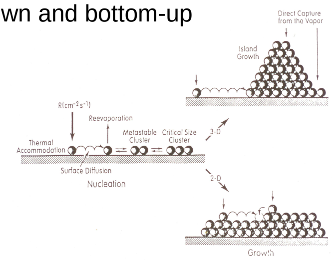
Lecture 14

Nucleation and growth of thin films and nanostructures

References:
1. Zangwill, Chapter 16
2. Luth, p.89-114
3. C.T. Campbell, Surf. Sci. Reports 27 (1997) 1-111
4. Kolasinski, Chapter 7



14.1 Thermodynamics and kinetics of thin film growth

What is a "thin film"?

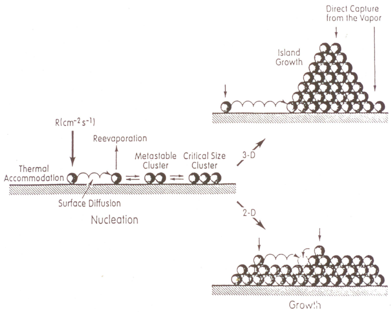
How thin films are different from the bulk materials?
Thin films may be:
- Lower in density (compared to bulk analog)
- Under stress
- Different defect structures from bulk
- Ultra-thin films (<10-20nm): quasi two dimensional
- Strongly influenced by surface and interface effects

Steps in thin film growth
- Separation of particles from source (heating, high voltage)
- Transport
- Condensation on substrate

Steps in film formation

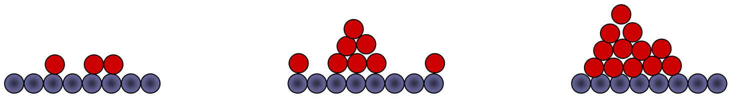
1. Thermal accommodation
2. Binding (physisorption and chemisorption)
3. Surface diffusion (typically larger than bulk diffusion)
4. Nucleation
5. Island growth
6. Coalescence
7. Continued growth

Nucleation and growth occurs on defects (or sites with higher bonding energy)

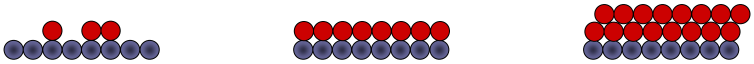


Three different growth modes

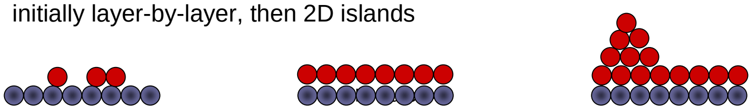
1. **Island growth (Volmer – Weber)**
   3D islands formation; film atoms more strongly bound to each other than to substrate and/ or slow diffusion



2. **Layer-by-layer growth (Frank – van der Merwe)**
   generally the highest crystalline quality; film atoms more strongly bound to substrate than to each other and/or fast diffusion

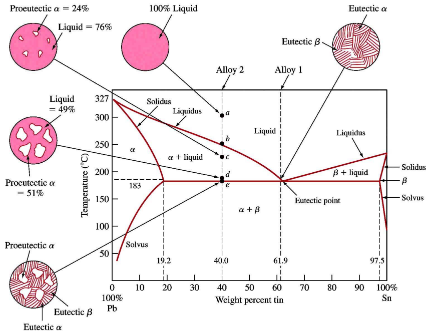


3. **Stranski – Krastanov (mixed growth)**
   initially layer-by-layer, then 2D islands



Thin film growth is not an equilibrium process!

1. Thermodynamics (Gibbs Free energy and phase diagram): can the sold phase be formed at the given temperature?



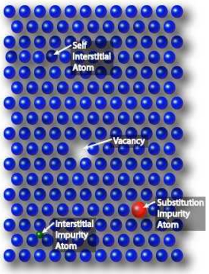
2. Kinetics (deposition rate and diffusion rate)

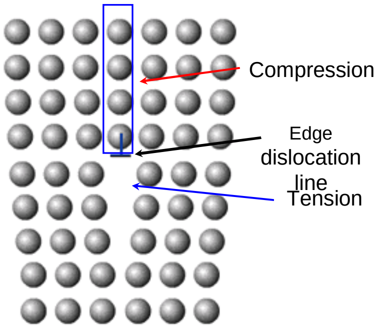
Artificial superlattice is the best example of manipulating kinetics and thermodynamics

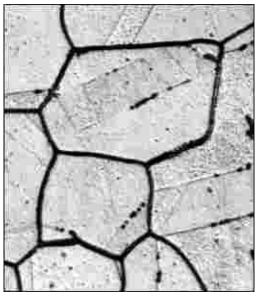
14.2 Defects in Films

Can be divided according to their geometry and shape

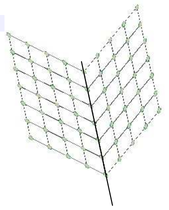
- 0-D or point defects
- 1-D or line defects (dislocations)
- 2-D and 3D (grain boundaries, crystal twins, twists, stacking faults, voids and precipitates)





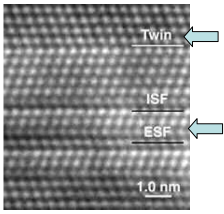


3D defects



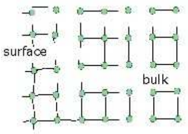
Crystal twins
Grain boundary is not random, but have a symmetry (ex.: mirror)

Stacking faults
fcc: …ABCABC…
…ABCABABCABC…



Crystal twin

Stacking fault



Voids the absence of a number of atoms to form internal surfaces; similar to microcracks (broken bonds at the surface)

Based on crystallinity:
amorphous; polycrystalline and epitaxal (single crystal)

14.3 Vacuum film deposition techniques

1. **Physical Vapour Deposition (PVD)**
   Evaporation: thermal and electron-beam assisted
   Sputtering: RF and DC Magnetron
   Pulsed Laser Deposition (PLD)

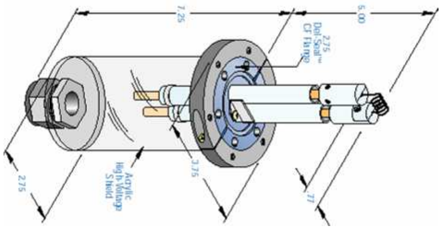
2. **Molecular Beam Epitaxy (MBE)**

3. **Chemical Vapour Deposition (CVD)**
   Plasma-Enhanced CVD (PE-CVD)
   Atomic Layer Deposition (ALD)

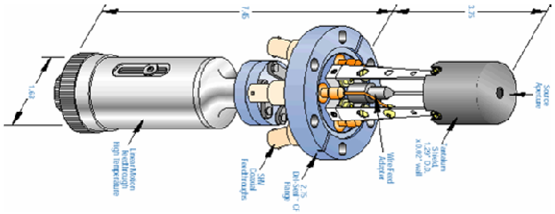
⇒ **Need good vacuum for thin film growth!**

14.3.1 Physical Vapour Deposition (PVD)

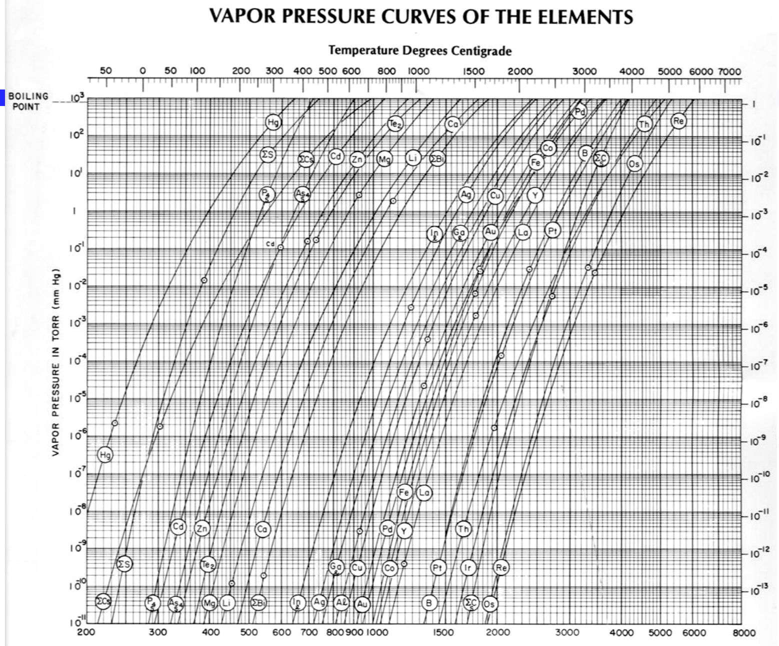
Thermal Evaporation for non-refractory materials



E-beam evaporation for refractory materials



http://www.mdc-vacuum.com

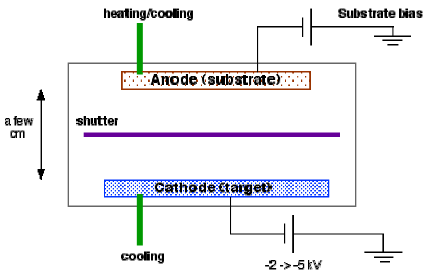


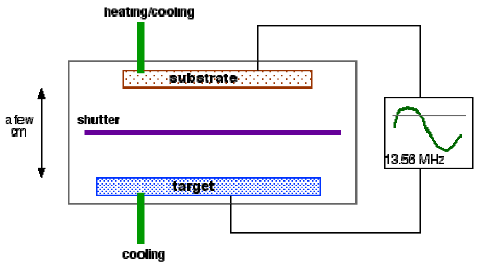
http://www.mcallister.com/vacuum.html – see a larger version attached in Appendix

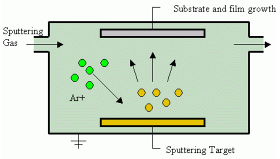
Sputtering Deposition

- DC for conducting materials
- RF for insulating materials

Magnetron sputtering is most popular due to high rate and low operation pressure

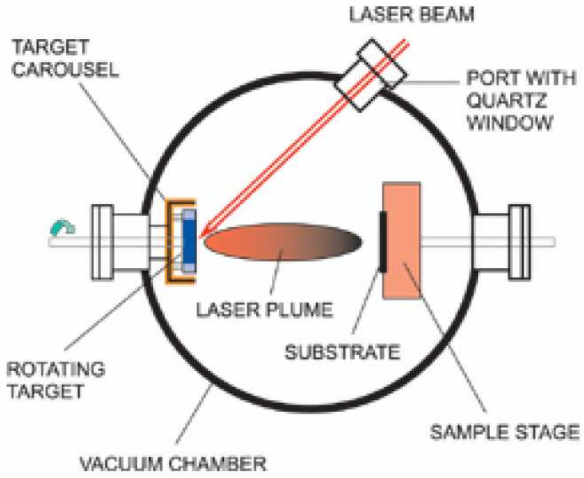






Pulsed Laser Deposition (PLD)

- Good for multielemental materials (P < 1 Torr)



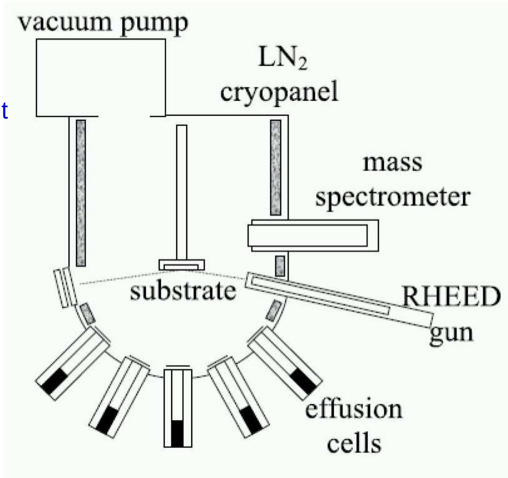
14.3.2 Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy
($p < 10^{-8}$Torr)

1. Elemental Superlattices: Giant Magneto-Resistiance (GMR) Devices

2. Binary III-V Superlattices

3. Complex Oxide Superlattices



Epitaxy

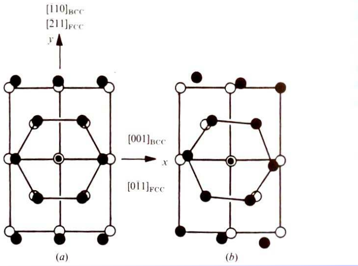
Epitaxy ("arrangement on") refers loosely to control of the orientation of the growing phase by the crystal structure of the substrate

homoepitaxy: host and growing phase are the same material
heteroepitaxy: host and growing phase are different

Orientation and Strain

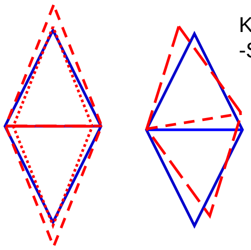
There exist orientational relations between dissimilar crystal lattices in contact (e.g., *fcc (111)/bcc (110); fcc (100) /rocksalt (100)*

Fig. 16.1. Overlay of an FCC(111) monolayer (filled circles) onto a BCC(110) substrate surface (open circles): (*a*) FCC [0$\bar{1}$1] parallel to BCC [001]; (*b*) 5.26° rotation relative to (*a*). The lattice constants of the two crystals are chosen to produce row-matching in the rotated case (Dahmen, 1982).



Nishiyama-Wasserman

Kurdjimov-Sachs



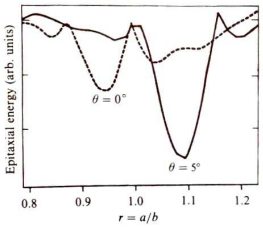
Zangwill, Ch.16

Epitaxial energy

NW: Θ = 0°, row-matching parallel to [001] bcc

KS: Θ = 5.26°, rotational epitaxy

Fig. 16.2. Model calculation of the total adsorbate–substrate interaction energy for rigid lattice FCC(111)/BCC(110) epitaxy as a function of the nearest neighbor distance ratio a/b for two angles of orientation relative to Fig. 16.1(a) (Ramirez, Rahman & Schuller, 1984).

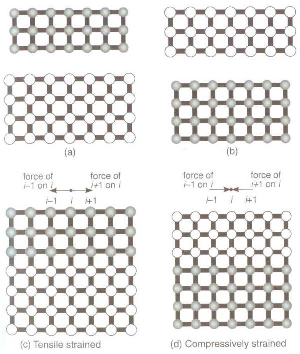


Epitaxial energy at interface calculated using Lennard-Jones pairwise 6-12 potential

Note minima for 0° and ~ 5°

E is indep. of r = a/b for other angles

Definition of misfit: $f = \dfrac{a-b}{a}$



(c) Tensile strained

(d) Compressively strained

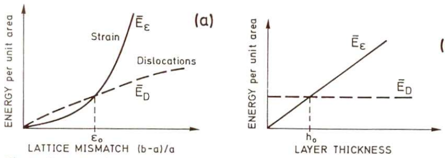
Heterointerface between 2 diff. crystals: the lattice mismatch is adjusted by **edge dislocations** or **strain**

Zangwill, Ch.16

Strained *vs* Dislocations

The type of interface (strained *vs* dislocations) depends on the *thickness of the film and lattice mismatch, f.*

The energy stored in an interface between epitaxial film and substrate is calculated from the relative contributions of elastic strain (deformation of the lattice of the film) and formation of edge dislocations



Left: film thickness = const.

Right: misfit = const.

Fig.3.16a,b. Qualitative plots of lattice energy stored at a crystalline hetero-interface per unit area: (**a**) as a function of lattice mismatch; beyond a critical lattice mismatch ϵ_0 (a and b are the lattice constants of the two materials) the adjustment of the two lattices by dislocations (*broken line*) is energetically more favorable than by strain (energy $\bar{E}_D < \bar{E}_\epsilon$), (**b**) as a function of overlayer thickness; for thicknesses exceeding the critical thickness h_0 dislocations are energetically more favorable than strain (energy $\bar{E}_D < \bar{E}_\epsilon$)

Often, **pseudomorphic growth** is found for the first monolayer or so in metals on metals (i.e., overlayer adopts atomic arrangements of substrate)

As film thickness ⇑, complexities develop….

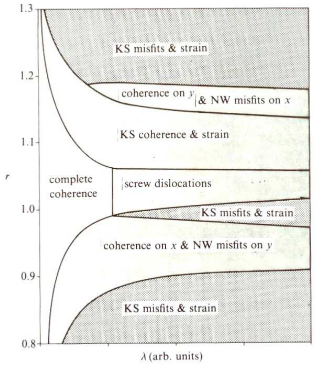
Structural phase diagram

We can illustrate the complexity of growth in the case of *fcc(111)/bcc(110)* inteface in plot of *r vs* λ

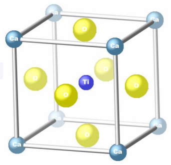
$$r = \frac{a}{b}$$

$$\lambda = \frac{\text{coupling strenth within film}}{\text{interlayer coupling strenth}}$$

Fig. 16.4. Structural phase diagram of an FCC(111)/BCC(110) bicrystal as a function of geometrical (r) and energetic (λ) parameters of the system. Dark shading denotes regions of one-dimensional coherence. Light shading denotes regions where all coherence with the substrate is lost. See text for discussion (Stoop & Van der Merwe, 1982).



Superlattices grown by MBE



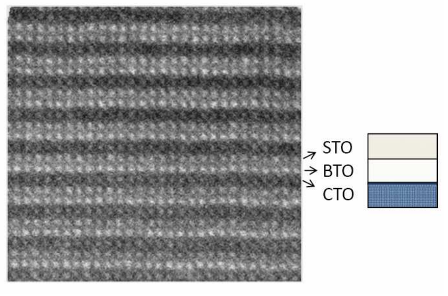
Complex oxides are not that complex: many of them are based on the ABO_3 cubic perovskite structure

Ex.:: $SrTiO_3$, $LaTiO_3$, $LaMnO_3$, $LaAlO_3$, …

⇒ Favorable to atomically smooth layered heterostructures

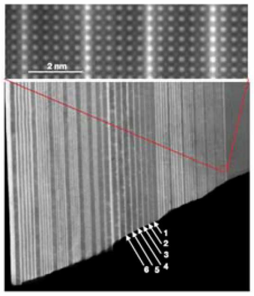
ABO_3
A: M^{2+} (Ca, Sr, Ba, La)
B: M^{4+} (Ti, Zr, Mn)

$SrTiO_3/BaTiO_3/CaTiO_3$



M. Warusawithana, J. Zuo, H. Chen and J. N. Eckstein

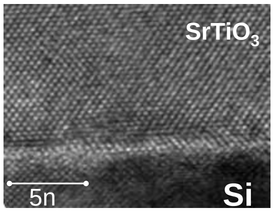
$LaTiO_3/SrTiO_3$ (PLD)



A. Ohtomo, H. Y. Hwang, *Nature* 419, 378 (2002)

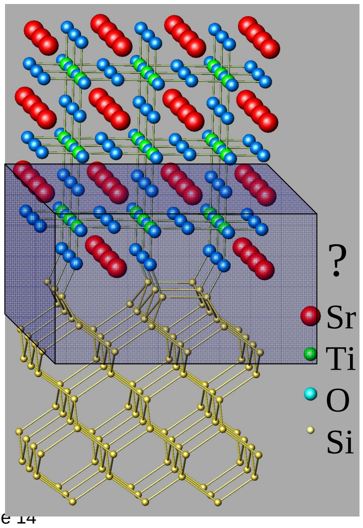
Epitaxial oxide material integrated with Si

1. Sc_2O_3/Si(111)
2. $SrTiO_3$/Si(001)



- Epitaxial structures may afford controllable interfaces (no dangling bonds…)
- Demonstration of interface stability and identification of potential stability problems under oxidizing/reducing conditions

Epitaxial *vs* amorphous or polycrystalline



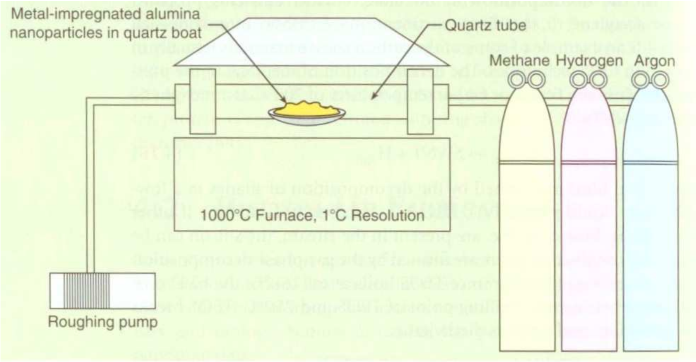
14.3.3 Chemical Vapour Deposition (CVD)

Precursors are needed!

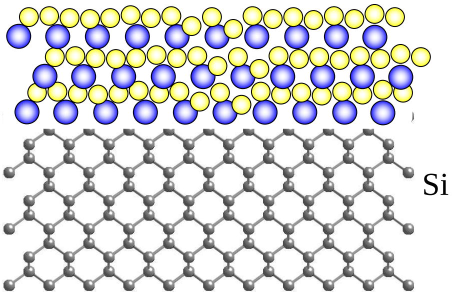
CH_4 (g) → SWNT + H_2 (g) ~ 700^{o}C, Fe, Ni catalysts

SiH_4(g) → Si + 2 H_2 (g)

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



14.3.4 Atomic Layer Deposition



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

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

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

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

14.4 Nanomaterials growth methods

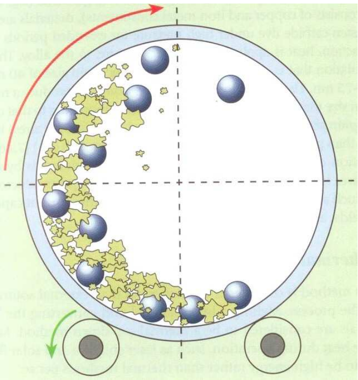
Two approaches

Top-down	Bottom-up
Patterning in bulk materials by combination of	Structure is assembled from well-defined chemically or physically synthesized building blocks
Lithography Etching Deposition	Self-assembly Selective growth
- can be applied for variety of materials	- require accurate control and tunable chemical composition, structure, size and morphology of building blocks
- limited by lithography resolution, selectivity of etching, etc.	- 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

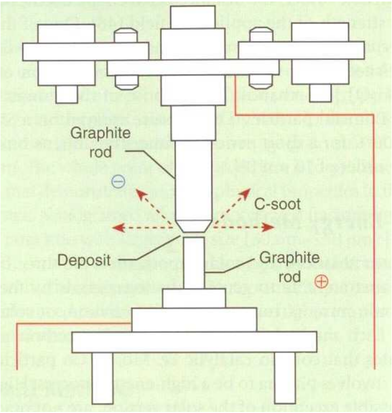
$$K_{IC} = Y\sigma_F\sqrt{\pi a} \qquad \sigma_F \sim \frac{1}{Y}\sqrt{\frac{K_{IC}}{a}} \sim \sqrt{\frac{\gamma E}{a}}$$

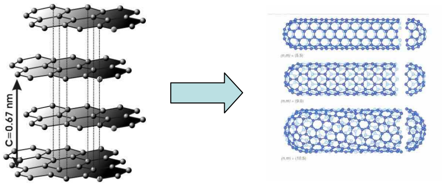
σ_F – stress level, when crack propagation leads to fracture; γ - surface energy of the particle; a - length of a crack

-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)





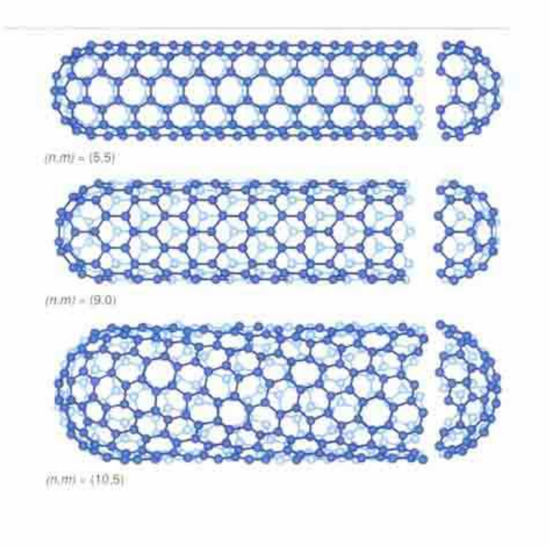
Can be used for fullerenes and C nanotubes

Process depend on:

-Pressure of He, process temperature, applied current

final product requires extensive purification

Structure of the carbon nanotubes

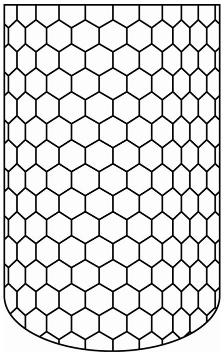


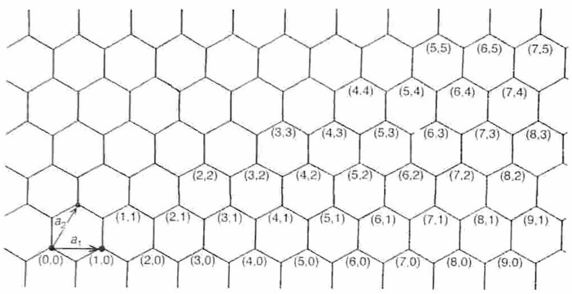
armchair

zig-zag

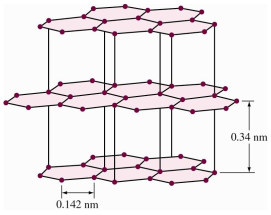
chiral

Carbon Nanotubes





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

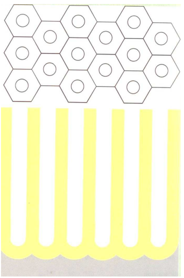


A nanotube with the indices (6,3): the sheet is rolled up so that the atom (0,0) is superimposed on the one labeled (6,3)

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

Chemical Fabrication Methods

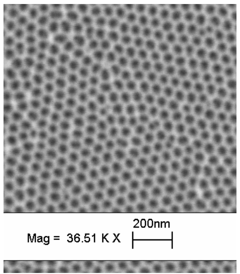
Anodizing (and electropolishing)
Insulating porous oxide layer is created on a conductive metal anode in electrolytic solution



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:

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



by J.Liu

Porous Al_2O_3 membranes can be considered as ultimate template or mask material

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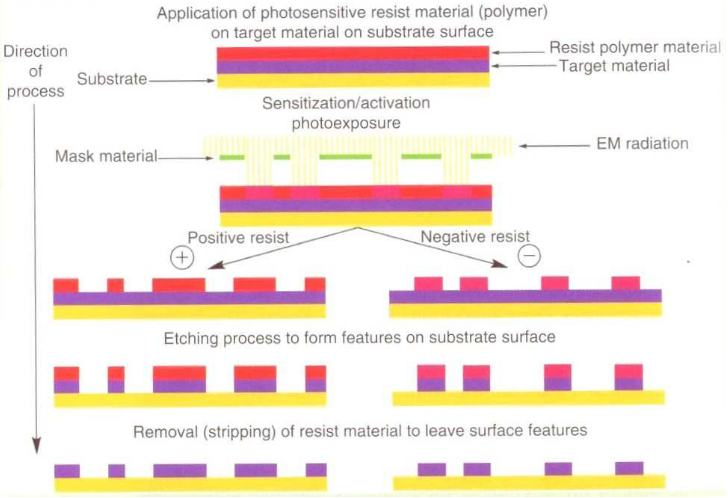
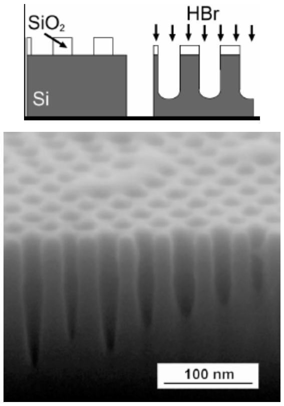
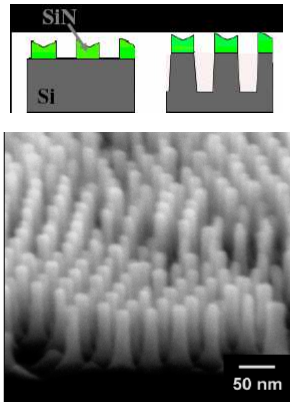
Lithographic Methods



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

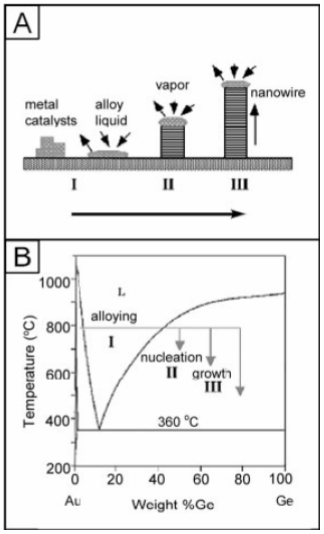


nanotextured Si surface



dense silicon pillar array

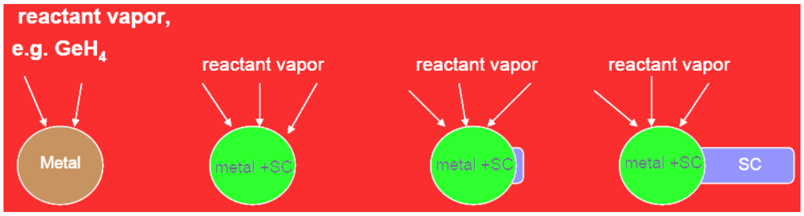
Bottom-up: vapor-liquid-solid growth



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

Cartoon of growth

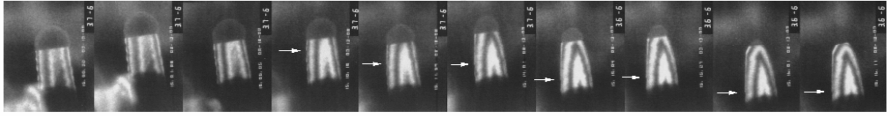


Metallic catalyst nanocluster

Eutectic (AuGe alloy) Temperature is controlled to keep it in the **liquid** state

Nanowire nucleation begins when the liquid become saturated with Ge

Nanowire growth continues as long as Au-Ge alloy stays liquid and Ge concentration is high enough



Au catalyzed growth of Si nanowire: Wire tapers off as Au is consumed in the reaction

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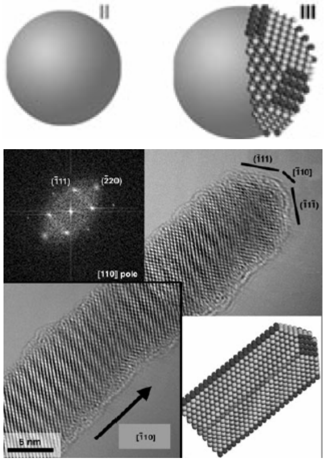
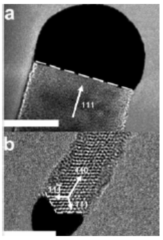
Preferred crystallographic orientation

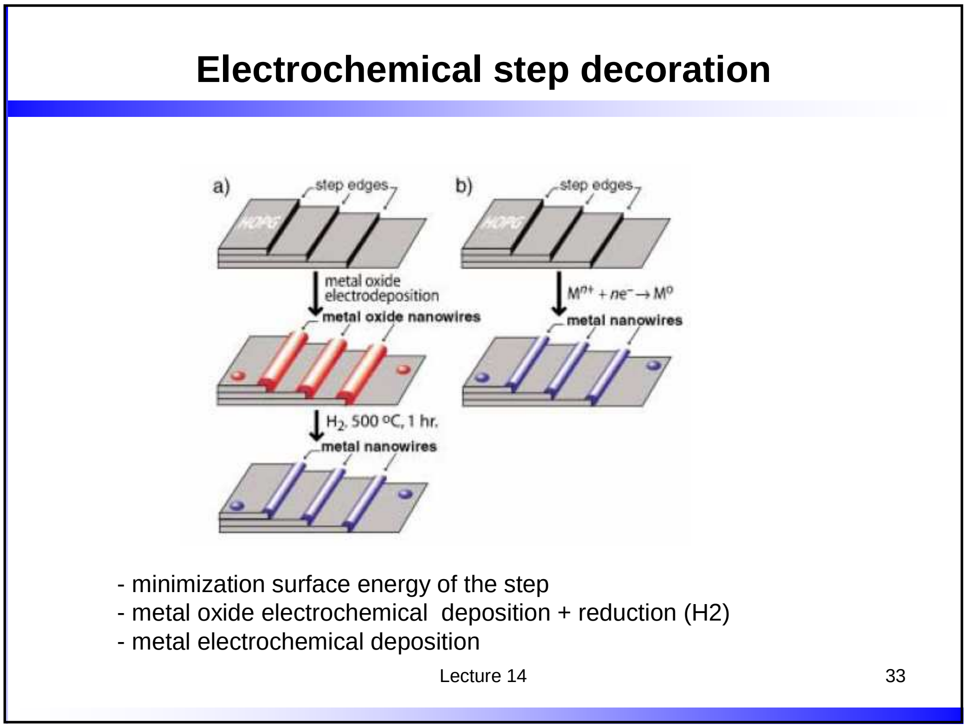
Proposed explanation:

- 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.



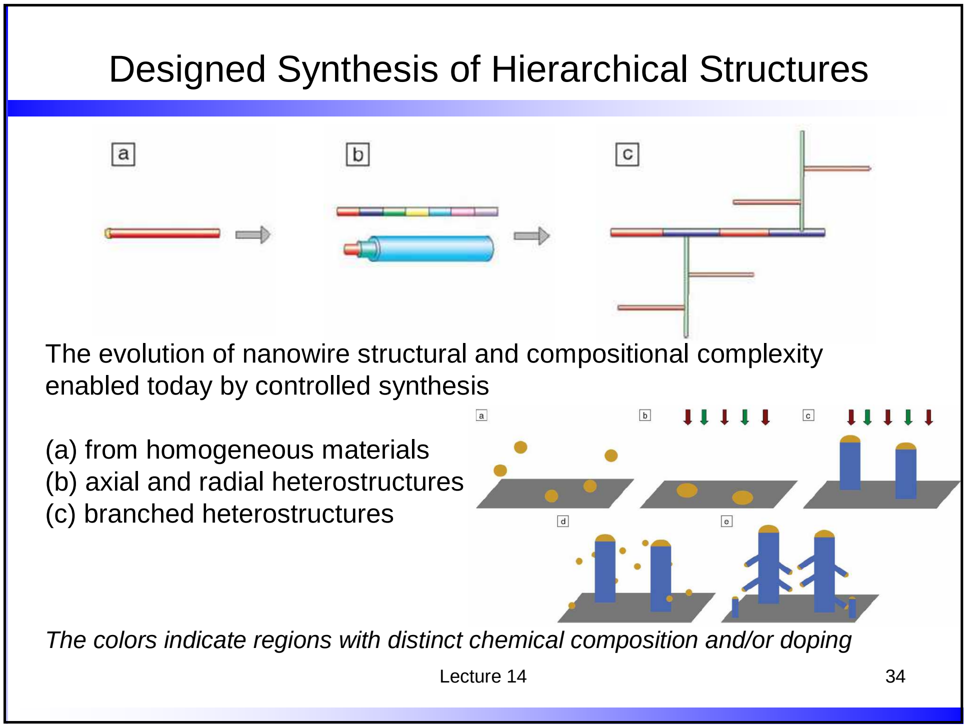


For <110> growth aixs, the solid-liquid interface is still (111), but surface energetics may drive the nucleation of a second (111) plane to enable <110> growth, which yields the lowest energy solid/vacuum interfaces



Electrochemical step decoration

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



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

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

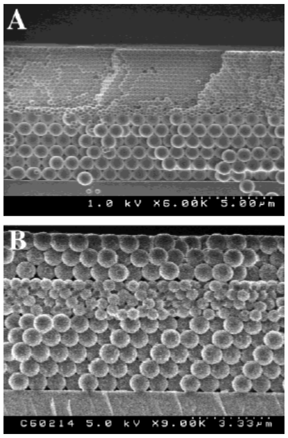
(1) electric - field – directed (highly anisotropic structures and large polarization)

(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) isothermal heating evaporation induced self-assembly (IHEISA) of spheres on a planar substrate

(5) patterned chemical assembly or imprint



S.Wong, V.Kitaev, G.A. Ozin, JACS 125 (2003) 15589

Imprint based patterning of metal nanoparticles