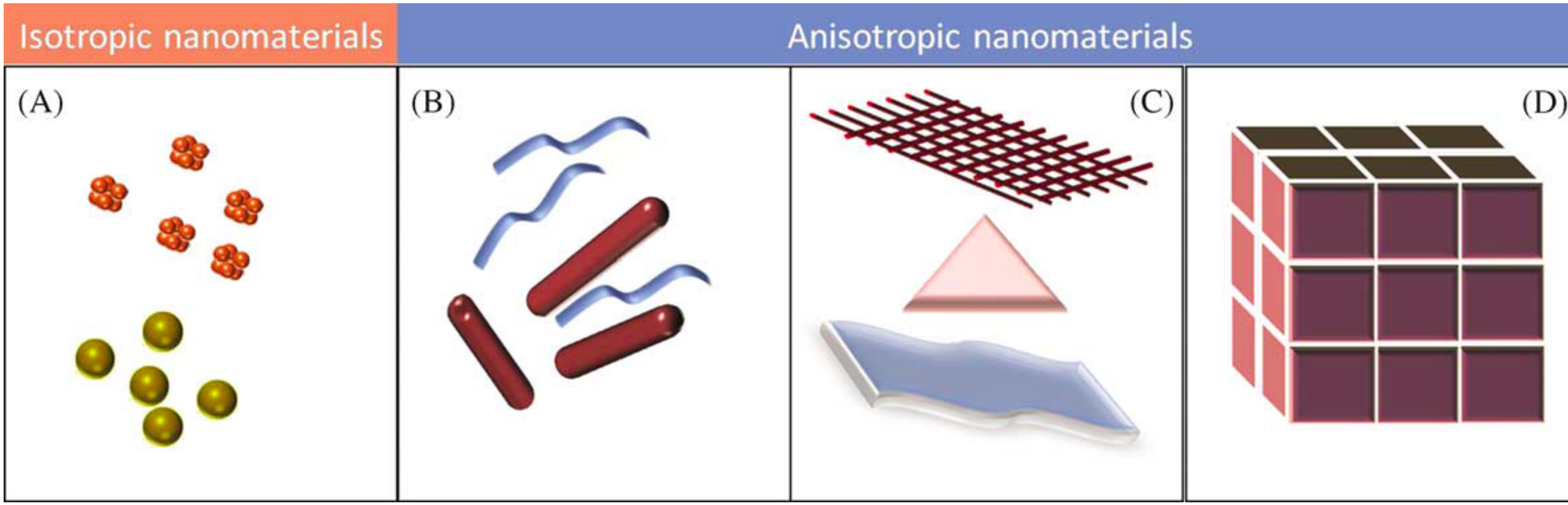
Growth of Nanostructures



0D spheres and clusters

1D nanofibers, wires, and rods

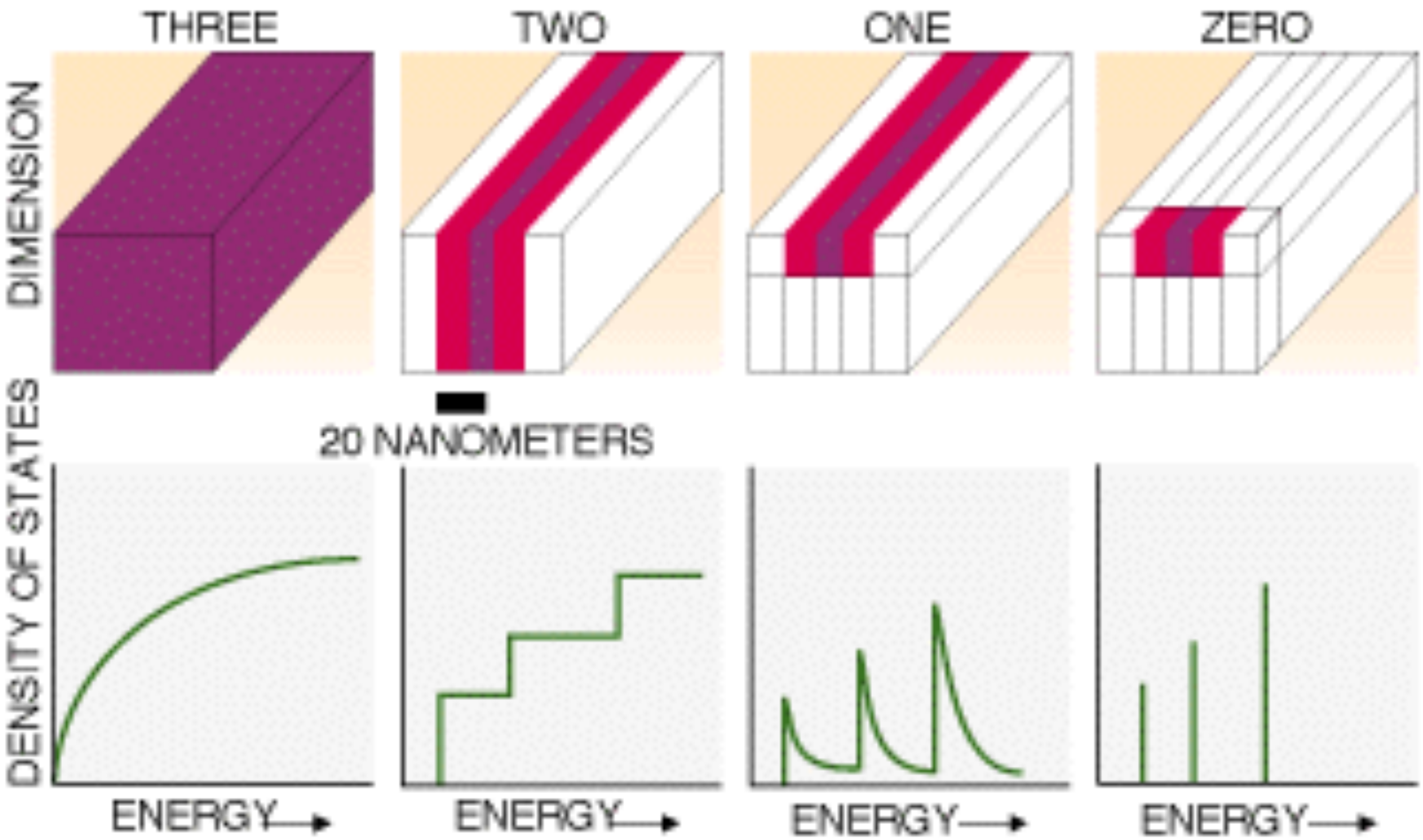
2D films, plates, and networks

3D nanomaterials

Various kinds of nanomaterials

Panikkanvalappil R. Sajanlal et al., Nano Reviews 2011, **2**: 5883

Quantum confinement



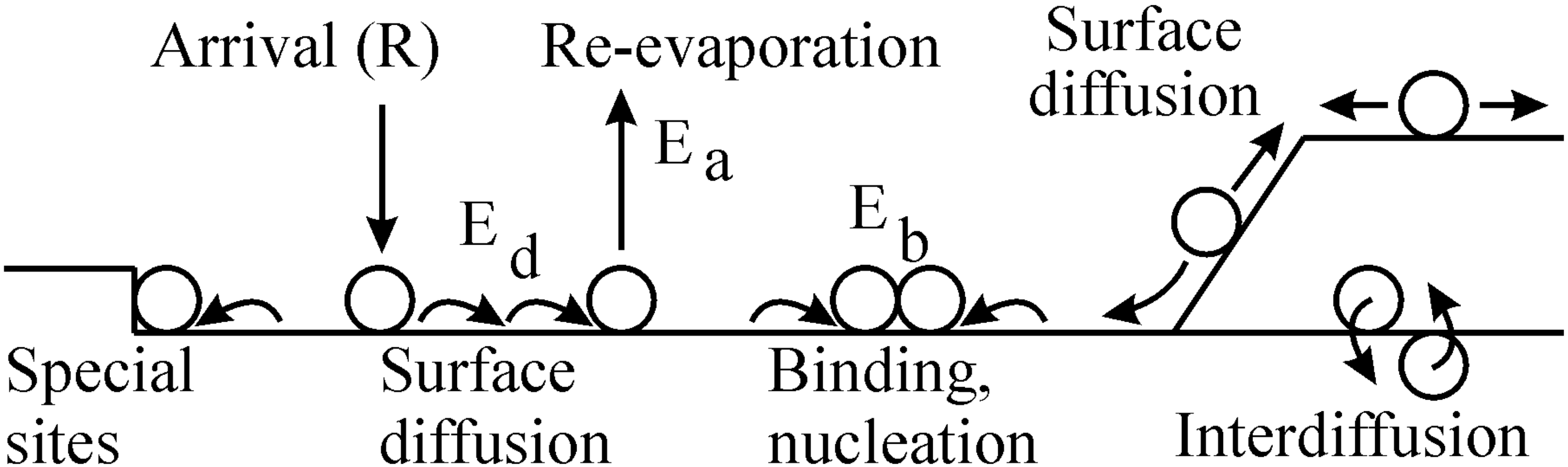
(Scientific American)

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

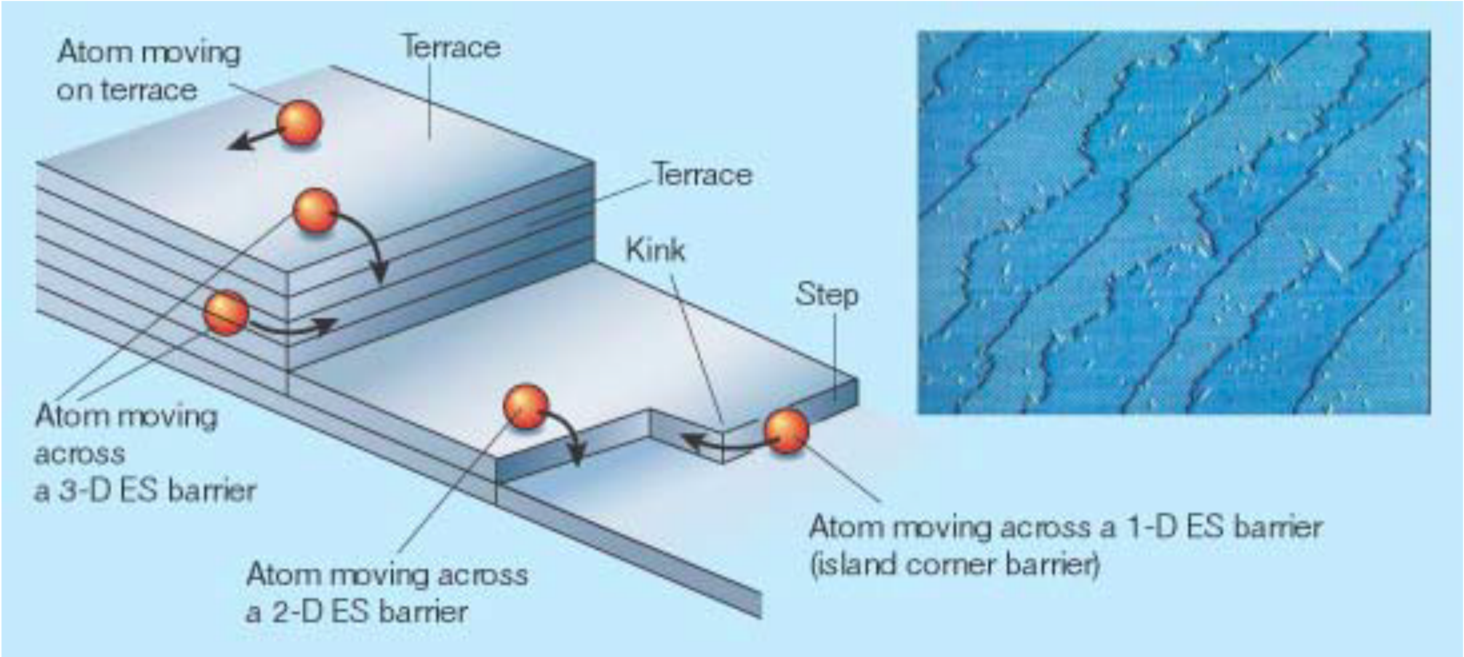
Atomic-level processes



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

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

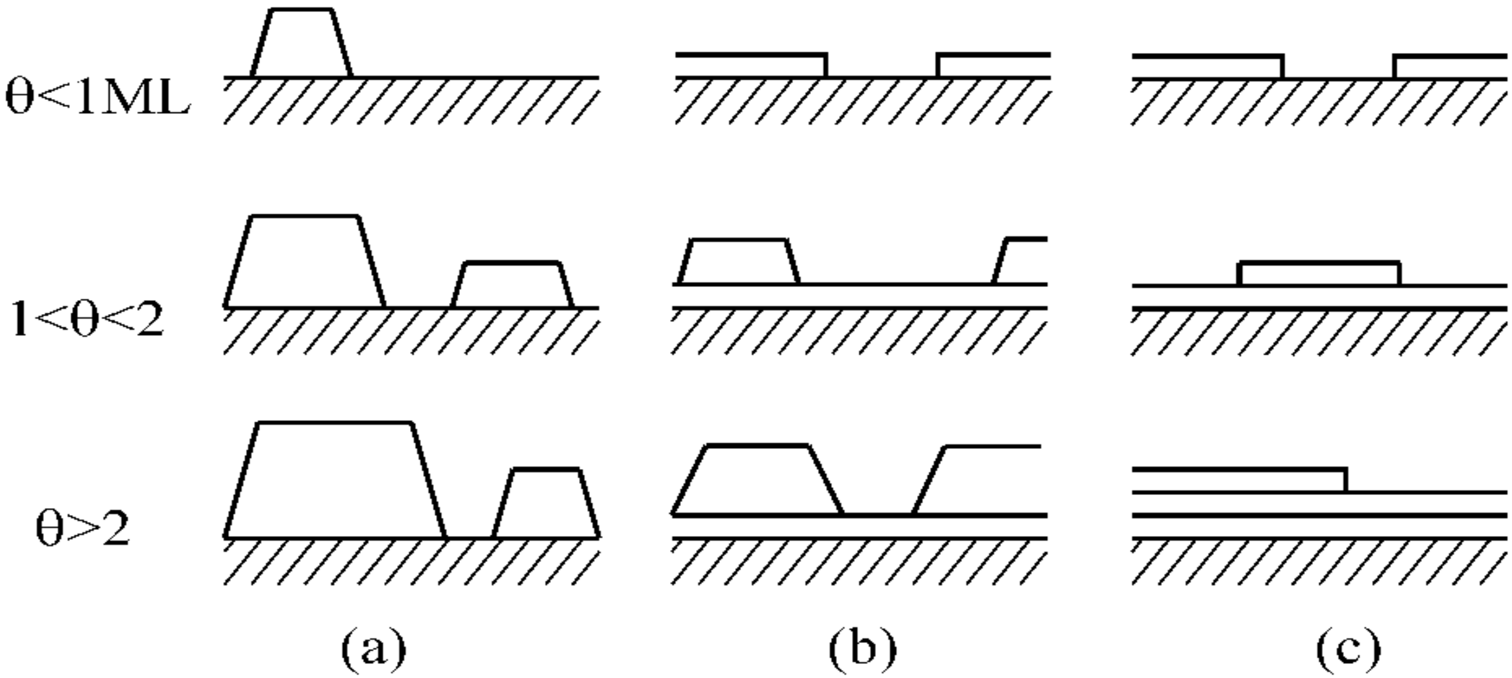
Atomistic Models for Crystalline Surfaces



Terrace Step Kink (TSK) model

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

Growth modes

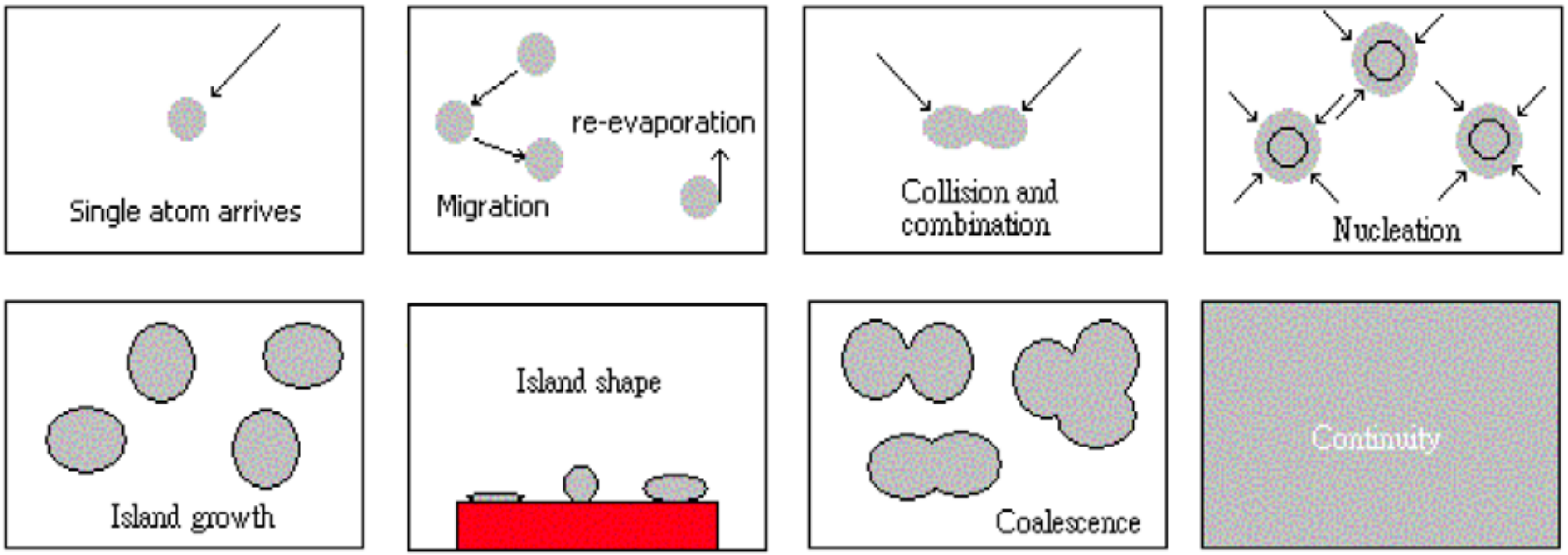


Island	Layer + Island	Layer
Volmer-Weber	*Stranski-Krastanov*	*Frank-VdM*

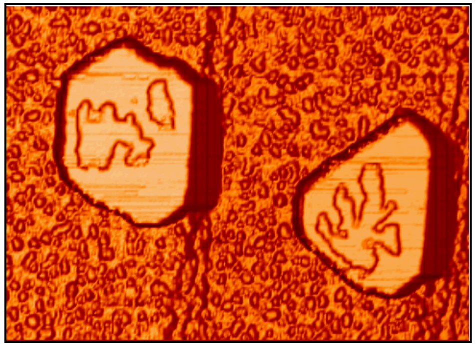
$\gamma_s < \gamma_f + \gamma_i$

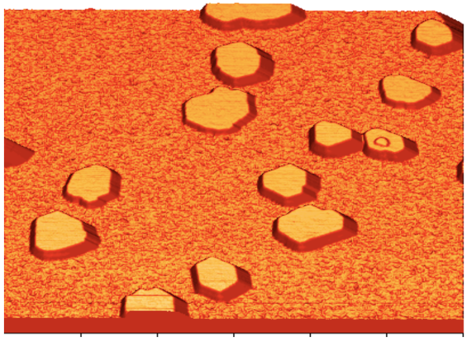
$\gamma_s \geq \gamma_f + \gamma_i$

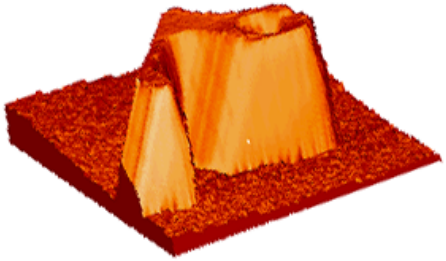
Thin Film Growth Process



Growth modes at diff. T







Non-crystalline | 2D islands | 3D islands

150 K | 300 K

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.

Techniques for making nanowires

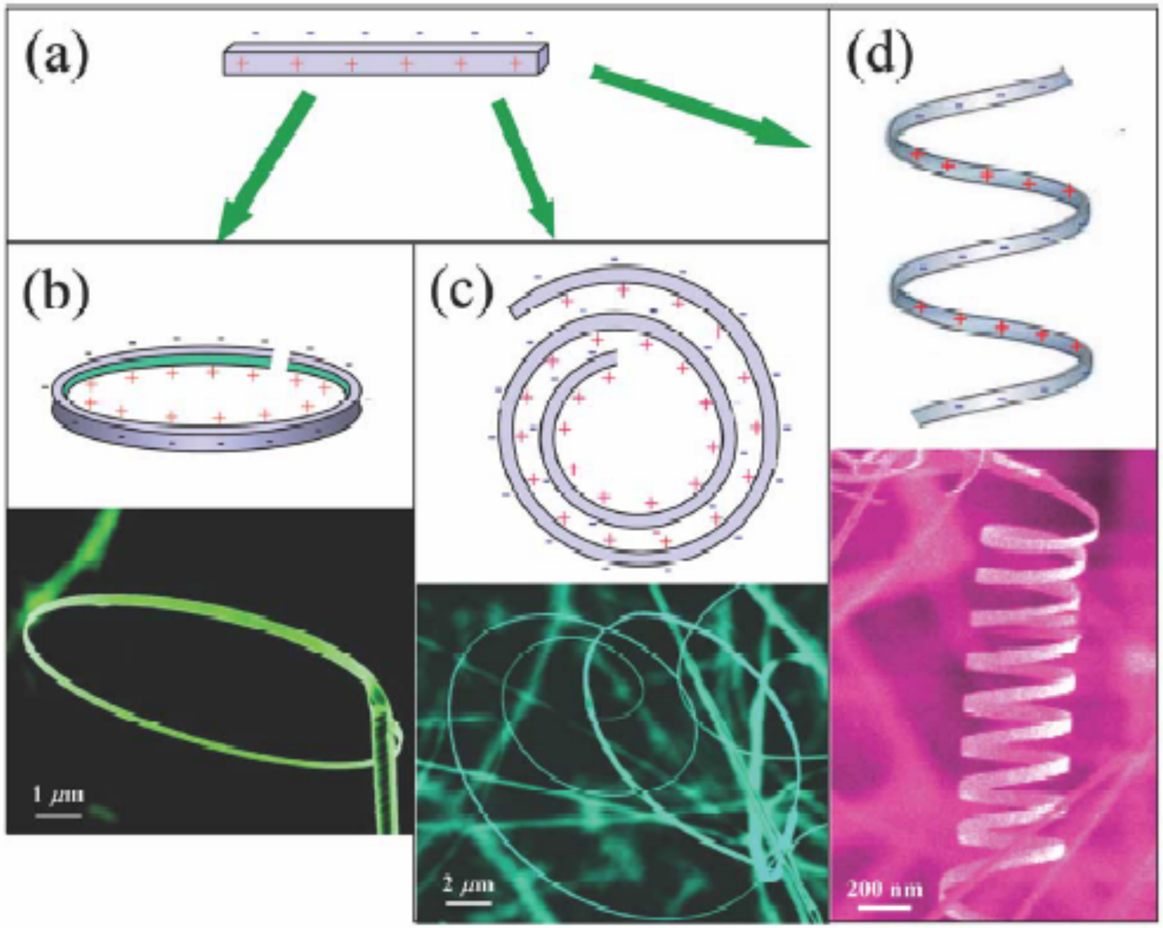
- **Spontaneous growth:**
  - Evaporation condensation
  - Dissolution condensation
  - Vapor-Liquid-Solid growth (VLS)
  - Stress induced re-crystallization
- **Template-based synthesis:**
  - Electrochemical deposition
  - Electrophoretic deposition
  - Colloid dispersion, melt, or solution filling
  - 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-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



“Nanostructures of zinc oxide,” by Zhon Lin Wang

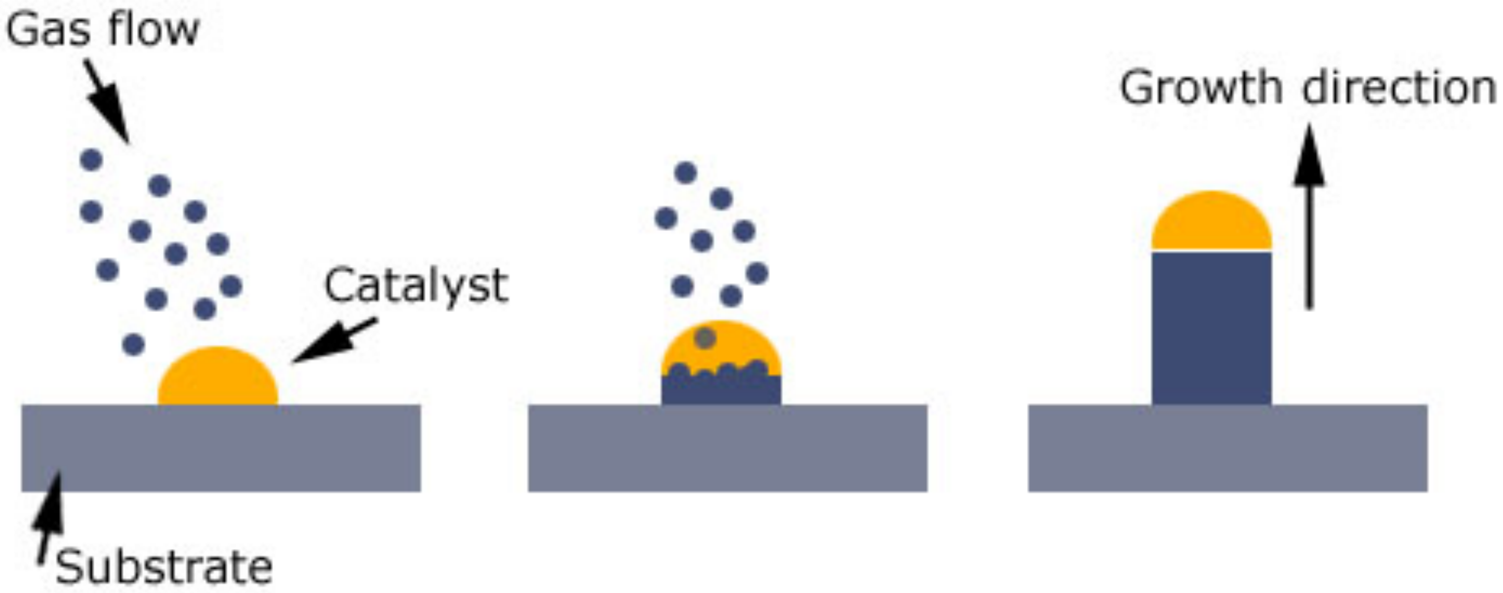
Vapor Liquid Solid Growth (VLS)

General Idea:

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

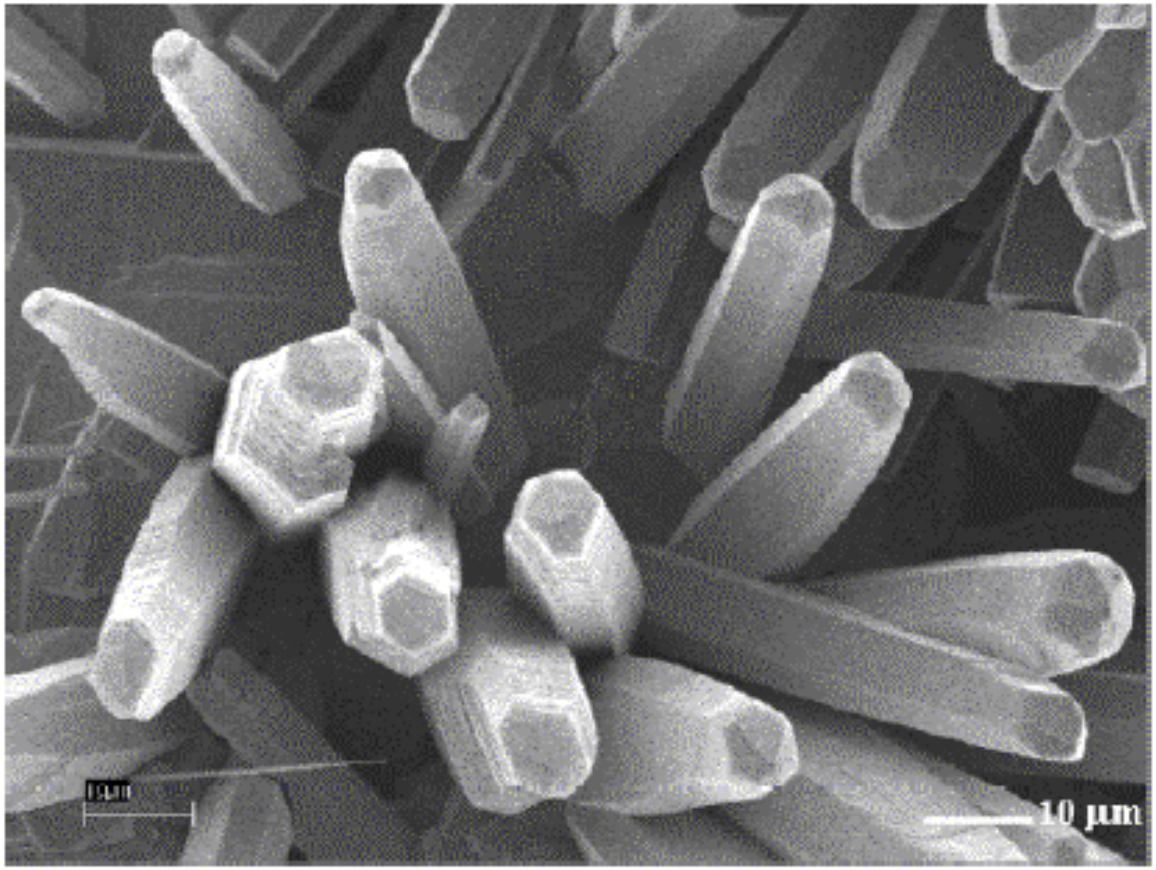
- Catalyst forms a **liquid droplet** by itself
- Acts as a trap for growth species
- The growth species is evaporated first and then diffuses and dissolves into a liquid droplet
- It precipitates at the interface between the substrate and the liquid

VLS Growth



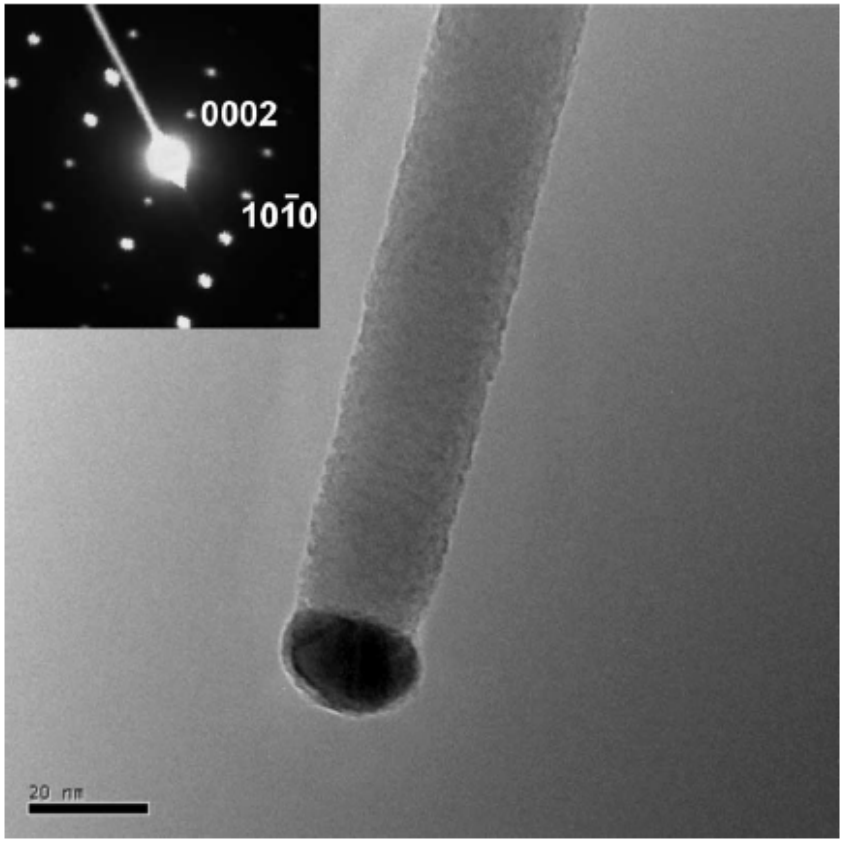
Growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in the ***one-directional growth***

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.**

Surface Energy

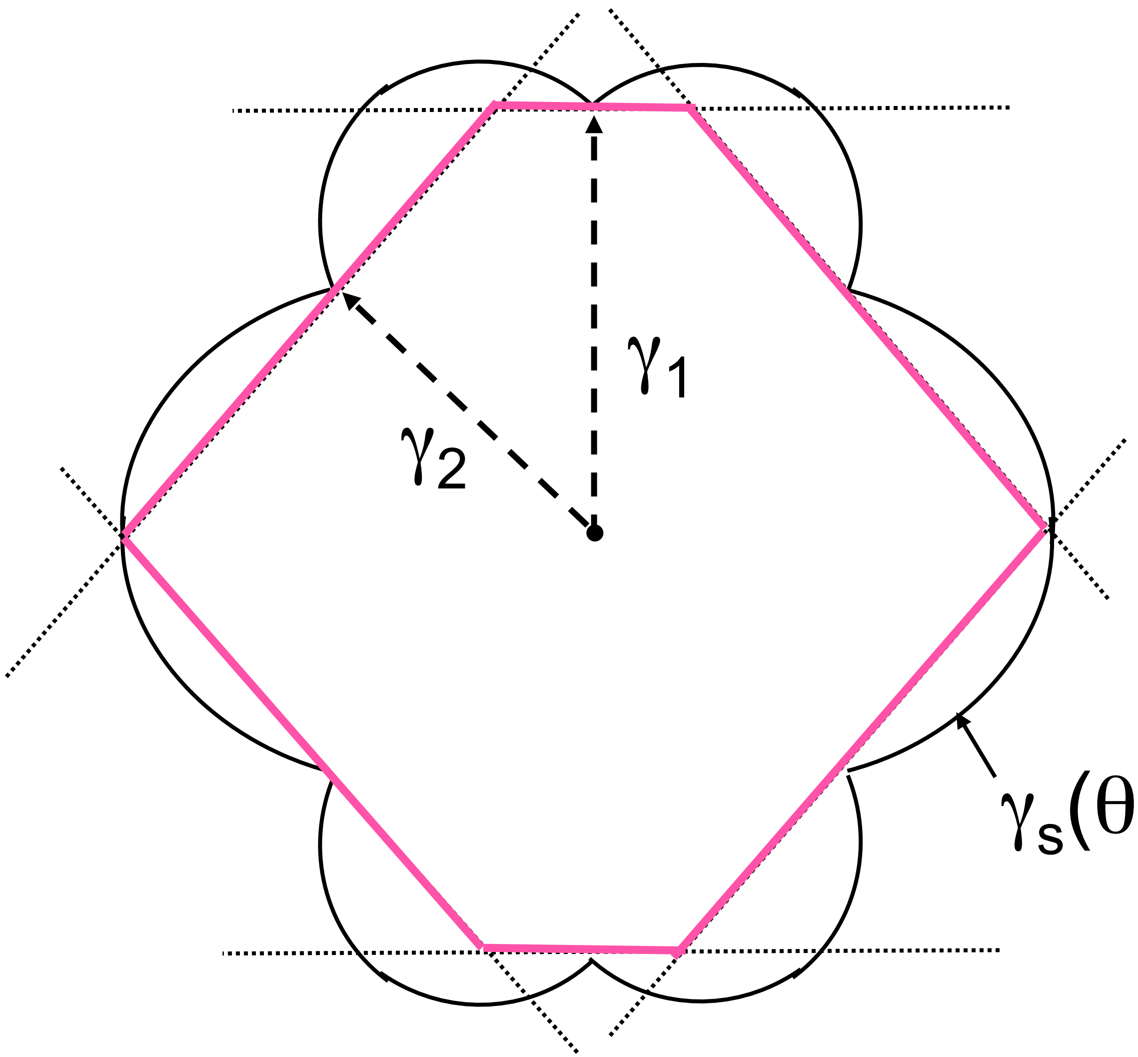
- Surface energy is given by

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

- Standard model for anisotropic surface free energy

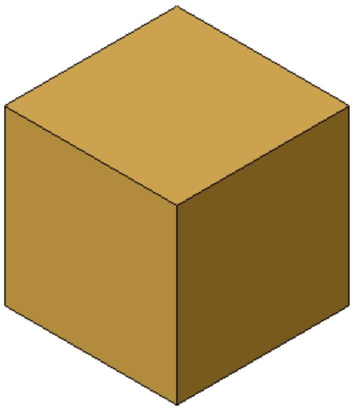
$$\gamma = \gamma_0(n)$$

Wulff construction

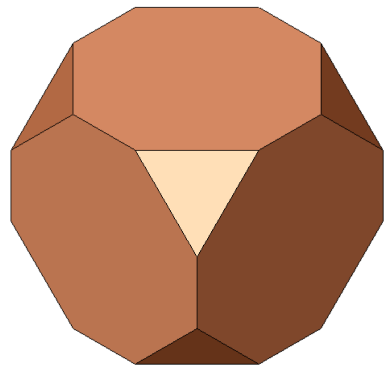


$$G = \int \gamma_s(\theta,\phi)\, dA$$

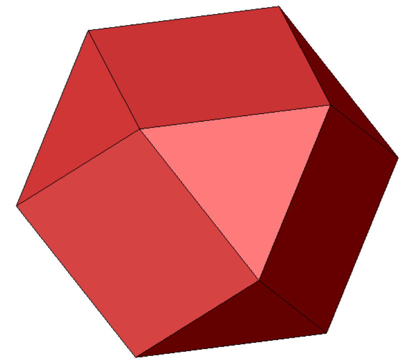
Single crystalline structures



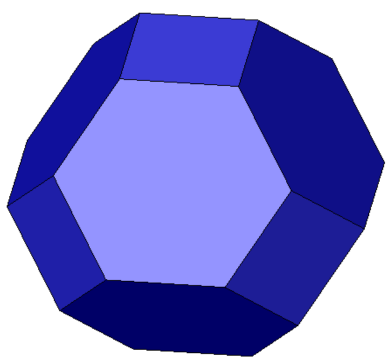
(a) cube



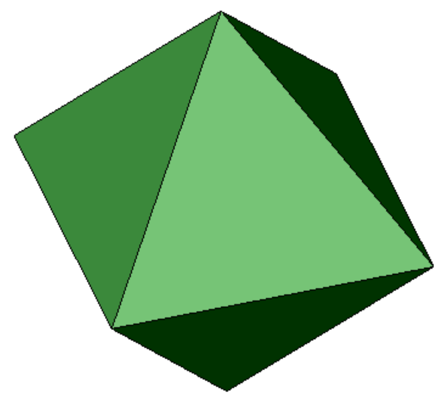
(b) truncated cube



(c) cuboctahedron

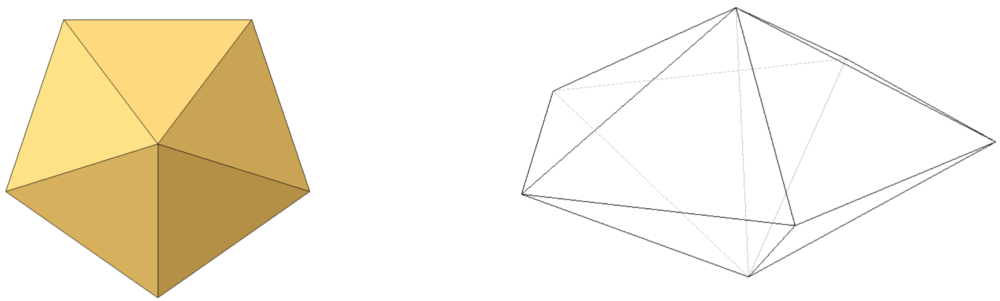


(d) truncated octahedron

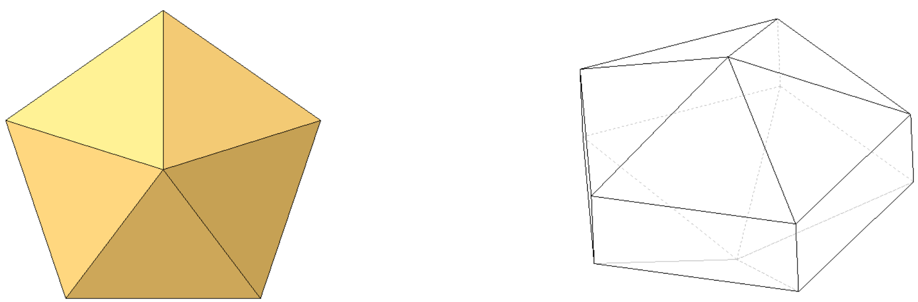


(e) octahedron

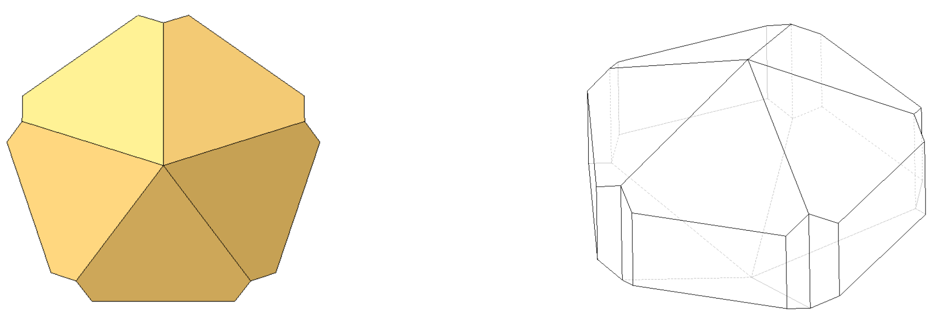
Decahedra



Classic

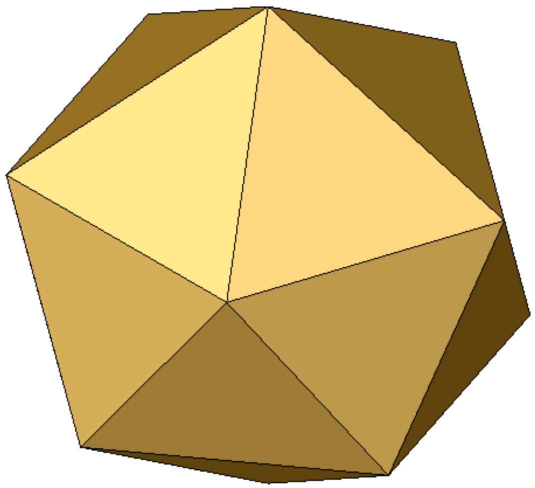


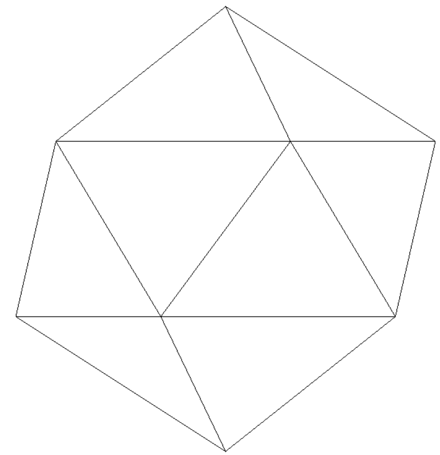
Ino's



Marks'

Icosahedra





Size-dependent structures calculated for Ni clusters:

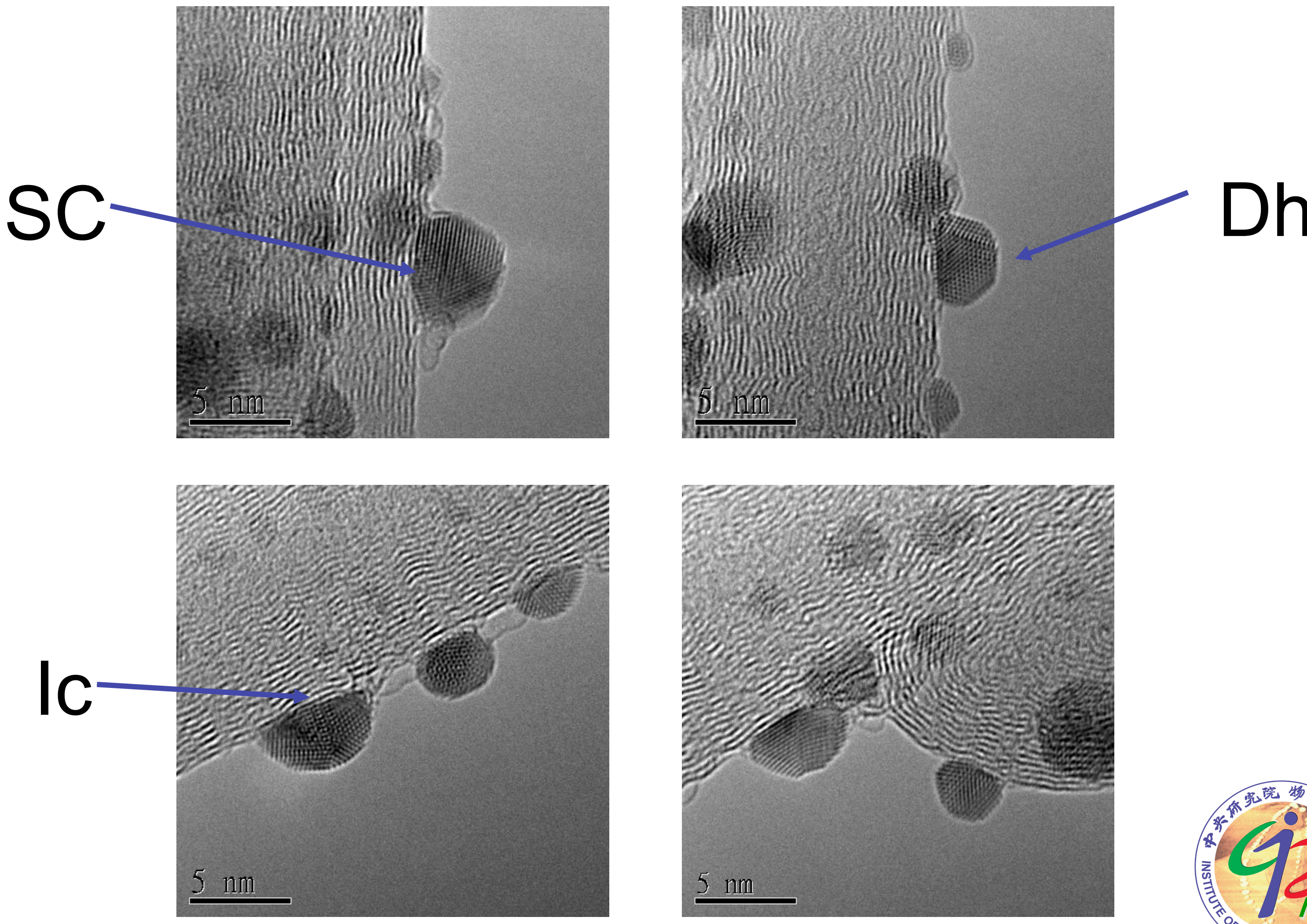
Icosahedra for 142 – 2300 atoms;

Marks' decahedra for 2300 – 17000 atoms;

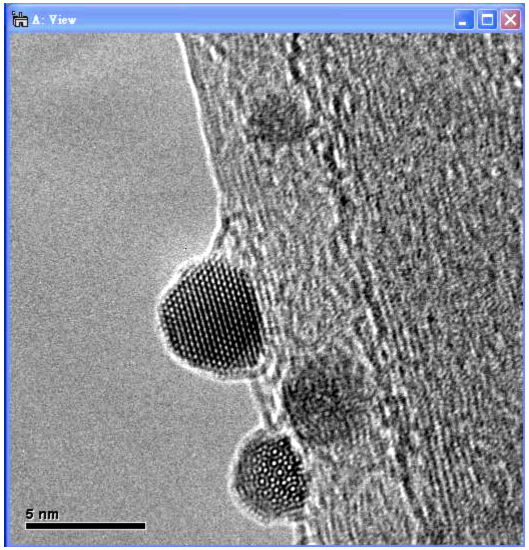
Single crystal for > 17000 atoms.

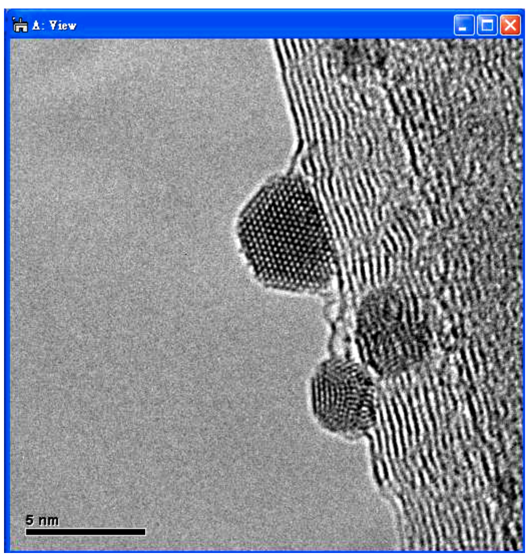
C.L. Cleveland and Uzi Landman, J. Chem. Phys. 94, 7376 (1991)

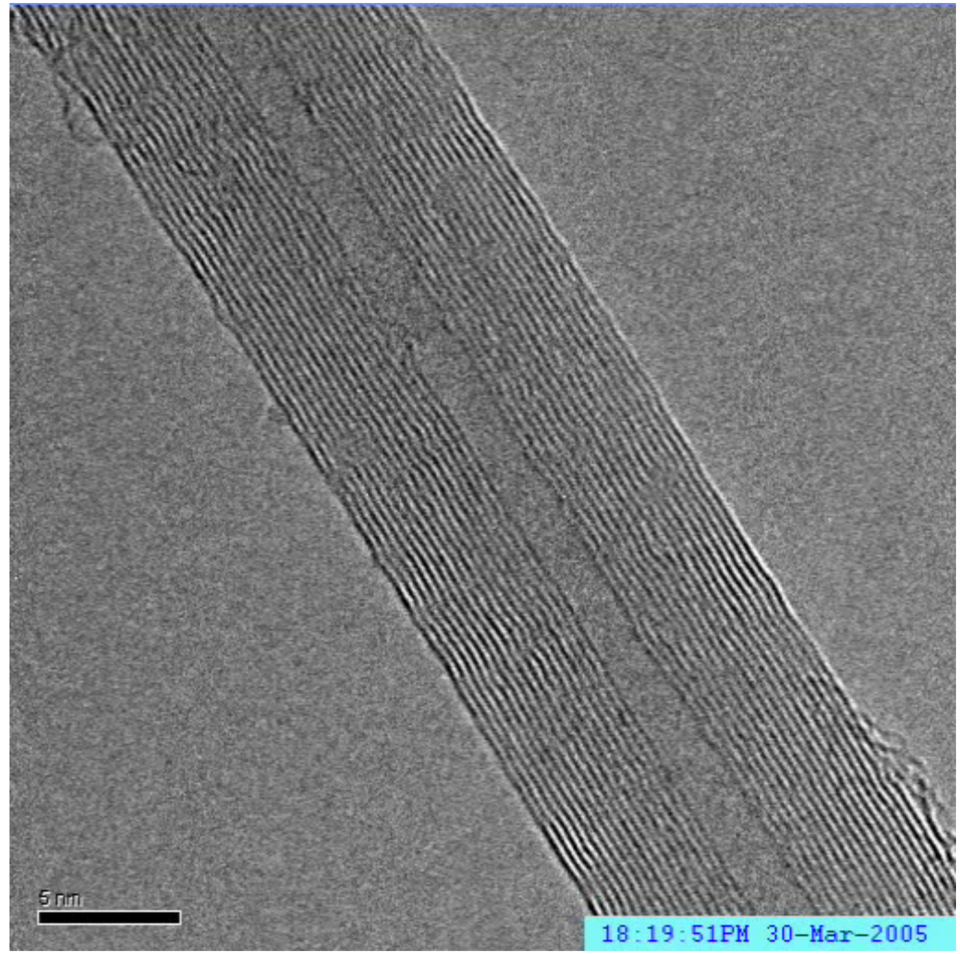
Varying structures of Ag clusters



Atomic motion and recrystallization

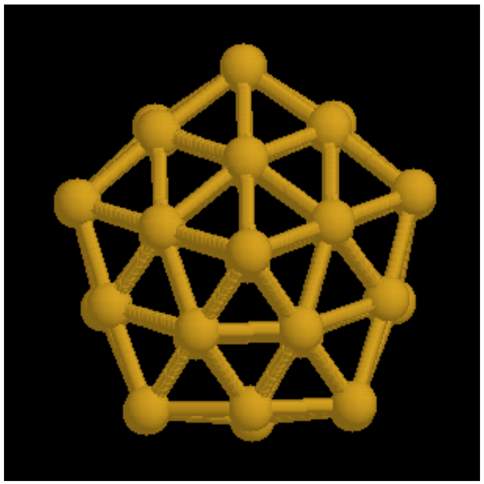




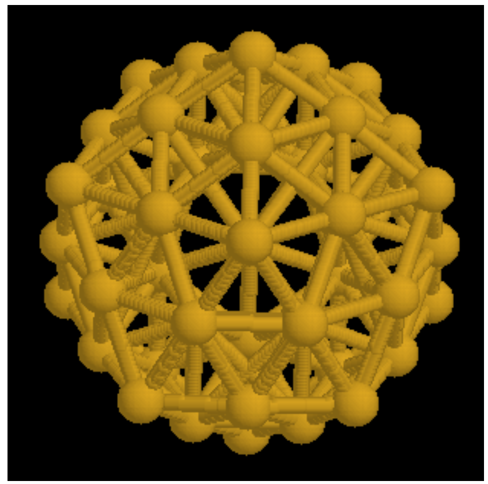


Room temperature

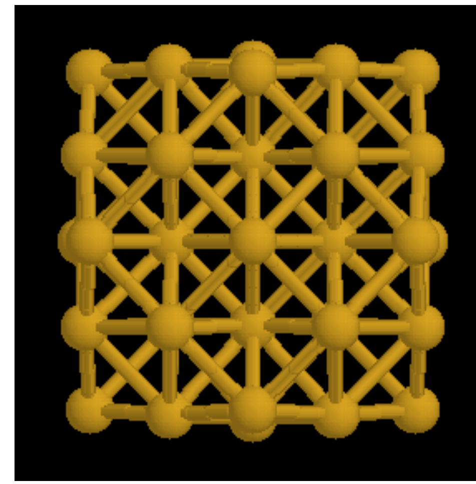
Possible shell structures of nano particles



Decahedr
al:
10 (111)
faces +
5 (100)



Icosahed
ral:
20 (111)
faces

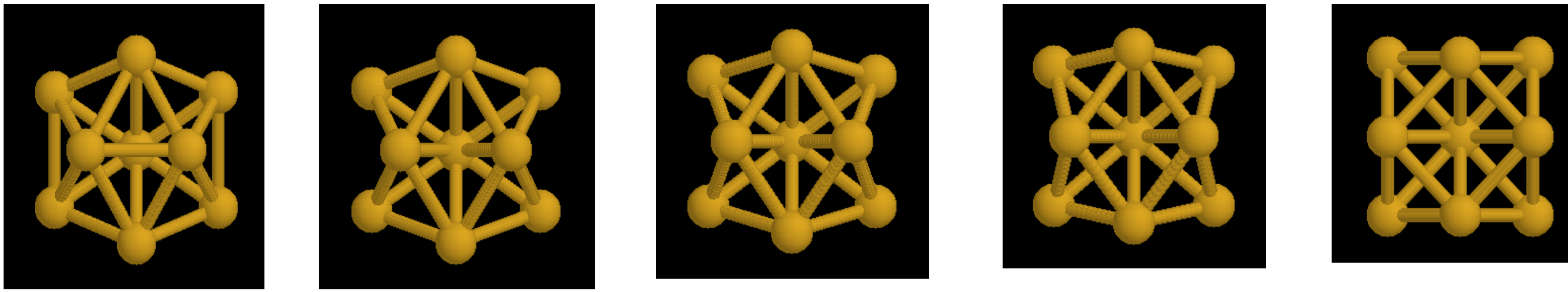


Cuboctah
edral:
8 (111)
fac
6 (1

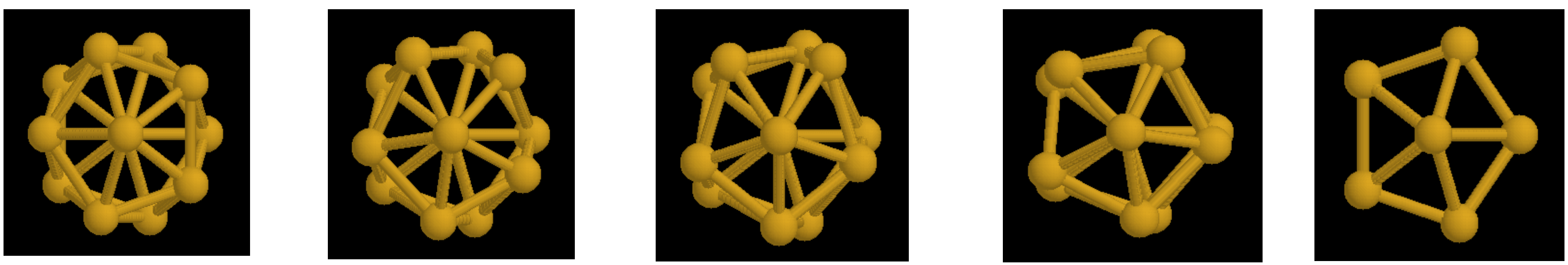
(Courtesy of C.M. Wei)

Structural phase transition

Icosahedral ⇔ Cubotohedral

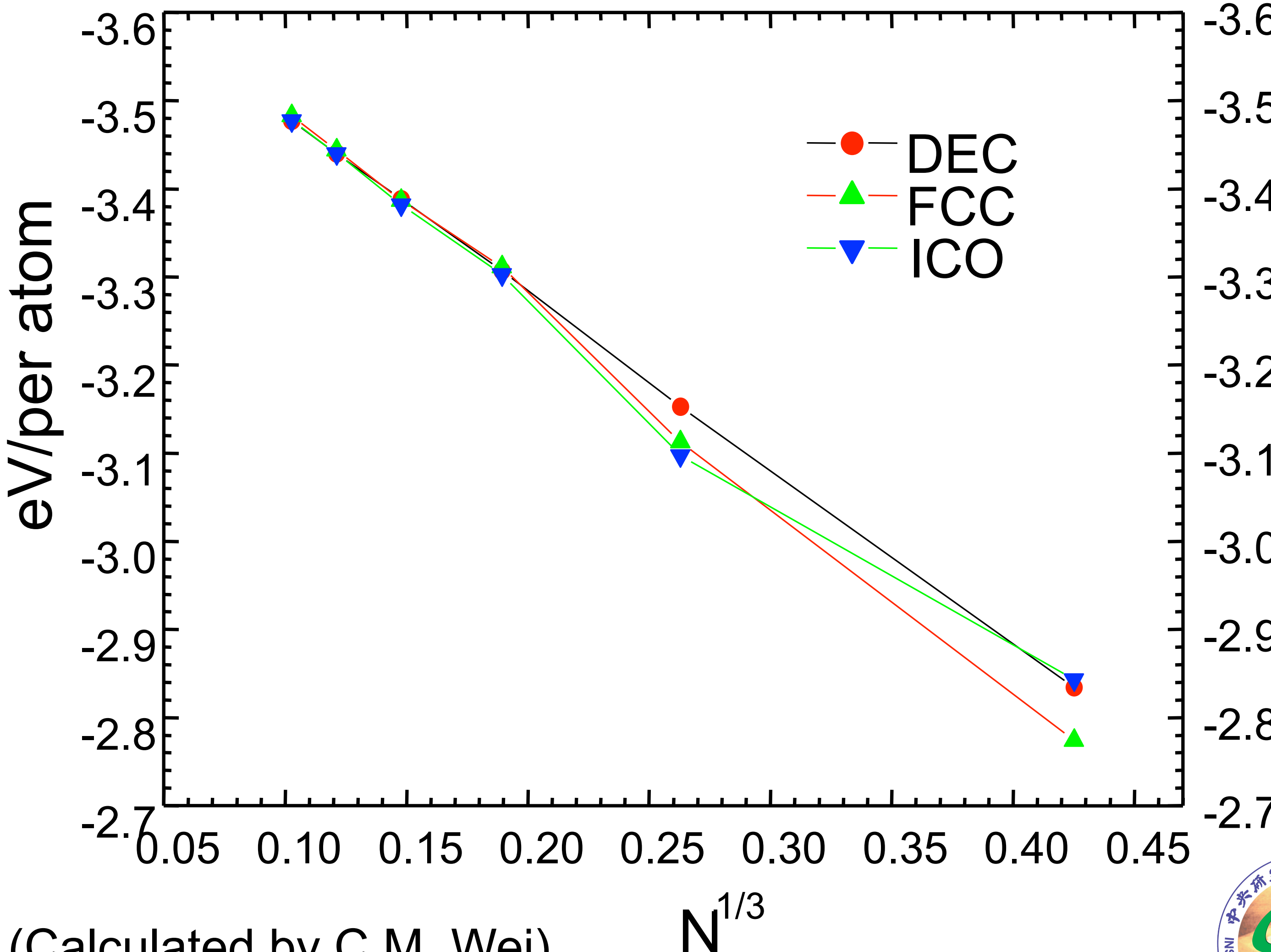


Icosahedral ⇔ Decahedral



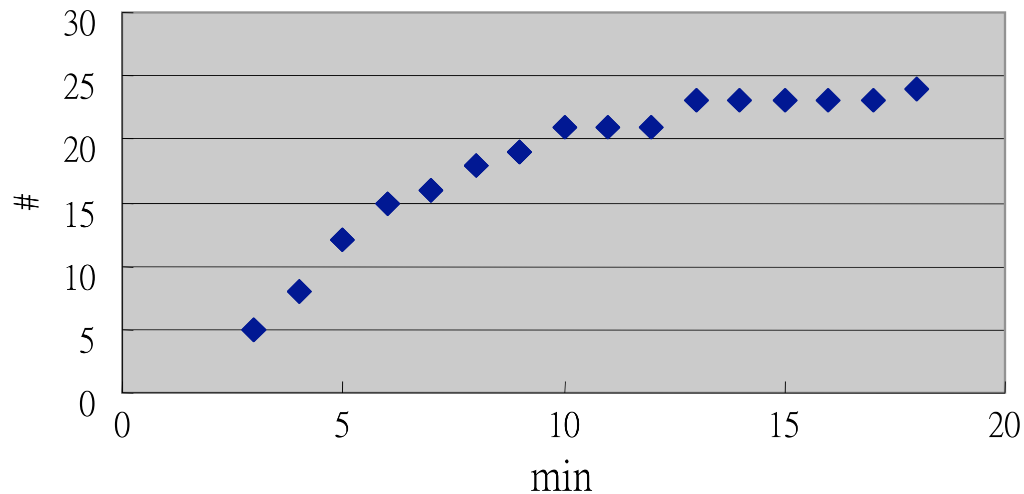
(Courtesy of C.M. Wei)

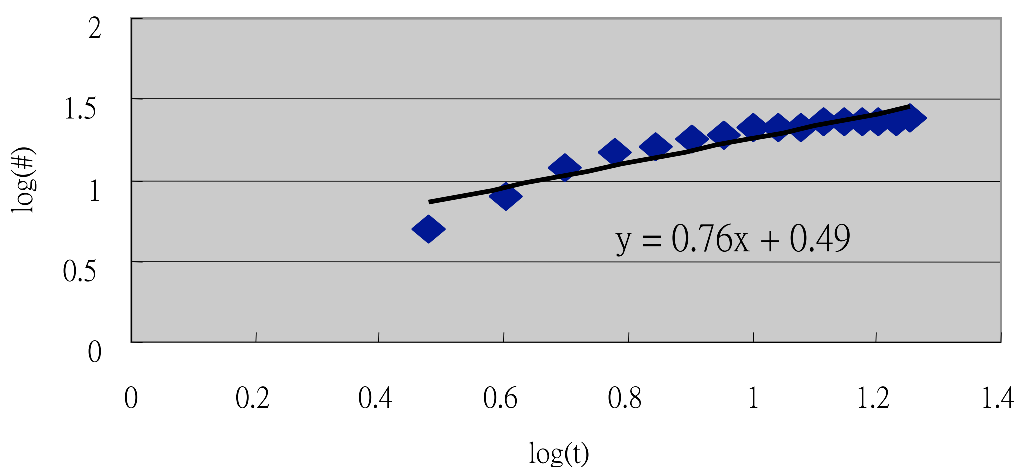
Binding energy for Al nano particles

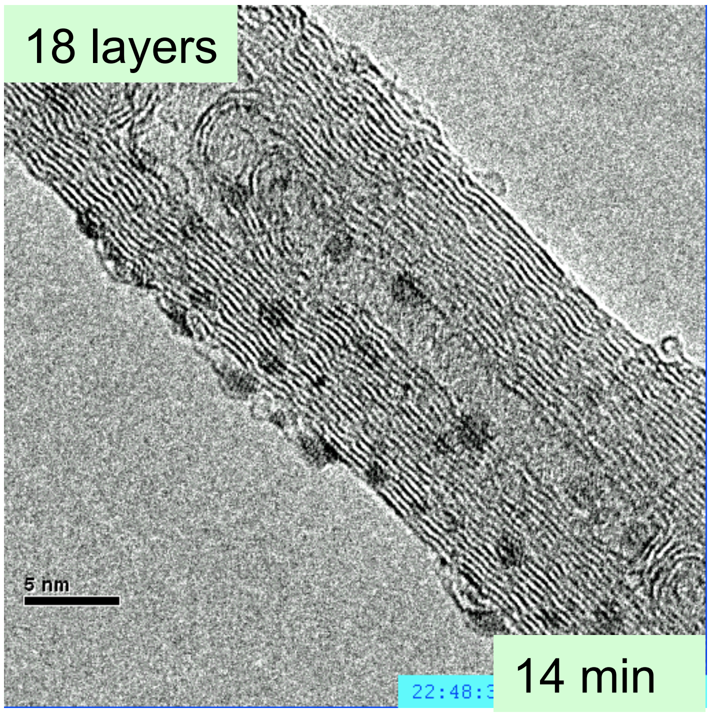


(Calculated by C.M. Wei)

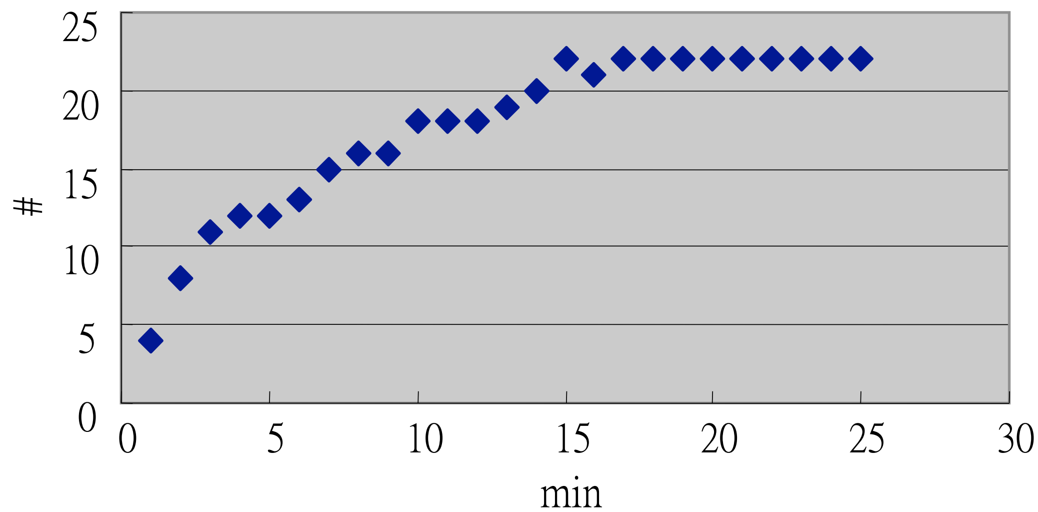
Growth of Ag clusters on 18-layer CNT

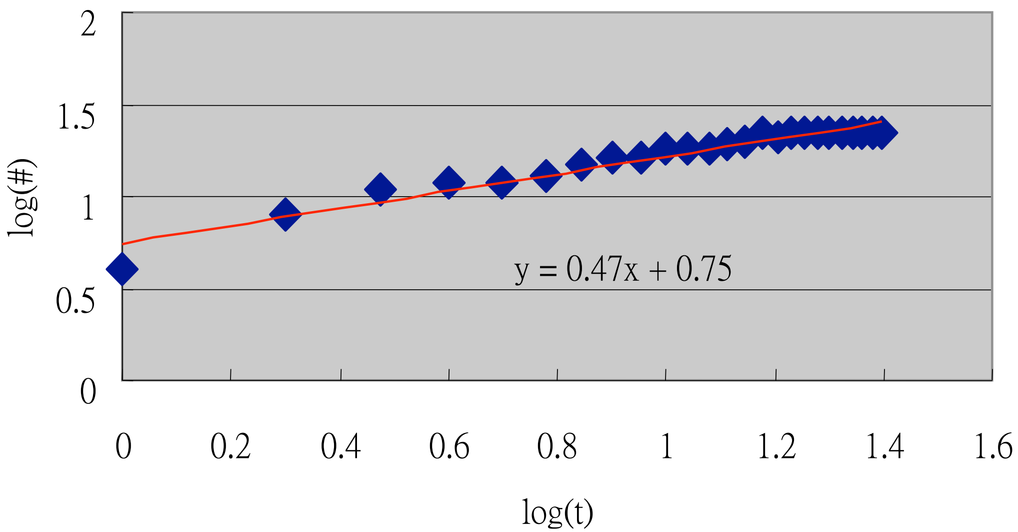


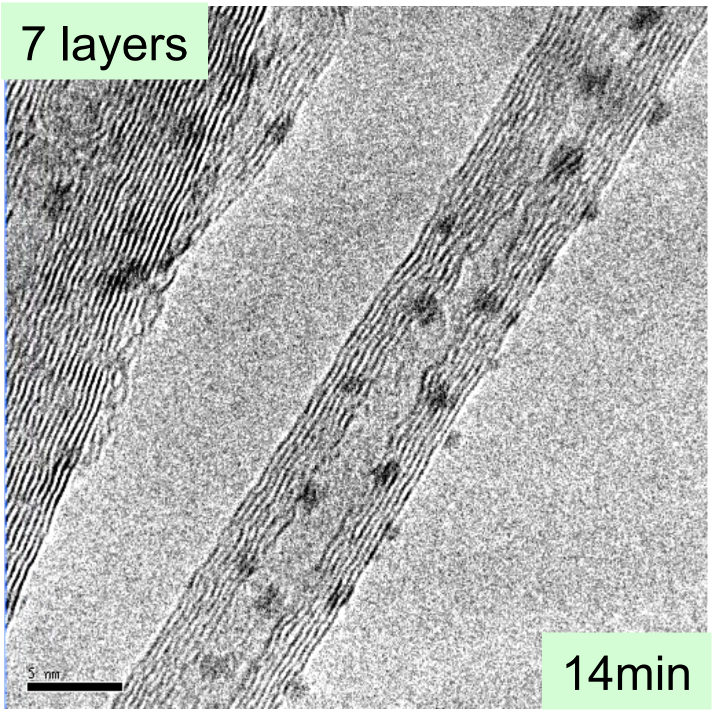




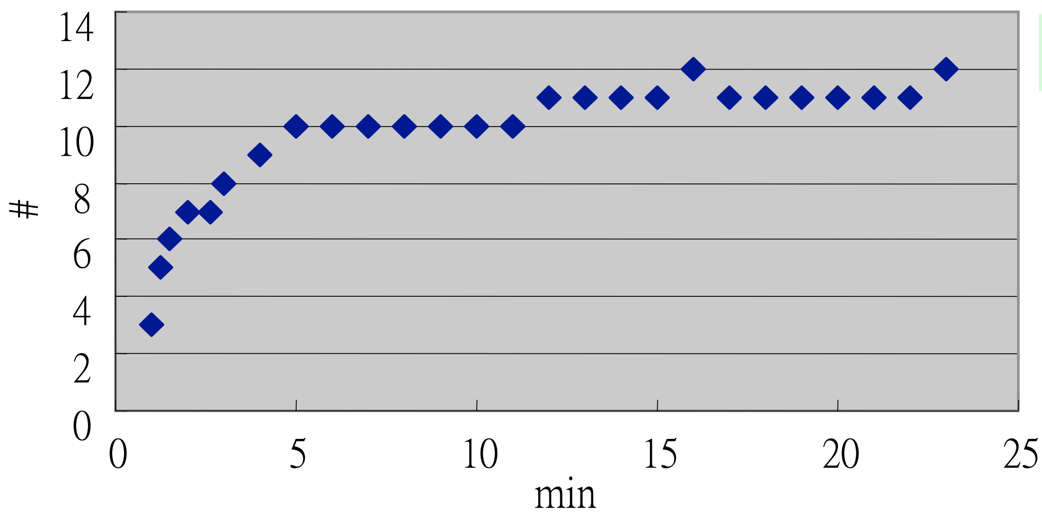
Growth of Ag clusters on 7-layer CNT

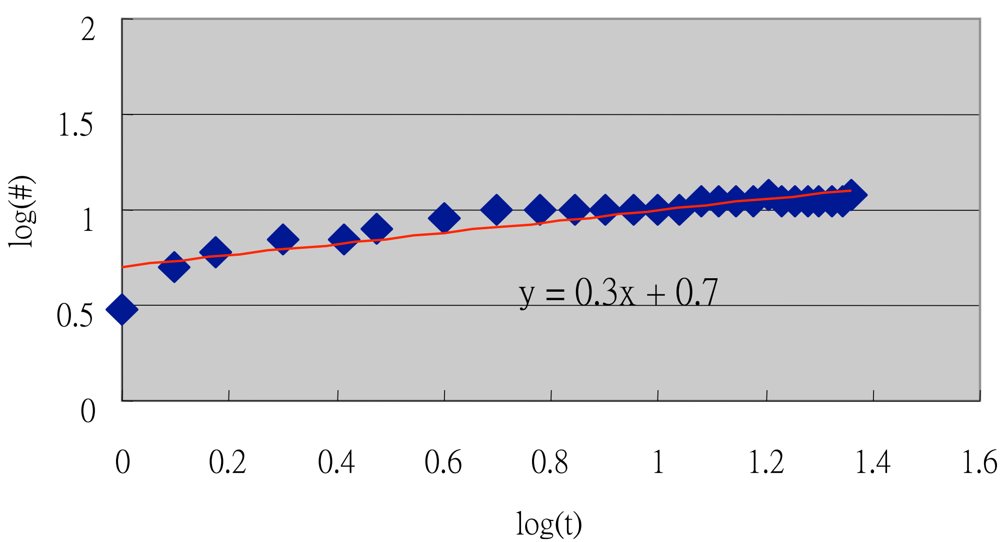


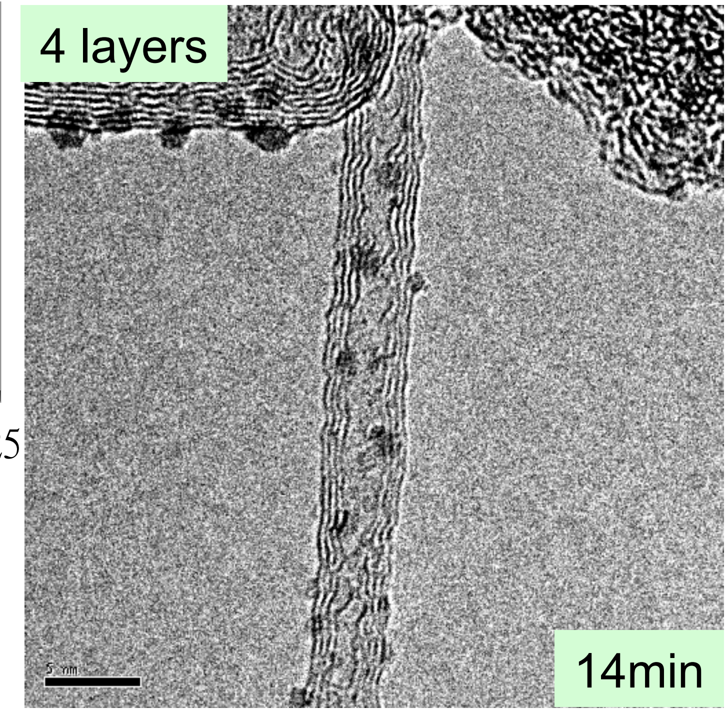




Growth of Ag clusters on 4-layer CNT







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**:

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

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 $n = R/ND$.

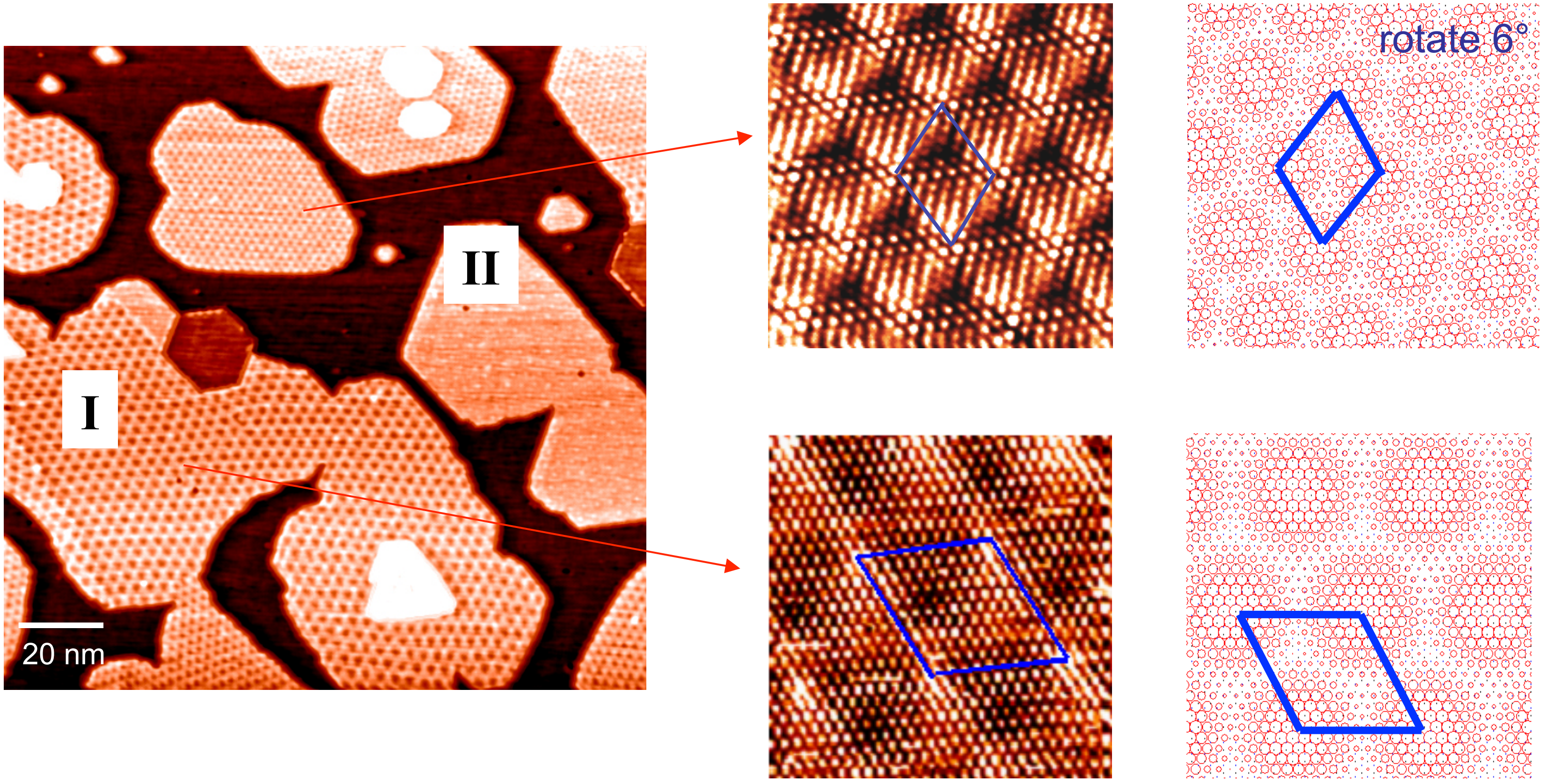
Then, integration leads to

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

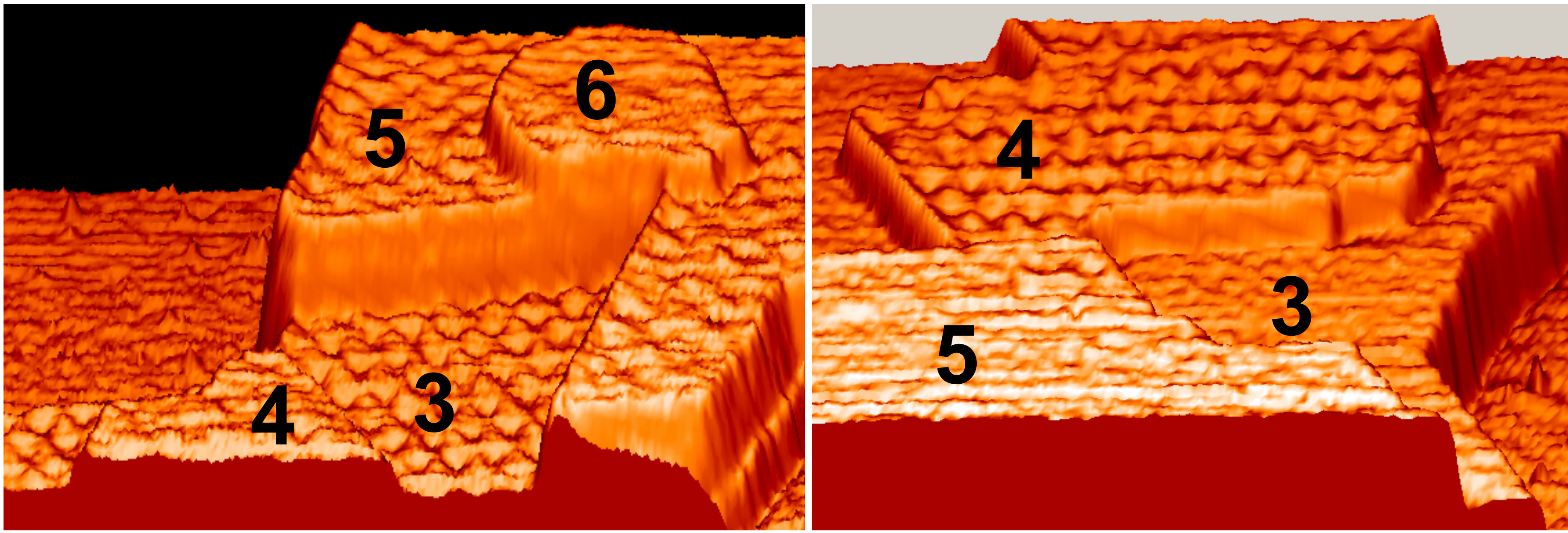
where, $\theta=Rt$ is the total coverage up to time t.

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

Superstructures of 2D islands



Characteristics of Pb island---
oscillatory and complementary contrast

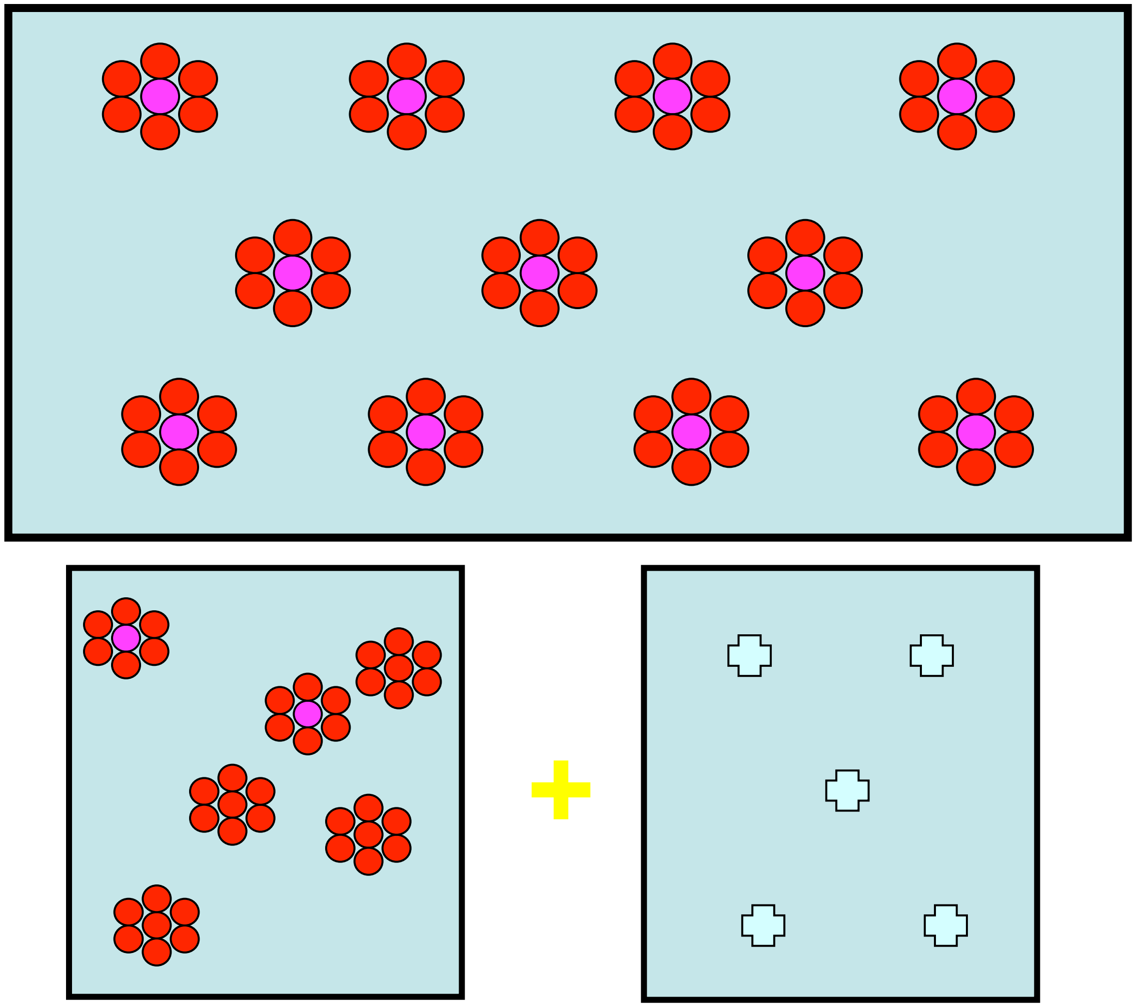


Type I

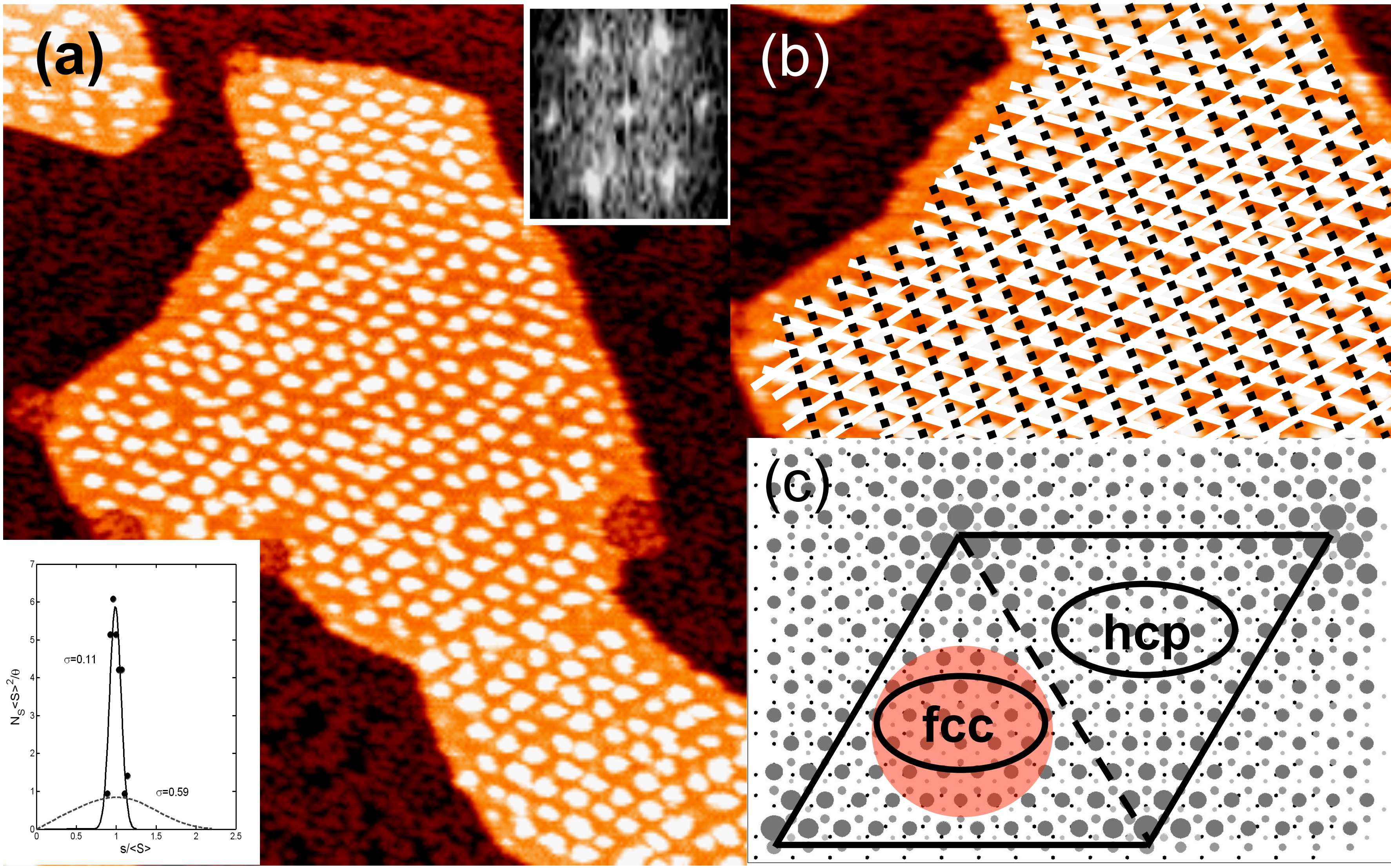
Type II

Self-organized growth

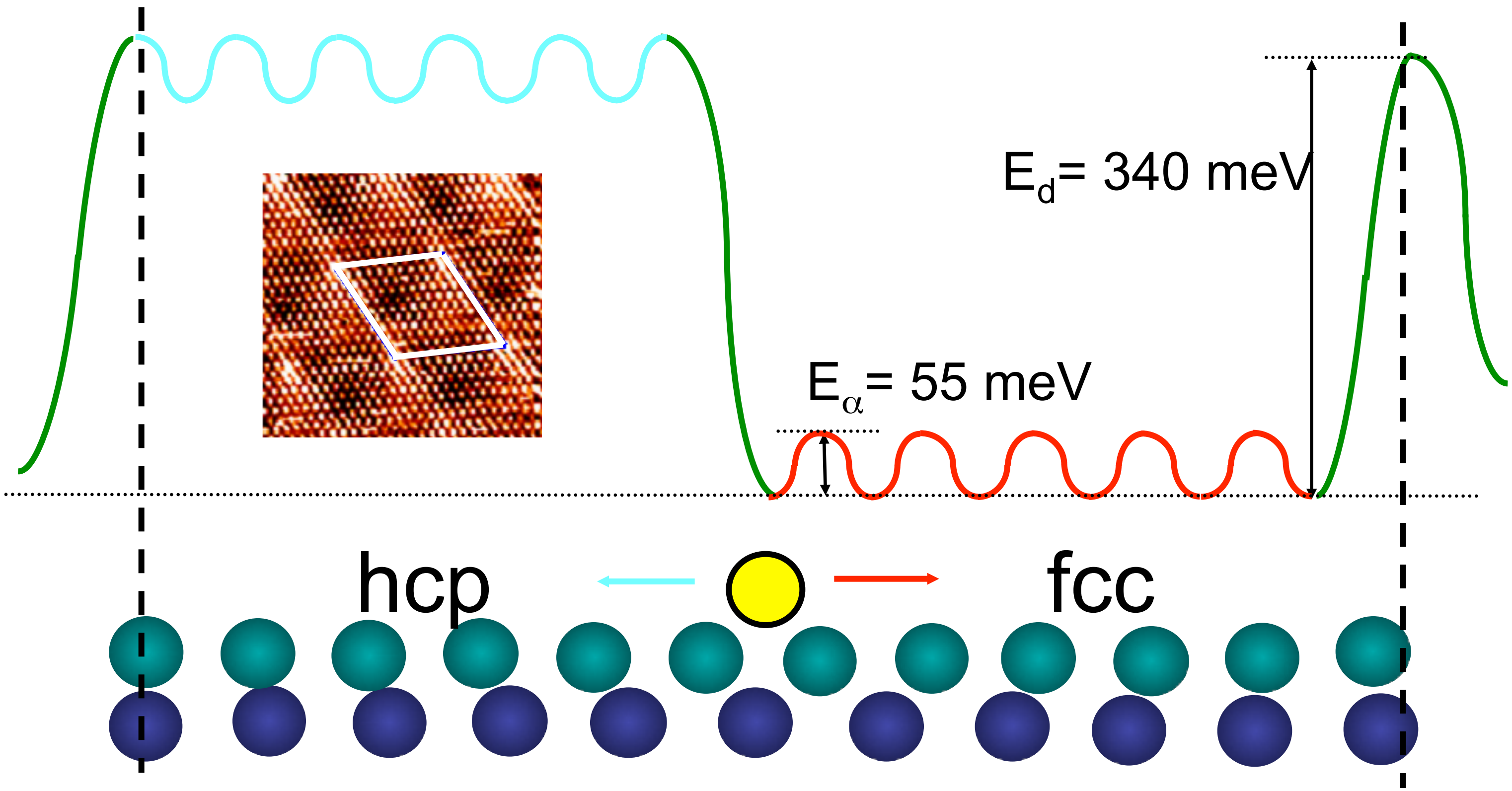
Size uniformity, Shape specification, Spatial orderliness and Functional homogeneity



Properties of nanopucks on Pb islands

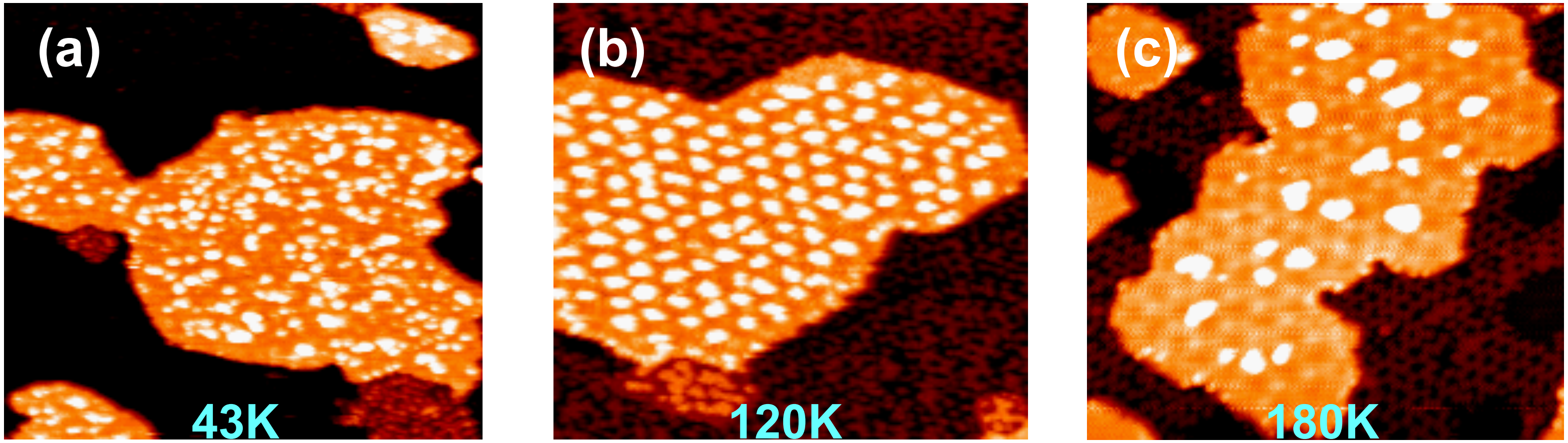


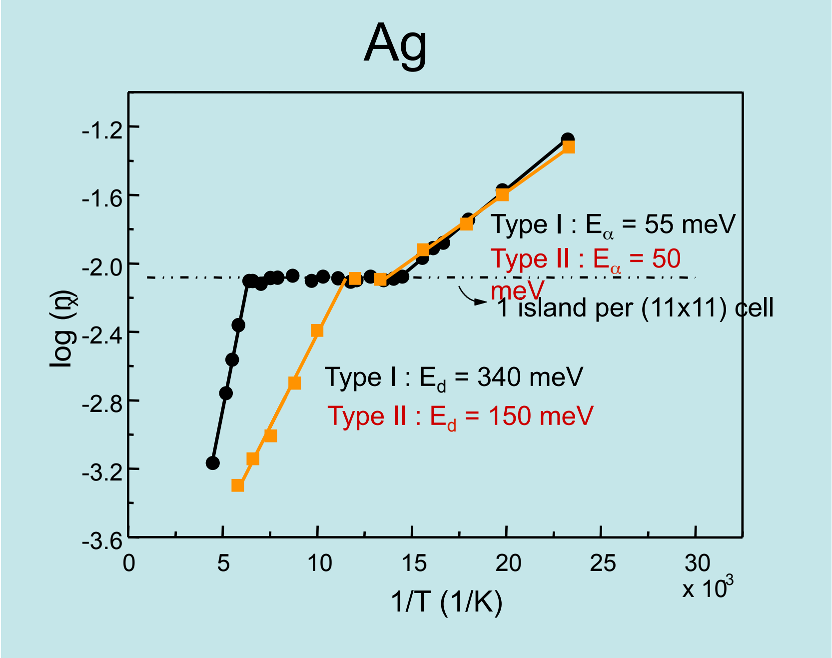
Various diffusion barriers

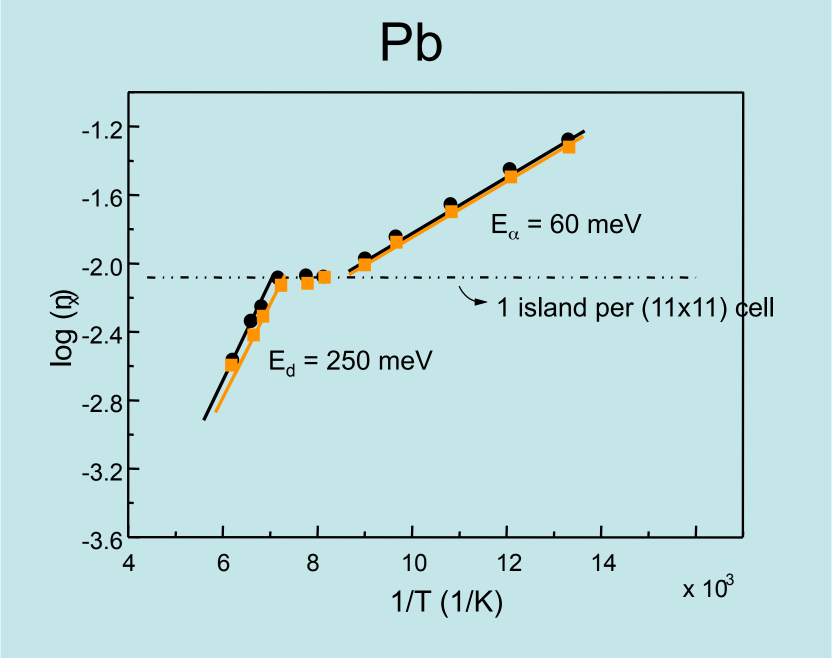


N ∝ E_d/[(i+2)kT], i : number of atoms in critical nucleus

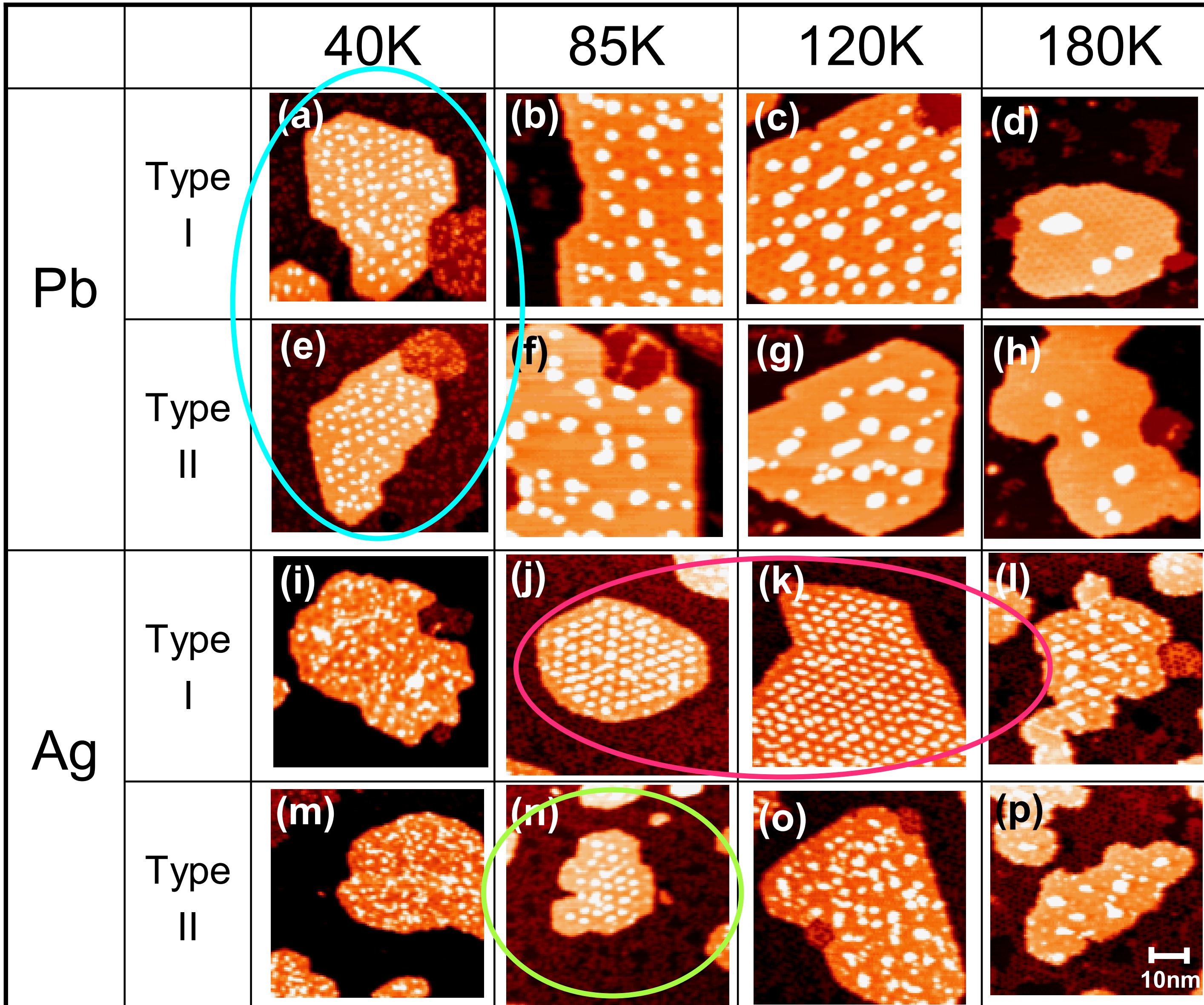
Diffusion barriers for Ag and Pb nanopucks



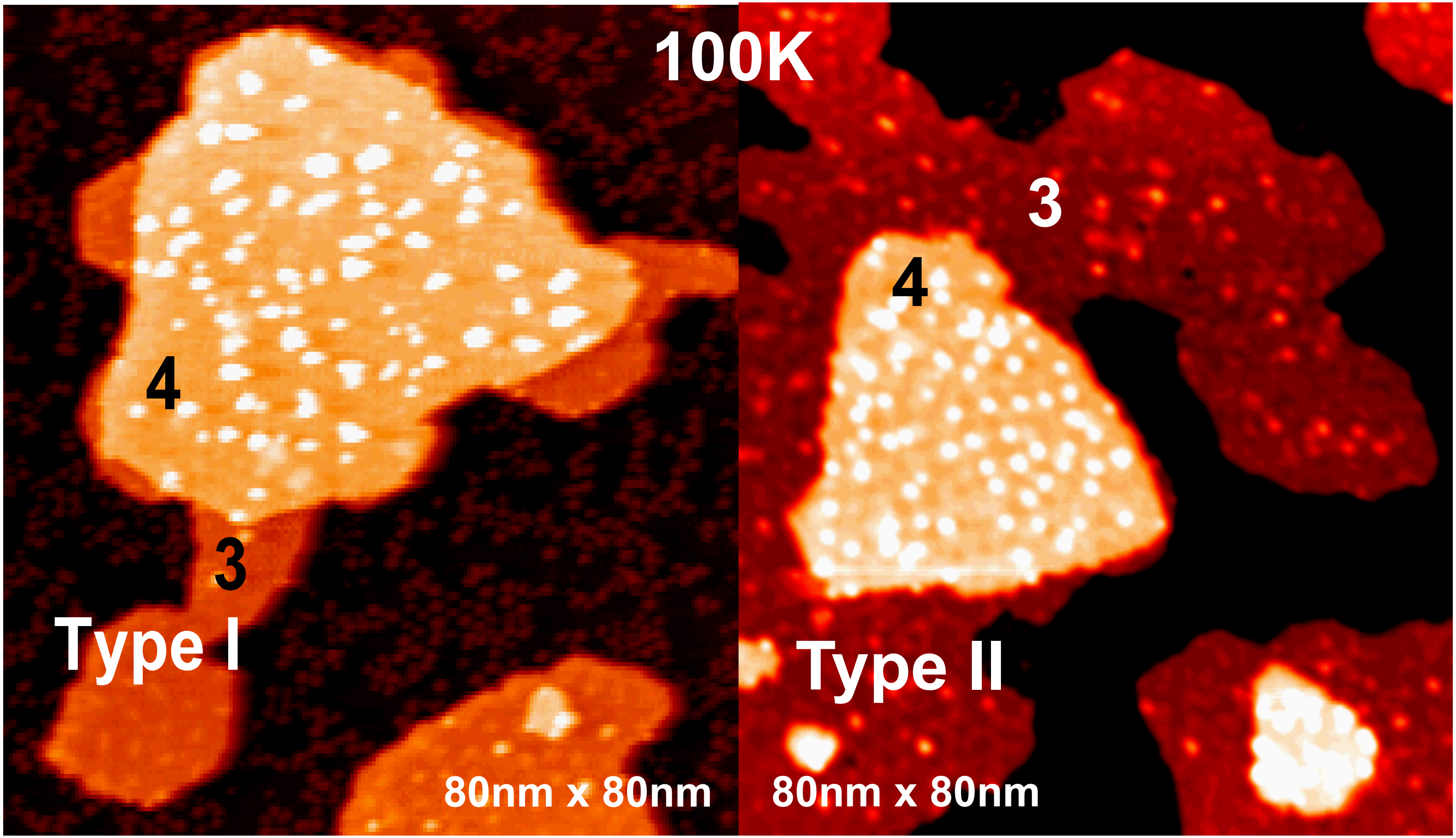




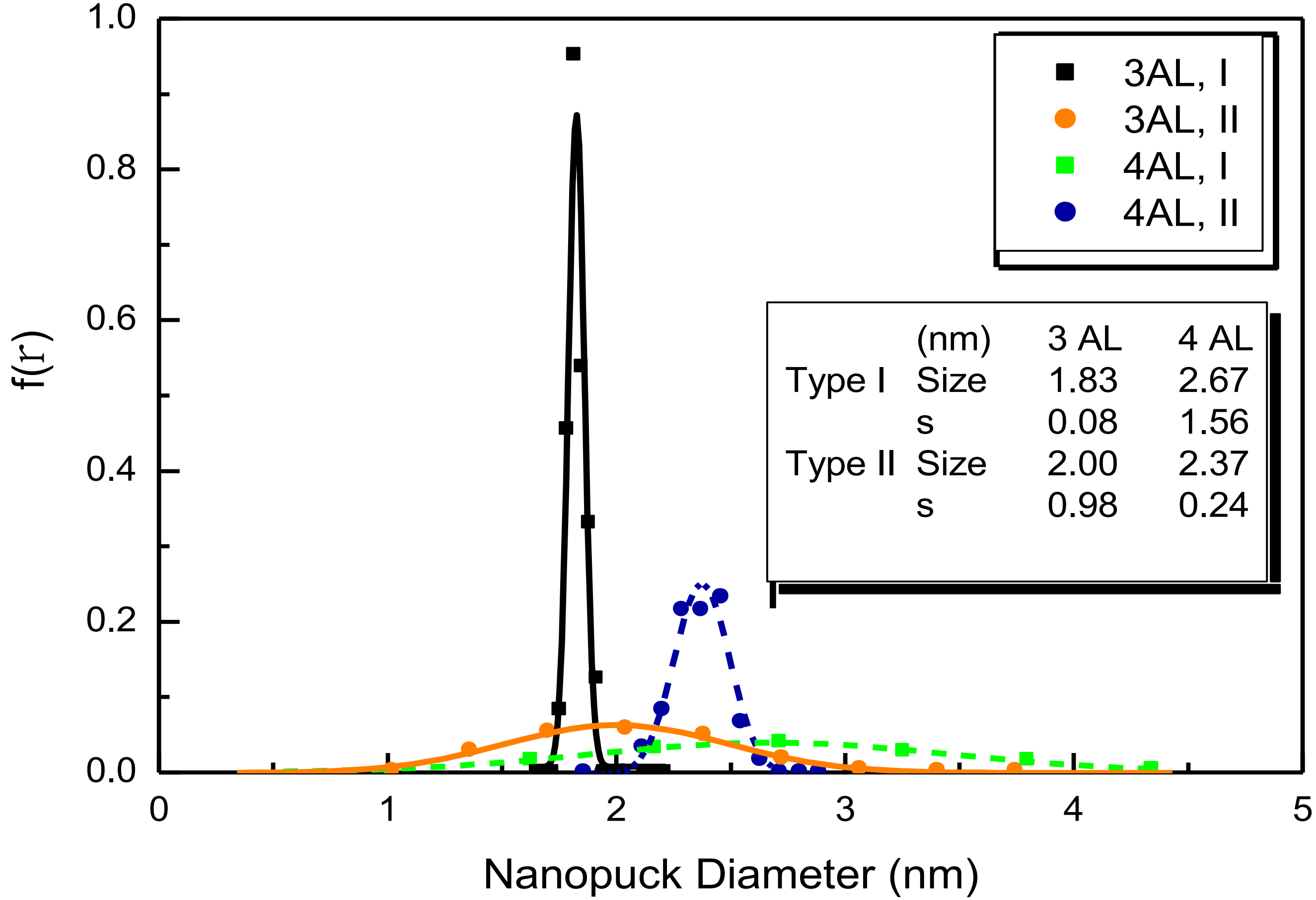
Formation of Pb and Ag nanopucks



Ag nanopucks on Pb islands of 4-layer thickness

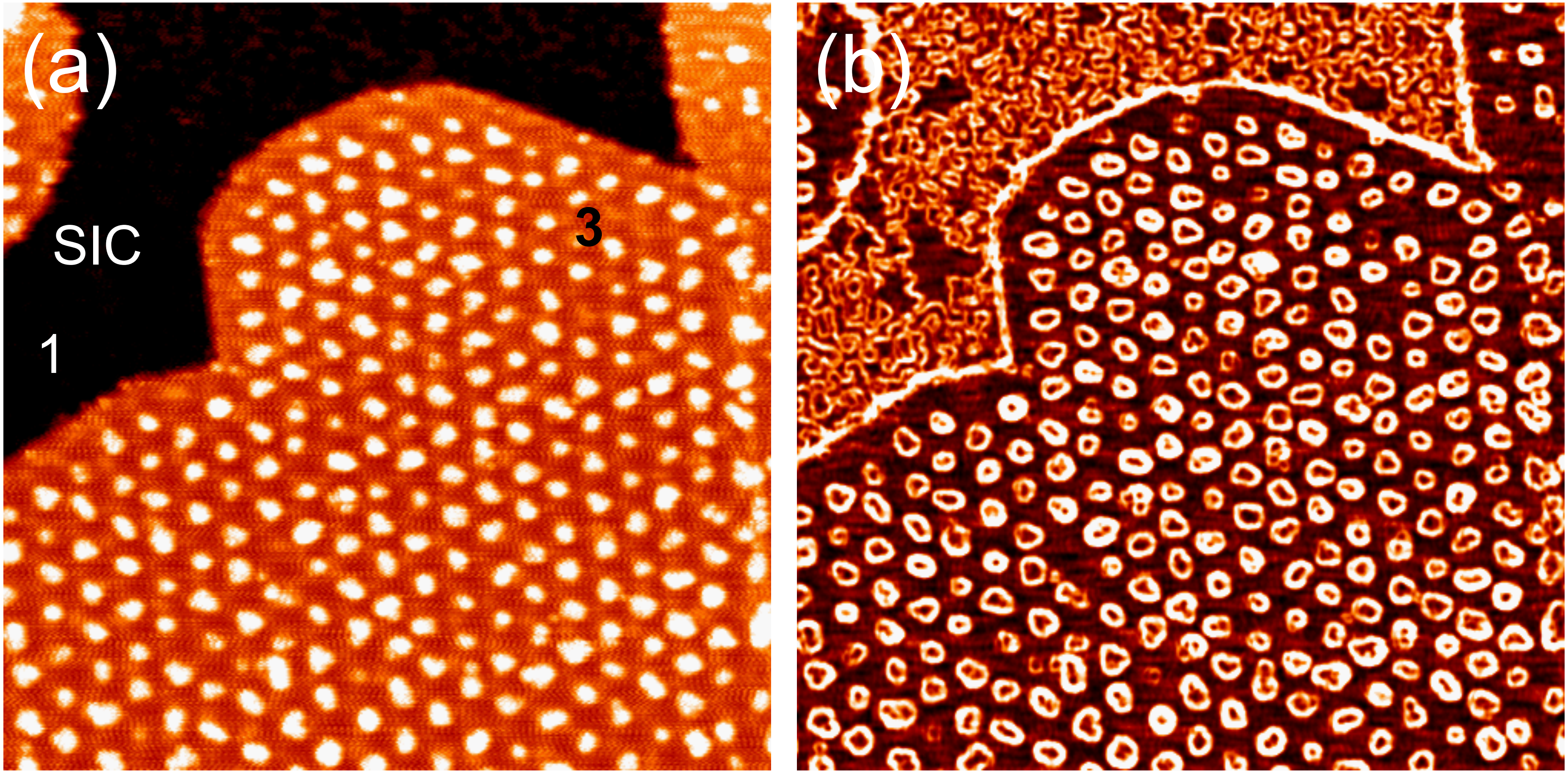


Size distribution of nanopucks



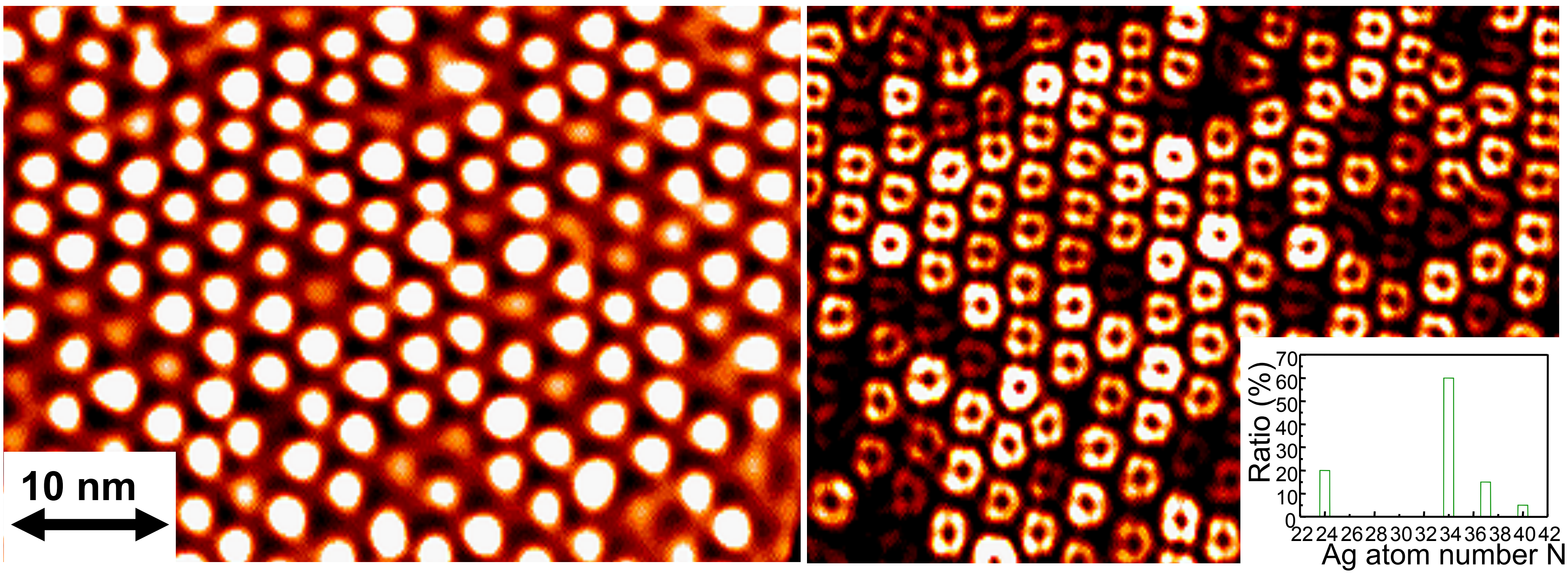
Spatial orderliness : **I (3AL) > II (4AL)** > II (3AL) > I (4AL)

Sizes and shapes of nanopucks



Ag 0.2 ML T = 120 K

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



Summary

- *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.*