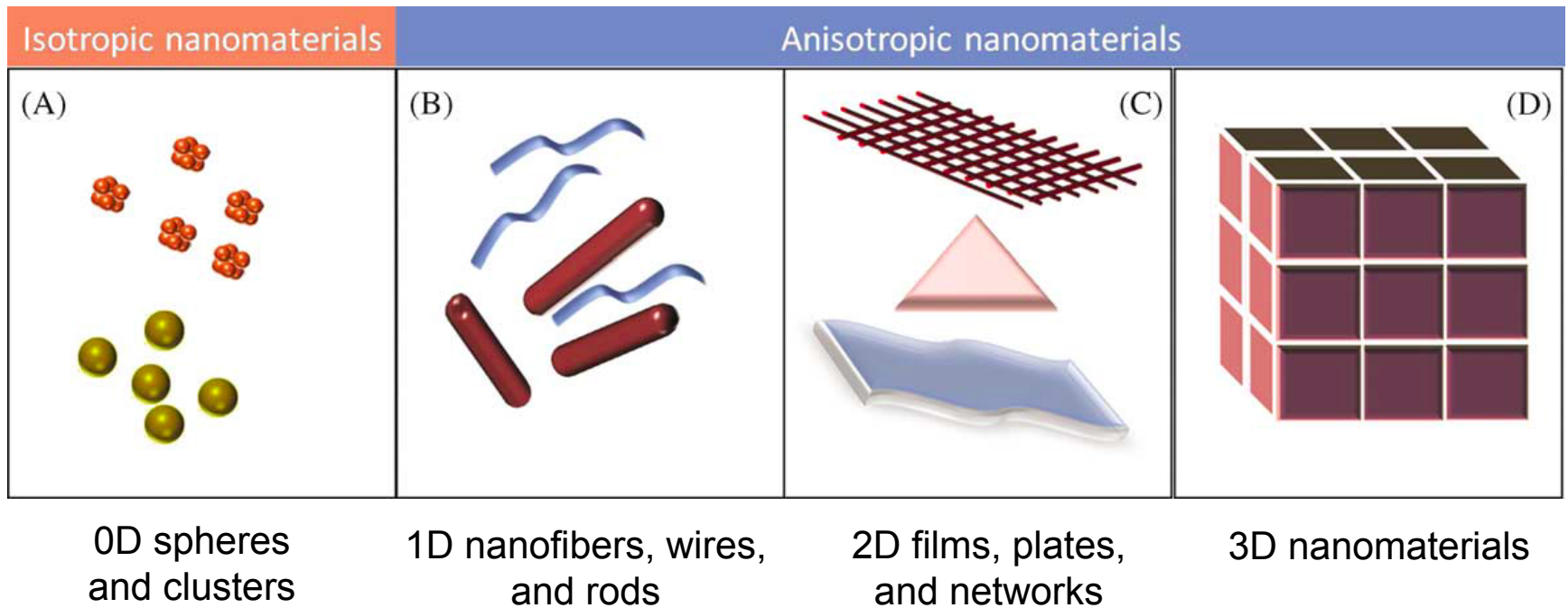


Growth of Nanostructures and Nanomaterials



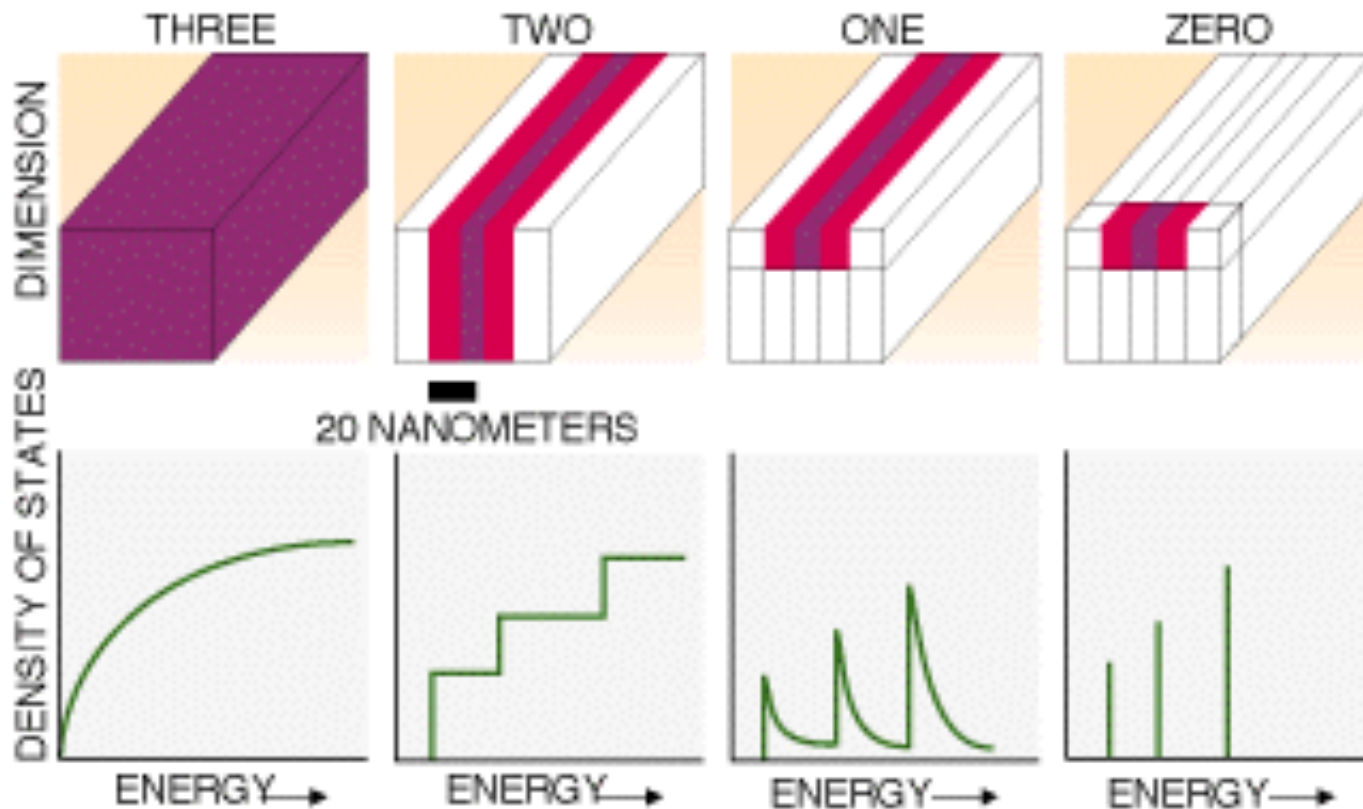
Various kinds of nanomaterials

Critical lengths for Nanostructures

Nanostructured materials derive their special properties from having one or more dimensions made small compared to a length scale critical to the physics of the process.

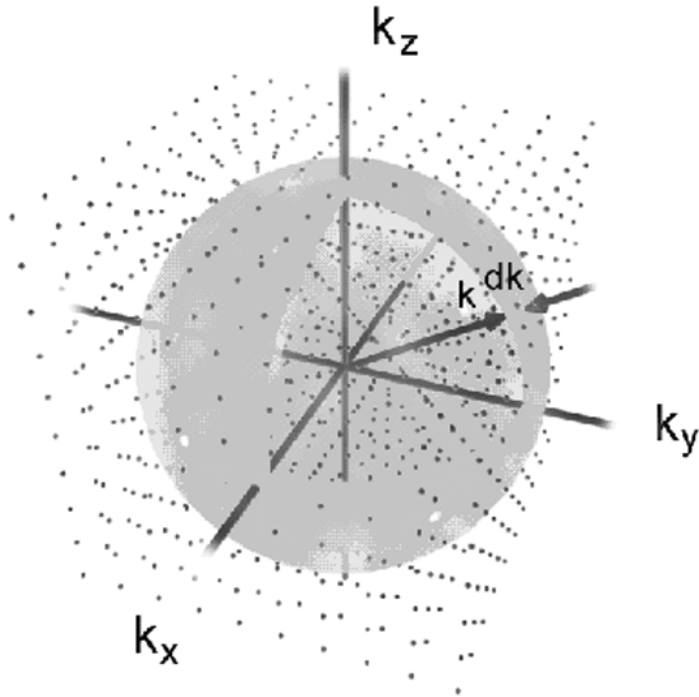
Phenomenon	Electronic Transport	Optical Interactions	Magnetic Interactions	Thermal	Fluidic Interactions
Physics	Fermi wavelength, λ_F Scattering length, ℓ	Wavelength of light in medium, $\lambda/2n$	Range of exchange interactions, range of magnetic dipole interactions	Phonon mean free path	Boundary layers, molecular dimensions
Length scale	$\lambda_F \approx 1\text{\AA}$ $\ell \approx 10\text{-}100\text{ nm}$	100 – 300 nm	Exchange 1-100 Å, Dipolar ca. microns	Hundreds of nm at 300K to very large at low T	Always in the low Reynolds number limit: Radius of gyration for dissolved molecules.

Quantum confinement



(Scientific American)

Size dependence of density of states



k-space is filled with an uniform grid of points each separated in units of $2\pi/L$ along any axis.

The volume (V_k) of k-space occupied by each point is:

$$\left(\frac{2\pi}{L} \right)^3$$

r-space:

$$\frac{4\pi r^2 dr}{V}$$

k-space:

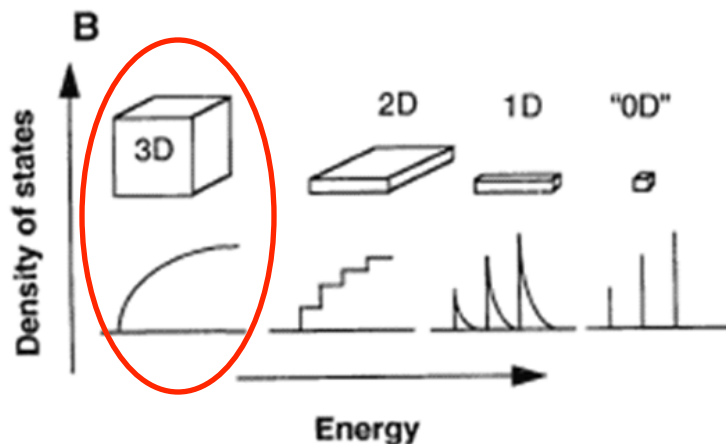
$$\frac{4\pi k^2 dk}{V_k} = \frac{4\pi L^3 k^2 dk}{8\pi^3}$$

3D DOS

Density of states in a volume V per unit wave vector: $\frac{dn}{dk} = \frac{Vk^2}{2\pi^2}$

For a free electron gas: $E = \frac{\hbar^2 k^2}{2m}$ $\frac{dE}{dk} = \frac{\hbar^2 k}{m}$

$$\frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{Vk^2}{2\pi^2} \frac{m}{\hbar^2 k} = \frac{Vm}{\hbar^2 2\pi^2} \sqrt{\frac{2mE}{\hbar^2}} \propto E^{\frac{1}{2}}$$

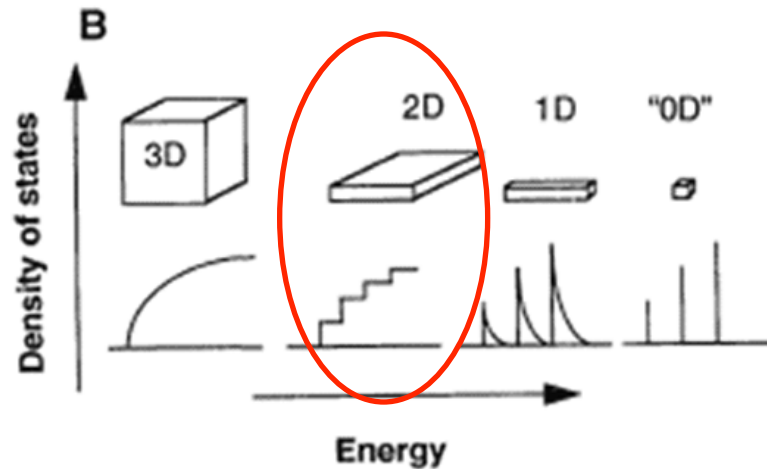


2D DOS

$$\frac{dn}{dk} = \frac{A2\pi k}{(2\pi)^2} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

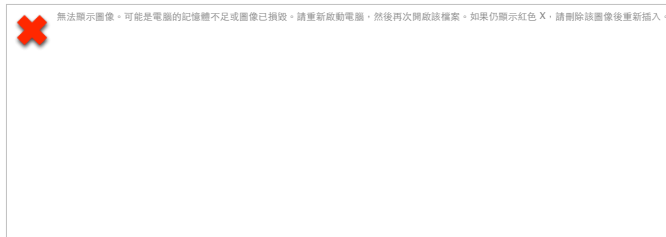
$$\frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{Am}{2\pi\hbar^2}$$

*Constant for each
electronic band*

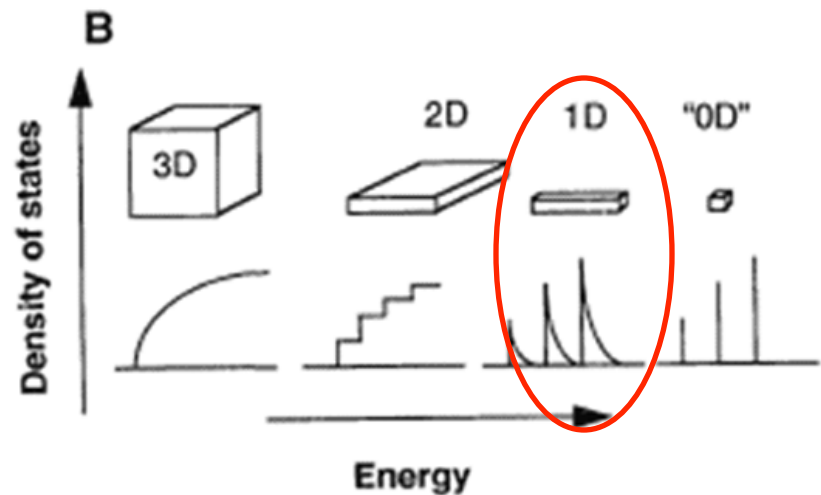


1D DOS

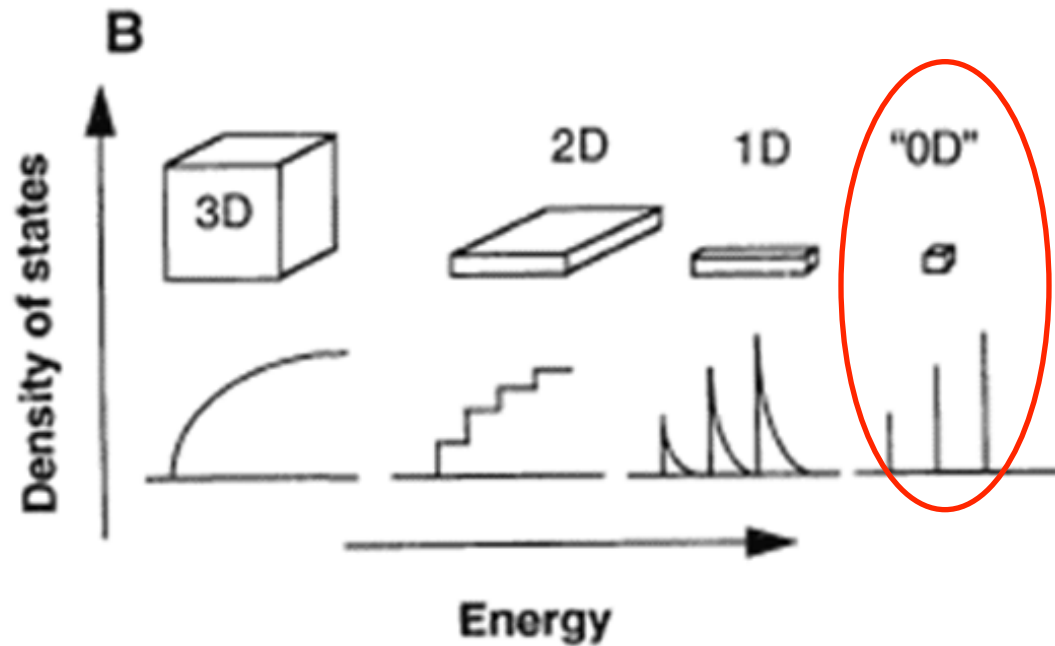
$$\frac{dn}{dk} = \frac{L}{2\pi} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$



At each atomic level, the DOS in the 1D solid decreases as the reciprocal of the square root of energy.

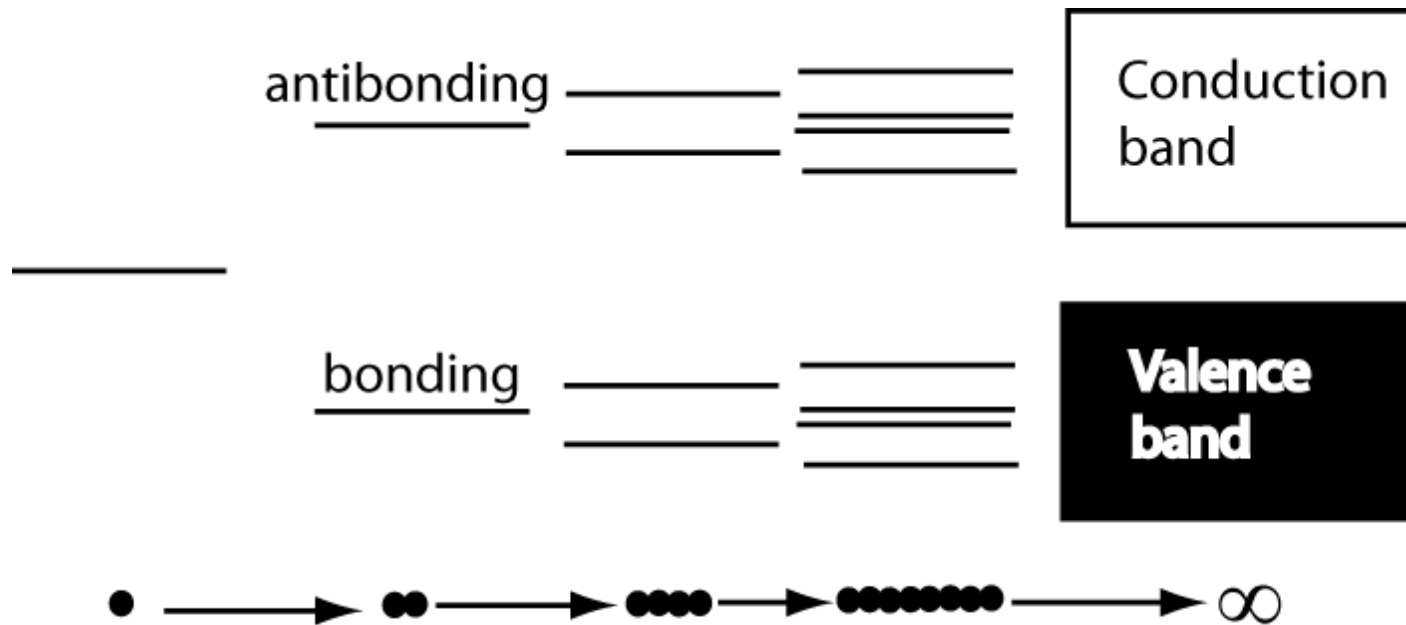


0 D DOS



In zero dimensions the energy states are sharp levels corresponding to the eigenstates of the system.

Development of electronic properties as a function of cluster size



Each band has a width that reflects the interaction between atoms, with a bandgap between the conduction and the valence bands that reflects the original separation of the bonding and antibonding states.

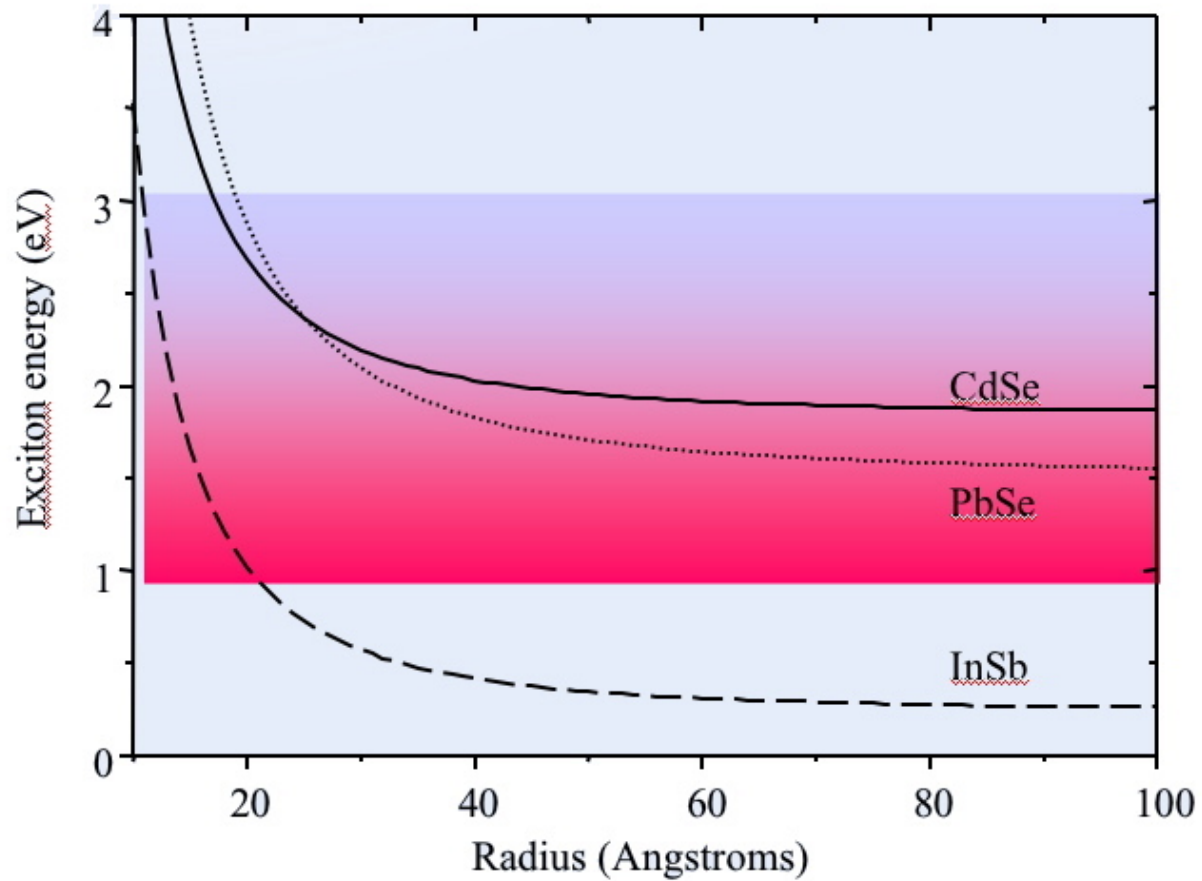
0D Electronic Structures: Quantum Dots



無法顯示圖像。可能是電腦的記憶體不足或圖像已損毀。請重新啟動電腦，然後再次開啟該檔案。如果仍顯示紅色 X，請刪除該圖像後重新插入。

Light incident on a semiconductor at an energy greater than the bandgap forms an exciton, i.e. an electron-hole quasiparticle, representing a bound state.

Exciton Energy



Nanostructure fabrications

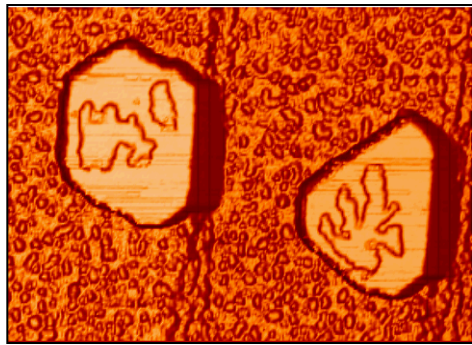
- Bottom-up approach: Growth and self-assembly to build nanostructures from atomic or molecular precursors.
- Top-down approach: Lithographic patterning to structure macroscopic materials at the nanoscale.

Epitaxial Growth

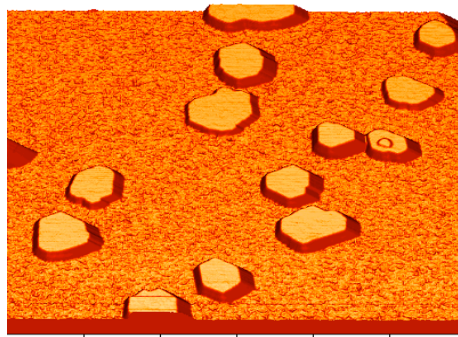
Epitaxial films take on a lattice structure and orientation identical to those of the substrate.

- **Homoepitaxy:** a crystalline film is grown on a substrate or film of the same material.
- **Heteroepitaxy:** a crystalline film grows on a crystalline substrate or film of a different material.

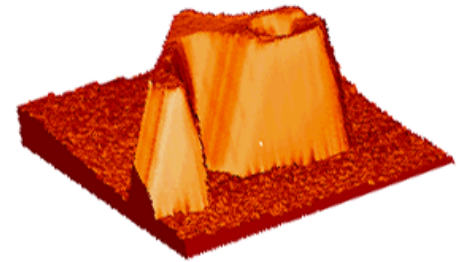
Growth modes at different temperature



Non-crystalline



2D islands



3D islands

150 K

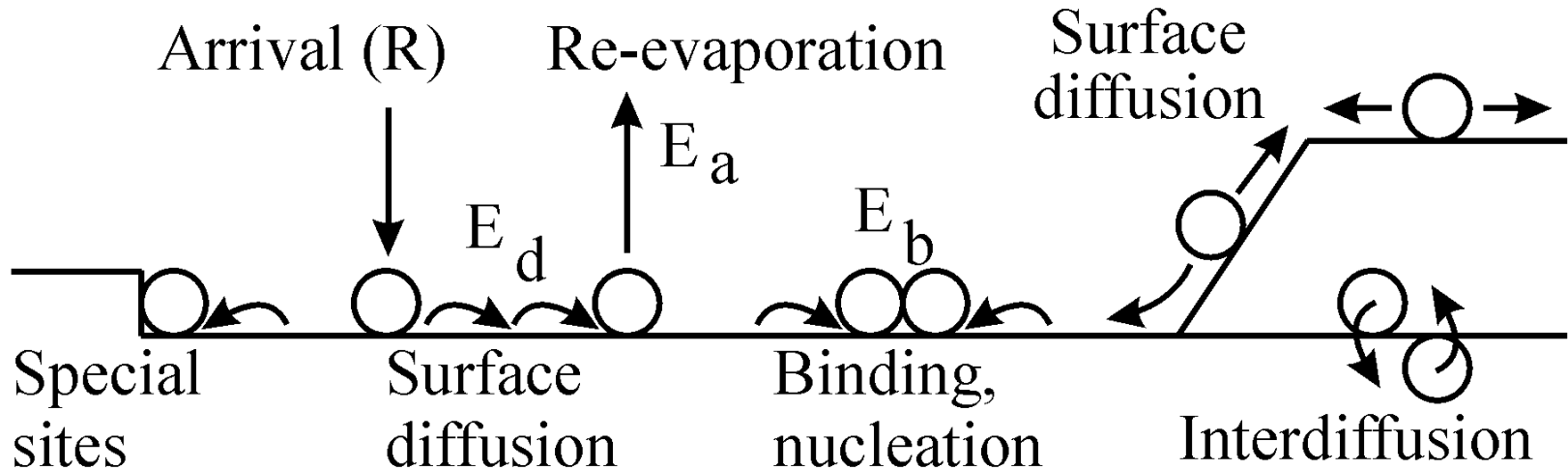
300 K

Growth kinetics

- Schematic description: particles are deposited on a surface and become adsorbed (adatoms). They diffuse around the surface and can be bound to the surface. Vice versa, unbinding and desorption happens.
- The kinetics of epitaxial growth is determined by the surface diffusion and nucleation.

Diffusion → Nucleation → Growth

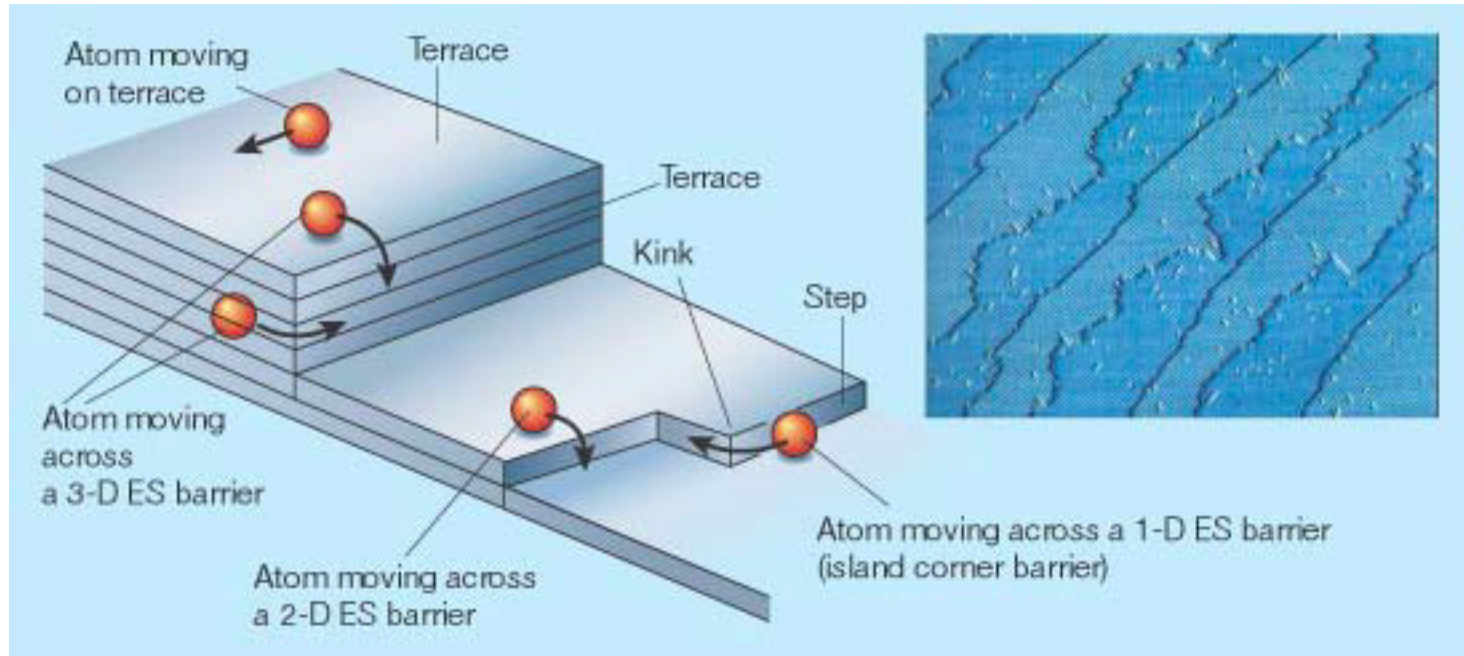
Atomic-level processes



Variables: R (or F), T , time sequences (t)

Parameters: E_a , E_d , E_b , mobility, defects...

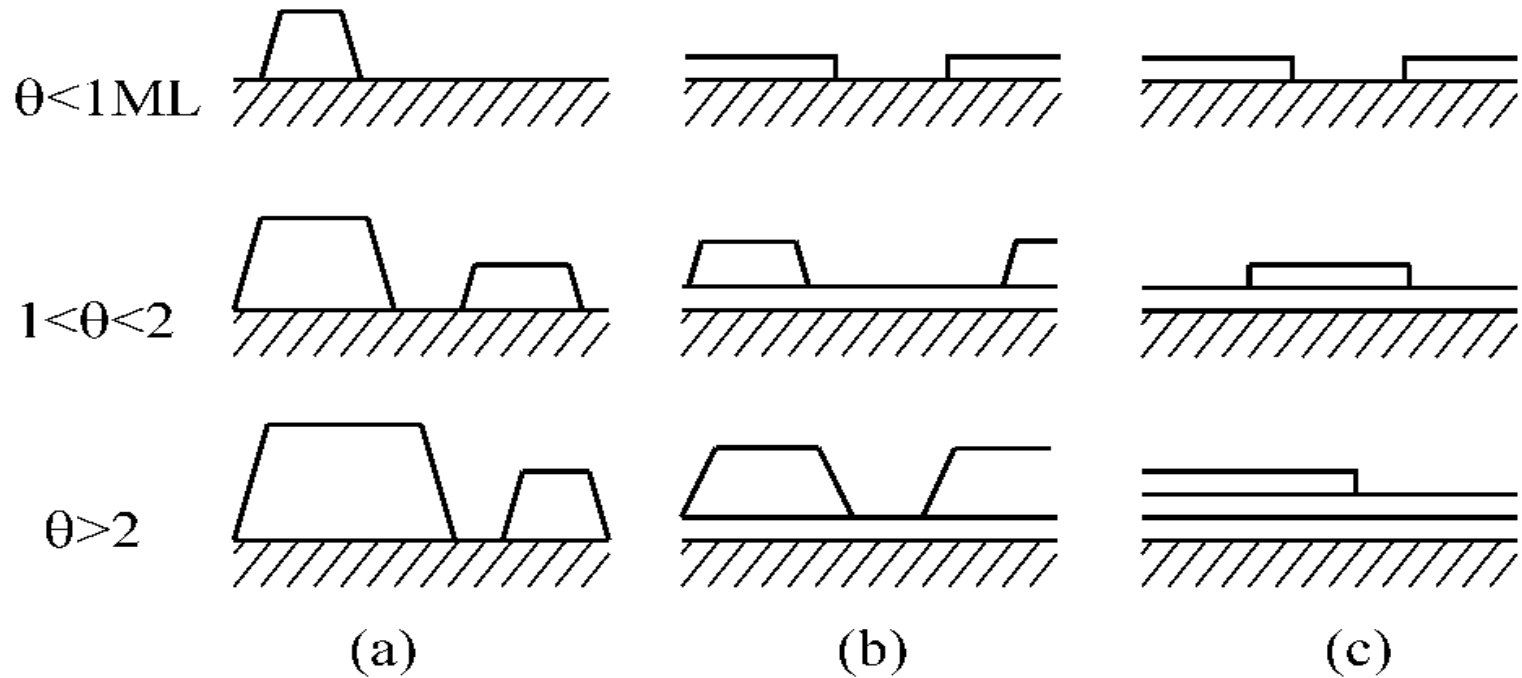
Atomistic Models for Crystalline Surfaces



Terrace Step Kink (TSK) model

Phase growth or transition simply involves the
bond forming and ***bond breaking***

Growth modes



Island

Volmer-Weber

$$\gamma_s < \gamma_f + \gamma_i$$

Layer + Island

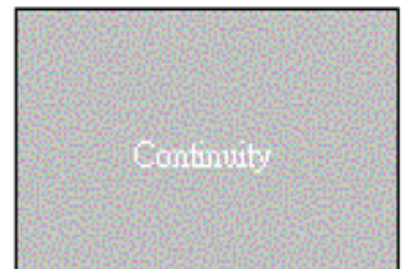
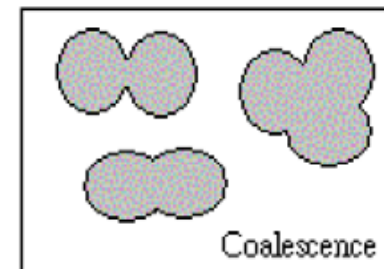
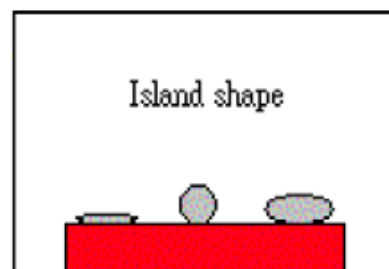
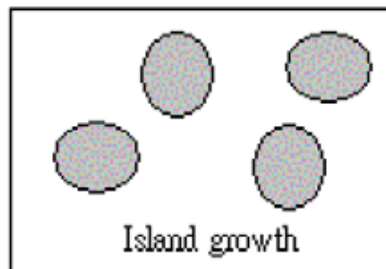
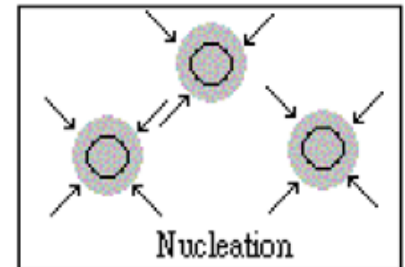
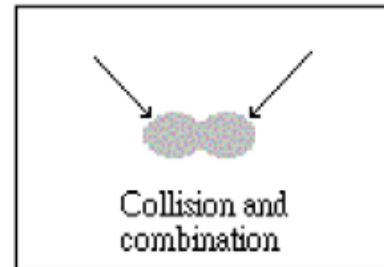
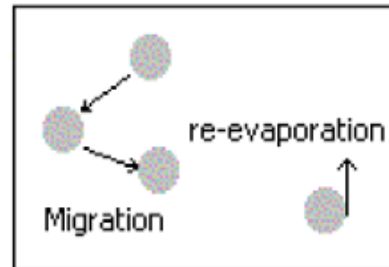
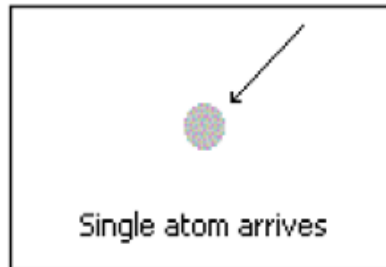
Stranski-Krastanov

Layer

Frank-VdM

$$\gamma_s \geq \gamma_f + \gamma_i$$

Thin Film Growth Process



Techniques for making nanowires

- **Spontaneous growth:**
 - Evaporation condensation
 - Dissolution condensation
 - Vapor-Liquid-Solid growth (VLS)
 - Stress induced re-crystallization
- **Template-based synthesis:**
 - Electrochemical deposition
 - Electrophoretic deposition
 - Colloid dispersion, melt, or solution filling
 - Conversion with chemical reaction
- **Electro-spinning**
- **Lithography** (*top-down*)

General characters for spontaneous growth

- Anisotropic growth is required
- Crystal growth proceeds along one direction, where as there is no growth along other direction.
- Uniformly sized nanowires (i.e. the same diameter along the longitudinal direction of a given nanowire)

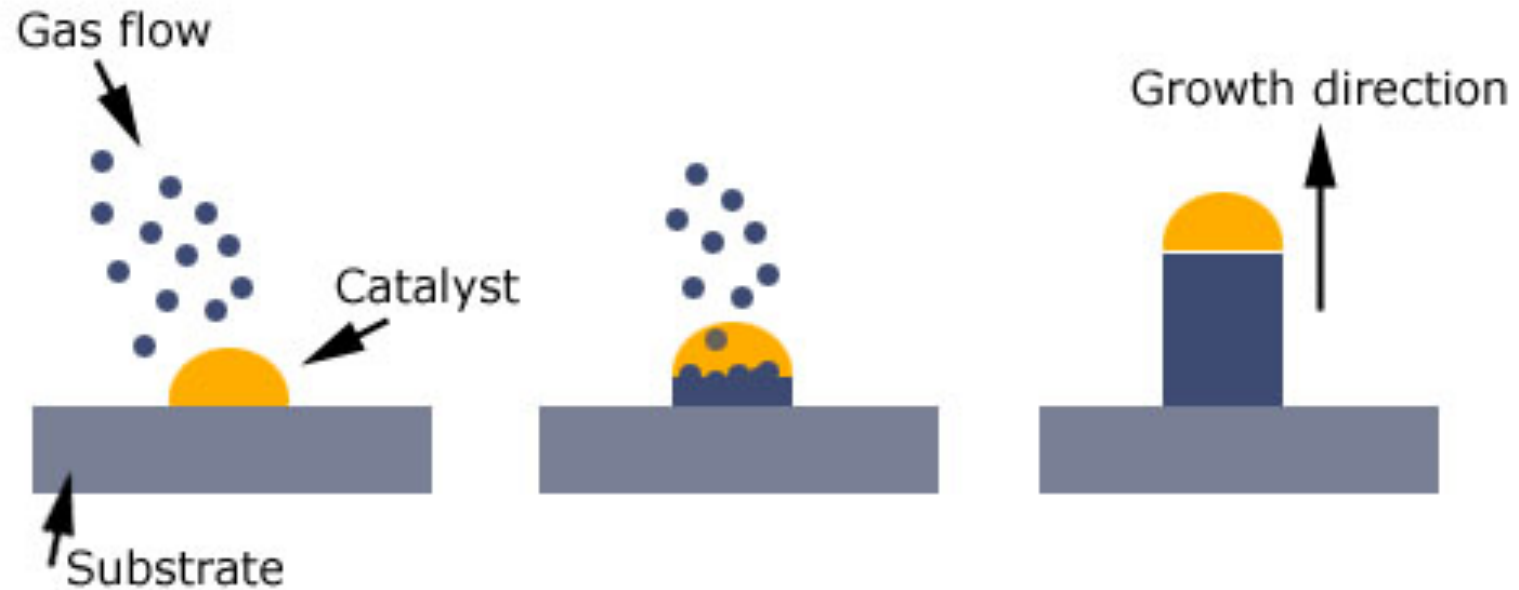
Vapor Liquid Solid Growth (VLS)

General Idea:

A second phase material, commonly referred to as ***catalyst***, is introduced to direct and confine the crystal growth on a specific orientation and within a confined area.

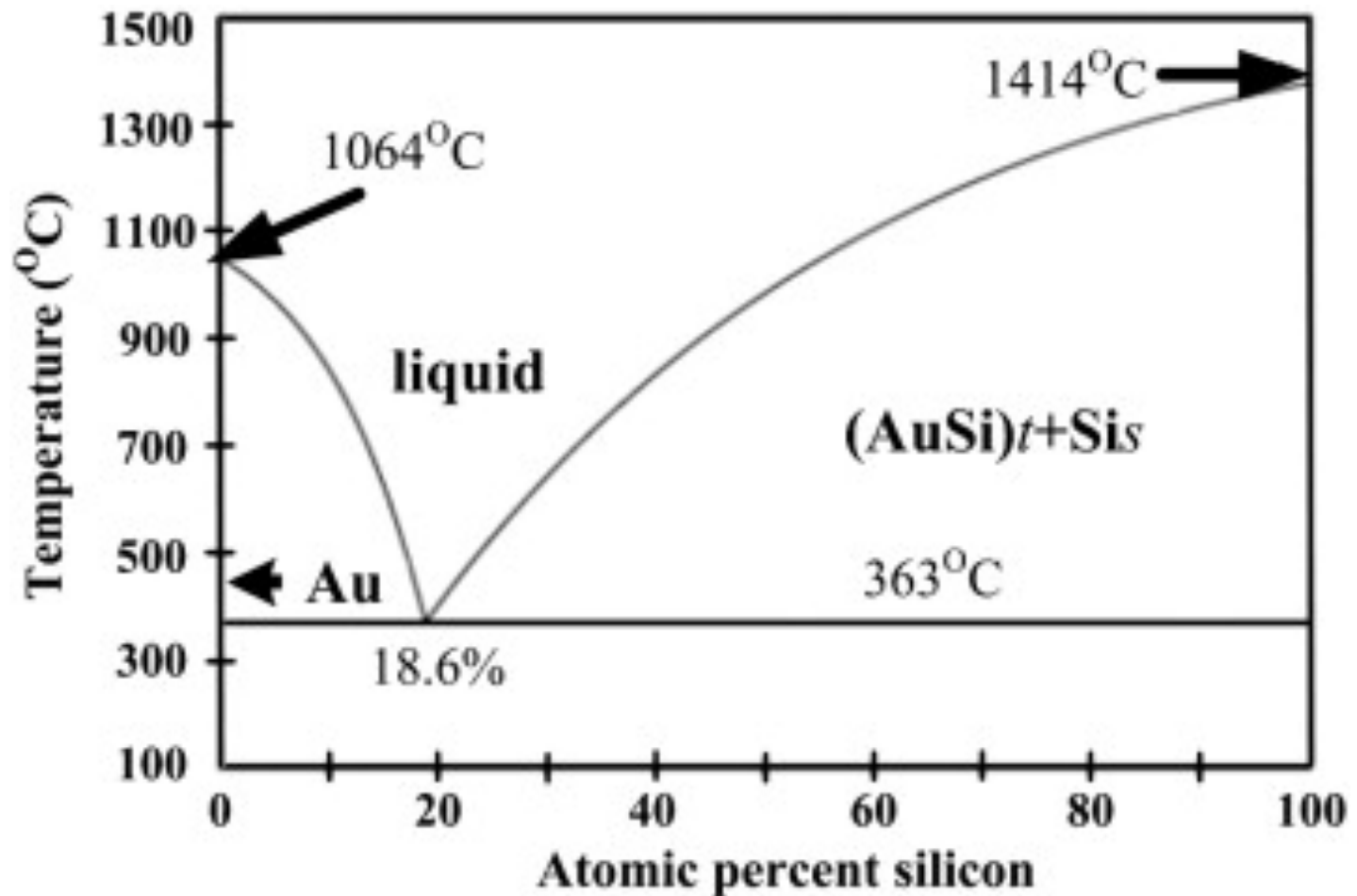
- Catalyst forms a **liquid droplet** by itself
- Acts as a trap for growth species
- The growth species is evaporated first and then diffuses and dissolves into a liquid droplet
- It precipitates at the interface between the substrate and the liquid

VLS Growth

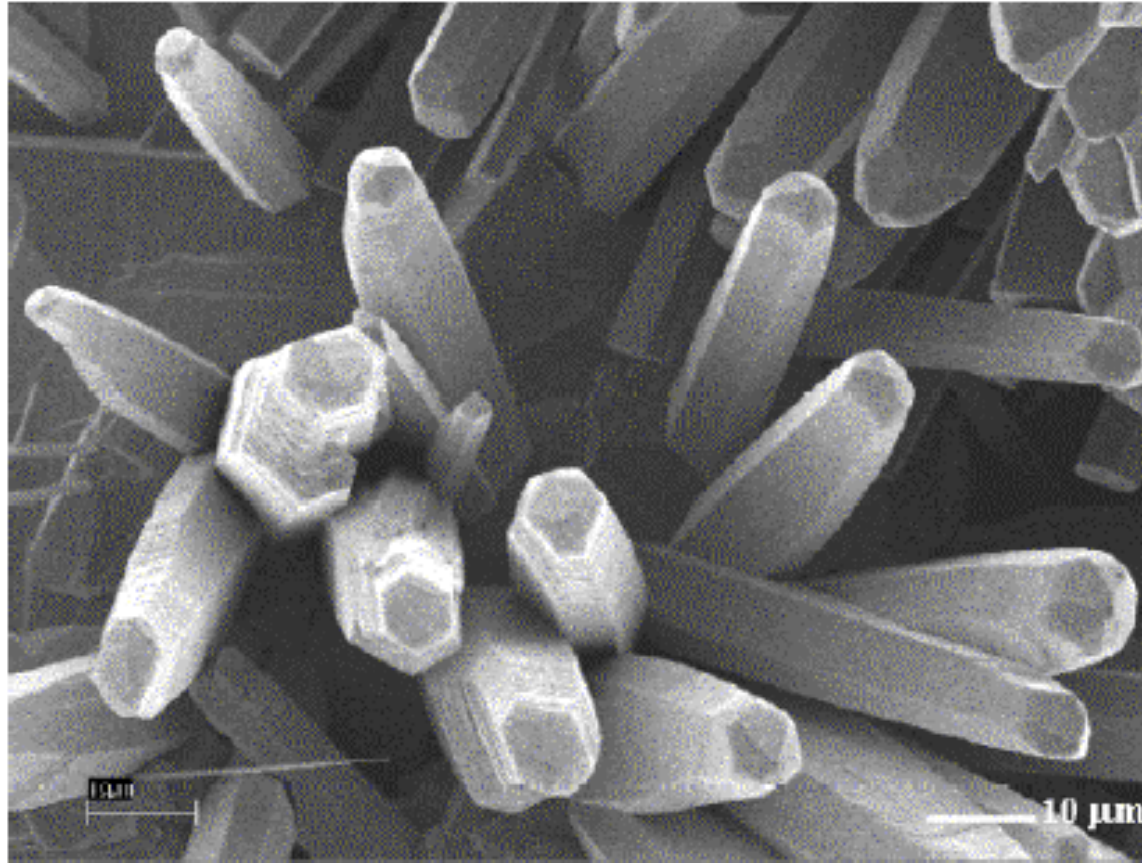


Growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in the ***one-directional growth***

Phase diagram of AuSi

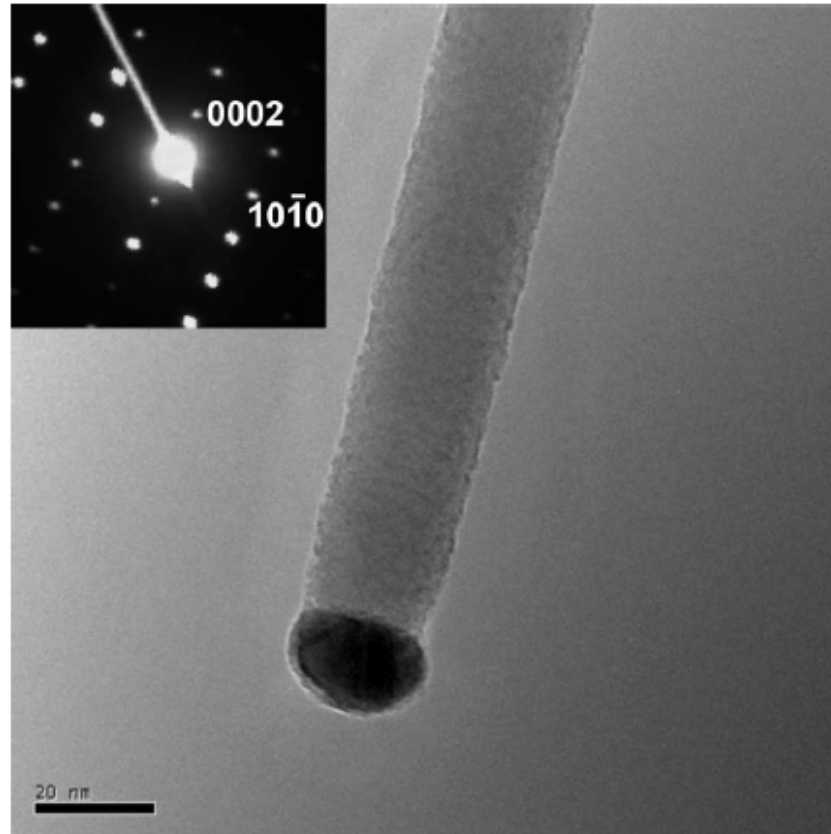


VLS Growth



“A Non-Traditional Vapor-Liquid-Solid Method for Bulk Synthesis of Semiconductor Nanowires,” Shashank Sharma, and Mahendra K. Sunkara

VLS Growth



TEM and selected area diffraction image of a single crystal ZnO nanorod.(~20 nm width).

“ZnO nanowire growth and devices,” Y.W. Heoa, D.P. Nortona, et al.

Vapor-Solid (VS) technique

- Nanowires and nanorods grown by this method are commonly single crystals with fewer imperfections
- The formation of nanowires or nanorods is due to the anisotropic growth.
- The general idea is that the different facets in a crystal have different growth rates
- There is no control on the direction of growth of nanowire in this method

Laser Assisted Catalytic growth

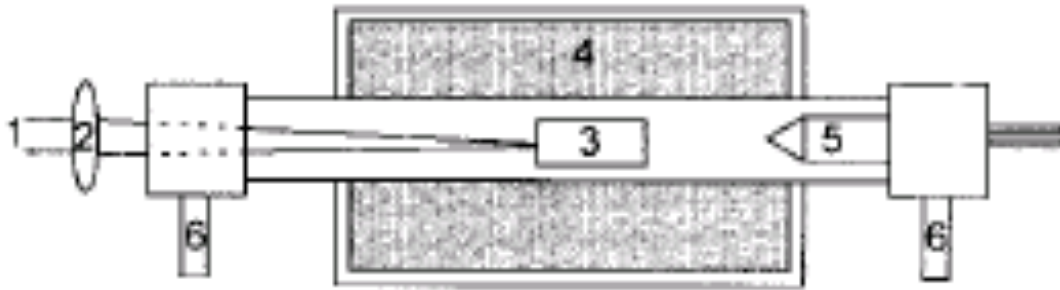


Fig. 2 Schematic of a nanowire growth set up using a combination of laser ablation and vapor-liquid- solid scheme

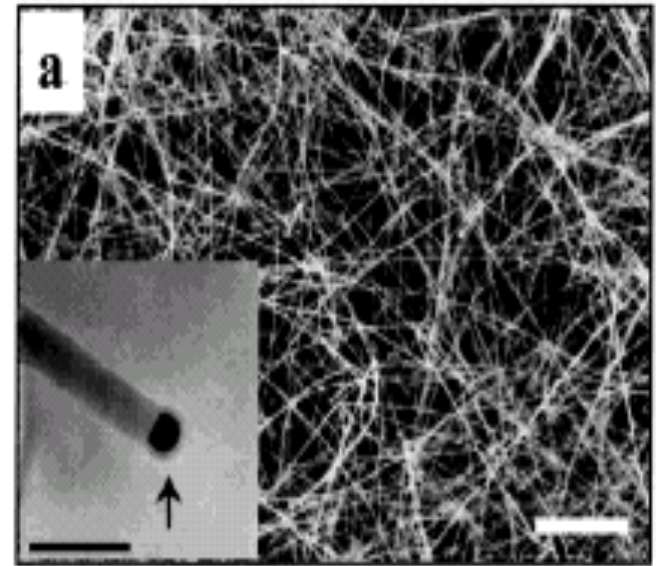
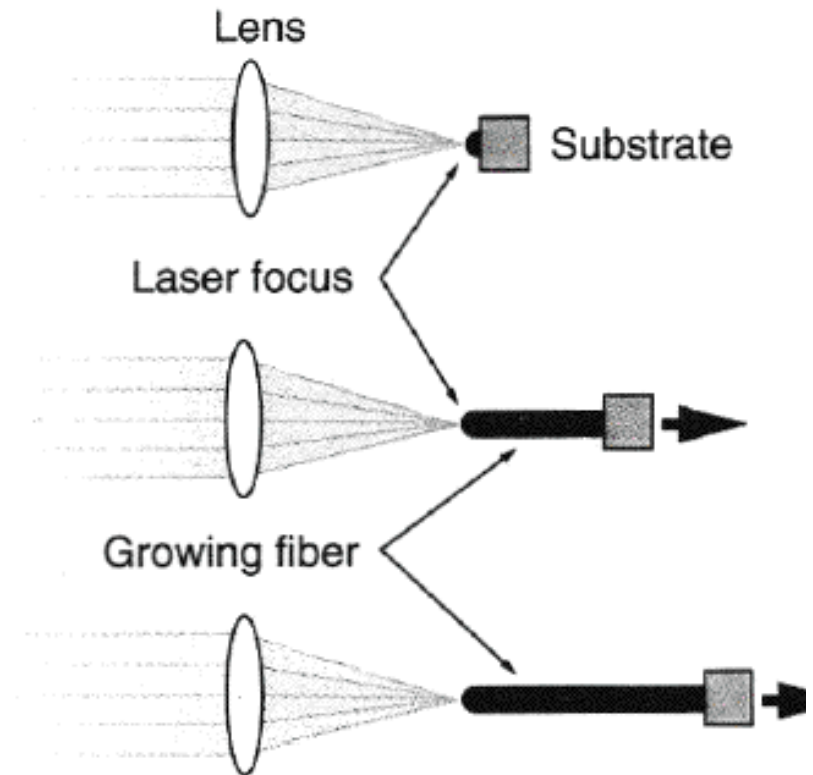


Fig.1 Semiconductor (GaAs) nanowires grown using laser assisted catalytic growth [1ref]. The scale bar corresponds to 50 nm.

Chemical vapor deposition (CVD) : L-CVD

- The L-CVD method is able to fabricate continuous thin rods and fibres by pulling the substrate away from the stationary laser focus at the linear growth speed of the material while keeping the laser focus on the rod tip, as shown in the Figure. LCVD was first demonstrated for carbon and silicon rods. However, fibers were grown from other substrates including silicon, carbon, boron, oxides, nitrides, carbides, borides, and metals such as aluminium. The L-CVD process can operate at low and high chamber pressures. The growth rate is normally less than $100\text{ }\mu\text{m/s}$ at low chamber pressure ($\ll 1\text{ bar}$). At high chamber pressure ($>1\text{ bar}$), high growth rate ($>1.1\text{ mm/s}$) has been achieved for small-diameter ($<20\text{ }\mu\text{m}$) amorphous boron fibers.



Template Base synthesis

- Use in fabrication of nanorods, nanowires, and nanotubes of polymers, metals, semiconductors, and oxides.
- Some porous membrane with nano-size channels (pores) are used as templates from conduct the growing of nanowires
- Pore size ranging from 10 nm to 100 nm can be achieved.

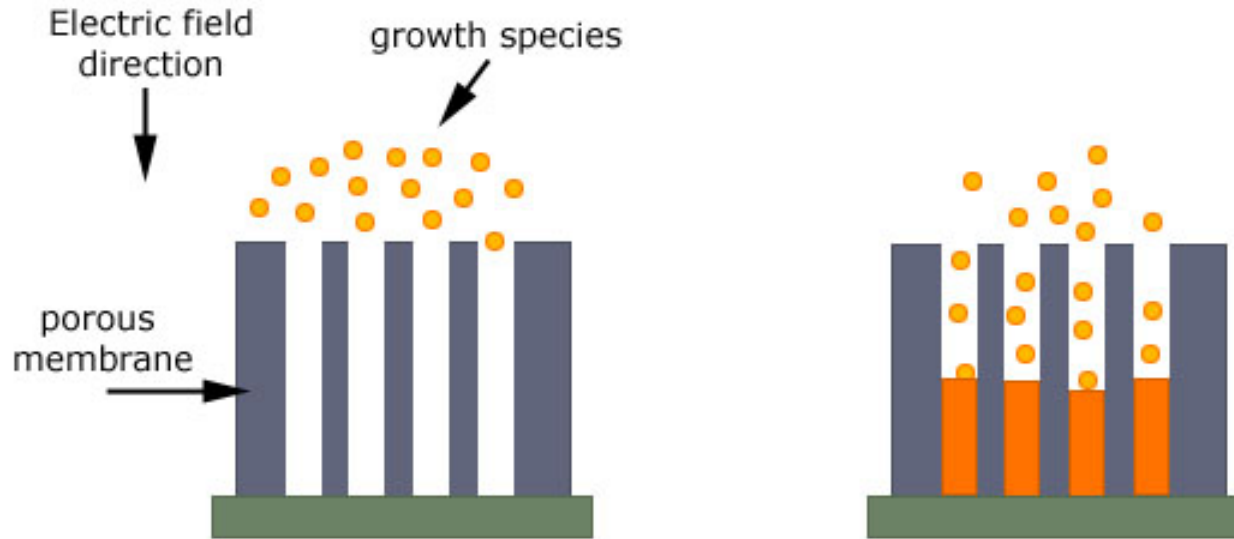
Electrochemical Deposition

- This method can be understood as a special electrolysis resulting in the deposition of solid material on an electrode
- The template can be electrically positive or negative
- Only applicable to electrically conductive materials: metals, alloys, semiconductors, and electrical conductive polymers.

Negative Template

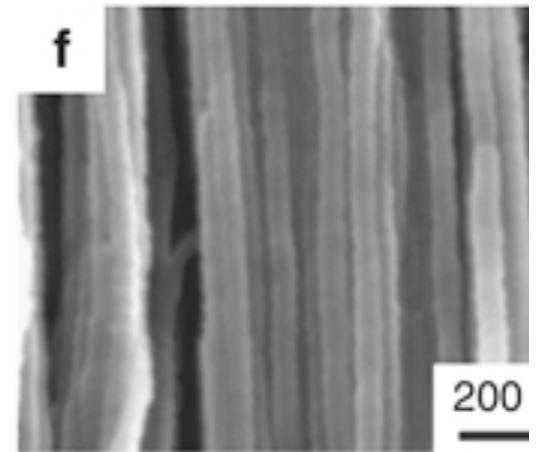
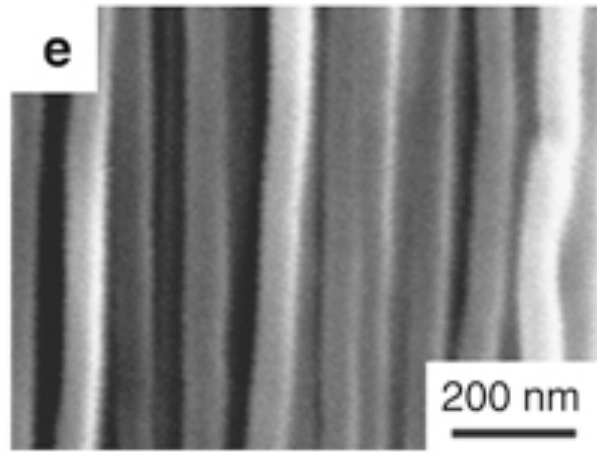
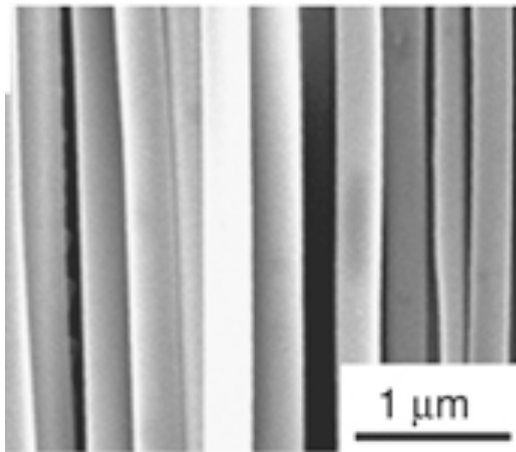
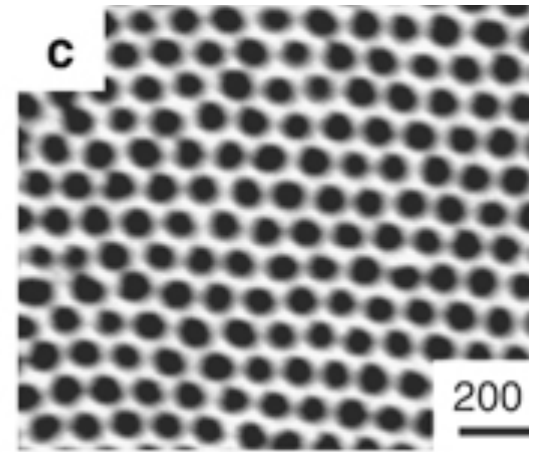
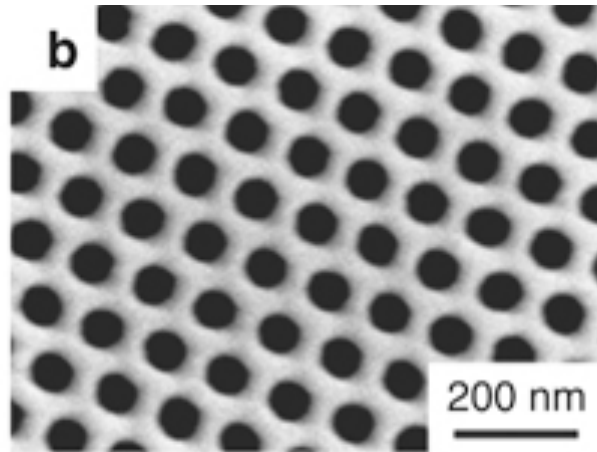
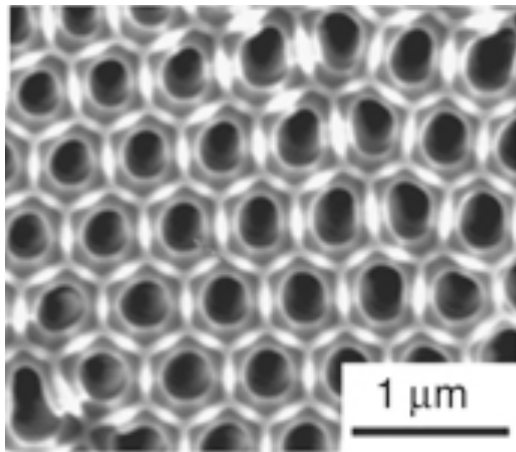
- use prefabricated cylindrical nanopores in a solid material as templates
- There are several ways to fill the nanopores to form nanowires, but the electrochemical method is a general and versatile method.
- Electrodeposition often requires a metal film on one side of the freestanding membrane to serve as a working electrode on which electrodeposition takes place
- If dissolve away the host solid material, free-standing nanowires are obtained.

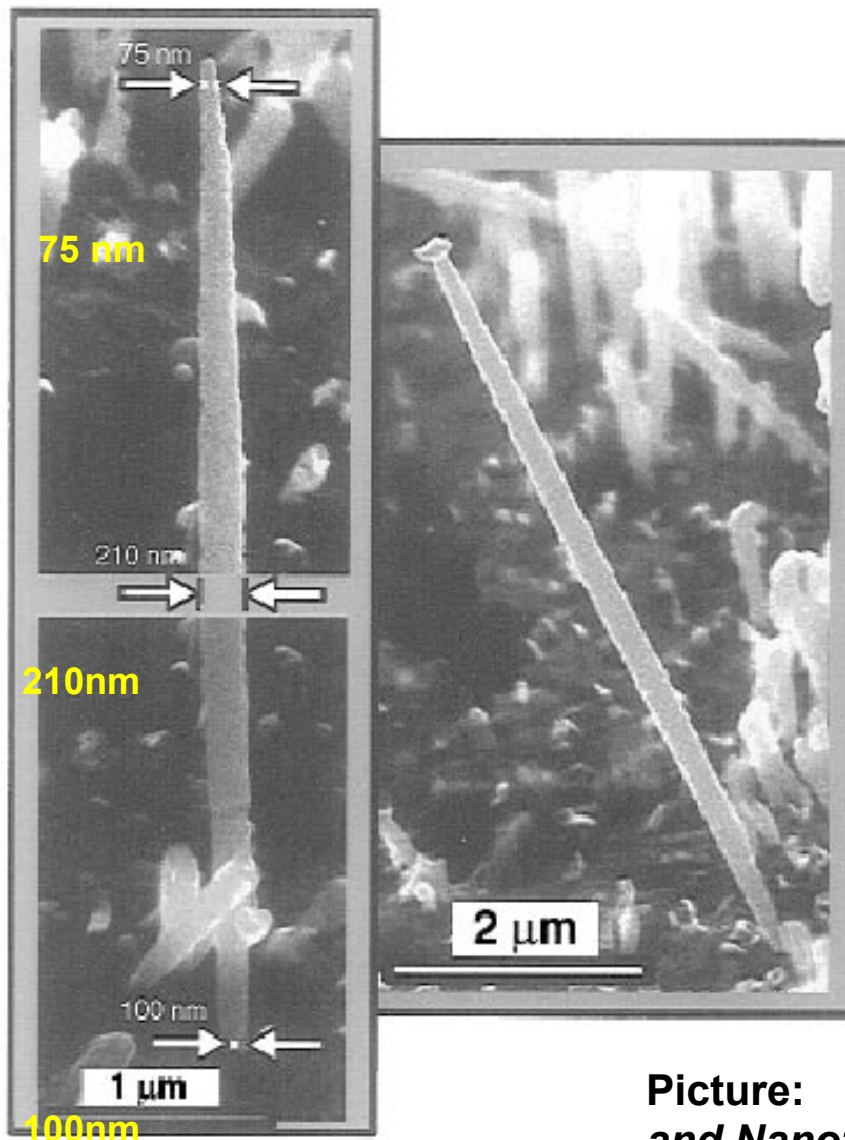
Electrochemical Deposition



- The diameter of the nanowires is determined by the geometrical constraint of the pores
- Fabrication of suitable templates is clearly a critical first step

Anodic Aluminum Oxide (AAO) templates





nano wires grown in
a **80nm** template
membrane after
dissolution of the
membrane.

Picture: *"Fabrication of Polypyrrole Nanowire and Nanotube Arrays,"* Fa-Liang Cheng*, Ming-Liang Zhang and Hong Wang, <http://www.mdpi.net/sensors/papers/s5040245.pdf>

Nanoparticle preparation

- Vapor condensation: Metallic and metal oxide ceramic nanoparticles. Inert gas condensation, thin film deposition (sputtering, thermal evaporation, chemical vapor deposition etc.).
- Chemical synthesis: In a liquid medium composed of various reactants. Sol-gel, electrodeposition.
- Solid-state processes: Mechanical processes (Grinding or milling) of bulk materials.

Surface Energy

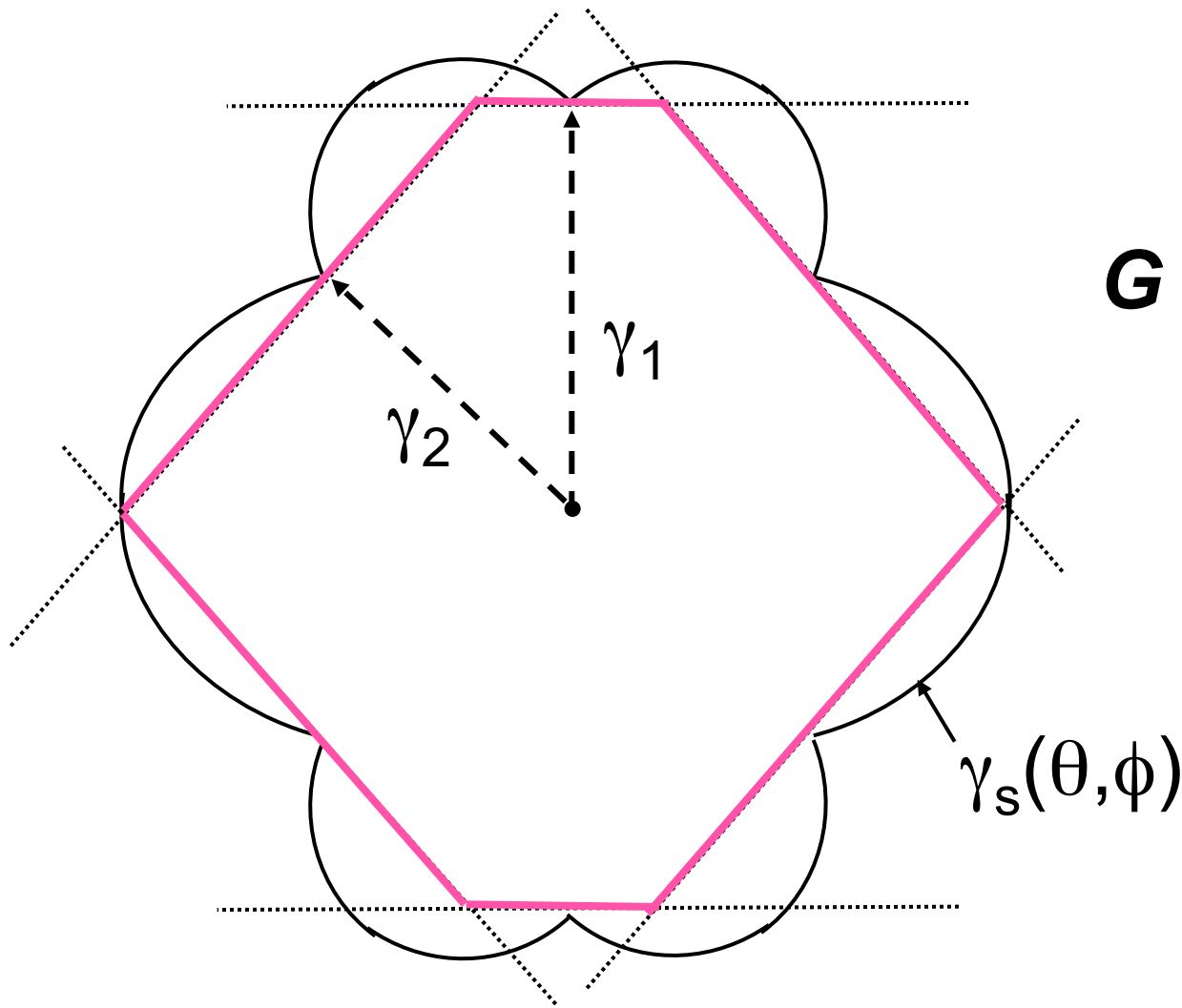
- Surface energy is given by

$$E(\Gamma) = \int_{\Gamma} \gamma \, dS$$

- Standard model for anisotropic surface free energy

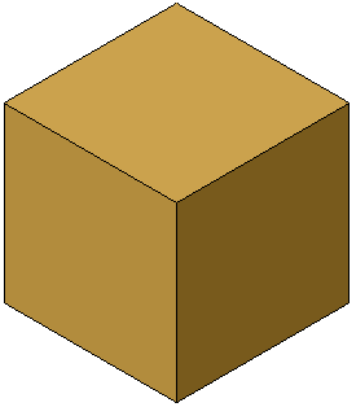
$$\gamma = \gamma_0(n)$$

Wulff construction

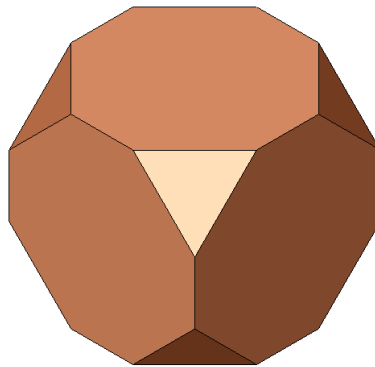


$$\mathbf{G} = \int \gamma_s(\theta, \phi) \, dA$$

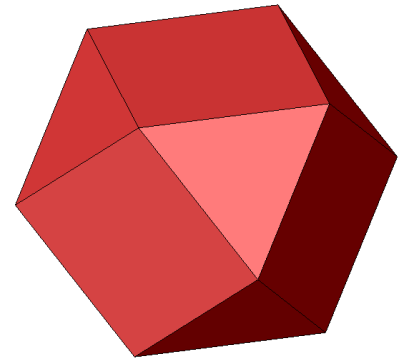
Single crystalline structures



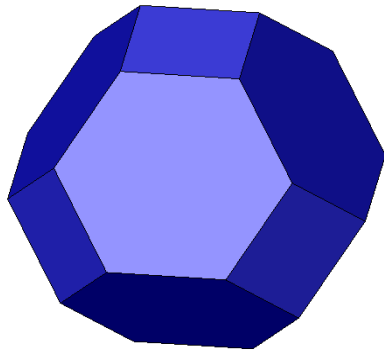
(a) cube



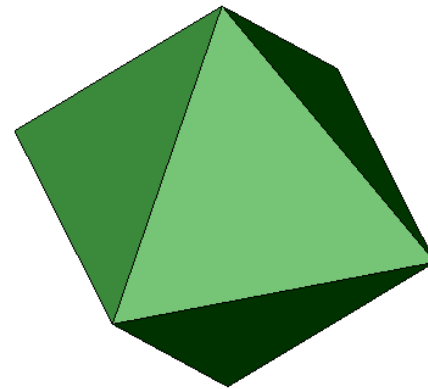
(b) truncated cube



(c) cuboctahedron

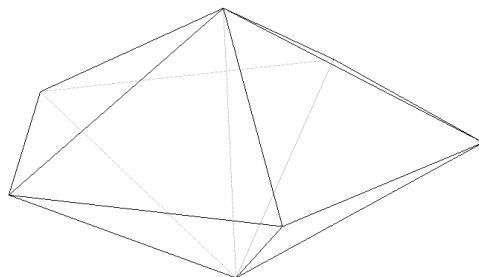
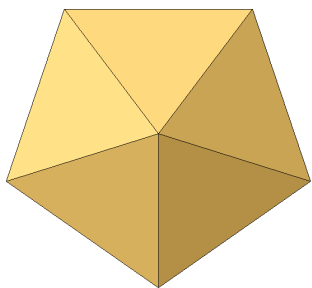


(d) truncated octahedron

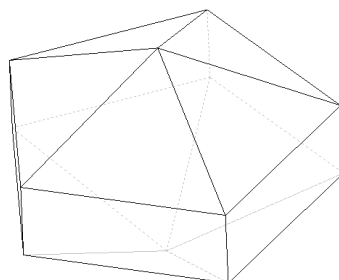
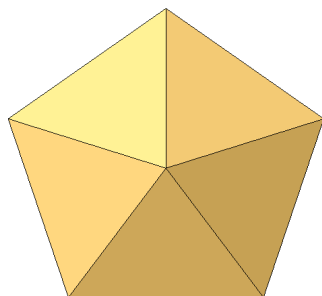


(e) octahedron

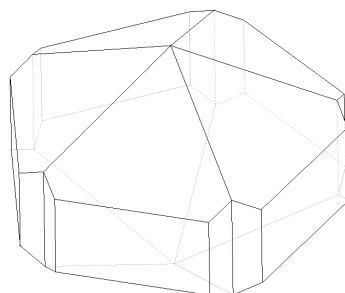
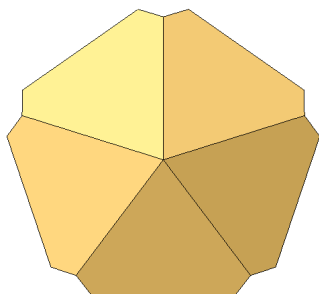
Decahedra



Classic

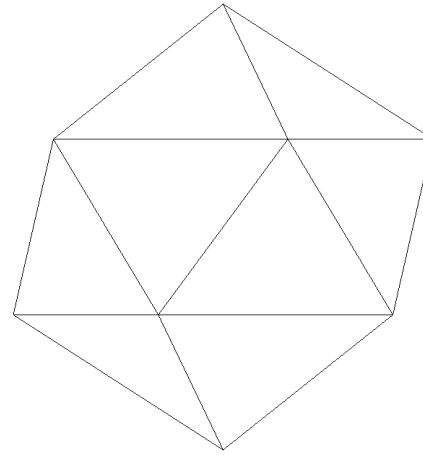
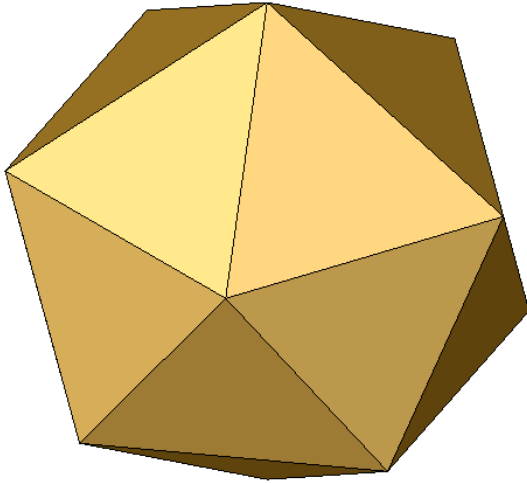


Ino's



Marks'

Icosahedra

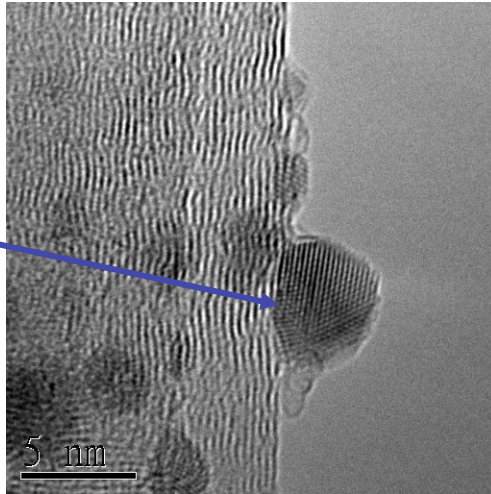


Size-dependent structures calculated for Ni clusters:
Icosahedra for 142 – 2300 atoms;
Marks' decahedra for 2300 – 17000 atoms;
Single crystal for > 17000 atoms.

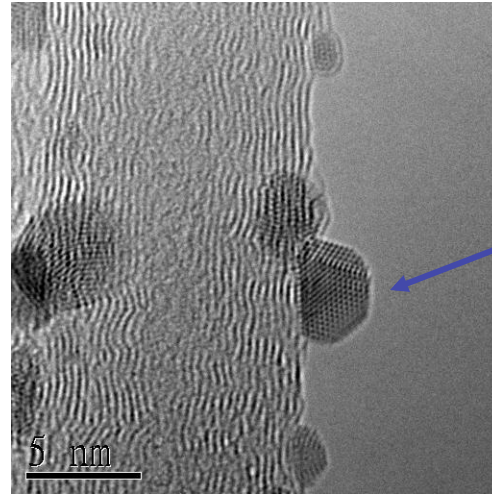
C.L. Cleveland and Uzi Landman, J. Chem. Phys. 94, 7376 (1991)

Varying structures of Ag clusters

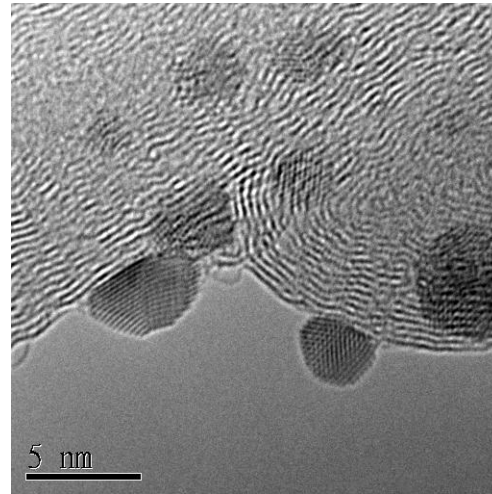
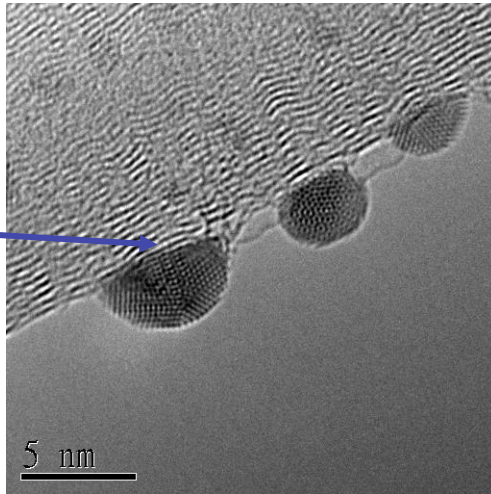
SC



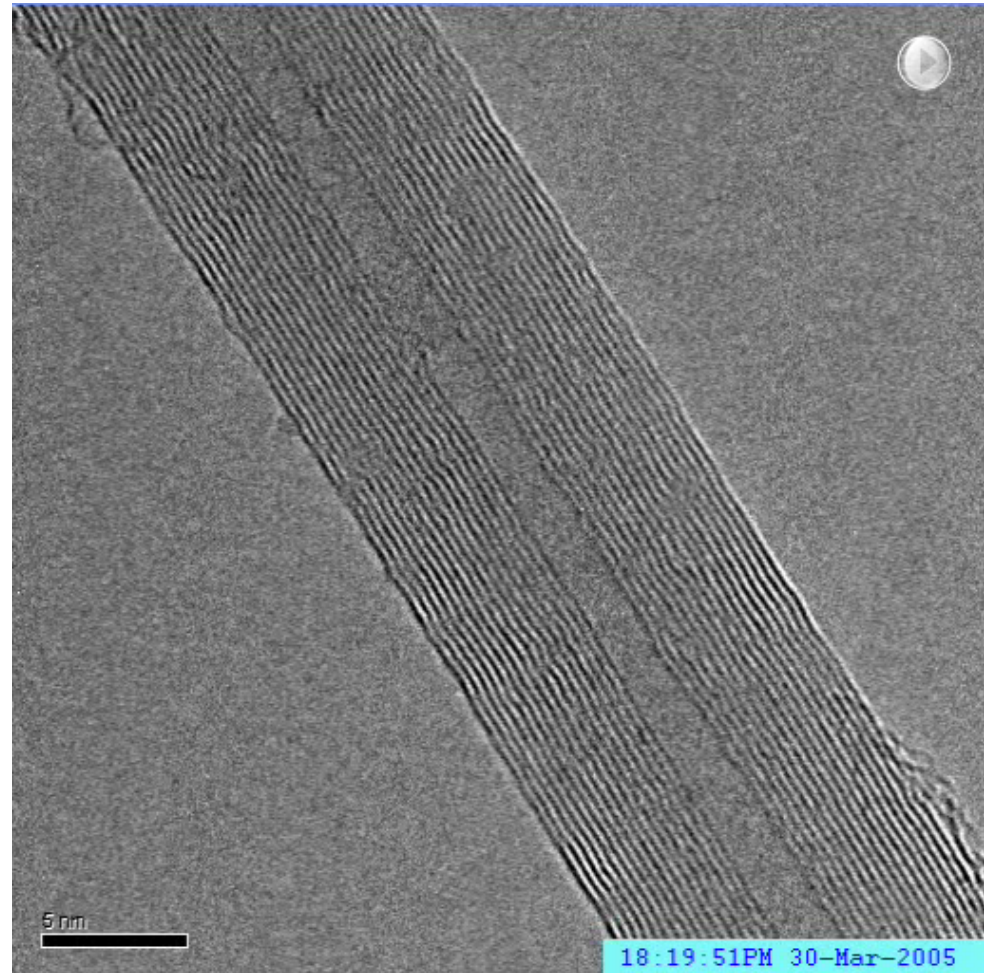
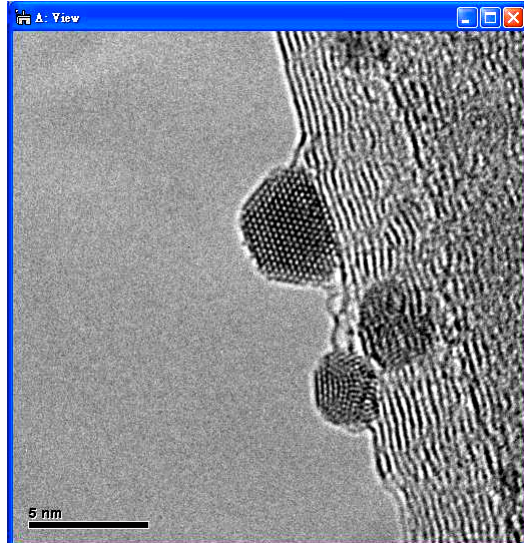
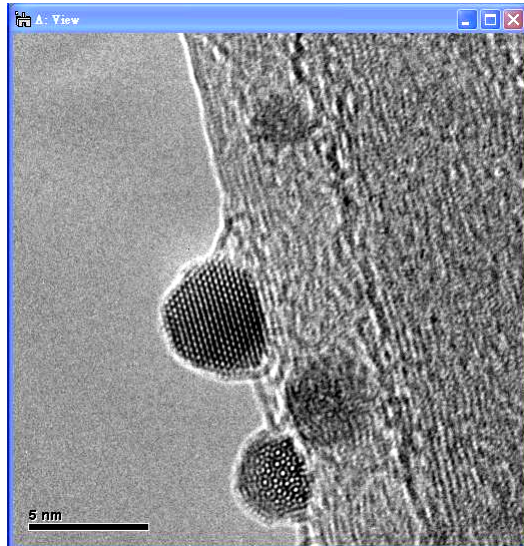
Dh



Ic

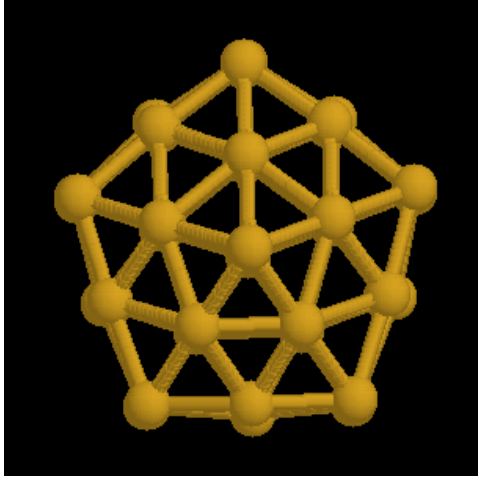


Atomic motion and recrystallization



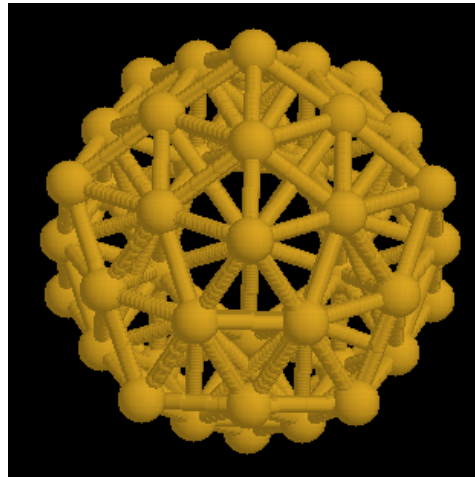
Room temperature

Possible shell structures of nano particles



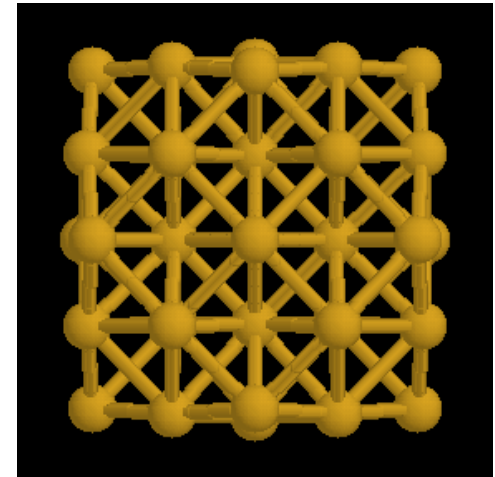
Decahedral:

10 (111) faces +
5 (100) faces



Icosahedral:

20 (111) faces



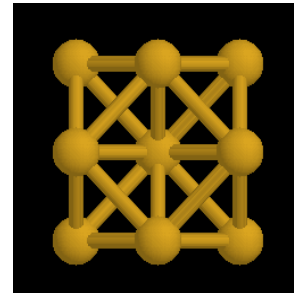
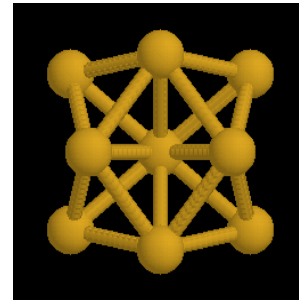
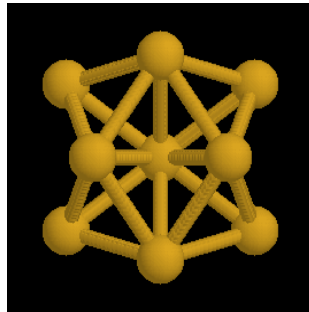
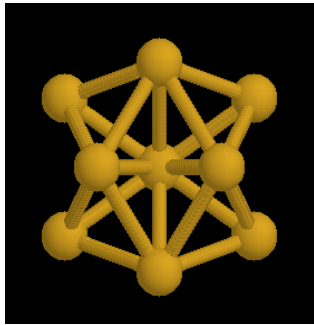
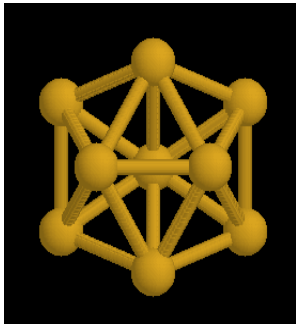
Cuboctahedral:

8 (111) faces +
6 (100) faces

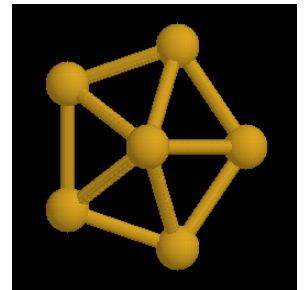
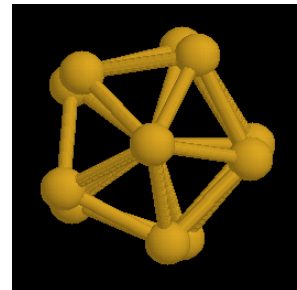
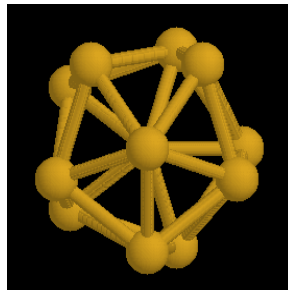
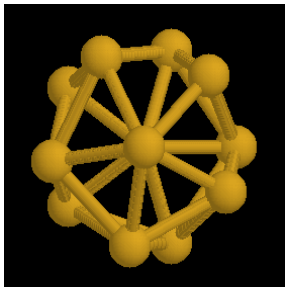
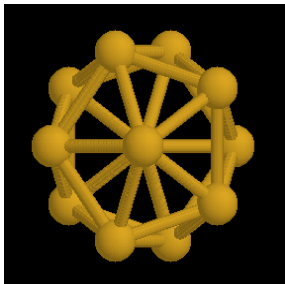
(Courtesy of C.M. Wei)

Structural phase transition

Icosahedral \Leftrightarrow Cubotohedral

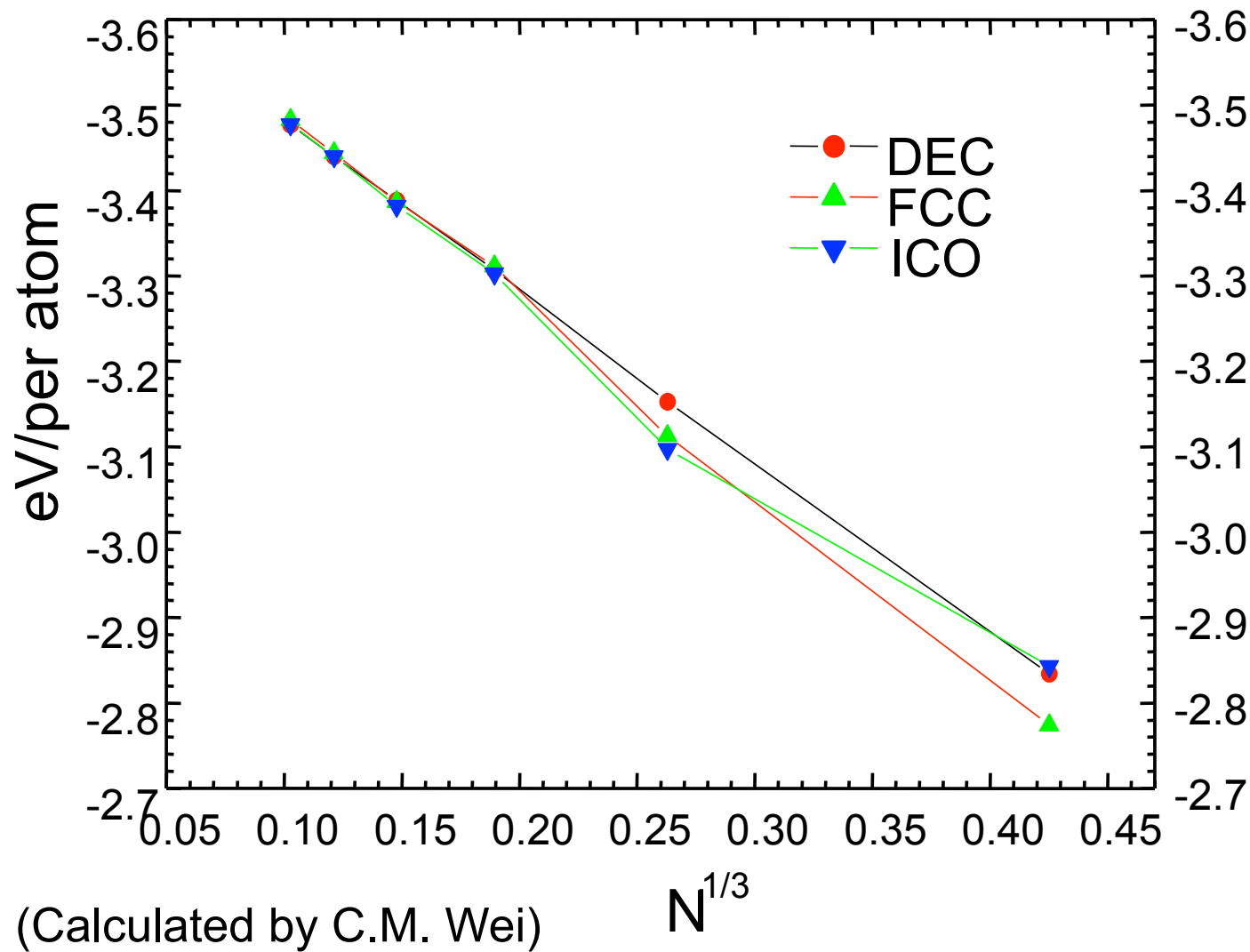


Icosahedral \Leftrightarrow Decahedral

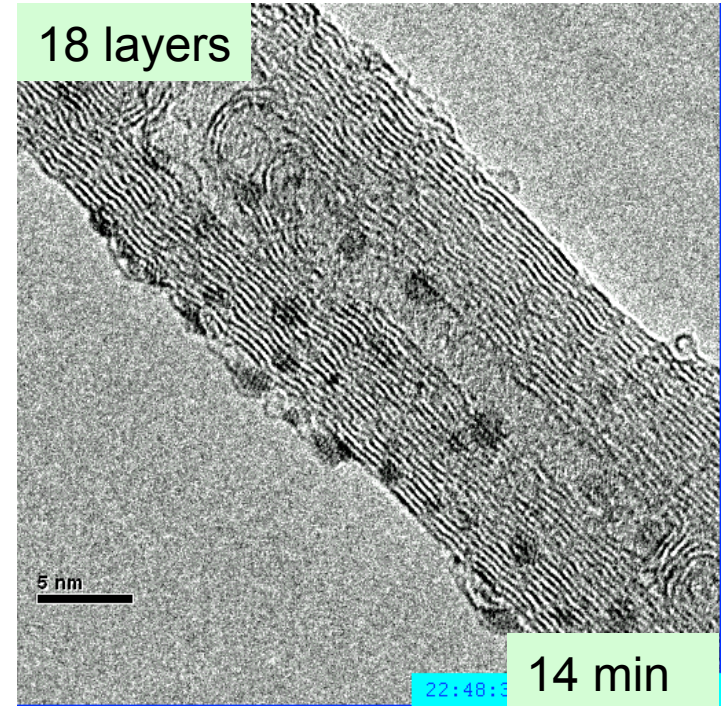
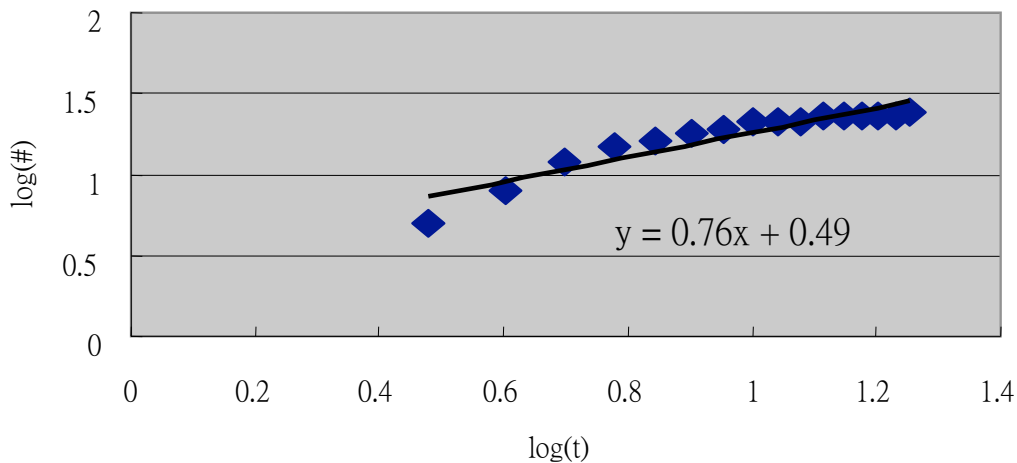
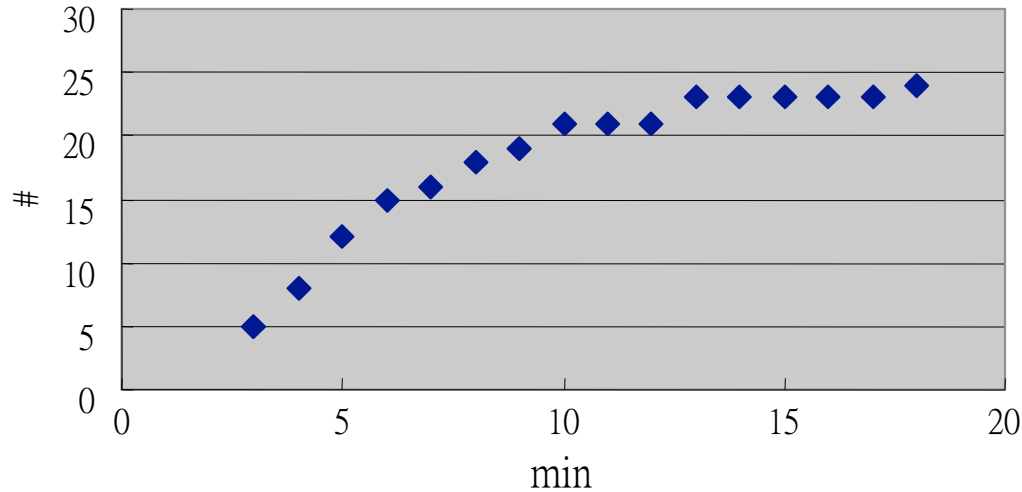


(Courtesy of C.M. Wei)

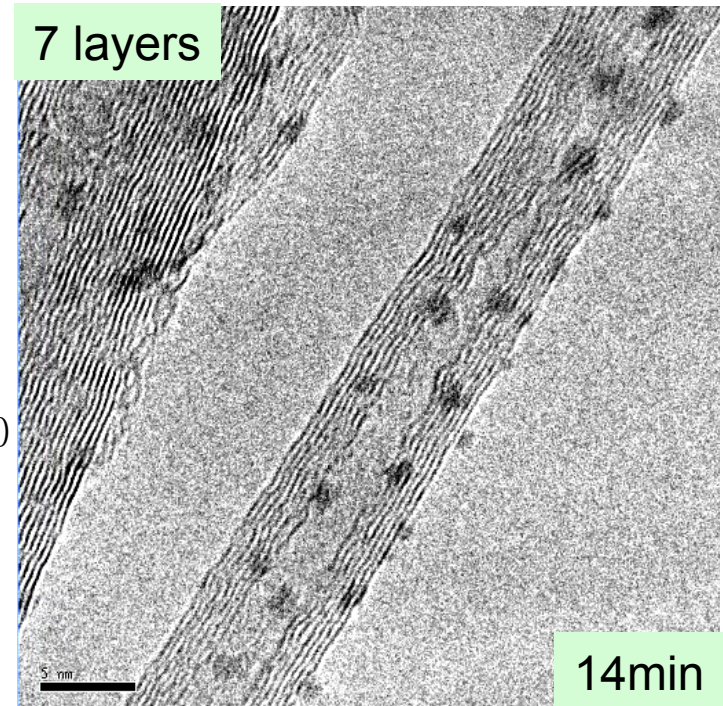
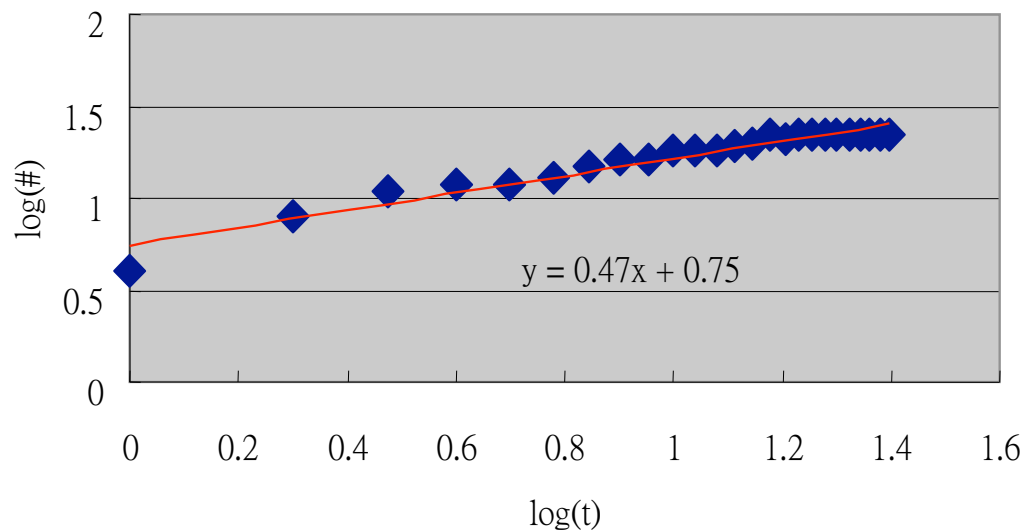
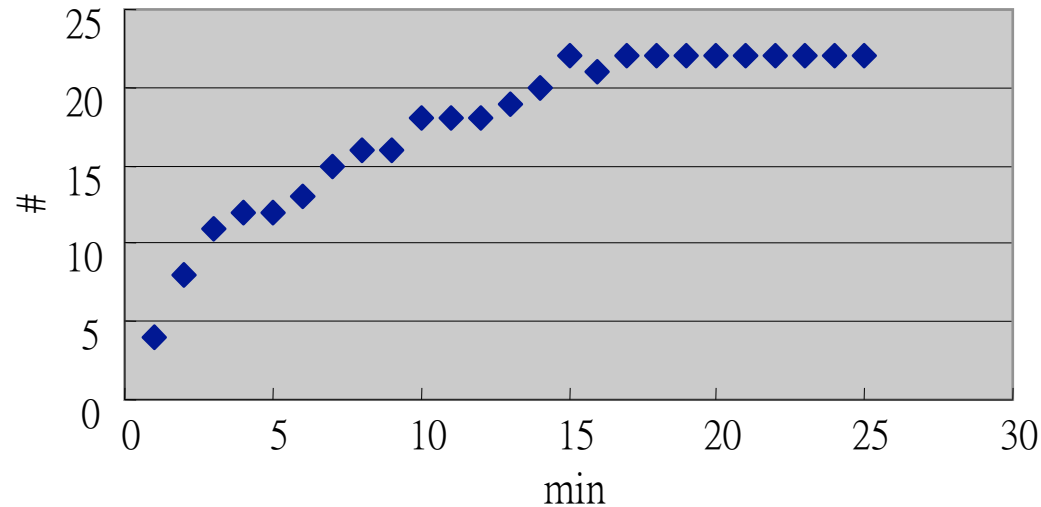
Binding energy for Al nano particles



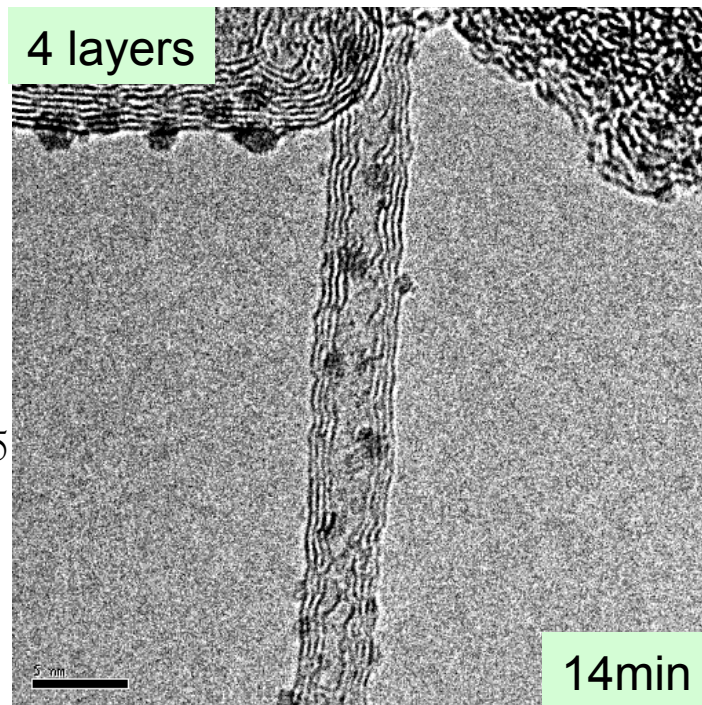
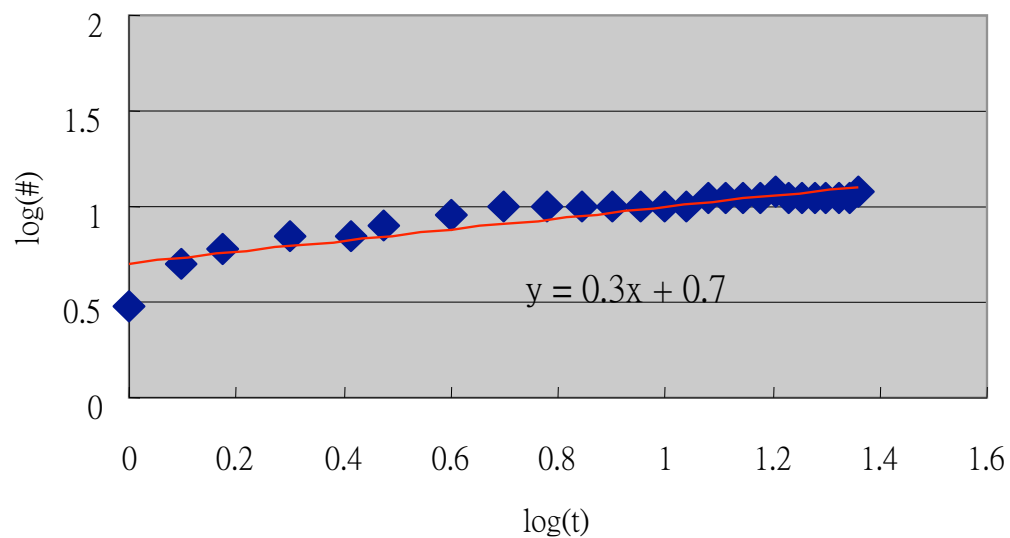
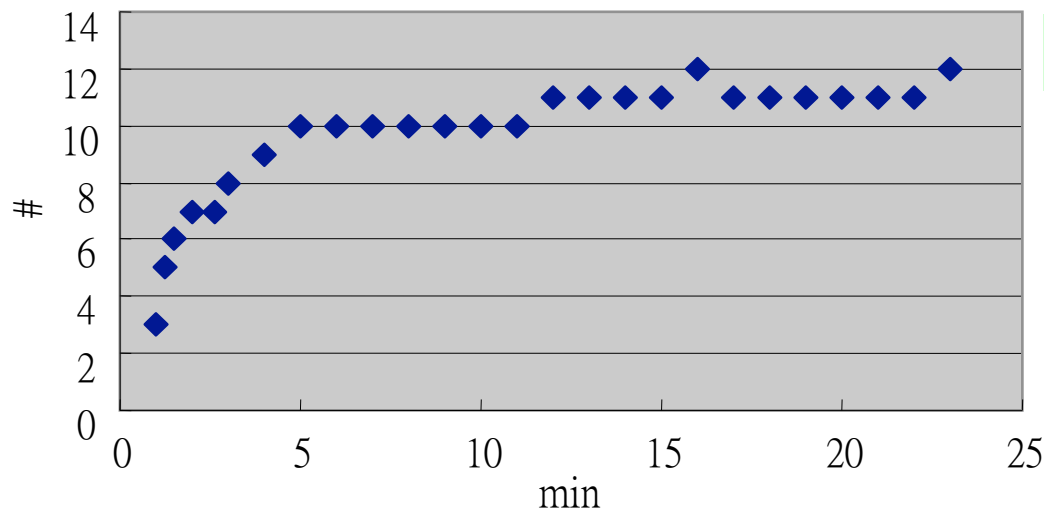
Growth of Ag clusters on 18-layer CNT



Growth of Ag clusters on 7-layer CNT



Growth of Ag clusters on 4-layer CNT



How surface diffusion related to island density

In a 2D random walk, the diffusion coefficient is

$$D = \Gamma \cdot a^2$$

Where Γ is the number of jumps in unit time (second) and a is the jumping step size, i.e., lattice spacing.

The lifetime of an adatom is controlled by two collision rates, W_{AA} (adatom-adatom collision) and W_{AI} (adatom-island collision).

The “death rate” of adatom, i.e., # of adatoms die in unit time (sec) is

$$n/\tau_A = 2W_{AA} + W_{AI}$$

Where τ_A is the lifetime, and n is the number density of adatoms --- # of adatoms per unit area.

Now, Let R be the deposition rate --- # of adatoms deposited on unit area in unit time, then

$$n = R\tau_A$$

The number of sites visited by an adatom during its lifetime is $\Gamma\tau_A = D\tau_A/a^2$. On average, # of sites occupied by one atom is $1/na^2$ and # of sites occupied by an island is $1/Na^2$.

where N is the number density of islands --- # of islands per unit area.

Hence, the *probability* of an arriving adatom to collide with an existing atom is

$$(D\tau_A/a^2)/(1/na^2) = nD\tau_A$$

Similarly, the *probability* of an arriving adatom to collide with an existing island is

$$(D\tau_A/a^2)/(1/Na^2) = ND\tau_A$$

Multiplying the above two terms by $R = n/\tau_A$ gives the collision rate, i.e., **# of collisions in unit time**:

$$W_{AA} = n^2D; \quad W_{AI} = nND$$

The nucleation rate, i.e., the rate of increase of the number density of islands, can be given as

$$dN/dt = W_{AA} = n^2D = R^2/(N^2D)$$

Substituting n with $n = R/ND$.

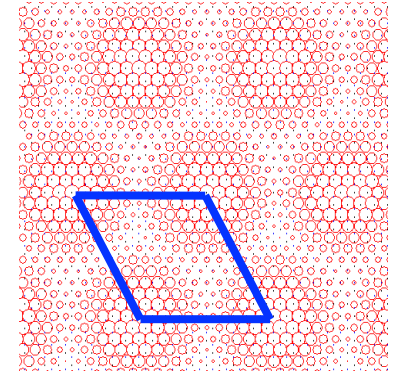
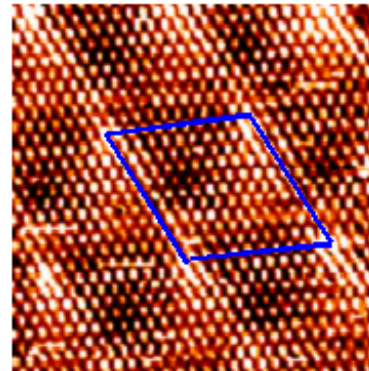
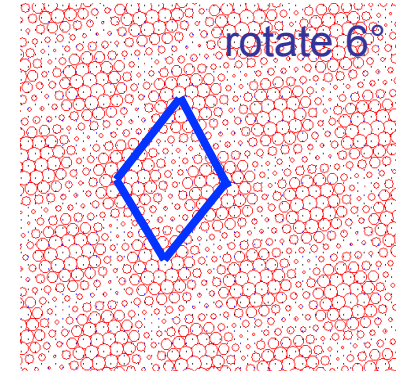
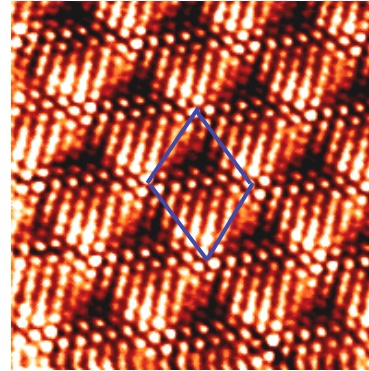
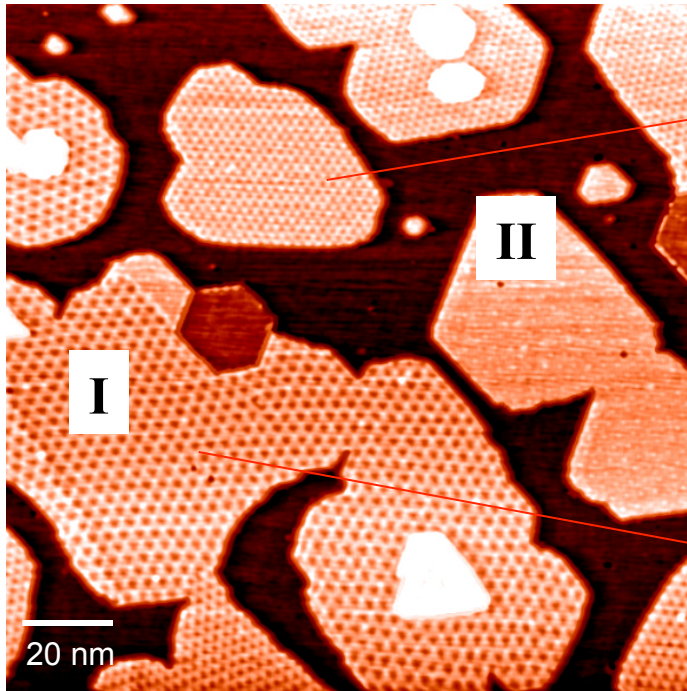
Then, integration leads to

$$N^3 = (3R^2/D)t = 3R\theta/D$$

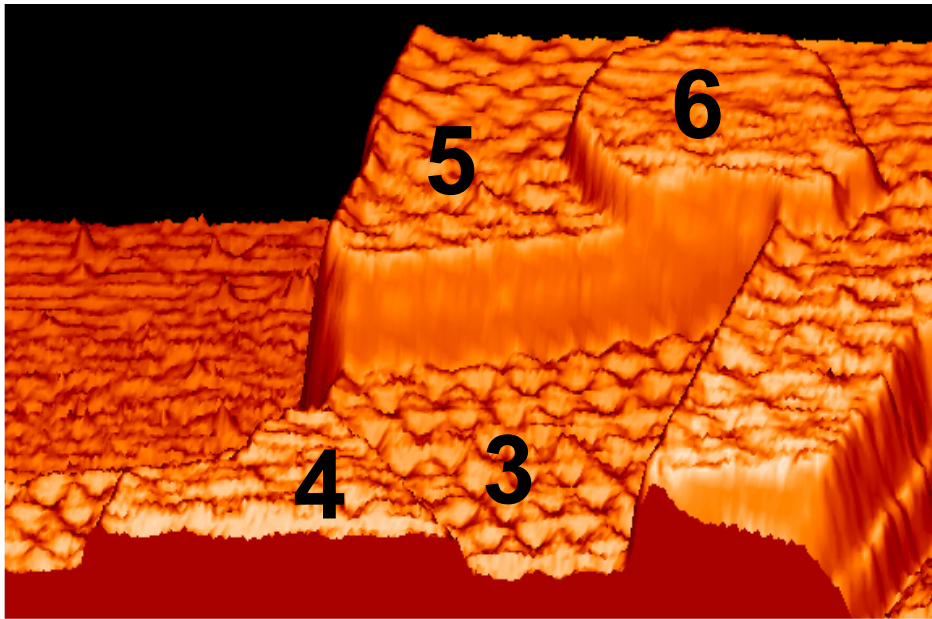
where, $\theta = Rt$ is the total coverage up to time t .

Experimentally, we can measure N , and from there we can determine D .

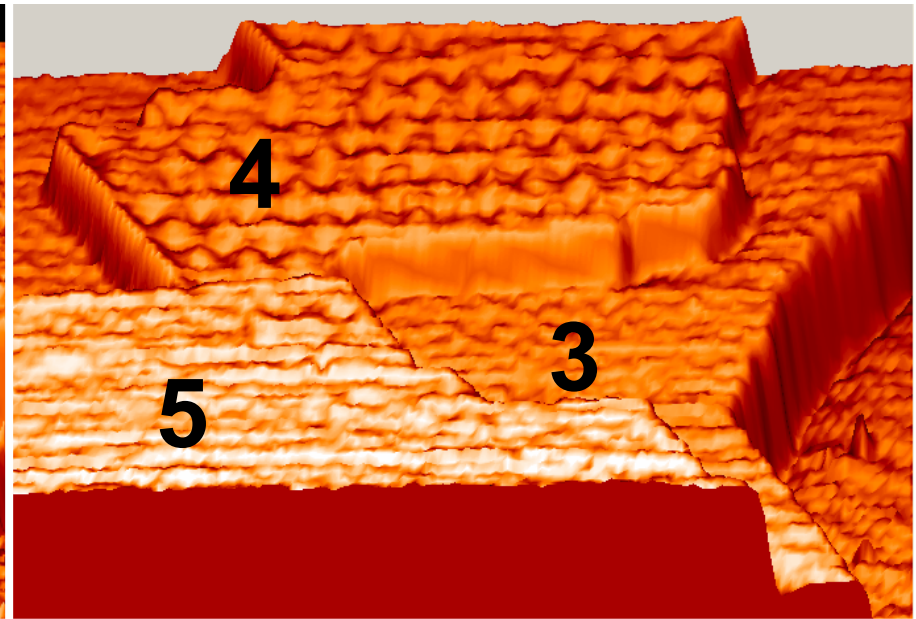
Superstructures of 2D islands



Characteristics of Pb island--- oscillatory and complementary contrast



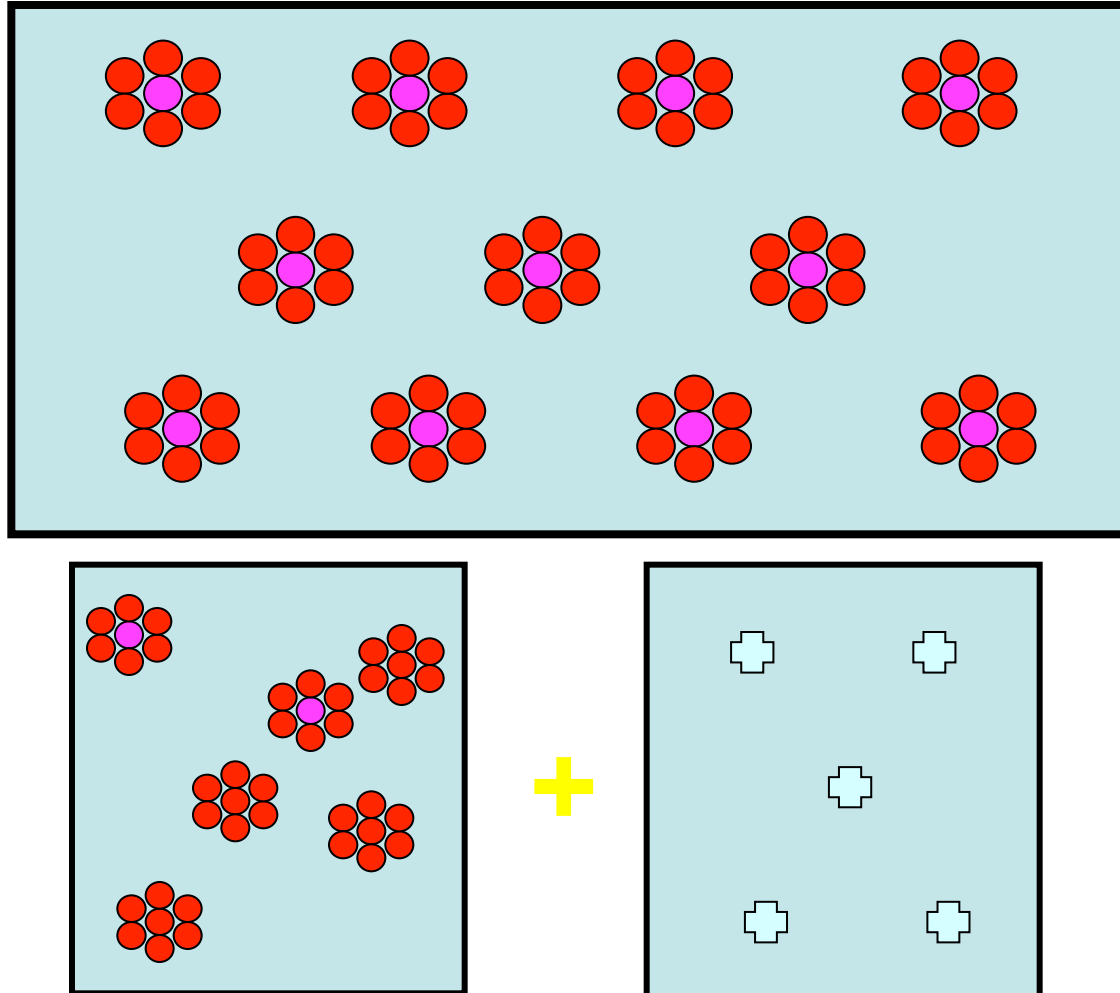
Type I



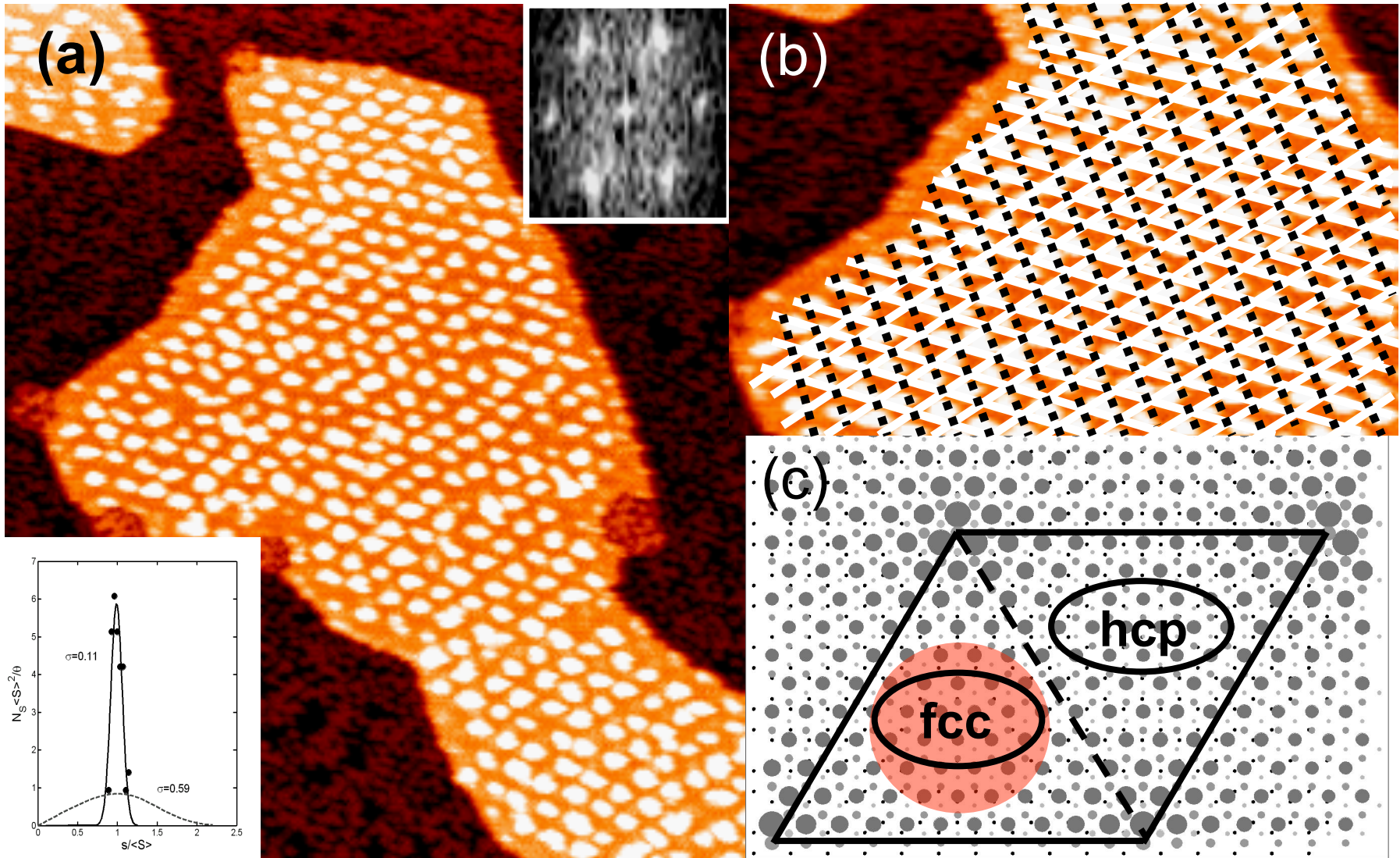
Type II

Self-organized growth

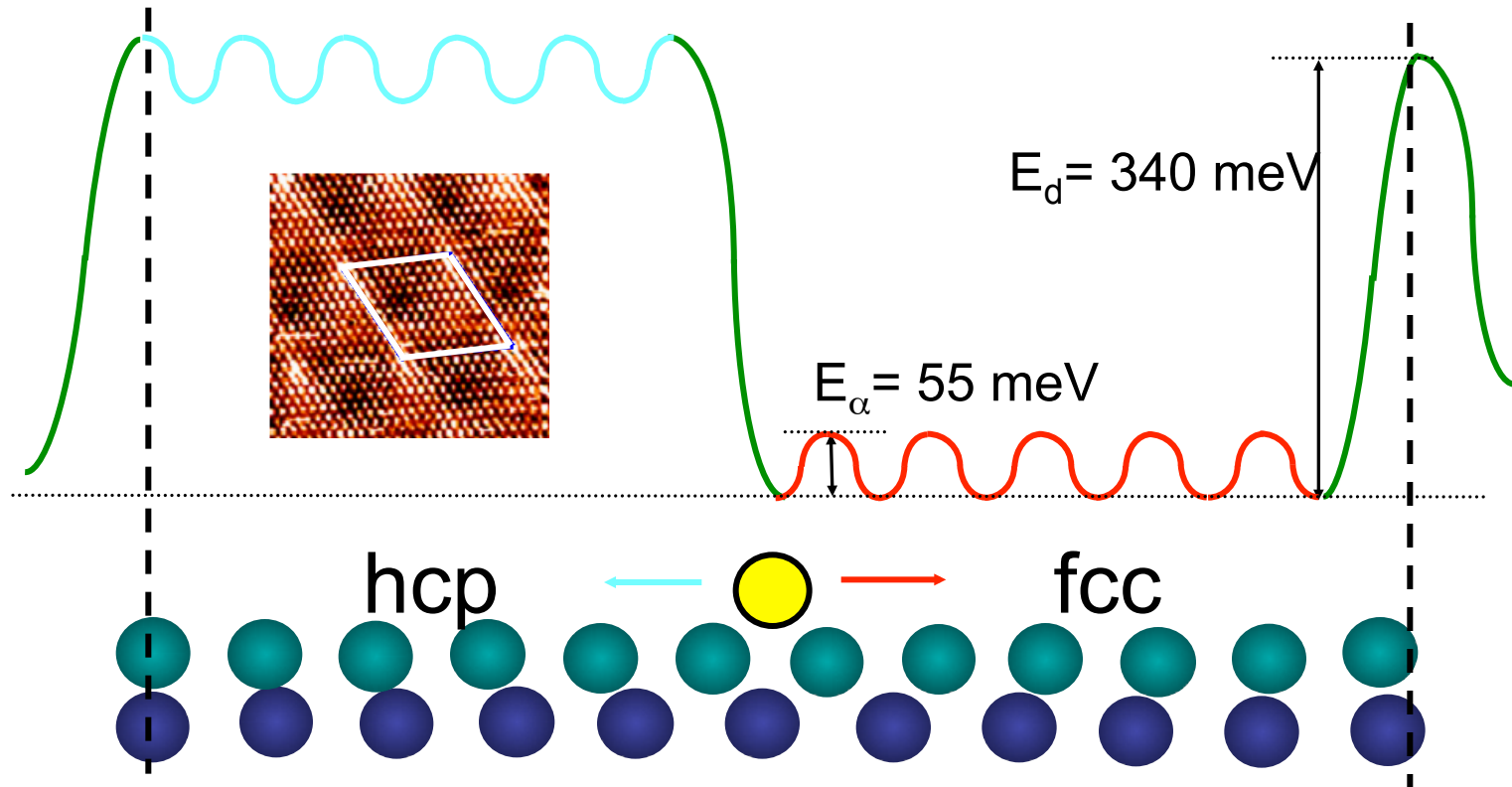
Size uniformity, Shape specification, Spatial orderliness and Functional homogeneity



Properties of nanopucks on Pb islands

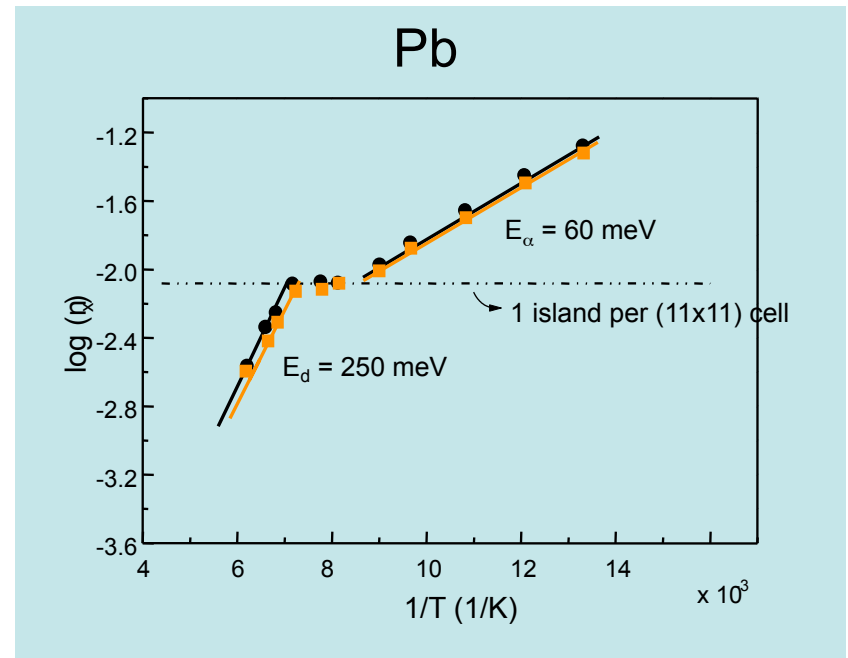
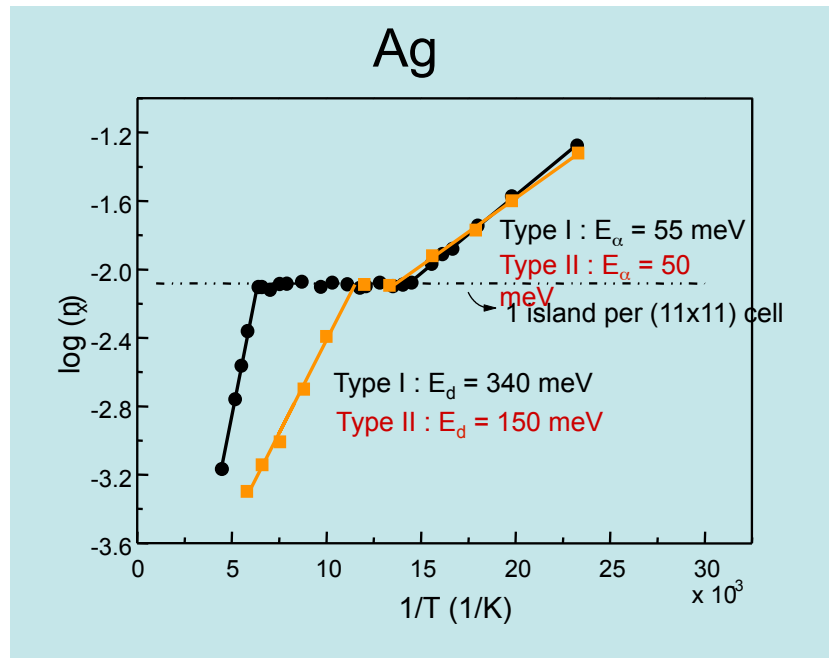
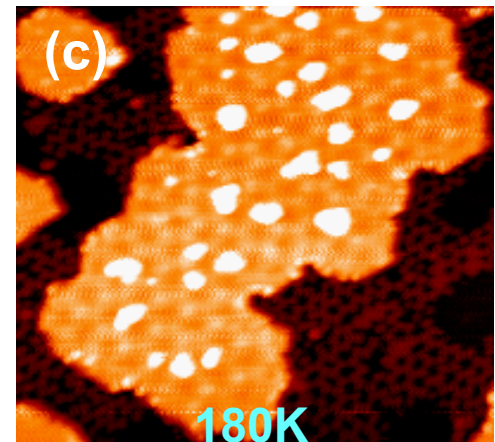
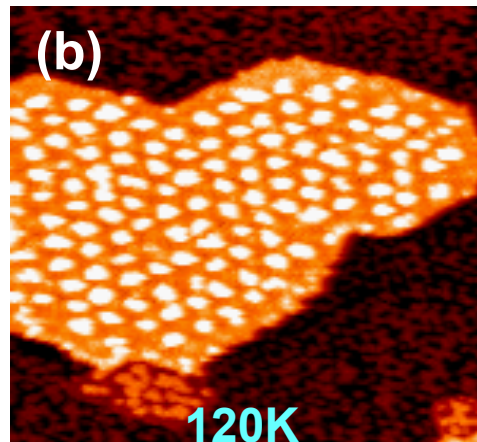
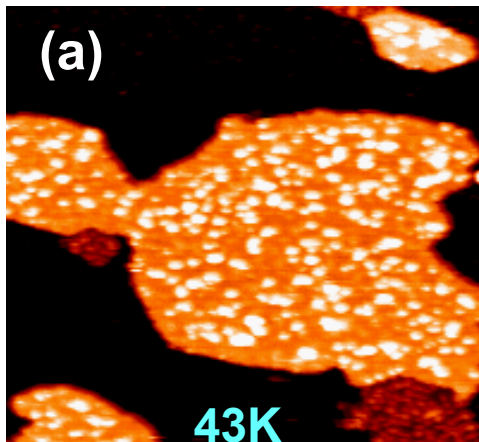


Various diffusion barriers

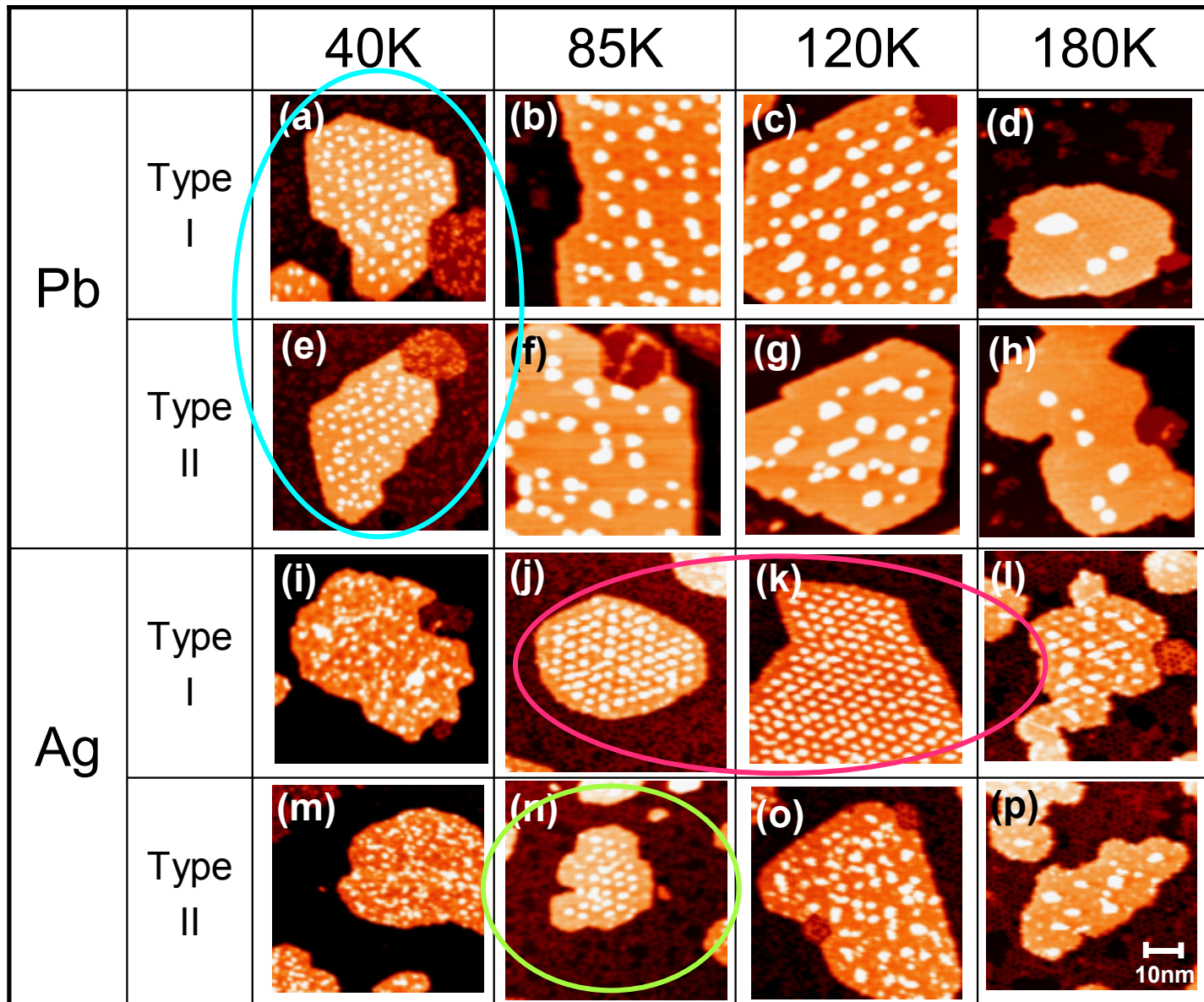


$N \propto E_d / [(i+2)kT]$, i : number of atoms in critical nucleus

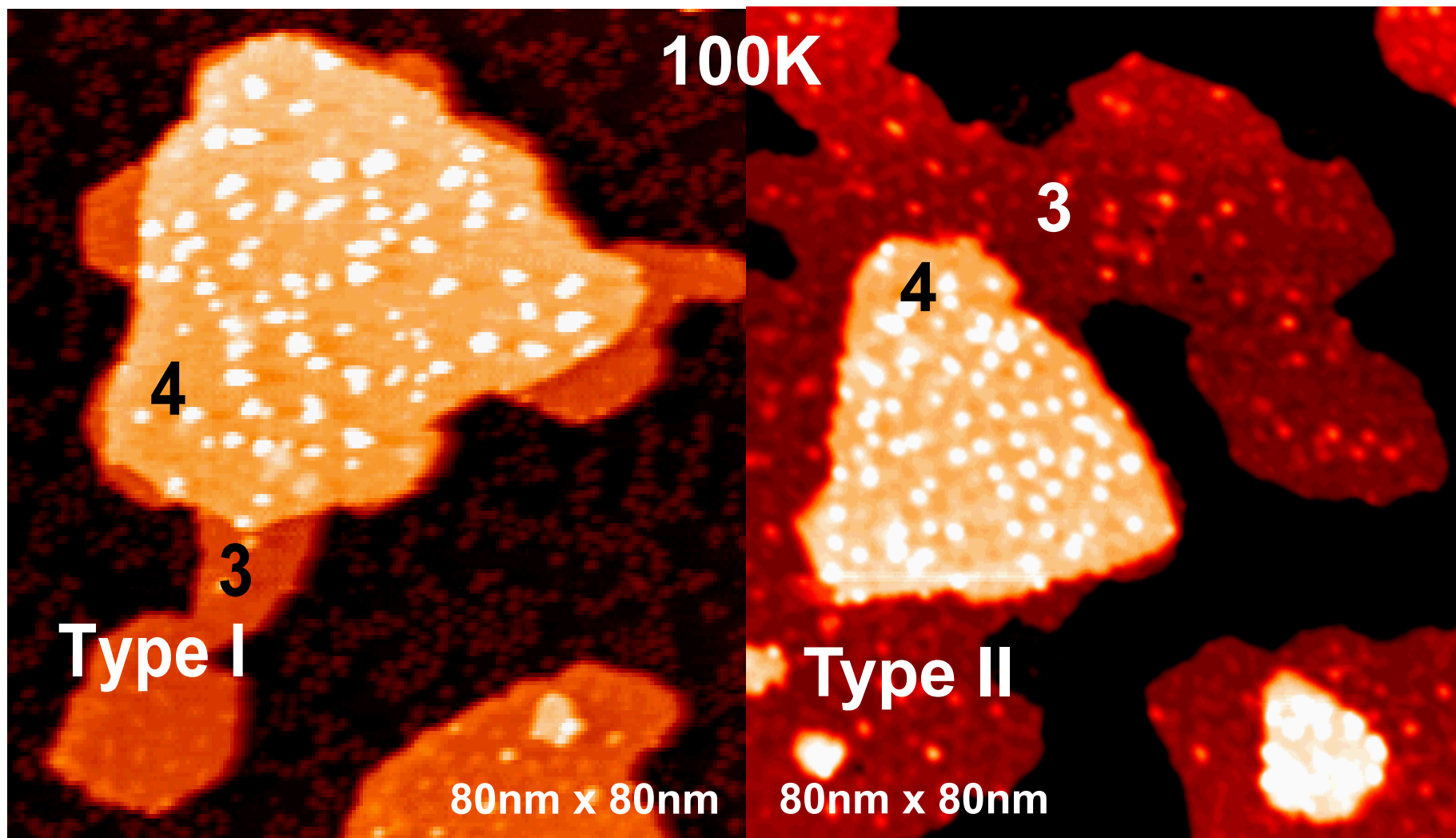
Diffusion barriers for Ag and Pb nanopucks



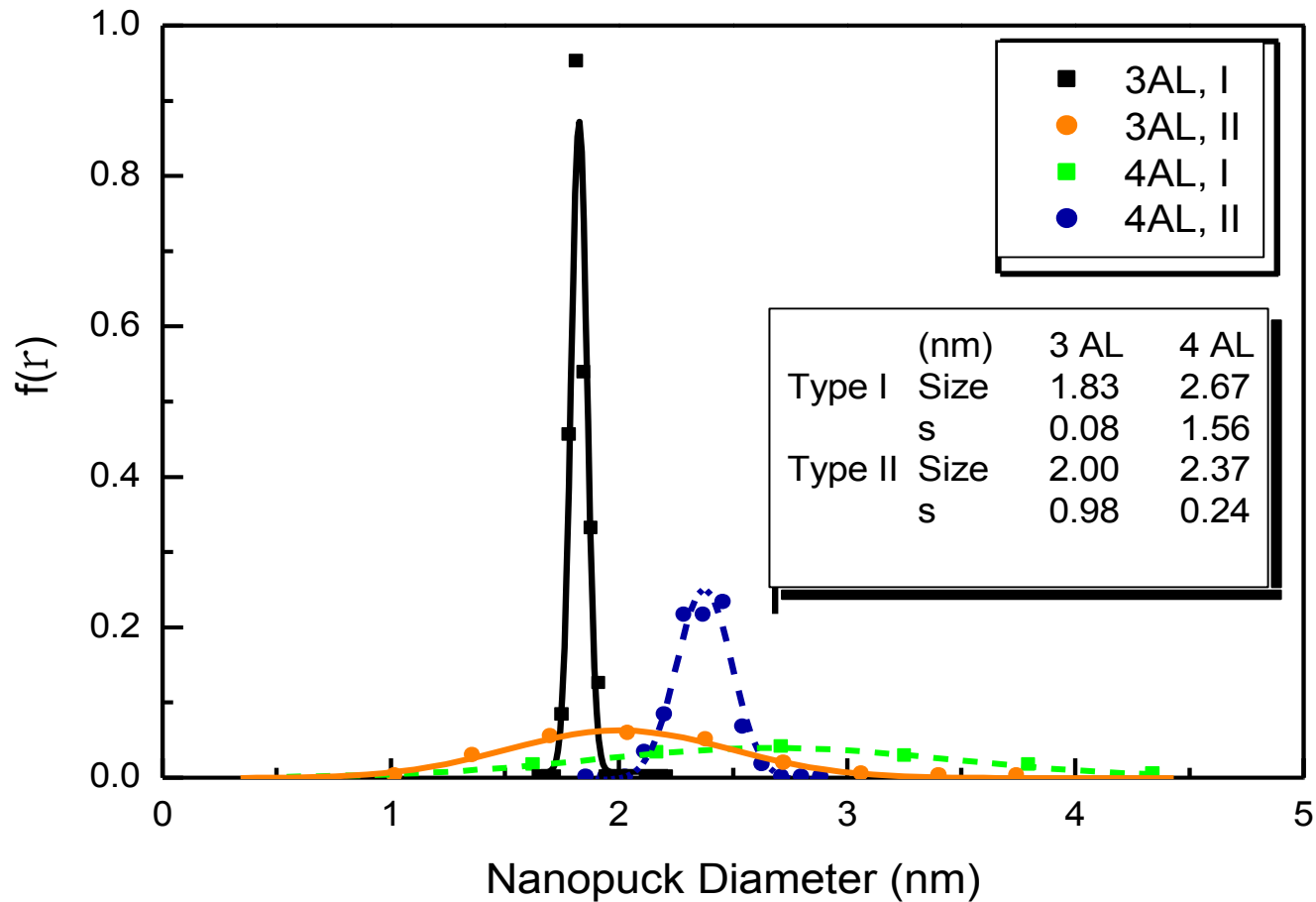
Formation of Pb and Ag nanopucks



Ag nanopucks on Pb islands of 4-layer thickness

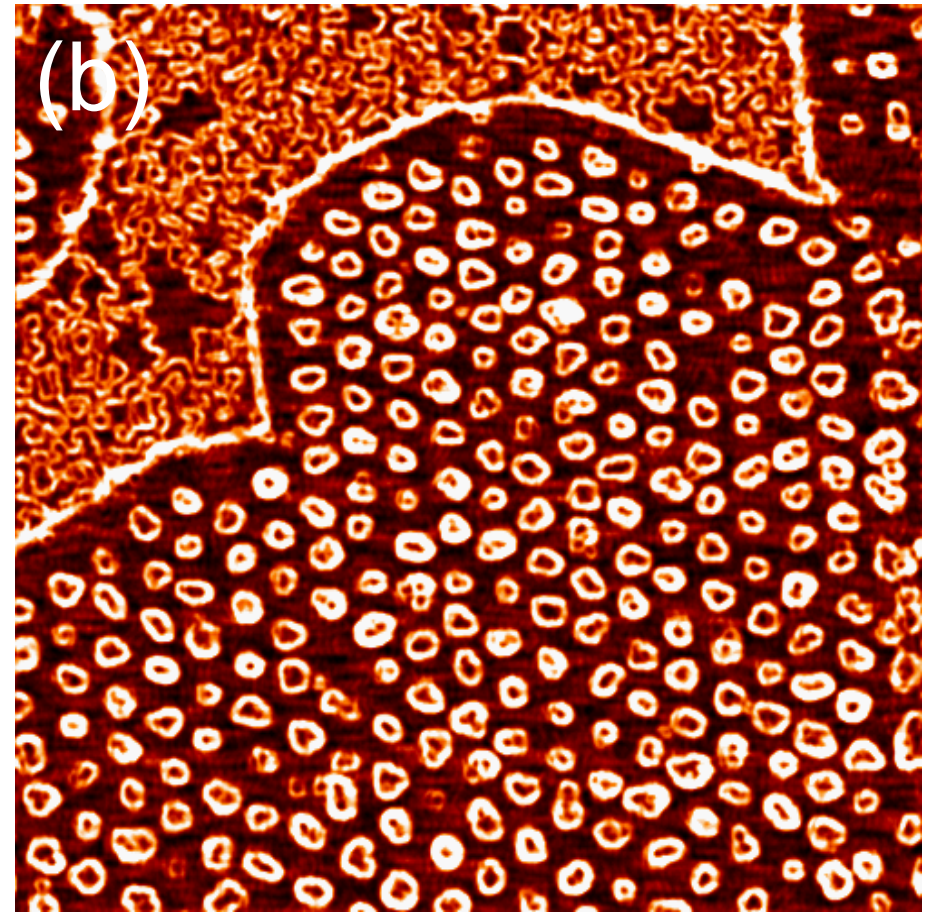
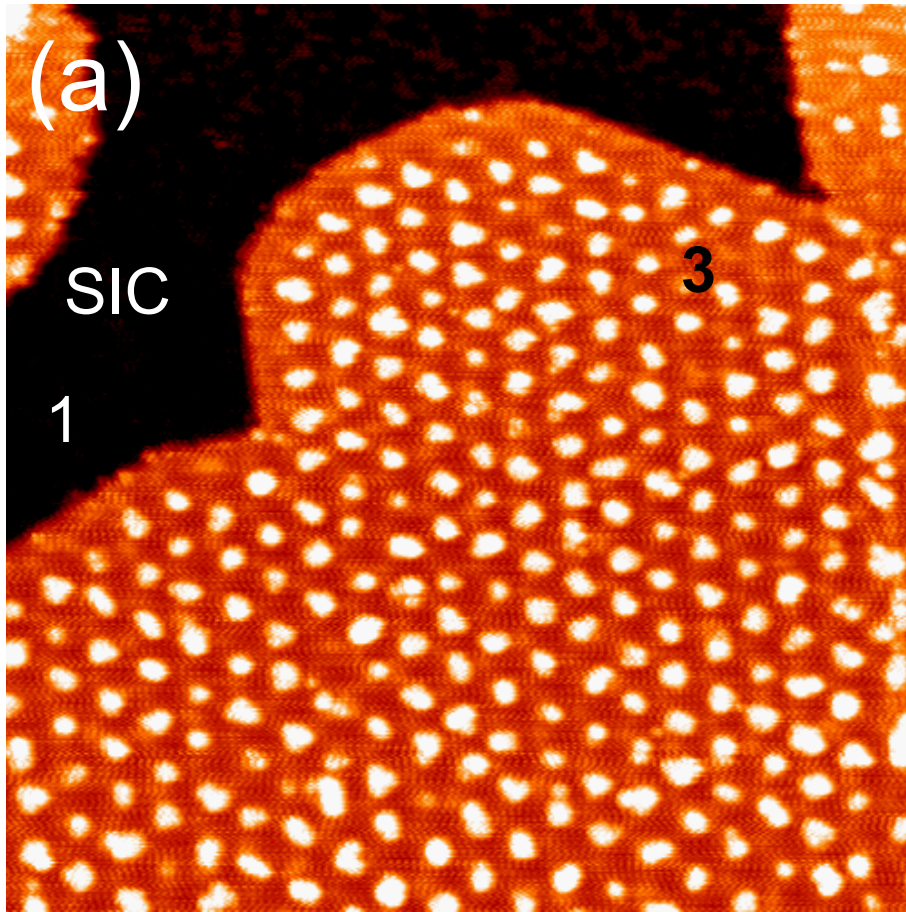


Size distribution of nanopucks



Spatial orderliness : I (3AL) > II (4AL) > II (3AL) > I (4AL)

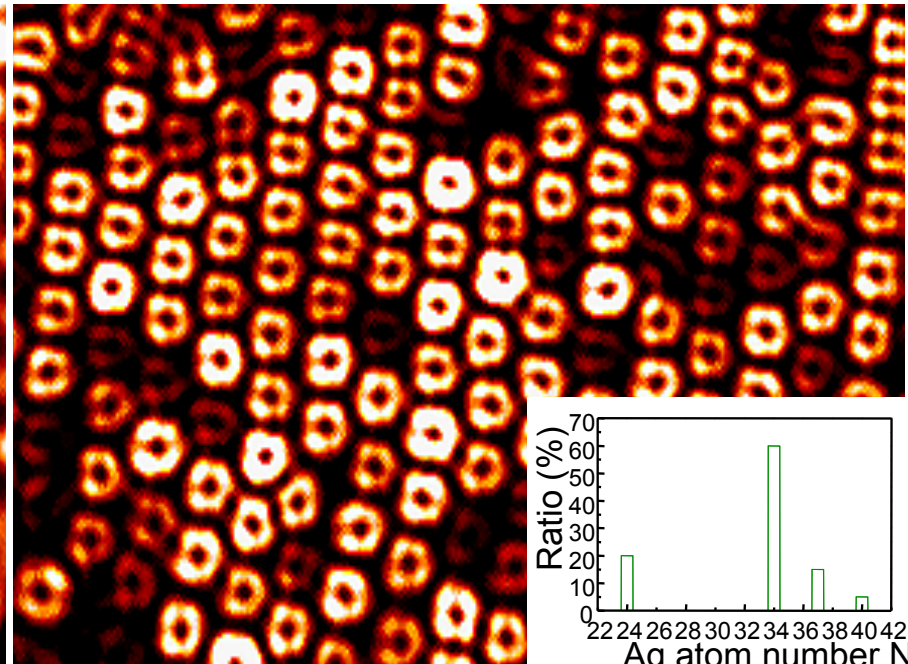
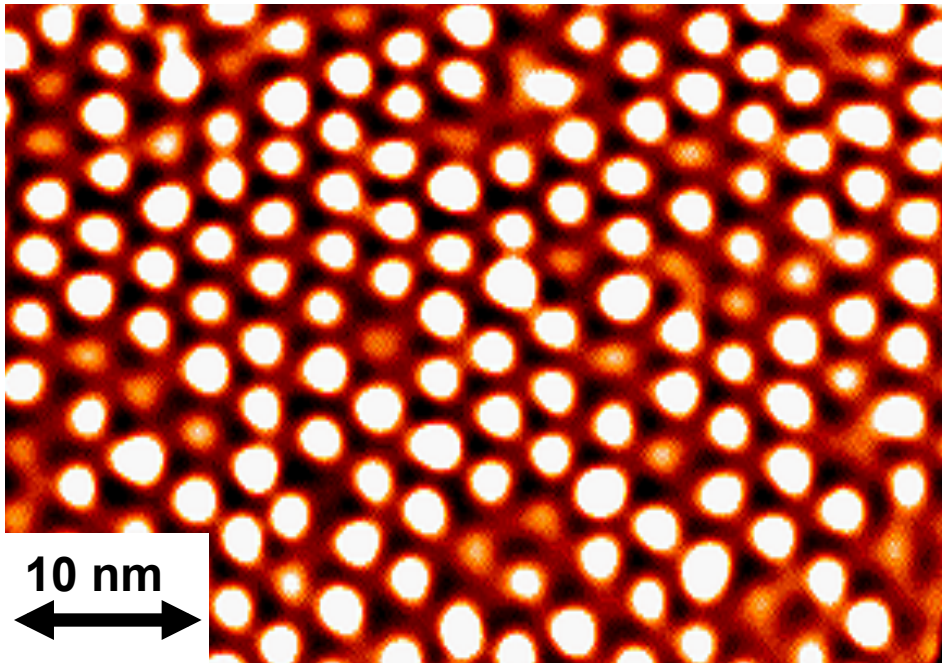
Sizes and shapes of nanopucks



Ag 0.2 ML

$T = 120 \text{ K}$

Size-, site- & shape-controlled self-organized growth



- *The quantitative derivations give the different binding energies of Ag adatoms on two triangular halves of a substrate unit cell.*
- *The difference in binding energy results in confined nucleation of Ag nanopucks at the fcc half cells exclusively and renders a site-specific arrangement.*
- *The order and size distribution of the nanopucks reveal a bi-layer oscillatory behavior, reflecting the electronic properties of the substrate.*

Definition of a composite

A material having two or more distinct constituents or phases, and have to satisfy the following criteria:

1. Both constituents have to present in reasonable proportions, say greater than 5%;
2. The constituents phases have different properties, and hence the composite properties are noticeably different from the properties of the constituents;
3. A man-made composite is usually produced by intimately mixing and combining the constituents by various means.

Nanocomposites: Composites contain two or more nano-sized fillers.
(Nano-structural composites)

Hierarchical nanocomposites

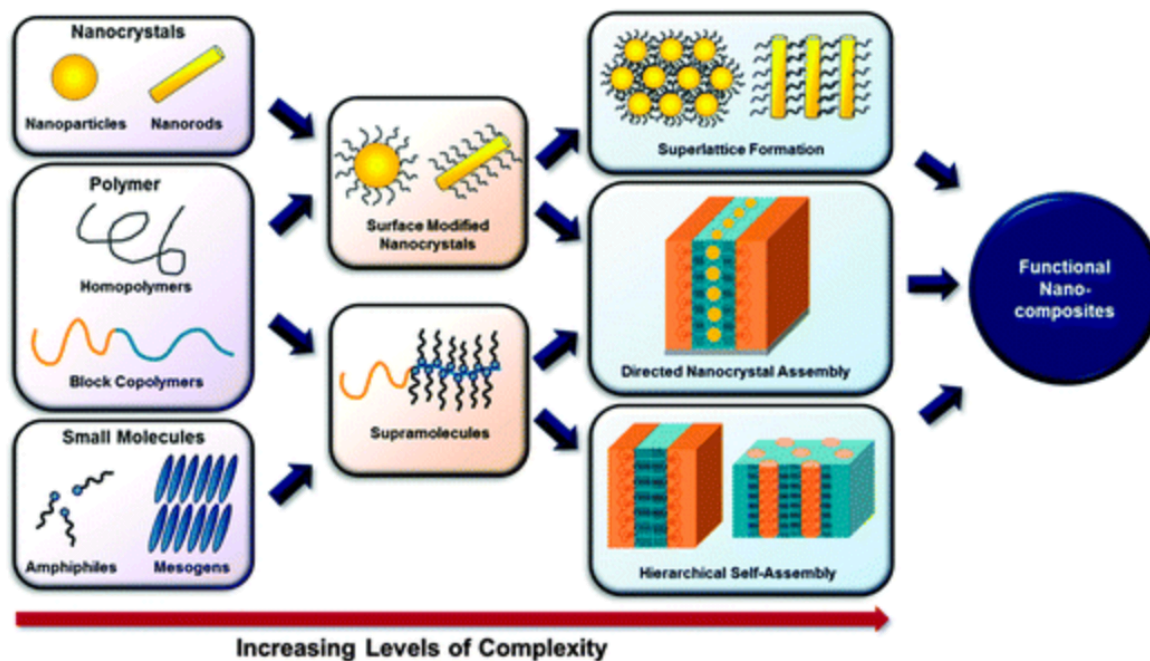
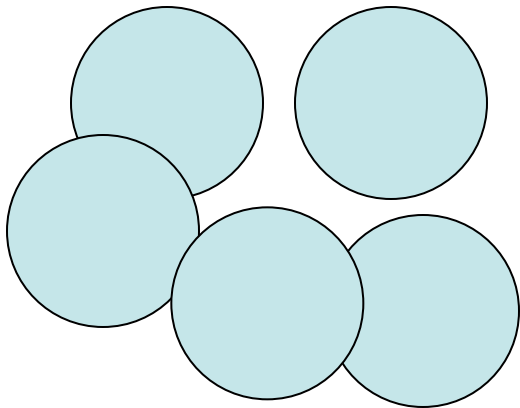
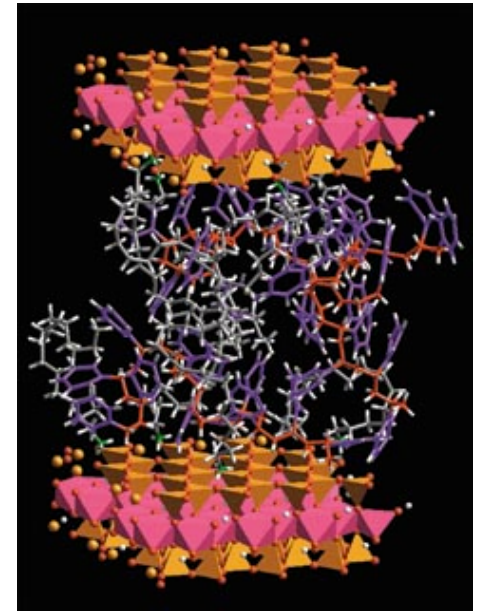


Fig. 1 Hierarchical co-assemblies of nanocrystals, polymers, and small molecules toward functional nanocomposites.

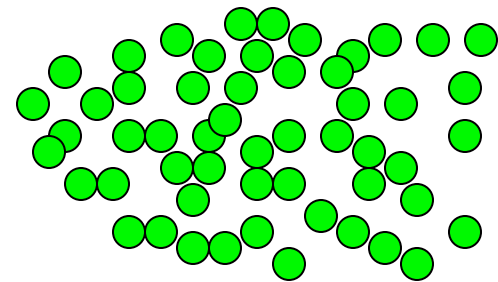
Why Nanocomposites?

Size does matter

Increased surface area on nanoparticles



Microparticles

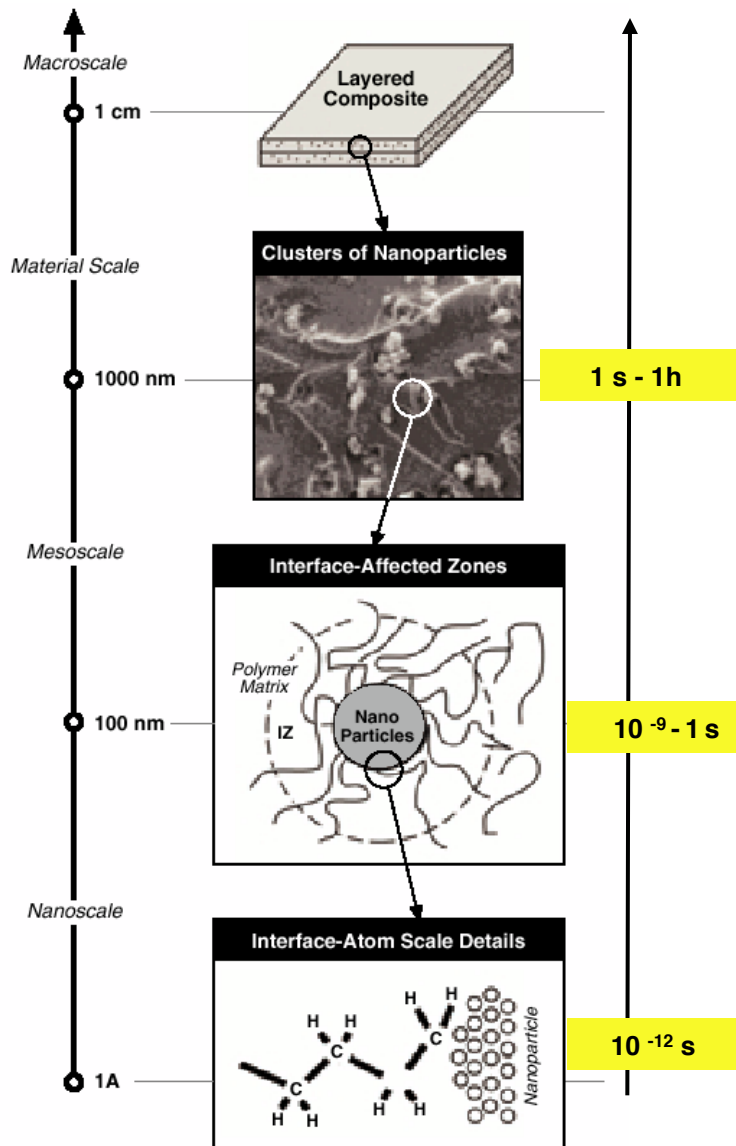


Nanoparticles

Why nanocomposites? → Multi-functionality

- Small filler size:
 - High surface to volume ratio
 - Small distance between fillers → bulk interfacial material
 - Mechanical Properties
 - Increased ductility with no decrease of strength,
 - Scratching resistance
 - Optical properties
 - Light transmission characteristics particle size dependent

Nanocomposite as a Multiscale System



– Macroscale composite structures

– Clustering of nanoparticles - micron scale

– Interface - affected zones - several to tens of nanometers - **gradient of properties**

– Polymer chain immobilization at particle surface is controlled by electronic and atomic level structure