

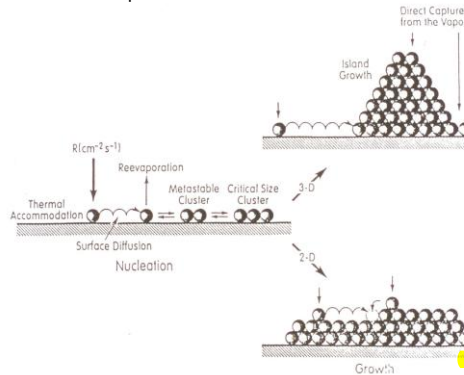
Lecture 6

Nucleation and growth of thin films and nanostructures

- 6.1 Thermodynamics and kinetics of thin film growth
- 6.2 Defects in films; amorphous, polycrystalline and epitaxial films
- 6.3 Nanomaterials growth approaches: top-down and bottom-up.
- 6.4 Capillary model of nucleation
- 6.5 Homogeneous nucleation kinetics
- 6.6 Epitaxy
- 6.7 Film deposition techniques
 - 6.7.1 Physical Vapour Deposition (PVD)
 - 6.7.2 Molecular Beam Epitaxy (MBE)
 - 6.7.3 Chemical Vapour Deposition (CVD)

References:

- 1) Zangwill, Chapter 16
- 2) Luth, p.89-114
- 3) Yates, pp. 627-668
- 4) Kolasinski, Chapter 7



6.1 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

Detailed 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

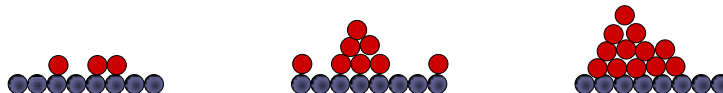
Nucleation and growth occurs on defects (or sites with higher bonding energy)

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Three different growth modes

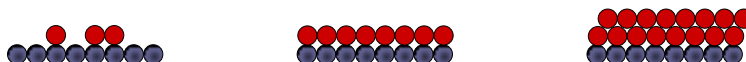
1. Island growth (Volmer – Weber)

3D islands formation; film atoms more strongly bound to each other than to substrate and/ or slow diffusion



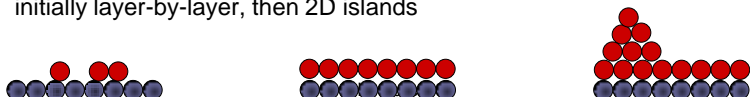
2. Layer-by-layer growth (Frank – van der Merwe)

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)

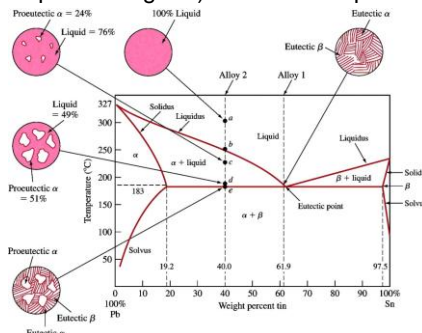
initially layer-by-layer, then 2D islands



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Thin film growth is not an equilibrium process!

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



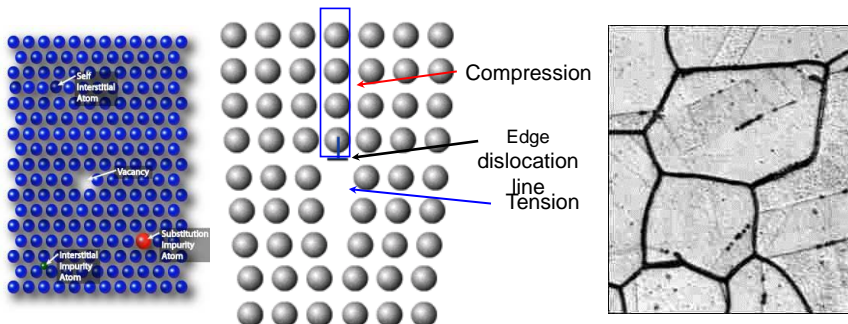
2. Kinetics (deposition rate and diffusion rate)

Artificial superlattice is the best example of manipulating kinetics and thermodynamics

6.2 Defects in Films

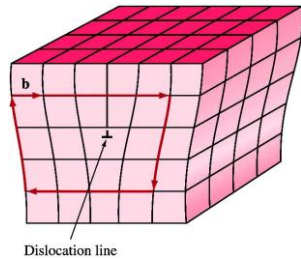
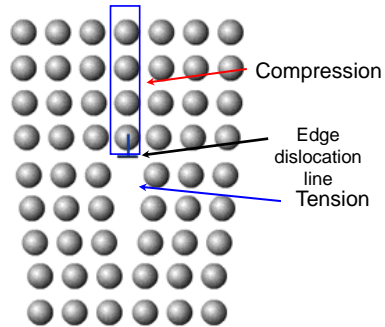
Can be divided according to their geometry and shape

- 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)



1D (Linear) defects

- 1D or linear defect - dislocations
 - edge dislocation
 - screw dislocation
- Edge dislocation (an extra partial plane of atoms)
- there will be local lattice distortion (relaxed at long distance)
- Strain fields (compression and tension)

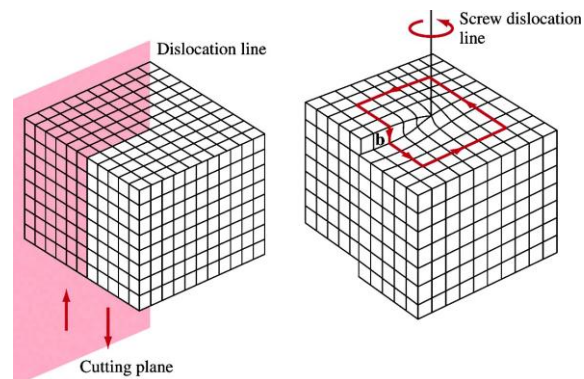


Mathematically *slip or Burger vector* \mathbf{b} is used to characterize displacement of atoms around the dislocation

\mathbf{b} is perpendicular to the edge-dislocation line

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1D - Screw dislocation

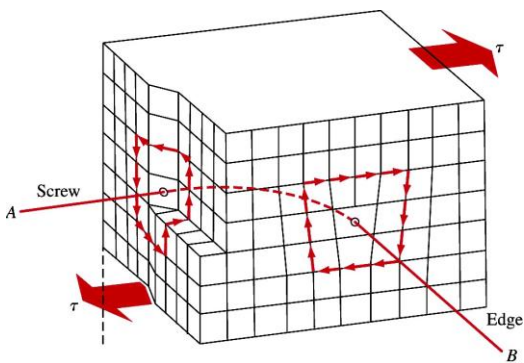


By following a loop of atoms around dislocation line \Rightarrow end up one plane up or down

Burger vector is parallel to the screw dislocation line

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Mixed edge and screw dislocations



Most dislocations found in crystalline material are neither pure edge nor pure screw, but exhibit components of both types

3D defects

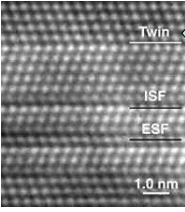
Crystal twins

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



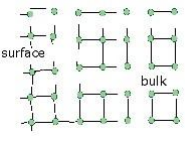
Stacking faults

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 epitaxial (single crystal)

6.3 Nanomaterials growth methods

Two approaches

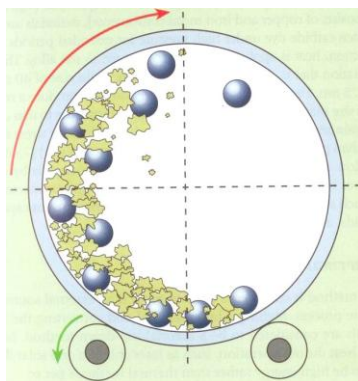
Top-down	Bottom-up
<p>Patterning in bulk materials by combination of</p> <p>Lithography</p> <p>Etching</p> <p>Deposition</p> <ul style="list-style-type: none"> - can be applied for variety of materials - limited by lithography resolution, selectivity of etching, etc. 	<p>Structure is assembled from well-defined chemically or physically synthesized building blocks</p> <p>Self-assembly</p> <p>Selective growth</p> <ul style="list-style-type: none"> - require accurate control and tunable chemical composition, structure, size and morphology of building blocks - in principle limited only by atomic dimensions

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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 \Rightarrow formation of defects and dislocations
- (3) Particle fracture and fragmentation with continuous size reduction \Rightarrow formation of nanograined material

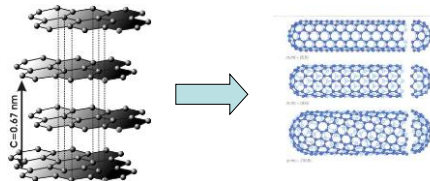
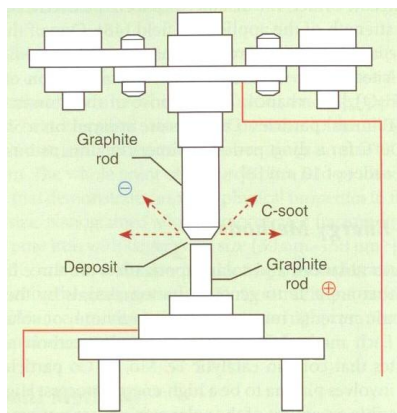
$$K_{IC} = Y\sigma_F\sqrt{\pi a} \quad \sigma_F \sim \frac{1}{Y}\sqrt{\frac{K_{IC}}{a}} \sim \sqrt{\frac{\gamma E}{a}}$$

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
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High-Energy Methods: Discharge Plasma Method

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



Can be used for fullerenes and C nanotubes

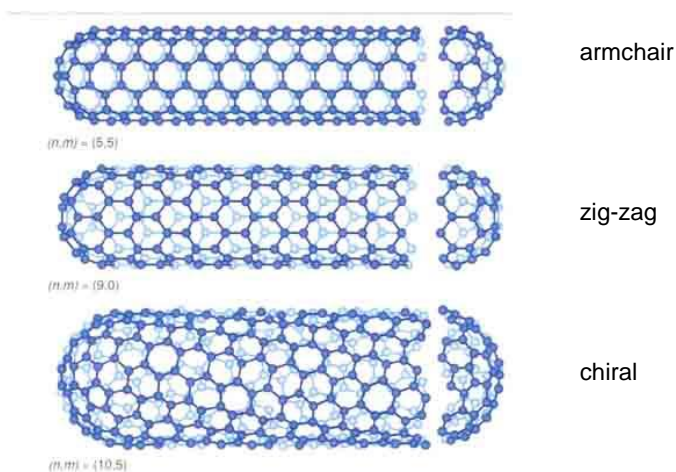
Process depend on:

- Pressure of He, process temperature, applied current

final product requires extensive purification

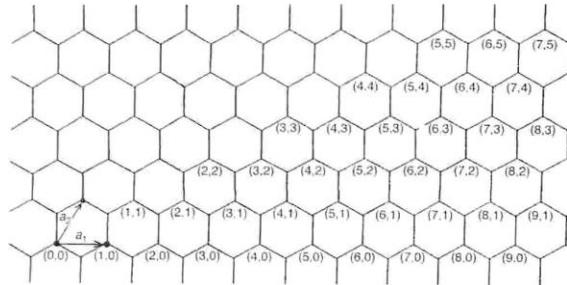
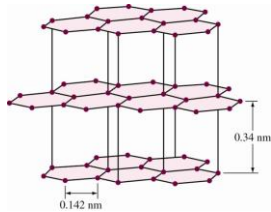
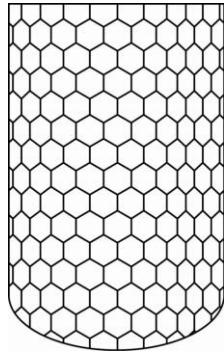
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Structure of the carbon nanotubes



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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 $(6,3)$

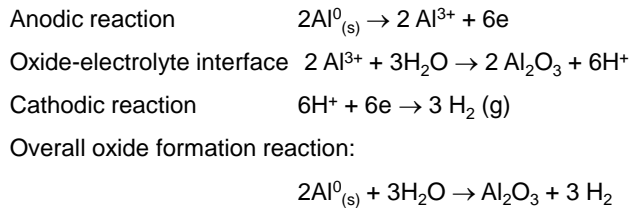
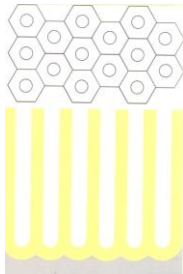
$m = 0$ for all zig-zag tubes, while $n = m$ for all armchair tubes

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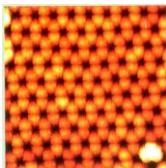
Chemical Fabrication Methods

Anodizing (and electropolishing)

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

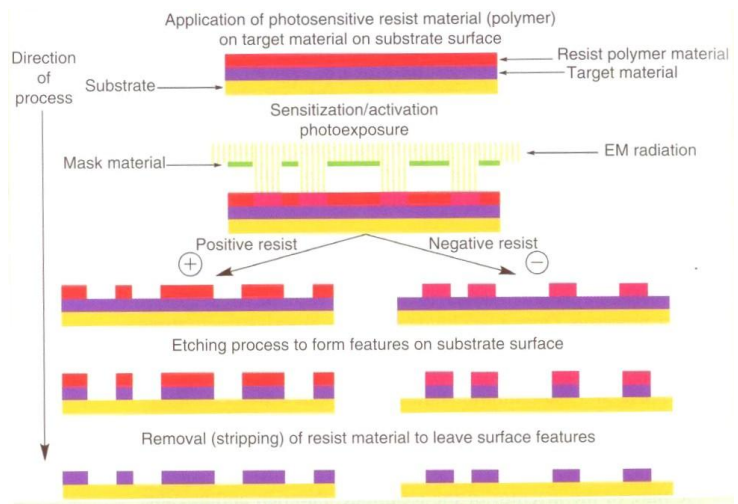


Porous Al_2O_3 membranes can be considered as ultimate template material



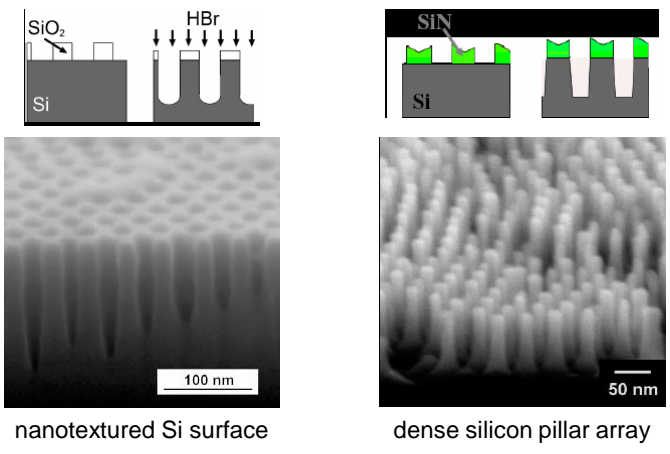
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Lithographic Methods



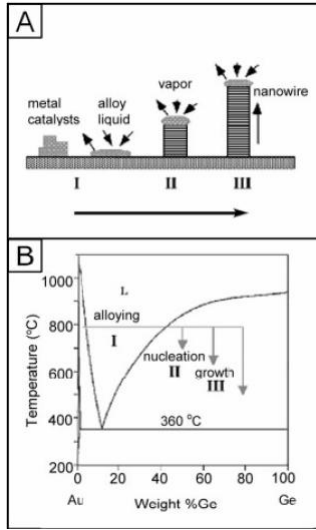
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Top-bottom: High-Aspect Aspect-Ratio Si Structures



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Bottom-up: vapor-liquid-solid growth



VLS growth of Ge NWs/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)

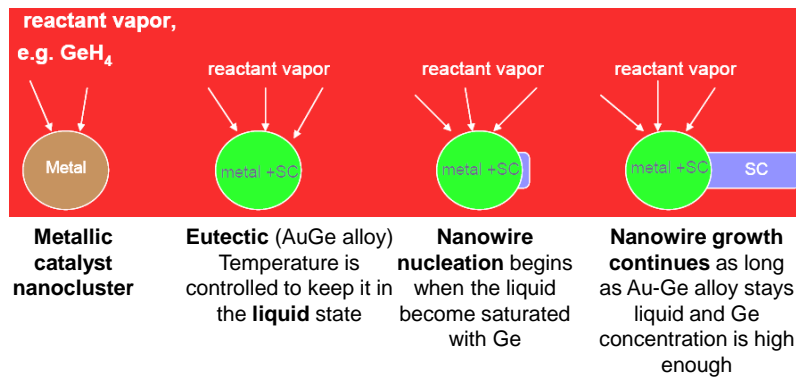
- When semiconductor reaches supersaturation, it precipitates out of the eutectic

- Metal prepared and deposited/grown on surface

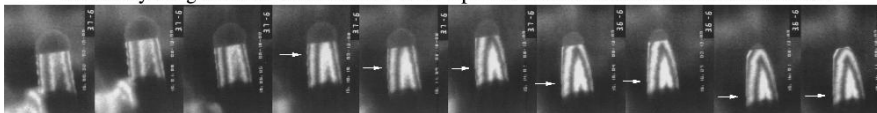
- Metal droplet size determines eventual wire diameter

(from E. Garfunkel) 19

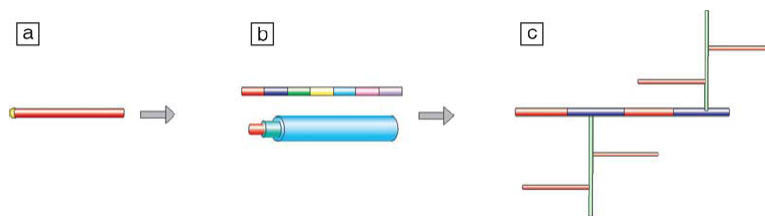
Cartoon of growth



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

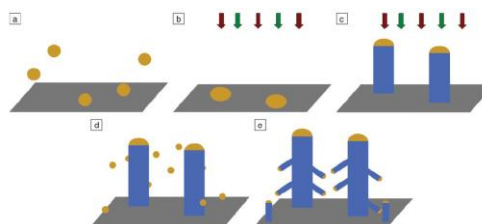


Designed Synthesis of Hierarchical Structures



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 21

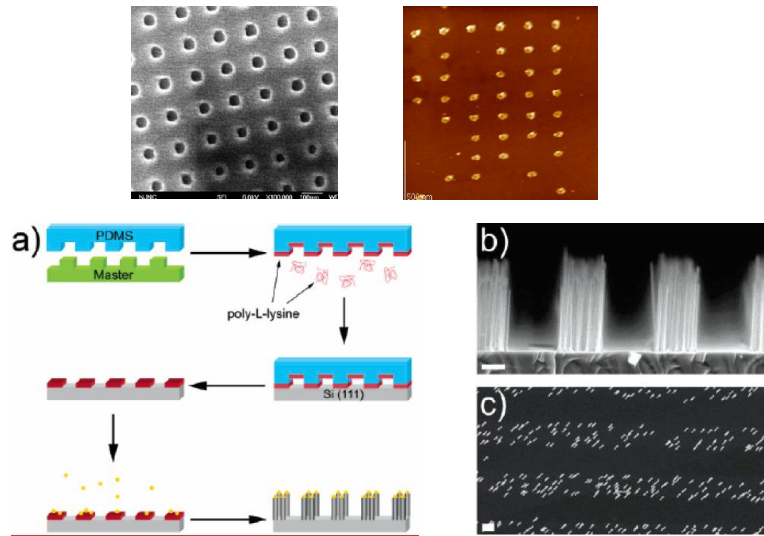
Organization and Assembly of Nanowires

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



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6.4 Homogeneous Capillary Model of Nucleation

$$\Delta G_{total} = \frac{4}{3} \frac{\pi r^3}{v} \Delta \mu + 4\pi r^2 \gamma$$

ΔG_{total} – total free-energy change
 r – radius of embryo or nucleus
 $\Delta \mu$ – volume free energy
 γ – specific surface free energy

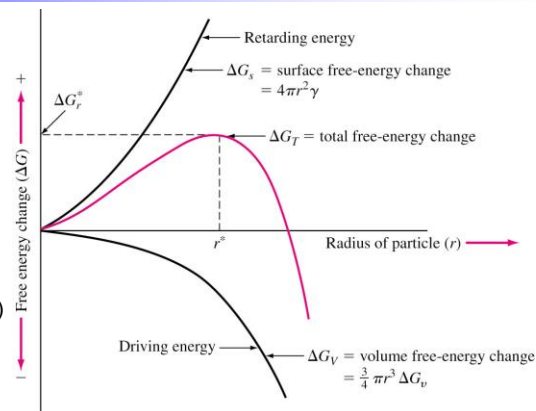
Two components: (i) volume free-energy change (ΔG_V or $\Delta \mu$) and (ii) surface free-energy change (ΔG_S)

$$\Delta \mu = \mu_S - \mu_L < 0;$$

$$\mu_S < \mu_L$$

(i) is negative,

(ii) ΔG_S is positive



r^* - critical radius

-if $r < r^*$, droplet can shrink or dissolve

-if $r > r^*$, droplet grows

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Critical radius, r^*

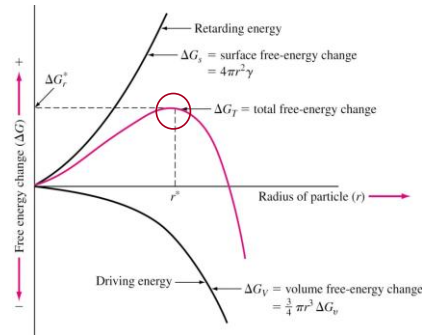
We can find the value of the critical radius by setting:

Growth cannot proceed until a droplet with radius at least as large as r^* forms

The energy of this critical nucleus relatively to the liquid phase is:

$$\Delta G^* = \frac{16\pi\gamma^3 v^2}{(\Delta\mu)^2}$$

r^* decreases as $T_C \downarrow$; $\Delta H_C \uparrow$, or $\gamma \uparrow$



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6.5 Homogeneous Nucleation Kinetics

(a) Nucleation in 1st layer: compact islands

The model:

- assume [nucleation in layer 1](#) and [slow adatom desorption](#)
 - assume [critical nucleus is 1 atom](#), so that a dimer, once formed, will not dissociate. New adatoms can form new nuclei by collision with another adatom, or can add to existing nuclei
 - calculate **saturation density N** of nuclei
- N is reached when adatom diffuses distance L to find existing nucleus before meeting another atom

The diffusion time τ_L over distance L, diffusion coefficient D is

$$\tau_L = \frac{L^2}{D}$$

$$Rate_{attach} = \frac{A \times n_2 D}{\tau_L}$$

$$Rate_{flux} = A \times F$$

Campbell, Surf. Sci. Rep. 27 (1997) 1-111

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Homogeneous Nucleation Kinetics

- At steady state, when no new nuclei are created

$$Rate_{flux} = Rate_{attach}$$

$$A \times F = A \frac{n_{2D}}{\tau_L} = A \frac{n_{2D} D}{L^2} \quad \text{Solve for } n_{2D}:$$

- Assume two atoms for a dimer when they sit on adjacent sites separated by a

$$Rate_{dimer} = A \times n_{2D} \times k_{hop} \times p_{occ} = A \times n_{2D} \times \frac{D}{a^2} \times 4n_{2D} a^2$$

$$Rate_{dimer} = 4ADn_{2D}^2$$

$$Rate_{dimer} = 4ADn_{2D}^2 \ll Rate_{attach} = A \frac{n_{2D}}{\tau_L}$$

$$4Dn_{2D} = \frac{1}{10\tau_L} = \frac{D}{10L^2} \Rightarrow L^2 = \frac{D}{40F}$$

- Saturation should be assured when enough nuclei have formed to have average separation L , so that saturation density is

(b) Dendritic Growth in 1st layer: - aside

C. Ratsch PRL 72 (1994) 3194

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6.6 Epitaxy

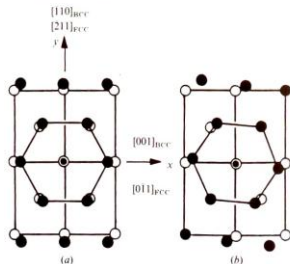
Epitaxy (“arrangement on”) refers loosely to control of the orientation of the growing phase by the crystal structure of the substrate

- homoeptitaxy: host and growing phase are the same material
- heteroepitaxy: host and growing phase are different

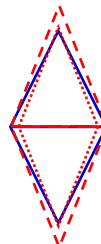
Orientation and Strain

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

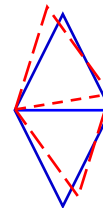
Fig. 16.1. Overlay of an FCC(111) monolayer (filled circles) onto a BCC(110) substrate surface (open circles): (a) FCC [011] parallel to BCC [001]; (b) 5.26° rotation relative to (a). The lattice constants of the two crystals are chosen to produce row-matching in the rotated case (Dahmen, 1982).



Nishiyama-Wasserman



Kurdjimov-Sachs

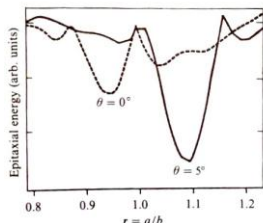


Zangwill, Ch.16

Epitaxial energy

NW: $\Theta = 0^\circ$, row-matching parallel to [001] bcc Definition of misfit: $f = \frac{a-b}{a}$
 KS: $\Theta = 5.26^\circ$, rotational epitaxy

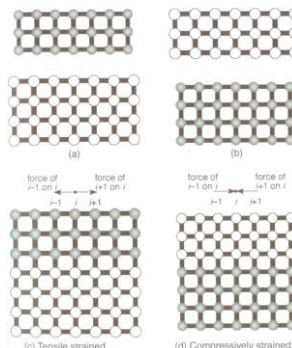
Fig. 16.2. Model calculation of the total adsorbate-substrate interaction energy for rigid lattice FCC(111)/BCC(110) epitaxy as a function of the nearest neighbor distance ratio a/b for two angles of orientation relative to Fig. 16.1(a) (Ramirez, Rahman & Schuller, 1984).



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

Note minima for 0° and $\sim 5^\circ$

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



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

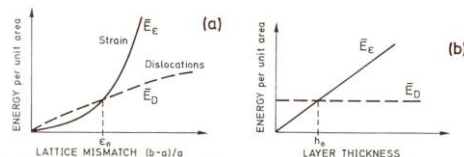


Fig.3.16a,b. Qualitative plots of lattice energy stored at a crystalline hetero-interface per unit area: (a) as a function of lattice mismatch; beyond a critical lattice mismatch ϵ_0 (a and b are the lattice constants of the two materials) the adjustment of the two lattices by dislocations (broken line)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

Left: film thickness = const.
 Right: misfit = const.

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 \uparrow , complexities develop....

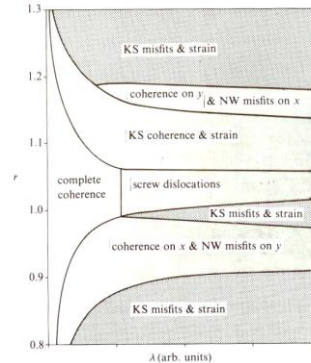
Structural phase diagram

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

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

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

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).



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6.7 Film deposition techniques

1. Physical Vapour Deposition (PVD)

Evaporation: thermal and electron-beam assisted

Sputtering: RF and DC Magnetron

Pulsed Laser Deposition (PLD)

3. Molecular Beam Epitaxy (MBE)

2. Chemical Vapour Deposition (CVD)

Plasma-Enhanced CVD (PE-CVD)

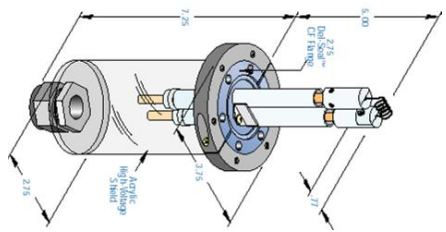
Atomic Layer Deposition (ALD)

⇒ Need good vacuum for thin film growth!

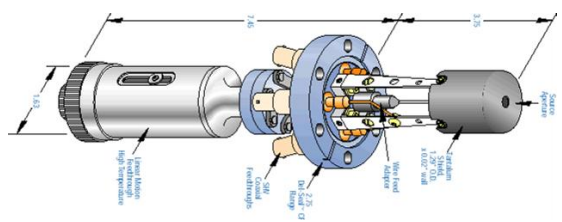
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6.7.1 Physical Vapour Deposition (PVD)

Thermal Evaporation for non-refractory materials



E-beam evaporation for refractory materials



<http://www.mdc-vacuum.com>

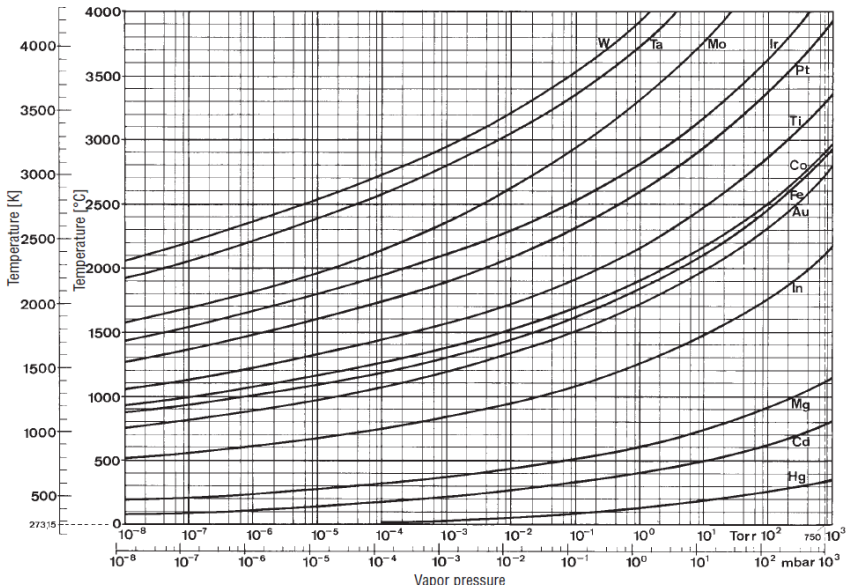


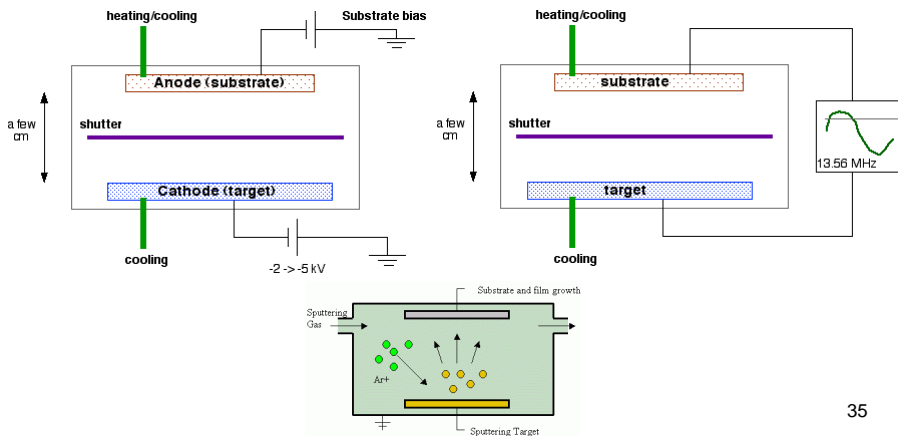
Fig. 9.13: Saturation vapor pressure of major metals used in vacuum technology

Leybold Product and Vacuum Technology Reference Book

Sputtering Deposition

- DC for conducting materials
- RF for insulating materials

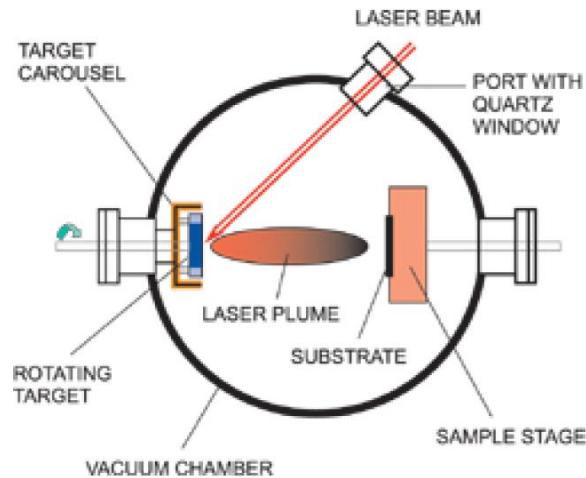
Magnetron sputtering is most popular due to high rate and low operation pressure



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Pulsed Laser Deposition (PLD)

- Good for multielemental materials ($P < 1$ Torr)

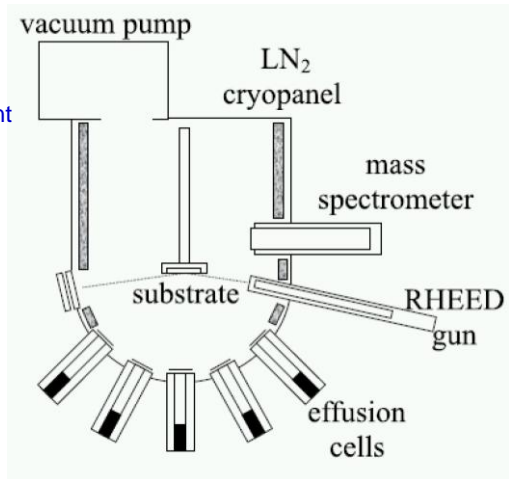


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6.7.2 Molecular Beam Epitaxy (MBE)

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

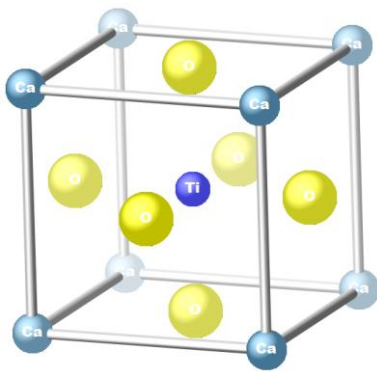
1. Elemental Superlattices: Giant Magneto-Resistance (GMR) Devices
2. Binary III-V Superlattices
3. Complex Oxide Superlattices



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Complex oxides are not that complex:

Most of them are based on the ABO₃ cubic perovskite structure
 Ex.: SrTiO₃, LaTiO₃, LaMnO₃, LaAlO₃, ...
 ⇒ Favorable to atomically smooth layered heterostructures

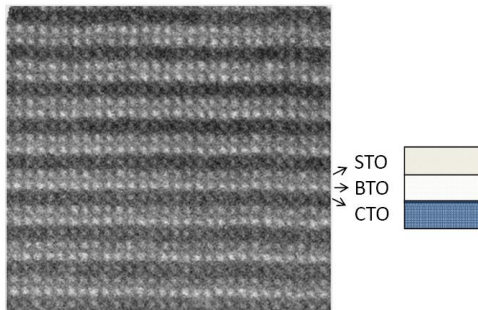


ABO₃
 A: M²⁺ (Ca, Sr, Ba, La)
 B: M⁴⁺ (Ti, Zr, Mn)

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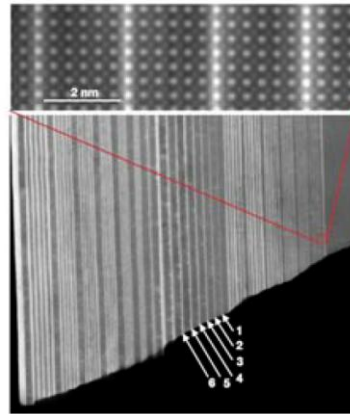
Superlattices grown by MBE

SrTiO₃/BaTiO₃/CaTiO₃



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

LaTiO₃/SrTiO₃ (PLD)

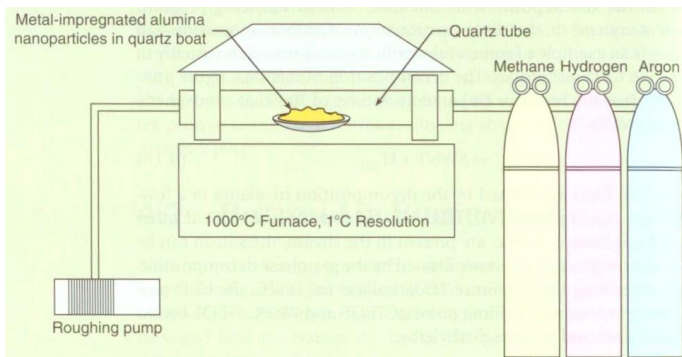
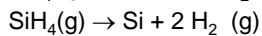
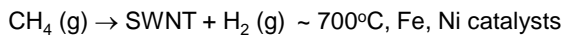


A. Ohtomo, H. Y. Hwang, *Nature* 419, 378 (2002)

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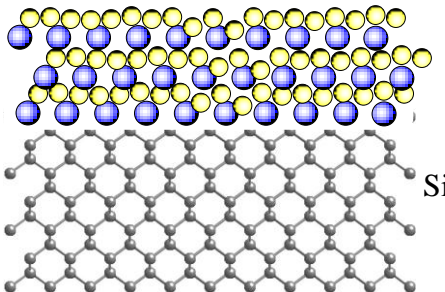
6.7.3 Chemical Vapour Deposition (CVD)

Precursors are needed!

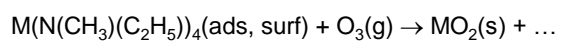
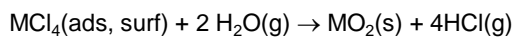


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Atomic Layer Deposition



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



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