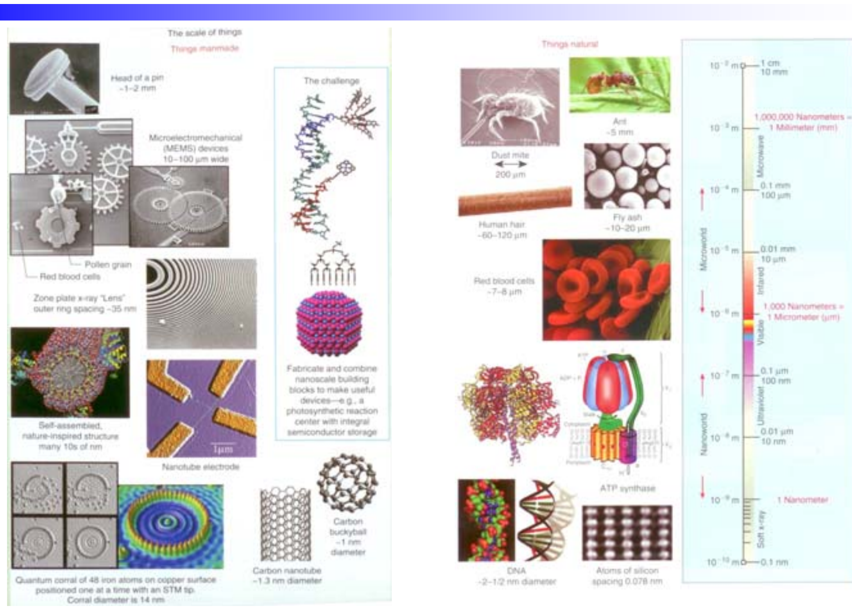
Chapter 13

Functional Nanomaterials (2D, 1D, and 0D)

Pure or doped **highly anisotropic** **crystalline** metals, semiconductors or insulators with a lateral dimension of 5-100nm

1. **Growth mechanism and processes**
2. **Structure: directionality and epitaxy**
3. **Organization and Assembly**

Manmade vs Nature



Motivation

Small size, low dimensionality and high surface to bulk ratio make nanowires ideal for many technological applications

- Electronics: transistors
- Photonics: lasers,
- LEDs
- Sensors: chemical, biological, photon, motion, etc.
- Nanoprobes for SPM
- Catalysis, filters, exotic devices….

Tools for studying nanowires:

- Microscopy: SEM, TEM, AFM and STM

- Spectroscopy: infra-red, X-ray diffraction, X-ray photoemission

1. Growth methods

Two approaches

Top-down

Patterning in bulk materials by combination of

Lithography

Etching

Deposition

- can be applied for variety of materials

- limited by lithography resolution, selectivity of etching, etc.

Bottom-up

Structure is assembled from well-defined chemically or physically synthesized building blocks

Self-assembly

Selective growth

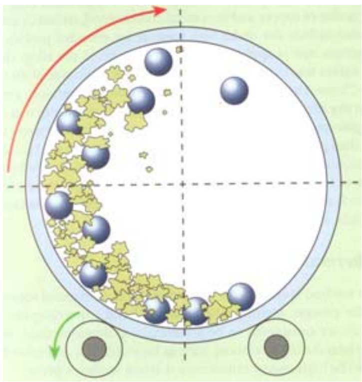
- require accurate control and tunable chemical composition, structure, size and morphology of building blocks

- in principle limited only by atomic dimensions

Mechanical Methods (Mechanosynthesis)

Low cost fabrication: ball milling or shaker milling

Kinetic energy from a rotating or vibrating canister is imparted to hard spherical ball bearings (under controlled atmosphere)



(1) Compaction and rearrangement of particles

(2) First elastic and then severe plastic deformation of the sample material ⇒ formation of defects and dislocations

(3) Particle fracture and fragmentation with continuous size reduction ⇒ formation of nanograined material

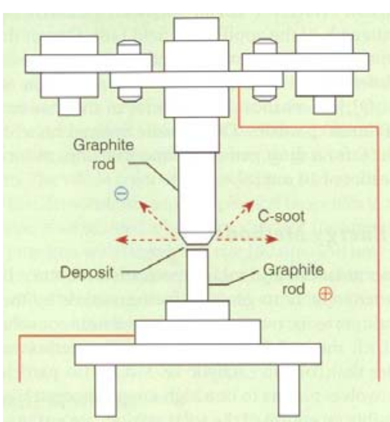
$$K_{IC} = Y\sigma_F\sqrt{\pi a} \qquad \sigma_F \sim \frac{1}{Y}\sqrt{\frac{K_{IC}}{a}} \sim \sqrt{\frac{\gamma E}{a}}$$

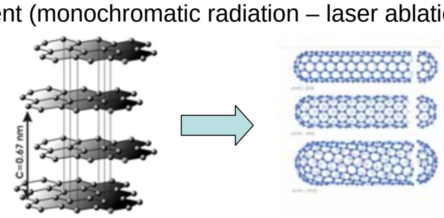
σ_F – stress level, when crack propagation leads to fracture; γ - surface energy of the particle; a - length of a crack

-material with defects with a wide distribution of size

High-Energy Methods: Discharge Plasma Method

Application of high energy electric current (monochromatic radiation – laser ablation)





Can be used for fullerenes and C nanotubes

Process depend on:

-Pressure of He, process temperature, applied current

final product requires extensive purification

Chemical Fabrication Methods

Anodizing (and electropolishing)

Insulating porous oxide layer is created on a conductive metal anode in electrolytic solution

Anodic reaction $2Al^0_{(s)} \rightarrow 2\ Al^{3+} + 6e$

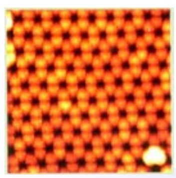
Oxide-electrolyte interface $2\ Al^{3+} + 3H_2O \rightarrow 2\ Al_2O_3 + 6H^+$

Cathodic reaction $6H^+ + 6e \rightarrow 3\ H_2\ (g)$

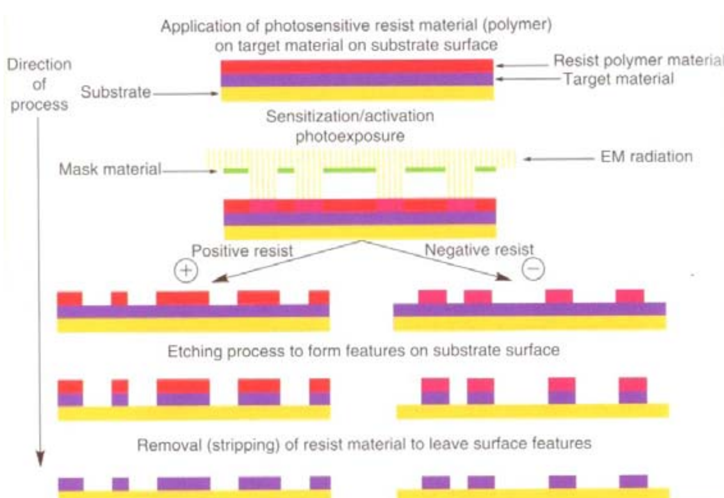
Overall oxide formation reaction:

$$2Al^0_{(s)} + 3H_2O \rightarrow Al_2O_3 + 3\ H_2$$

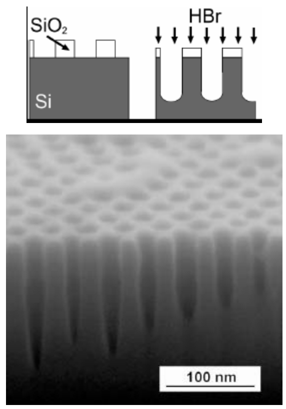
Porous Al_2O_3 membranes can be considered as ultimate template material



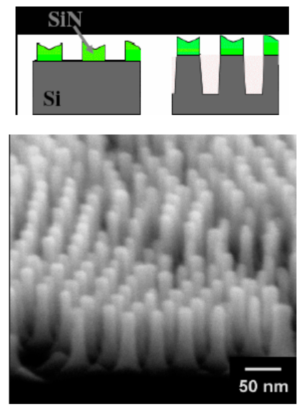
Lithographic Methods



Top-bottom: High-Aspect Aspect-Ratio Si Structures



nanotextured Si surface



dense silicon pillar array

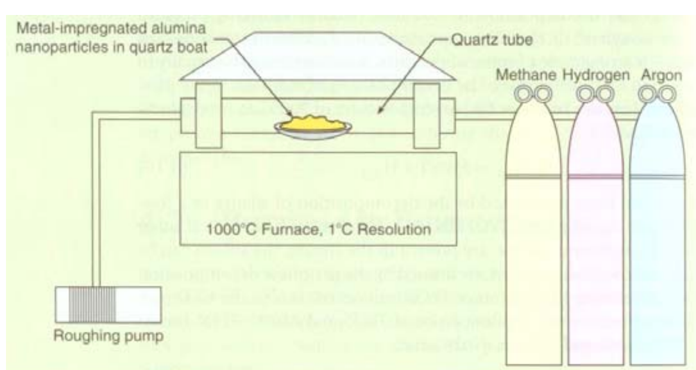
Bottom-Up Fabrication: Gas Phase Methods

Chemical Vapour Deposition

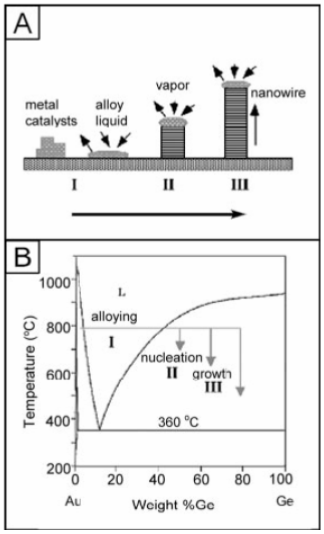
CH_4 (g) → SWNT + H_2 (g)   ~ 700°C, Fe, Ni catalysts

SiH_4(g) → Si + 2 H_2 (g)

$Si(OC_2H_5)_4$ (g) → SiO_2(s) + $(C_2H_5)_2O$ (g)



Bottom-up: vapor-liquid-solid growth

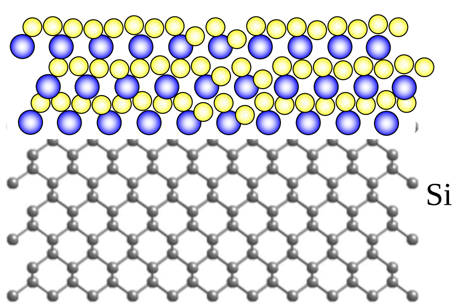


VLS growth of Ge NWsw/Au

- Metal particle catalyzed the decomposition of a gaseous species containing the semiconductor components, e.g. Ge, or Ga and As
- Metal catalyst particles absorb species, becoming saturated with them at eutectic point (relatively low temperature)
- When semiconductor reaches supersaturation, it precipitates out of the eutectic
- Metal prepared and deposited/grown on surface
- Metal droplet size determines eventual wire diameter

(from E. Garfunkel)

Atomic Layer Deposition



1. MCl_4 exposure
2. Purge
3. H_2O exposure
4. Purge $\Rightarrow$ MO_2 ML

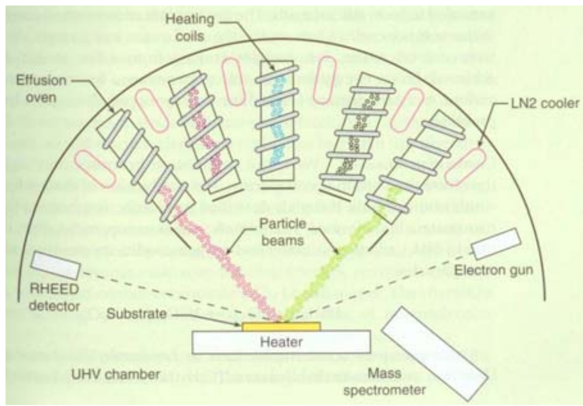
MCl_4(ads, surf) + 2 H_2O(g) $\rightarrow$ MO_2(s) + 4HCl(g)

$M(N(CH_3)(C_2H_5))_4$(ads, surf) + O_3(g) $\rightarrow$ MO_2(s) + …

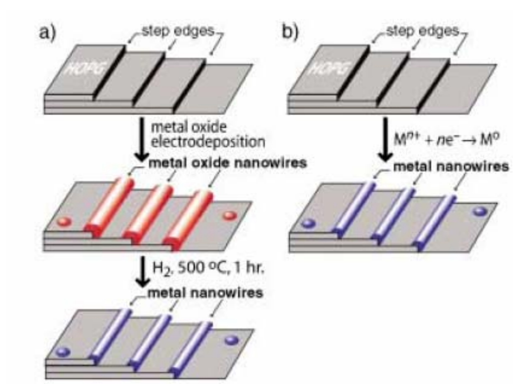
- Surface saturation controlled process
- Excellent film quality and step coverage

Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy – a single crystal film growth technique



Electrochemical step decoration

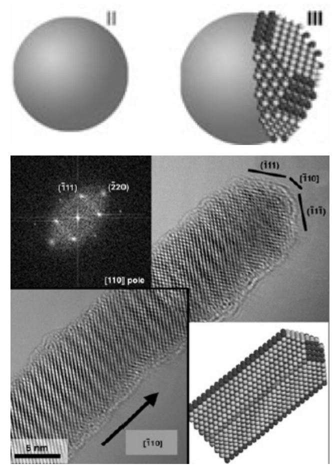


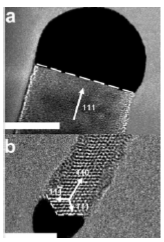
- minimization surface energy of the step
- metal oxide electrochemical deposition + reduction (H2)
- metal electrochemical deposition

2. Preferred crystallographic orientation

Proposed explanation:

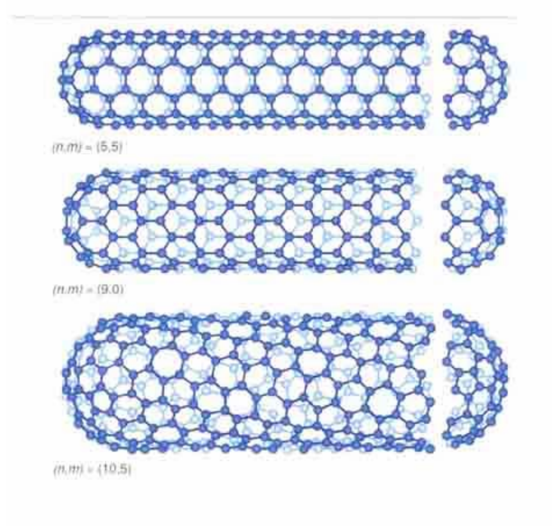
- For small diameter VLS nanowire, the surface energy minimization of the Si or Ge cap influences the Si NW nucleus structure and the growth direction during NW nucleation event
- Alternatively, Au/Si interface decides growth direction, <111> is favored for the lowest-free-energy (111) solid – liquid interface.





For <110> growth aixs, the solid-liquid interface is still (111), but surface energetics may drive the nucleation of a second (111) plane to enable <110> growth, which yields the lowest energy solid/vacuum interfaces

Structure of the carbon nanotubes

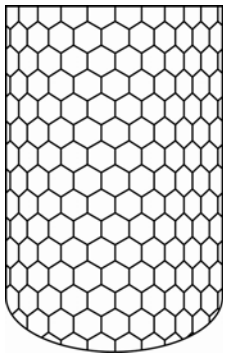


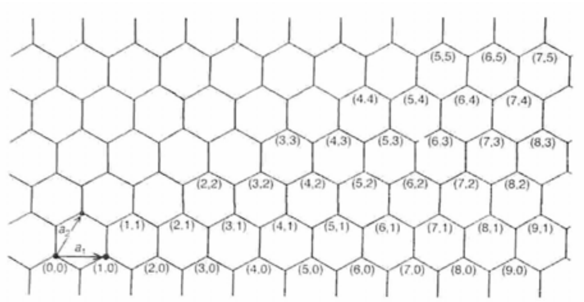
armchair

zig-zag

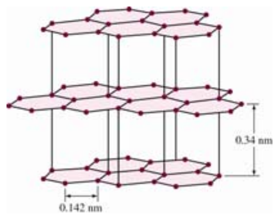
chiral

Carbon Nanotubes





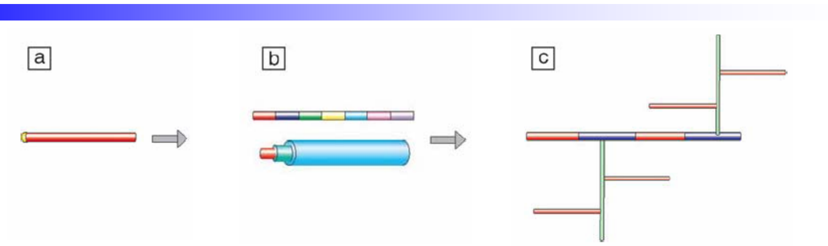
The structure can be specified by vector **(n, m)** which defines how the graphene sheet is rolled up



A nanotube with the indices (6,3): the sheet is rolled up so that the atom (0,0) is superimposed on the one labeled (6,3)

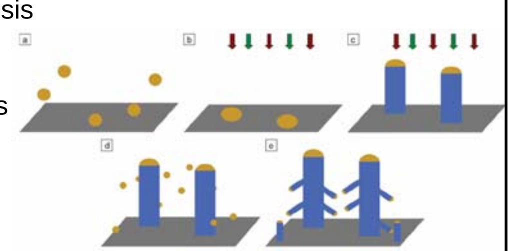
m = 0 for all zig-zag tubes, while n = m for all armchair tubes

3. Designed Synthesis of Hierarchical Structures



The evolution of nanowire structural and compositional complexity enabled today by controlled synthesis

(a) from homogeneous materials
(b) axial and radial heterostructures
(c) branched heterostructures



The colors indicate regions with distinct chemical composition and/or doping

Organization and Assembly of Nanowires

Using a patterned catalyst, NWs can be directly grown on a solid substrate in a designed configuration

NW materials produced under synthetic conditions optimized for their growth can be organized into arrays by several techniques

(1) electric - field – directed (highly anisotropic structures and large polarization)

(2) fluidic - flow – directed (passing a suspension of NWs through microfluidic channel structure)

(3) Langmuir–Blodgett (ordered monolayer is formed on water and transferred to a substrate)

(4) patterned chemical assembly or imprint

Imprint based patterning of metal nanoparticles