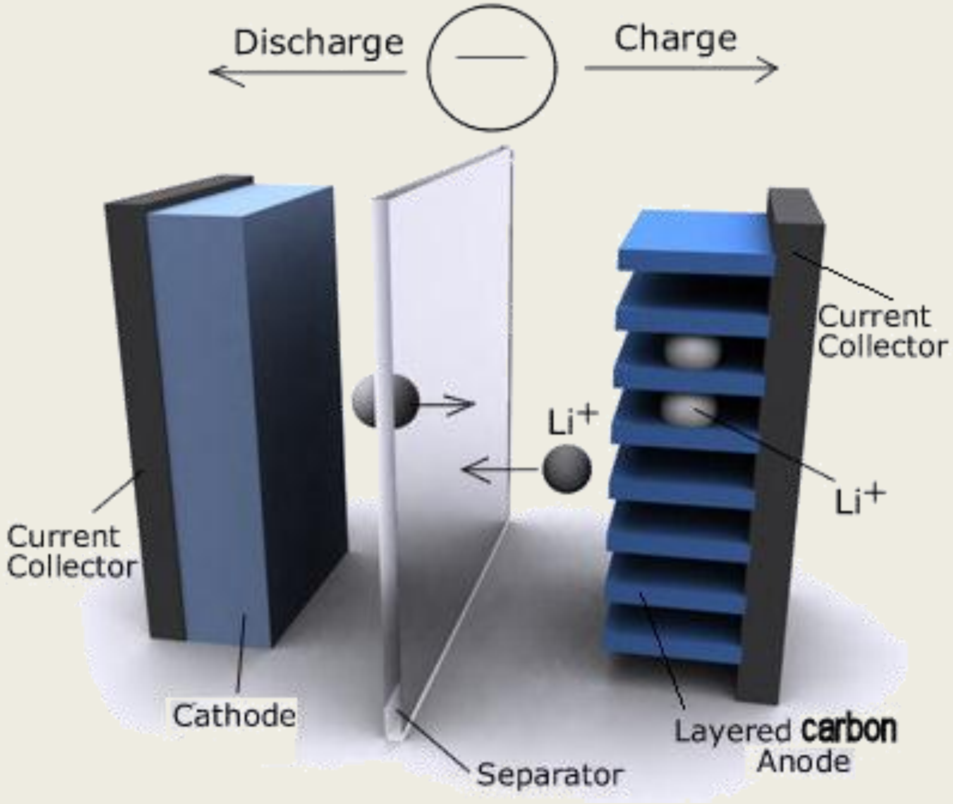


Ref.
P.M.Ajayan, Appl. Phys. Lett. 90 (2007) 123105

5.2. Energy applications

Lithium-ion batteries

Components

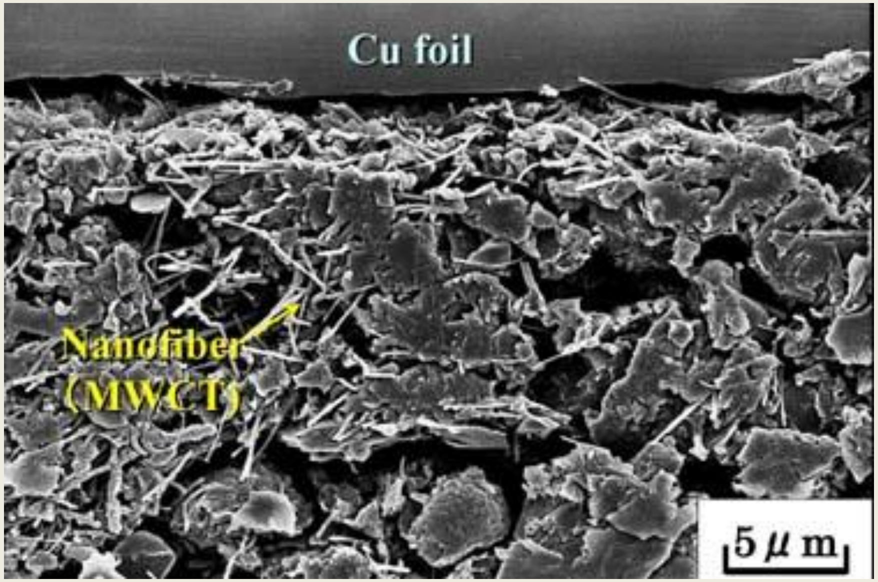


<Mechanism> $\mathrm{LiCoO_2 + C \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Li_{1-x}CoO_2 + Li_xC}$

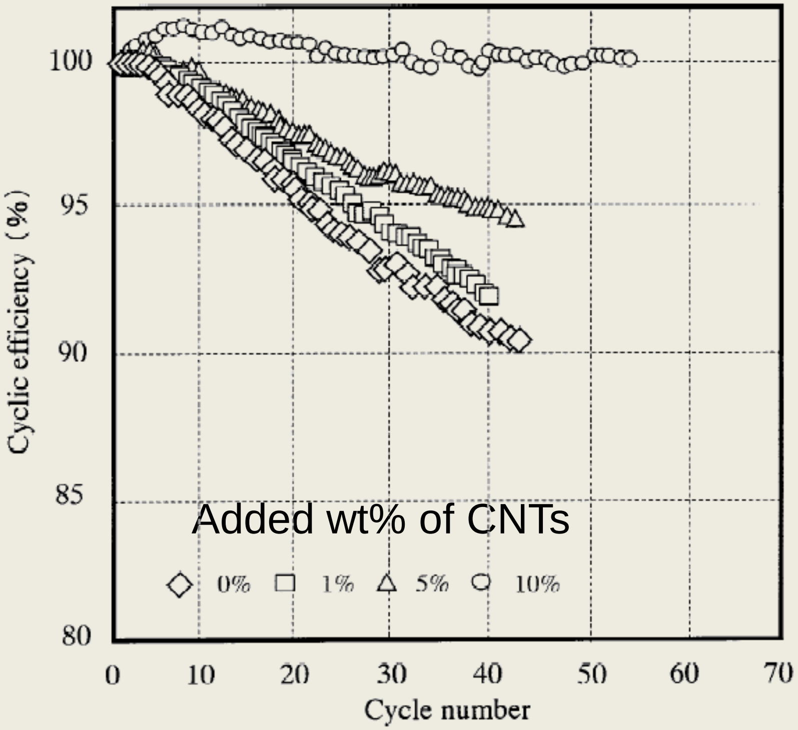
5.2. Energy applications

Lithium-ion batteries

FE-SEM micrographs of the anode sheet containing CNFs/CNTs in a Li-ion battery



The cyclic efficiency for samples with various wt% CNTs



Ref. M. Endo, et.al., *Carbon* **39** (2001) 1287

5.2. Energy applications

Fuell cells

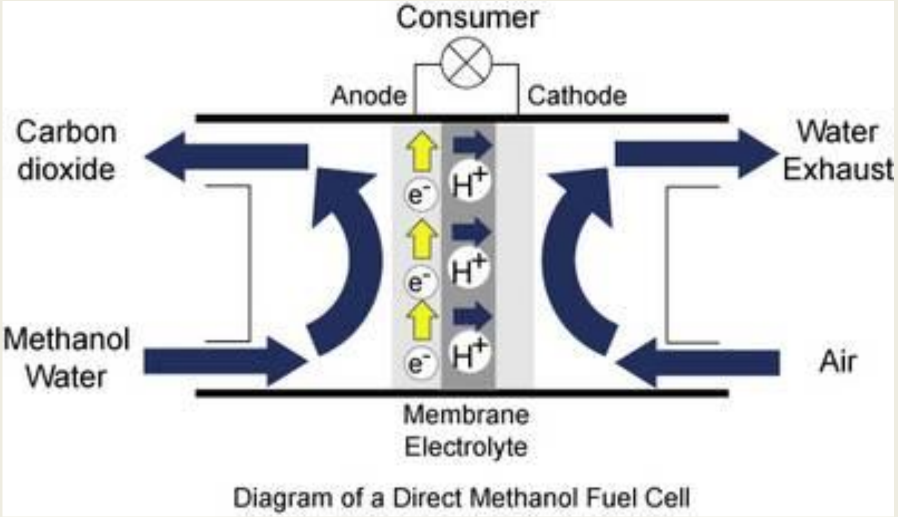
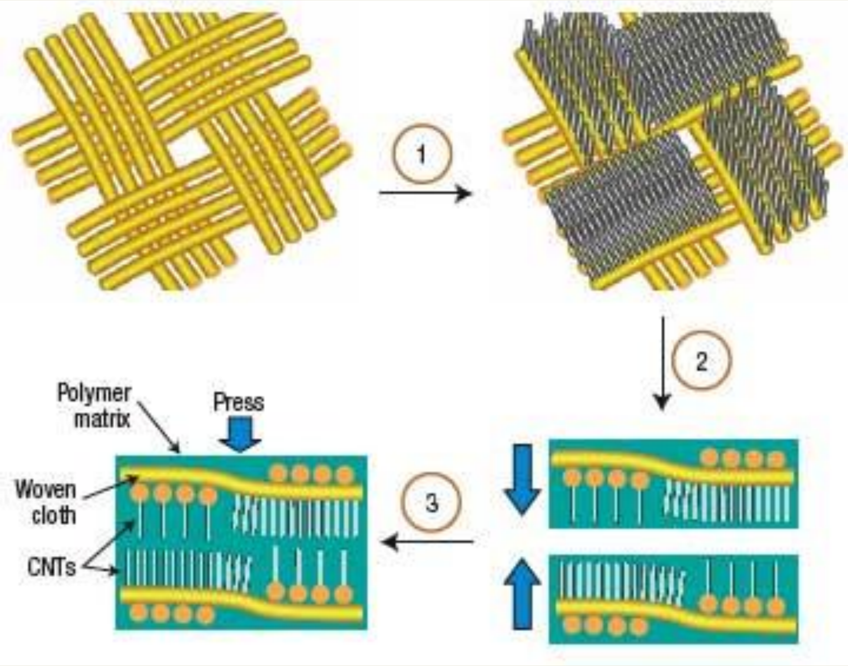


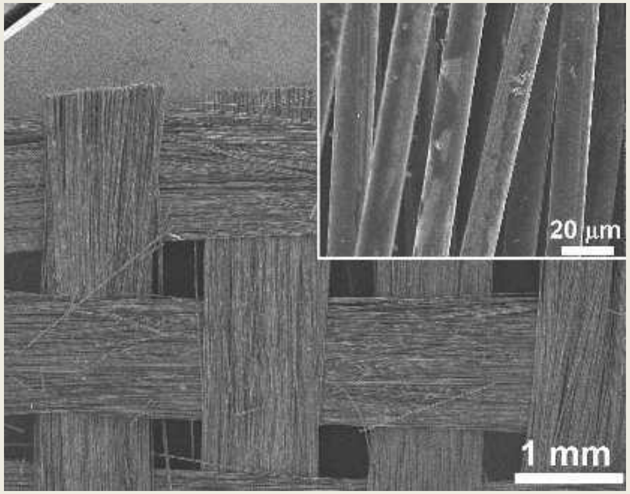
Diagram of a Direct Methanol Fuel Cell

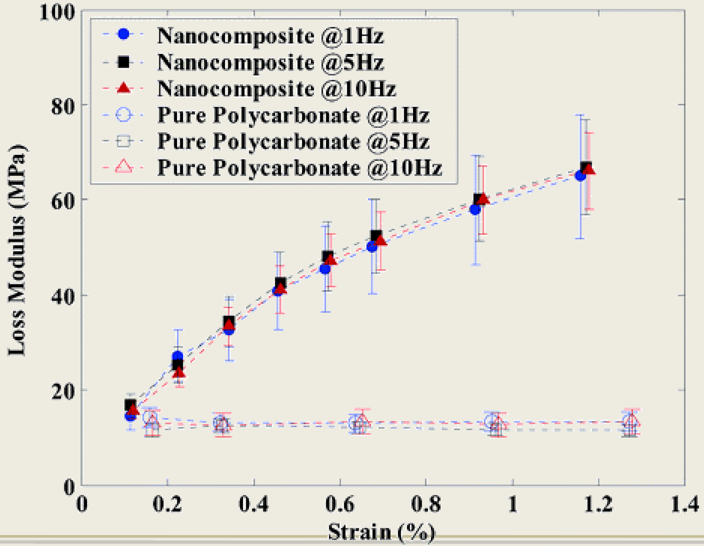
5. Applications of CNTs

5.3. Mechanical applications

CNT-filled polymer composites

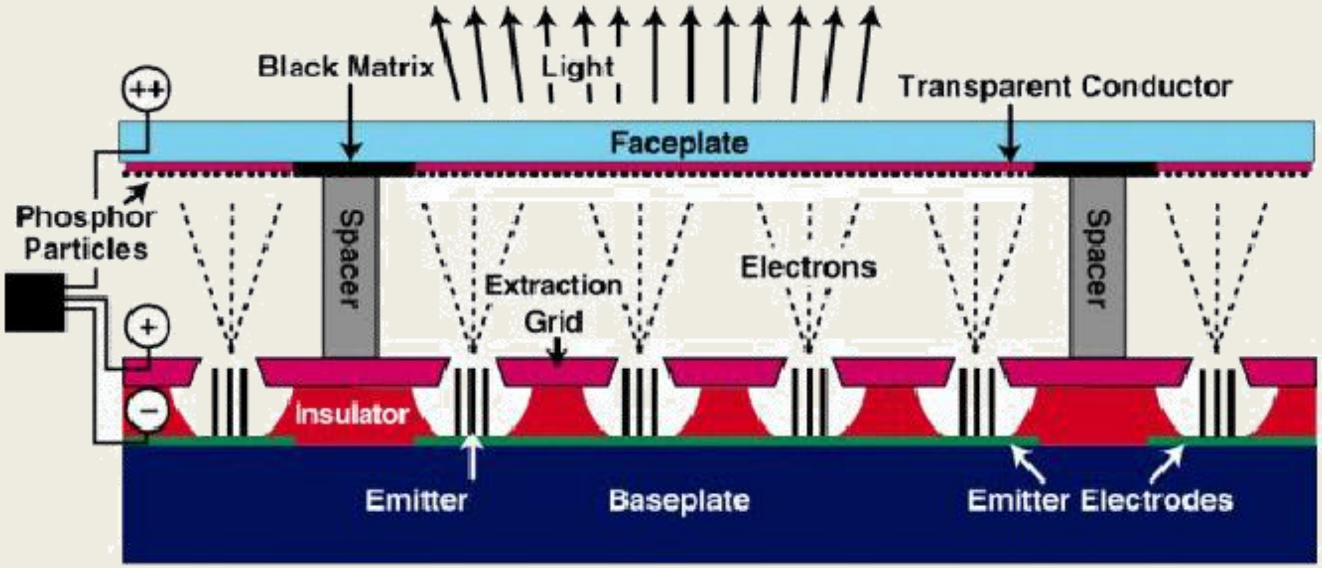






Ref. P.M.Ajayan, et.al., *Nature Mater.* **5** (2006) 457

5.4. Field emission display

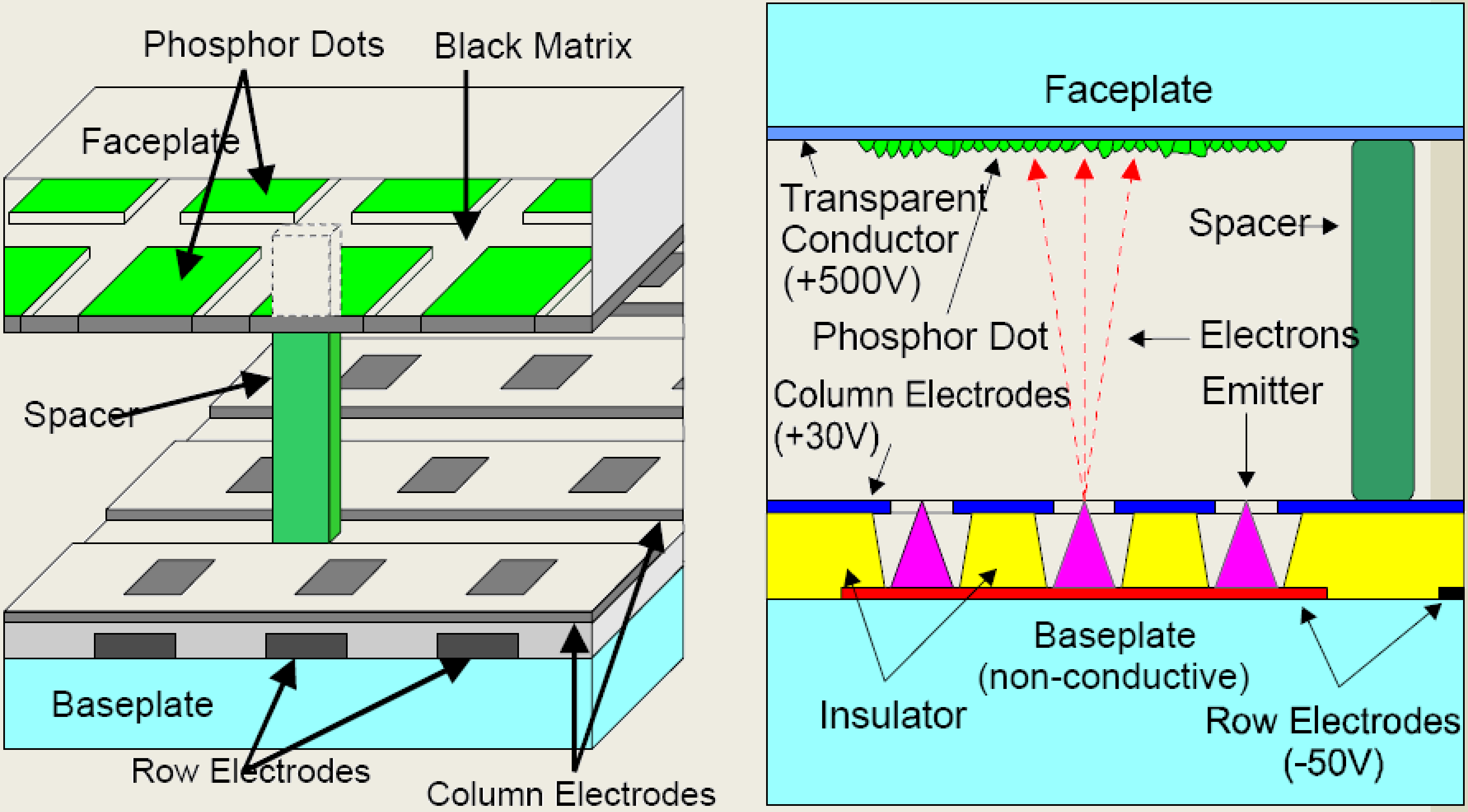


- Mechanism of the electron emission is basically similar to that of a lightning rod: the sharp tips center the electrons and make the possible of electron emission.
- When the Gate and the Emitter are supplied with voltage electrons are released, and when intense electric field is applied into the space between the two glasses electrons are accelerated and retain high kinetic energy.
- The accelerated electrons hit the phosphors inside the anode plate and emit light.

Ref. http://www.samsungsdi.co.kr

5.4. Field emission display

Structure of FED



5.4. Field emission display

- Low threshold voltage
  good emission stability → preferred field emitters
  long emitter lifetime

- Electron relaxation process (SWNTs)
  : fabrication of cathode-ray lighting elements and flat panel displays
  : 4.5" diodetype flat panel display using arc-based SWNTs
  : simply degraded at high emission current

- DWNTs or thin MWNTs
  : best field emitting materials
  : low threshold voltage comparable to SWNTs
  : better structural stability compared to SWNTs, almost comparable to MWNTs

- Doping of nanotubes
  : B-doped MWNTs – enhanced field emission compared to pure carbon MWNTs
  : presence of B atoms at the nanotube tips
  → increase density of state close to the Fermi level
  : N-doped MWNTs – emit electrons at relatively low turn-on voltages
  high current density
  excellent field emission properties

5. Applications of CNTs

- Research is moving forward in the field of fabrication methods, but there are still several remaining issues. For example, we still cannot control the chirality of the tube, which determines the electrical property of CNT.

- In the future, we will see the establishment of large-scale synthesis of carbon nanotubes as well as an acceleration in research targeting their applications.

- Without doubt, carbon nanotubes represent a material that offers great potential, bringing with it the possibility of breakthroughs in a new generation of devices, electric equipment and bio fields.