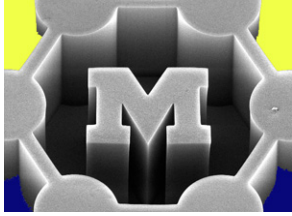
Nanomanufacturing
University of Michigan
ME599-002 | Winter 2010



13: **Overview of synthesis; nucleation kinetics**

March 8, 2010

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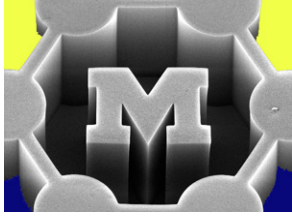
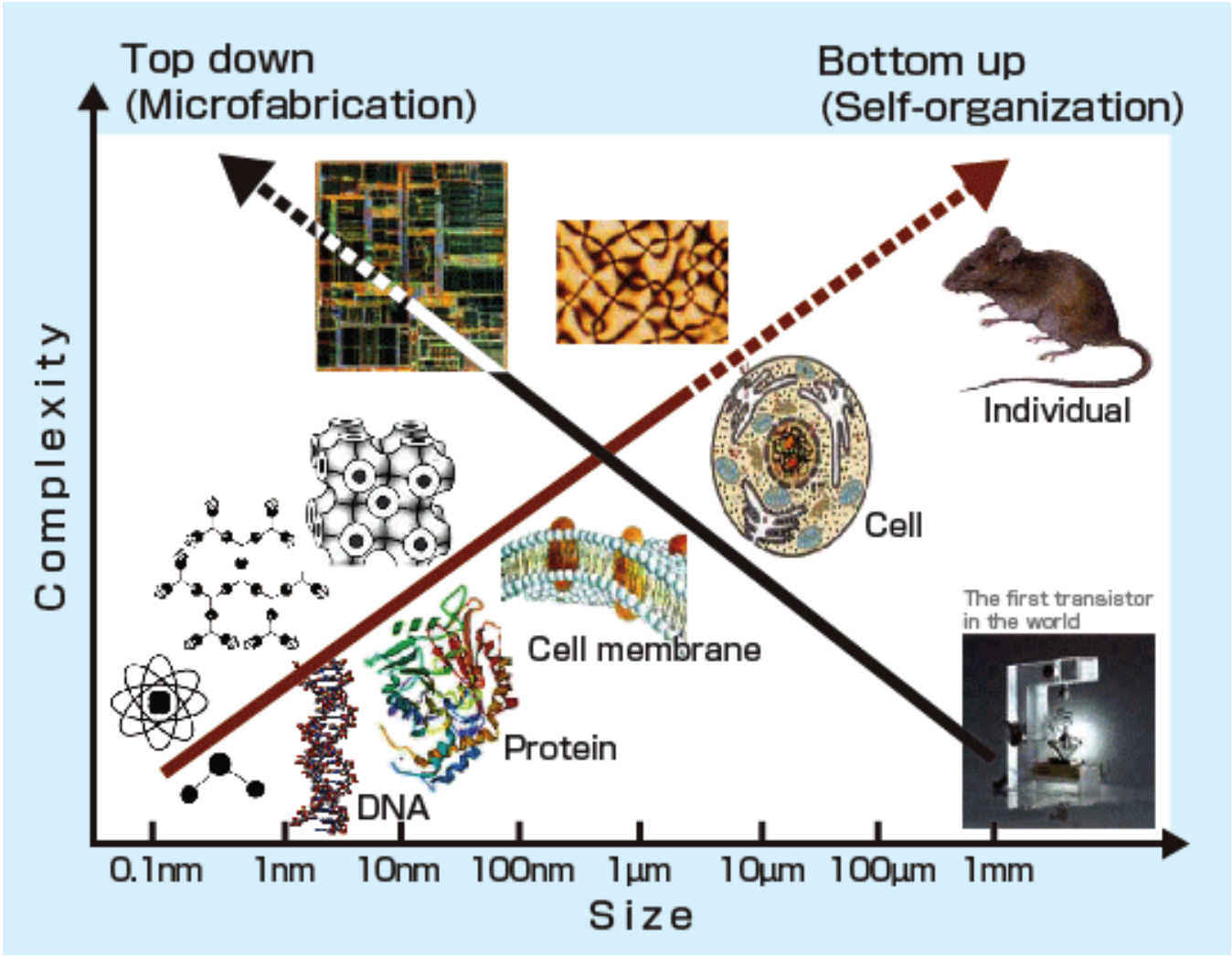
Announcements



- Project/video questions?
- Video due next Mon; upload details soon
- HW3 due next Wed (Mar/17)

Recap: top-down vs. bottom-up



http://www.aist.go.jp/aist_e/aist_today/2007_23/nanotec/nanotec_02.html

Templated self-assembly

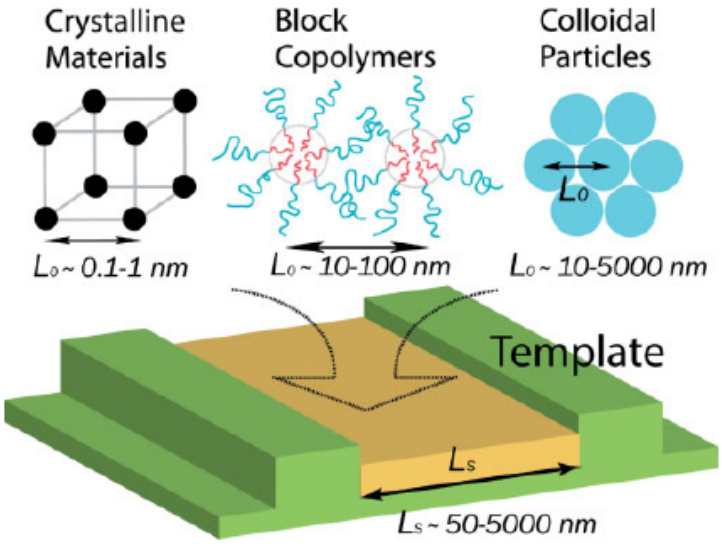


Figure 1. Illustration of some types of TSA systems. Characteristic lengths (L_0) of crystalline materials, block copolymers, and colloid assemblies and the characteristic length (L_S) of the template are indicated.

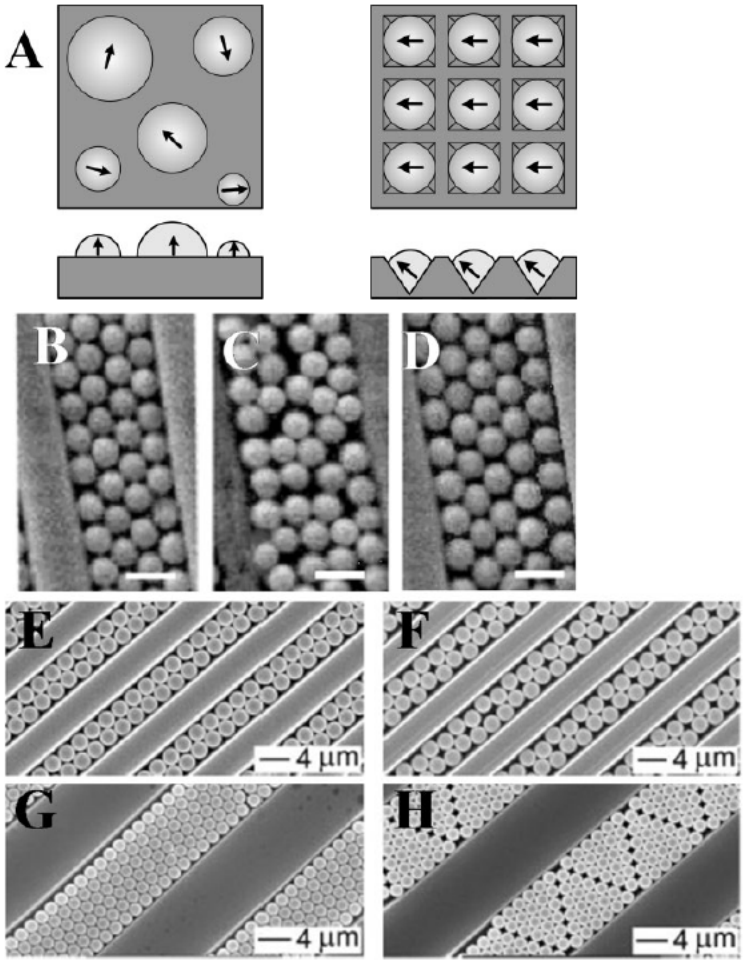
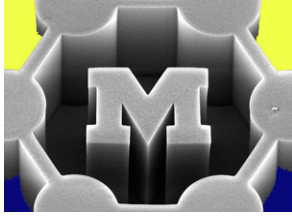


Figure 2. A) Use of topography and dewetting of Au films to create ordered particle arrays [14]. Particles on a flat substrate have random in-plane orientations, while particles on a topologically patterned substrate are crystallographically oriented. The arrows indicate the [111] direction. B–D) Effect of confinement on organization of colloidal particles deposited by an electrophoretic method [17]. The order–disorder–order transition in the colloidal array depends on commensurability of particle diameter and groove width. (Widths of the grooves: B) 2.22 μm, C) 2.51 μm, D) 2.72 μm.) Reprinted from [17]. E–H) Effect of incommensurability on colloidal particles deposited by flow technique [18]. E,F) 2.5 μm polystyrene (PS) bead arrays within channels 5.0 and 5.8 μm in width, respectively. G,H) 1.75 μm PS beads within channels 10.0 and 10.5 μm in width, respectively. Reprinted from [18].

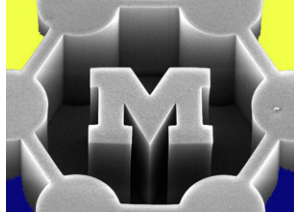
http://doi.wiley.com/10.1002/adma.200502651

Important considerations for synthesis and assembly

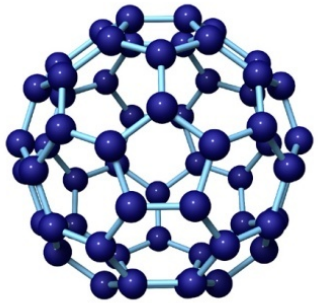


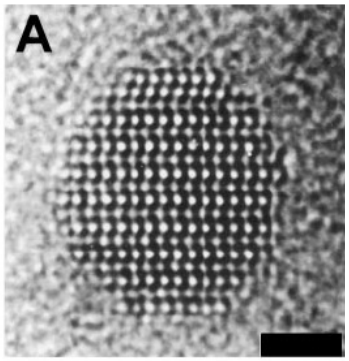
- Size and size distribution of nanostructures
- Process compatibility (chemistry, temperature)
- Defect density; purity
- Interface structure and profiles
- Specificity and strength of interactions with other structures, substrate
- Alignment
- Registry
- …

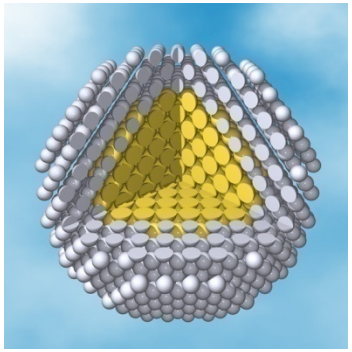
Building blocks



0-D







Nanoclusters

Magic #'s of atoms

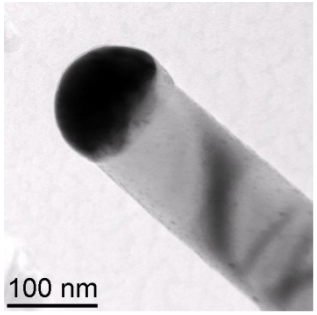
≤1 nm size

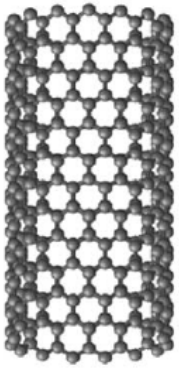
Nanoparticles

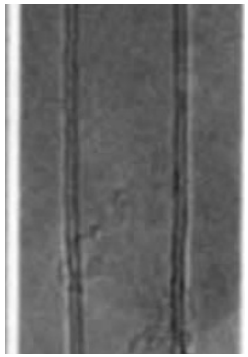
100's-1000's of atoms

~1-100 nm diameter

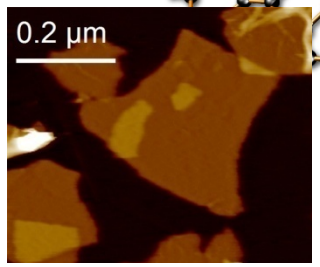
1-D

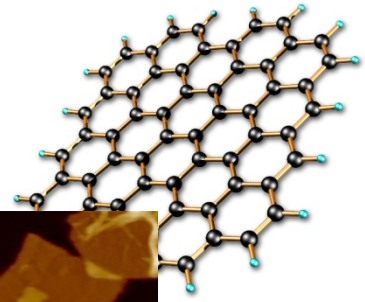






2-D





Nanowires

Filled

Nanotubes

Hollow

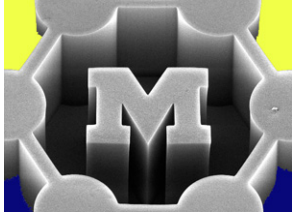
Nanosheets

~1 atom thick

~1-100 nm dia, up to mm long and beyond!

The best way to make monodisperse nanostructures is to employ a large number of very small people.

Today's agenda

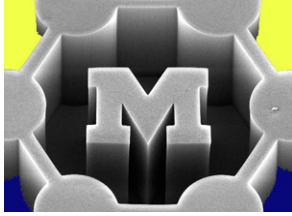


- Overview of synthesis methods for nanoparticles, nanowires, nanotubes
- Thermodynamic model of homogeneous nucleation

→ **Wednesday:** implications/applications in nanoparticle synthesis; evolution of size distributions

→ **Monday:** implications/applications in nanotube/wire synthesis; integration with top-down methods and device fabrication

Readings for lectures 13-15

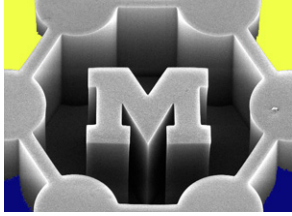


Nominal: (ctools)

- AJH written notes (one file for today and wednesday)
- Sugimoto, "Preparation of monodispersed colloidal particles"
  - Through page 73, needed as backup to lecture notes only
- Peng et al., "Kinetics of II-VI and III-V colloidal semiconductor nanocrystal growth: focusing of size distributions"

- Kodambaka et al., "Growth kinetics of Si and Ge nanowires"
- Hochbaum et al., "Controlled growth of Si nanowire arrays for device integration"
- Terranova et al., "The world of carbon nanotubes: an overview of CVD growth methodologies"
- Wirth et al., "Diffusion- and reaction-limited growth of carbon nanotube forests"

Readings for lectures 13-15



Extras: (ctools)

- Burda et al., excerpt from "Chemistry and properties of nanocrystals of different shapes"

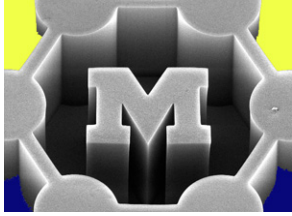
  → More detail on chemical methods of NP synthesis, self-assembly

- Xia et al., "One-dimensional nanostructures: synthesis, characterizaton, and applications"

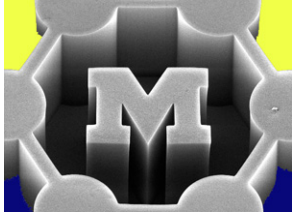
  → Broad overview of top-down and bottom-up NW/NT synthesis

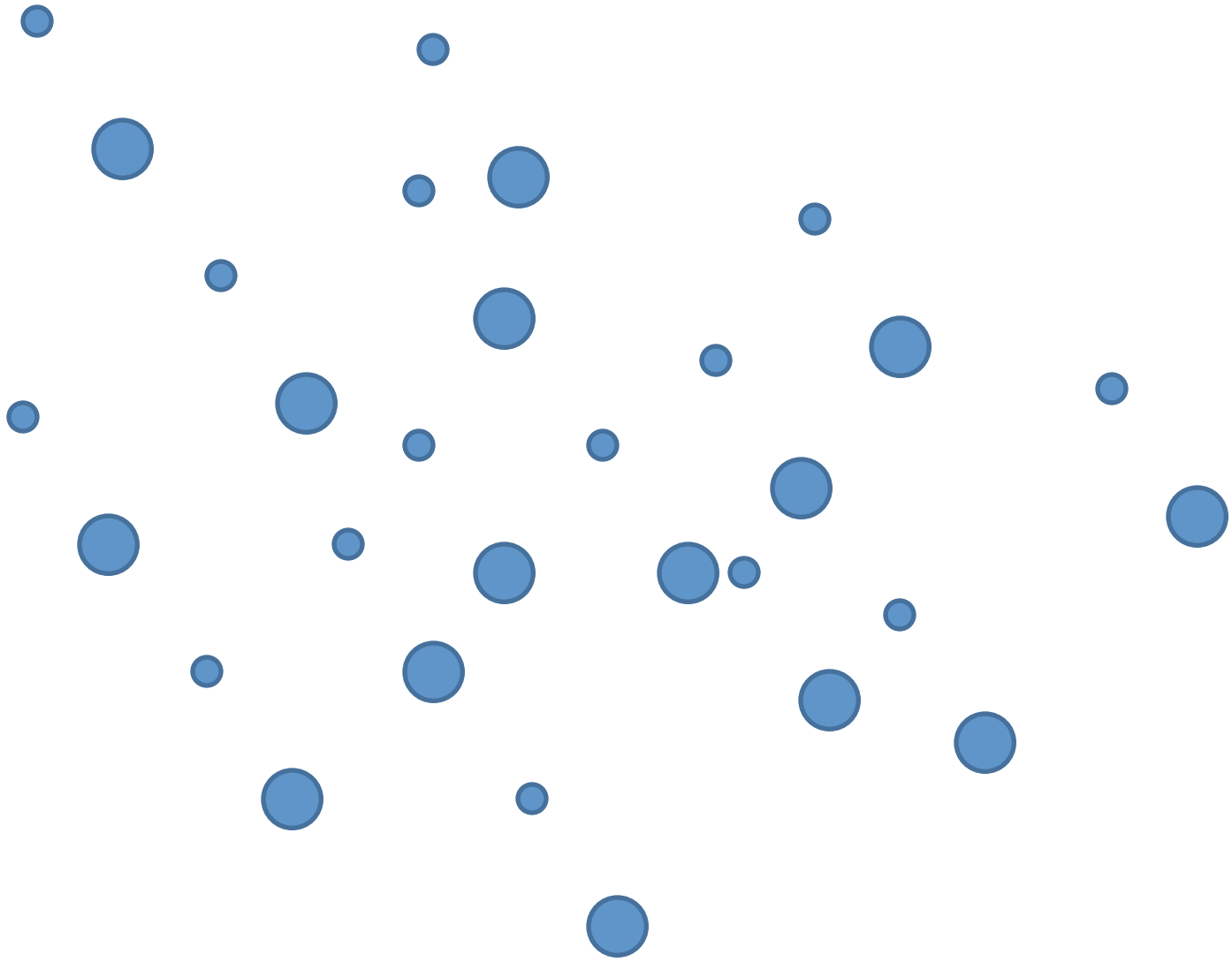
- Wagner and Ellis, "The vapor-liquid-solid method of crystal growth and its application to silicon"
- Hofmann et al., "Ledge-flow-controlled catalyst interface dynamics during Si nanowire growth"
- Harutyunyan et al., "Preferential growth of single-walled carbon nanotubes with metallic conductivity"

Start: nucleate!

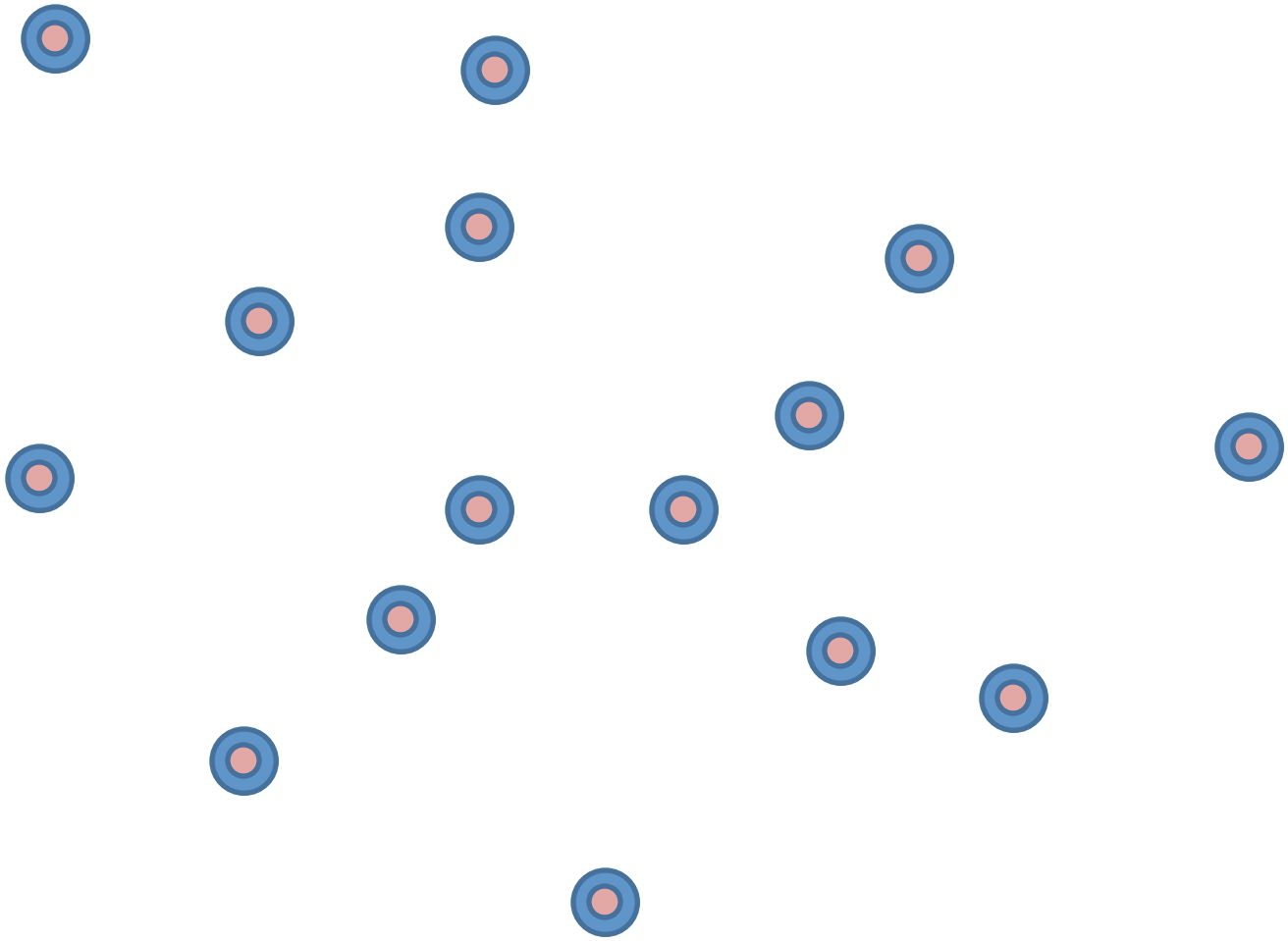


Nucleate *and* grow





Nucleate *then* grow



- This could be the final nanostructure, or an intermediate nanostructure for a subsequent process (e.g., NT/NW growth)

Liquid-phase nanoparticle synthesis

Strategy to separate nucleation and growth events

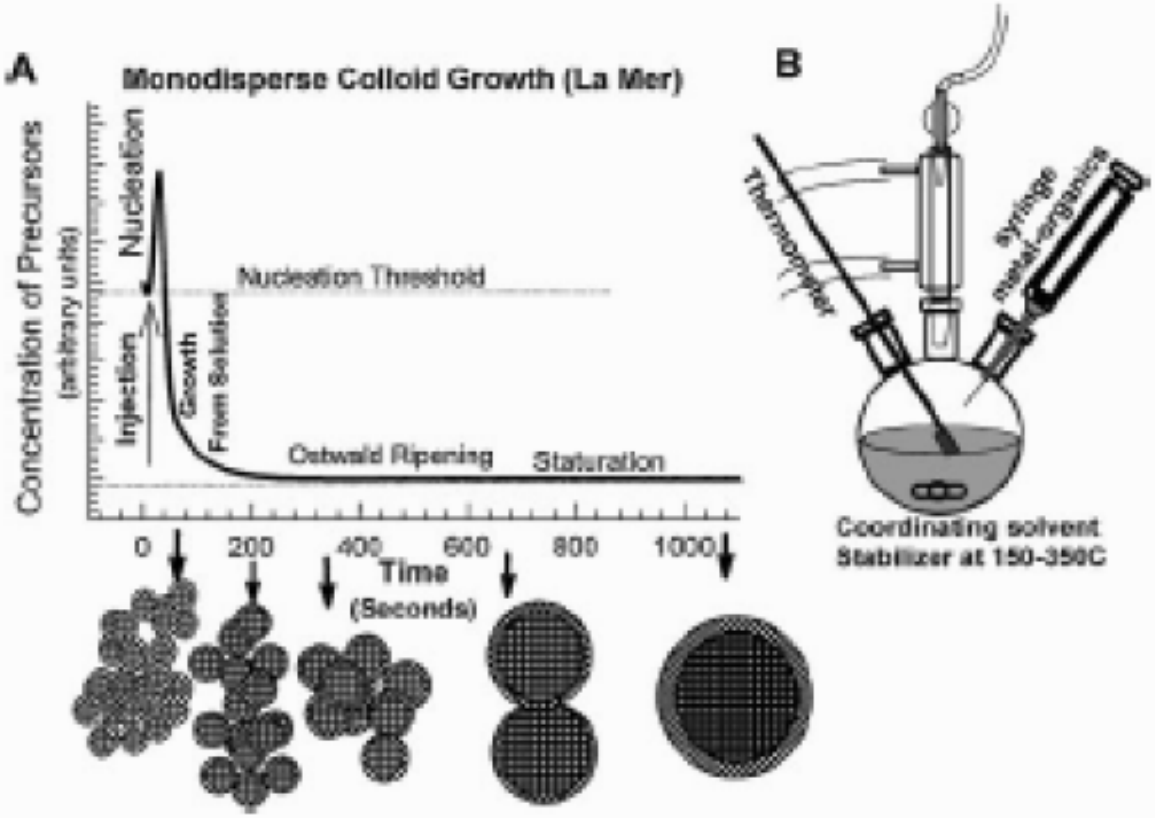
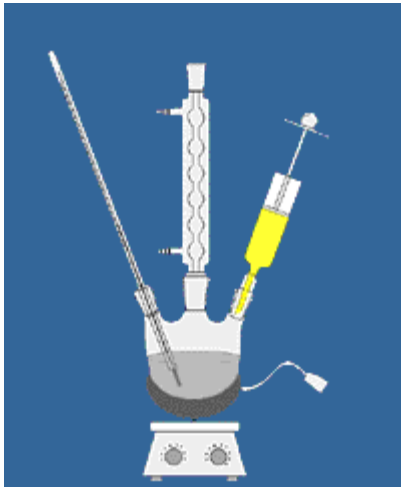


Figure 1 (*A*) Cartoon depicting the stages of nucleation and growth for the preparation of monodisperse NCs in the framework of the La Mer model. As NCs grow with time, a size series of NCs may be isolated by periodically removing aliquots from the reaction vessel. (*B*) Representation of the simple synthetic apparatus employed in the preparation of monodisperse NC samples.



Maximize energy difference between nucleation and growth steps

Gas-phase nanoparticle synthesis

Condensation from vapor at high inert gas pressure

Add oxygen to oxidize particles, stopping growth

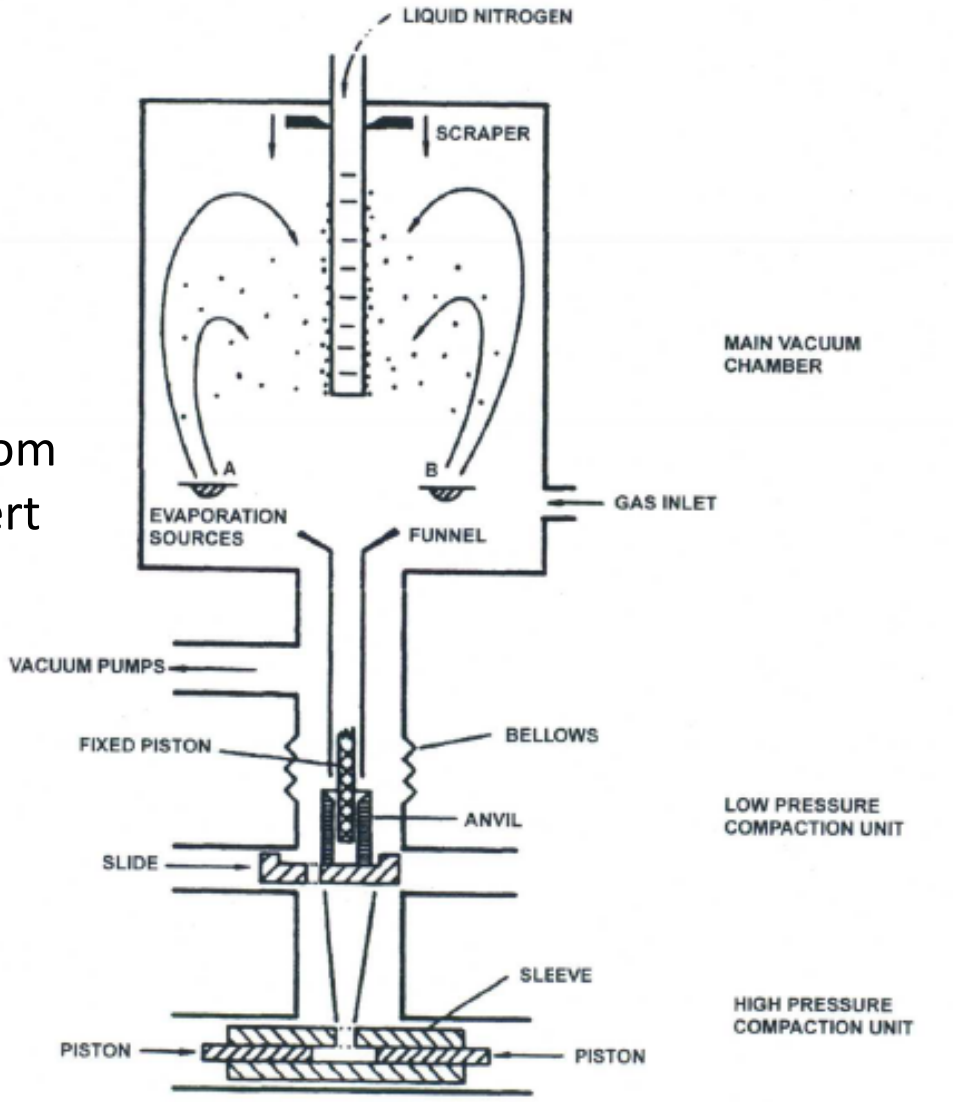
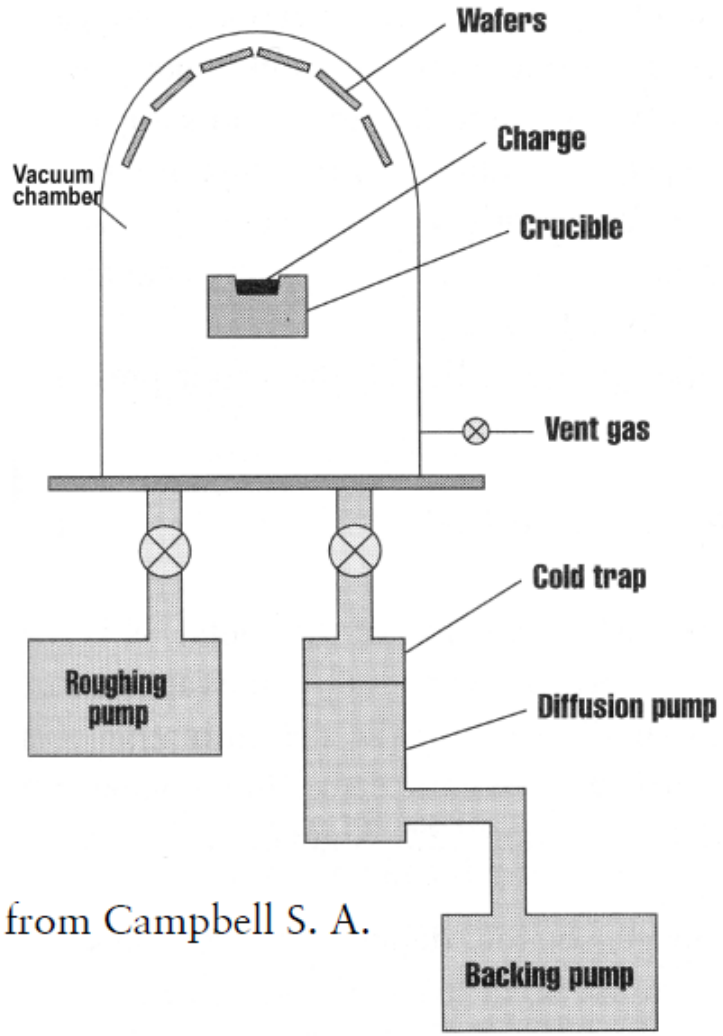
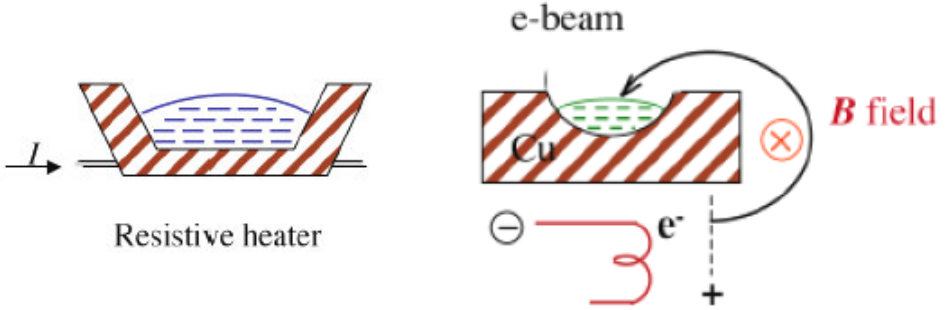


FIGURE 4.1 Typical apparatus for producing nanoparticles from supersaturated vapor.[53] Reprinted with permission from A S Edelstein and R C Cammarato, (eds), *Nanoparticles: Synthesis, Properties and Applications*, IOP Publishing, Philadelphia, (1996).

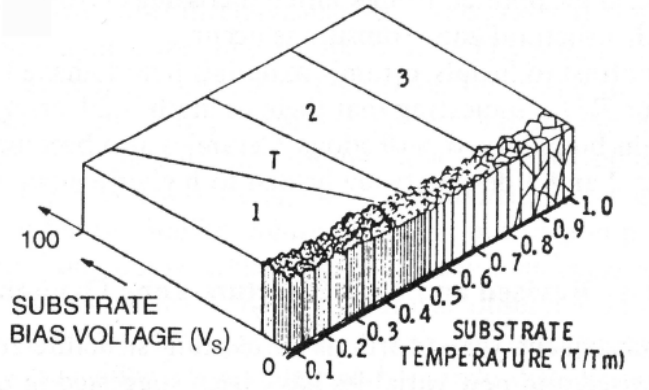
Thin-film deposition and growth



from Campbell S. A.

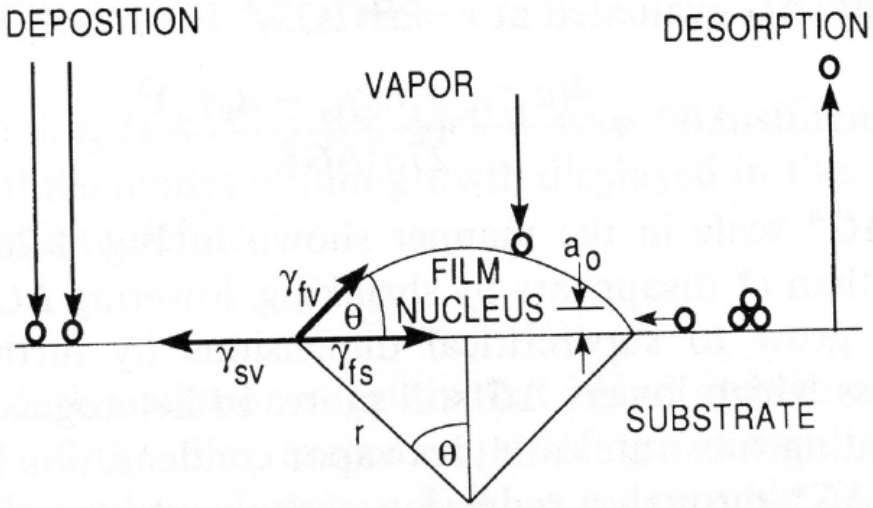


thin film structure is given by thin film properties and deposition parameters. The influence of deposition variables on structural features is typically depicted in (empirical) structure-zone diagrams or models (SZM)



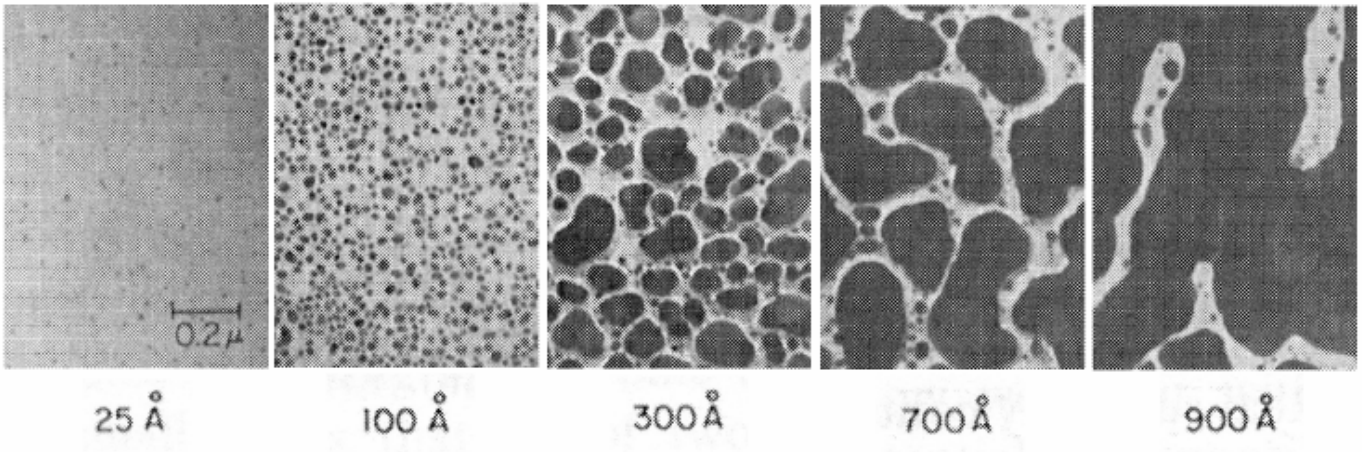
SZM for RF-sputtered films

Formation of nuclei by adsorption and diffusion on the substrate



ML = Monolayer	Θ < 1ML	1 ML < Θ < 2 ML	Θ > 2ML
Volmer – Weber			
Frank - van der Merwe			
Stranski – Krastanov			

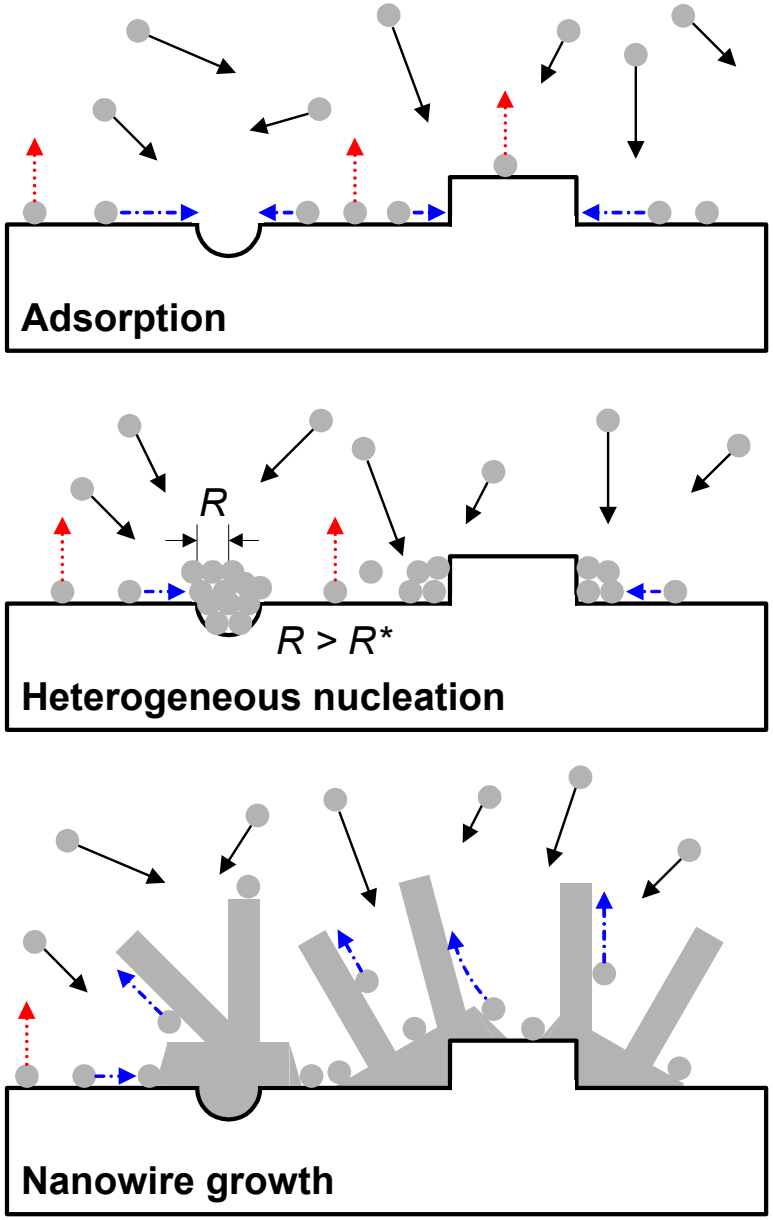
Different modes/models of nucleation and growth based on film-substrate wetting

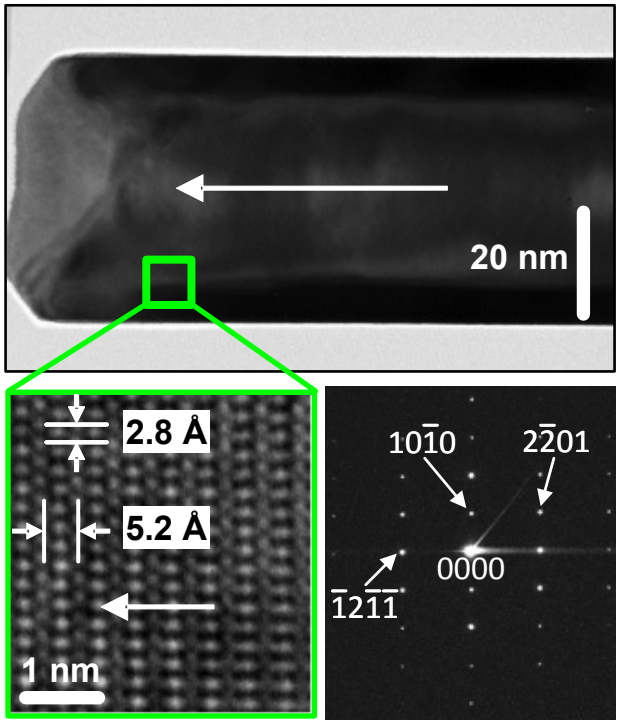


Nucleation of Ag on NaCl

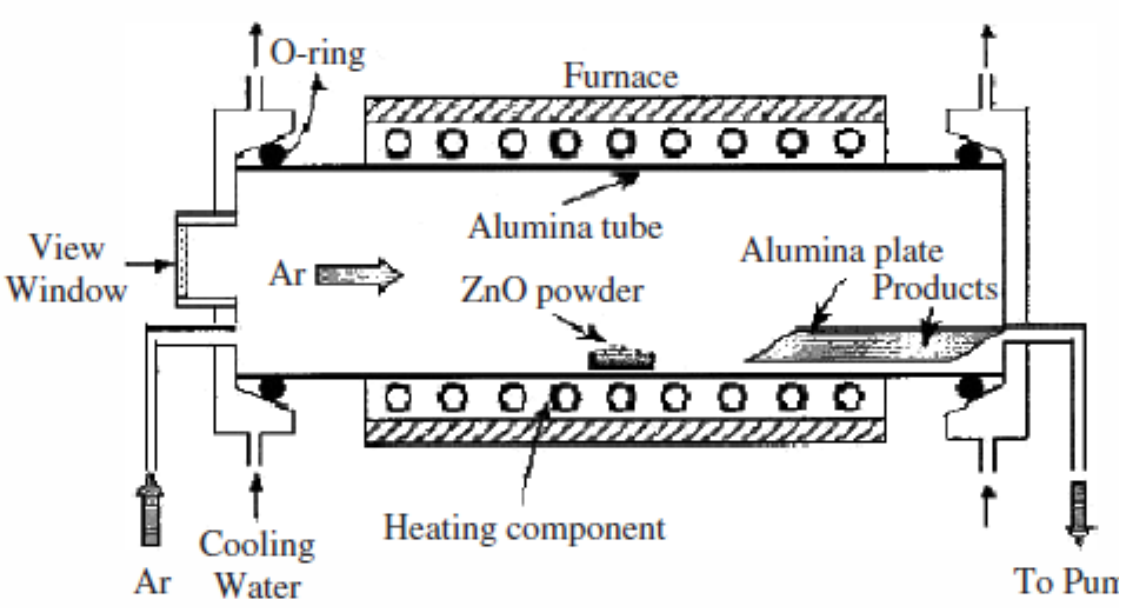
S. Hoffman (Cambridge)

Vapor-solid (VS) nanowire growth





ZnO NW growth: vapor transfer method



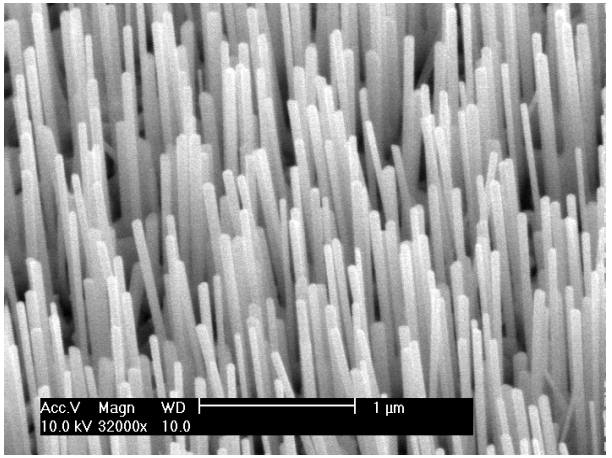


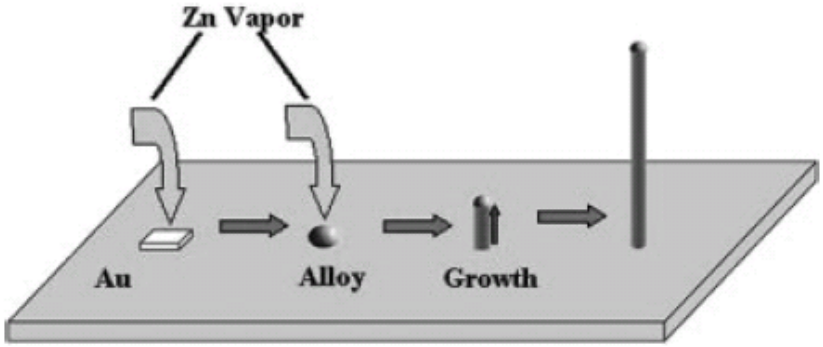
Figure 3. A schematic diagram of the experimental apparatus for growth of ox
by the solid–vapour phase process.

$$ZnO_{(solid)} + C_{(solid)} \leftrightarrow Zn_{(vapour)} + CO_{(gas)} \quad (T > 970\,^{\circ}C) \tag{1}$$

$$2C + O_2 = 2CO \tag{2}$$

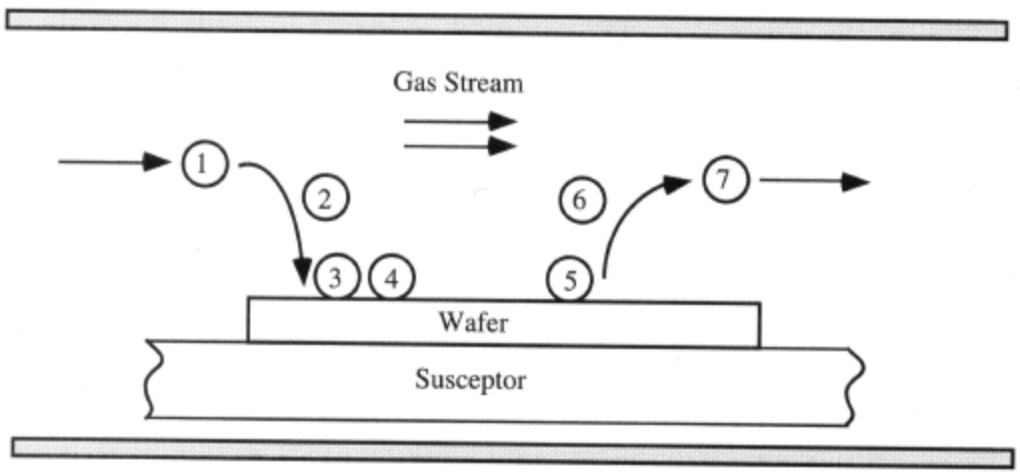
$$2CO + O_2 = 2CO_2 \tag{3}$$

$$2Zn + O_2 = 2ZnO. \tag{4}$$



P. Yang, et al., Adv. Funct. Mat. 12, 323 (2002)
S. H. Dalal, et al., Nanotechnology **17,** 4811 (2006)

Chemical vapor deposition (CVD)

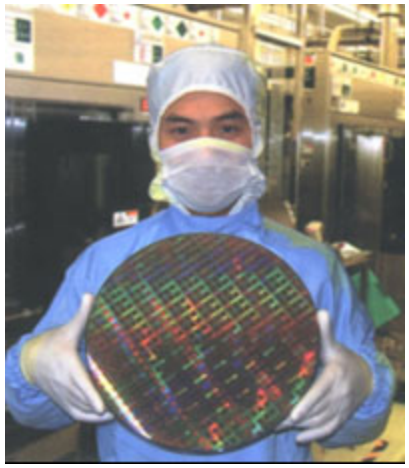


volatile gas(es) are introduced, which decompose when heated/plasma excited and produce non-volatile film

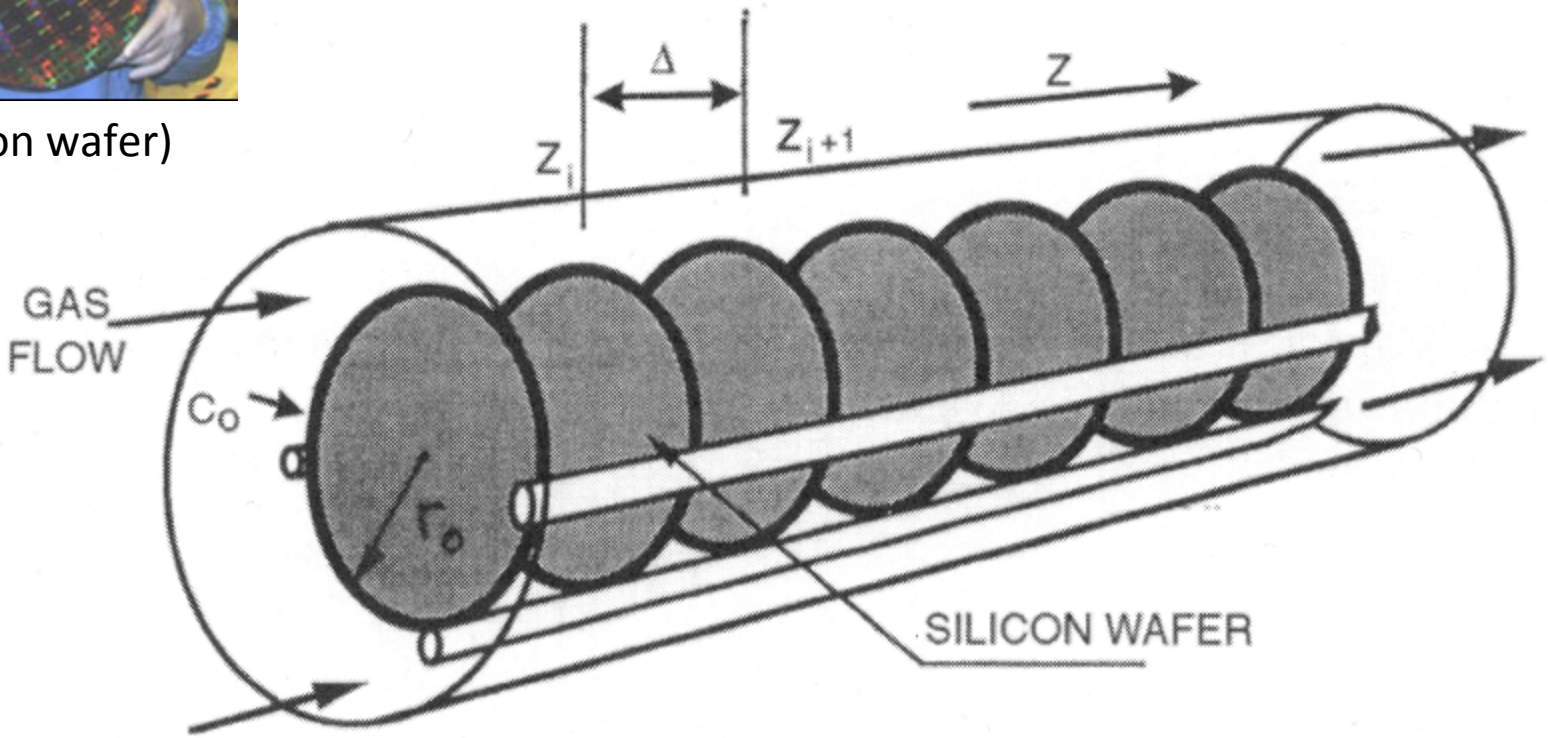
Steps involved in a CVD process:

1. Transport of reactants
2. Reactant diffusion from main gas stream through boundary layer
3. Adsorption of reactants
4. Surface processes (e.g., migration, reaction, incorporation)
5. Desorption of byproducts; diffusion and transport away…

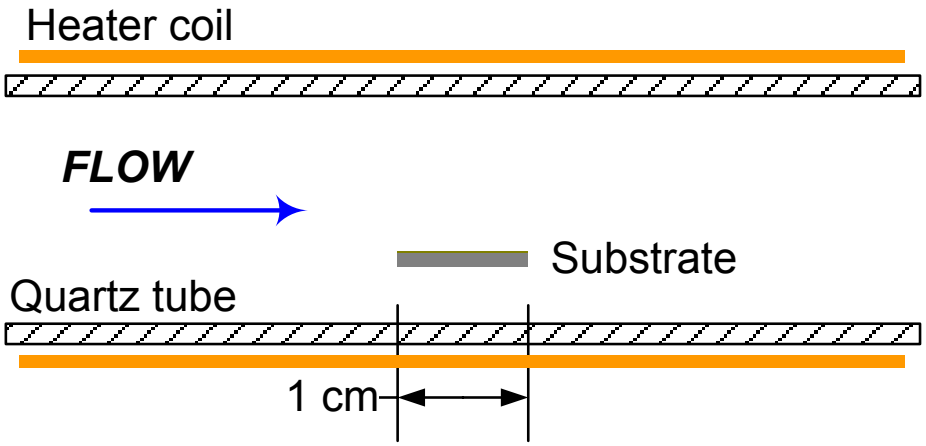
CVD on silicon wafer substrates



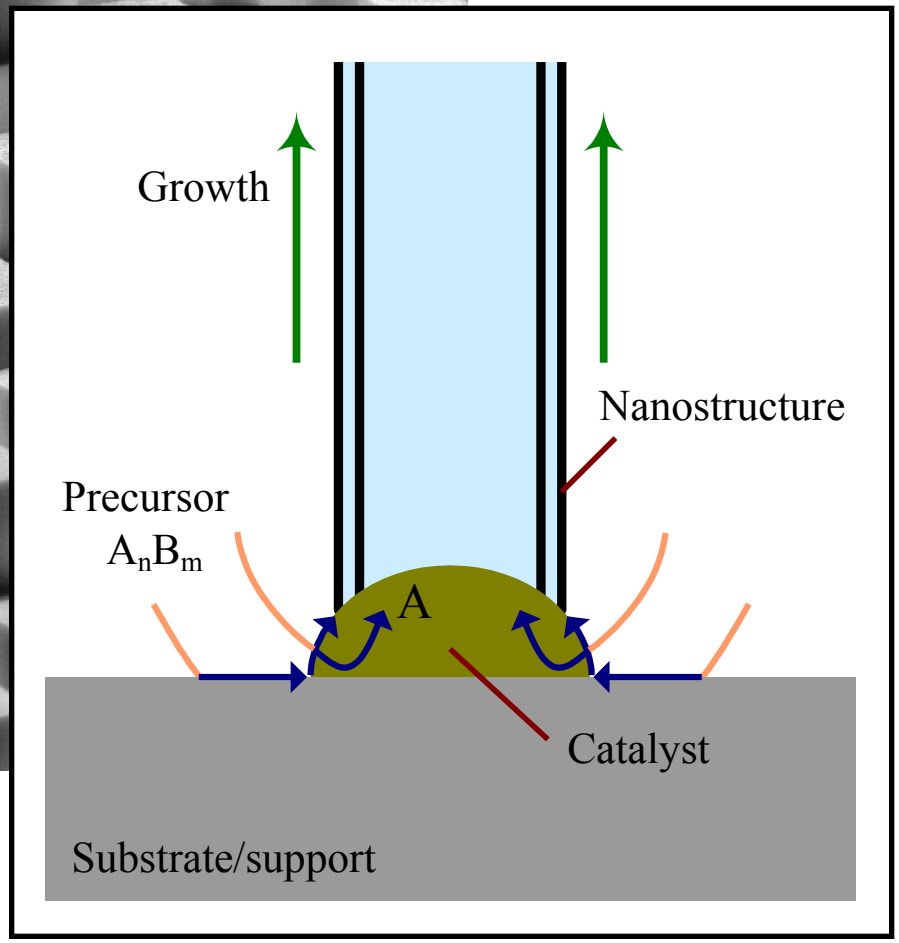
(silicon wafer)



CVD system with horizontal tube furnace



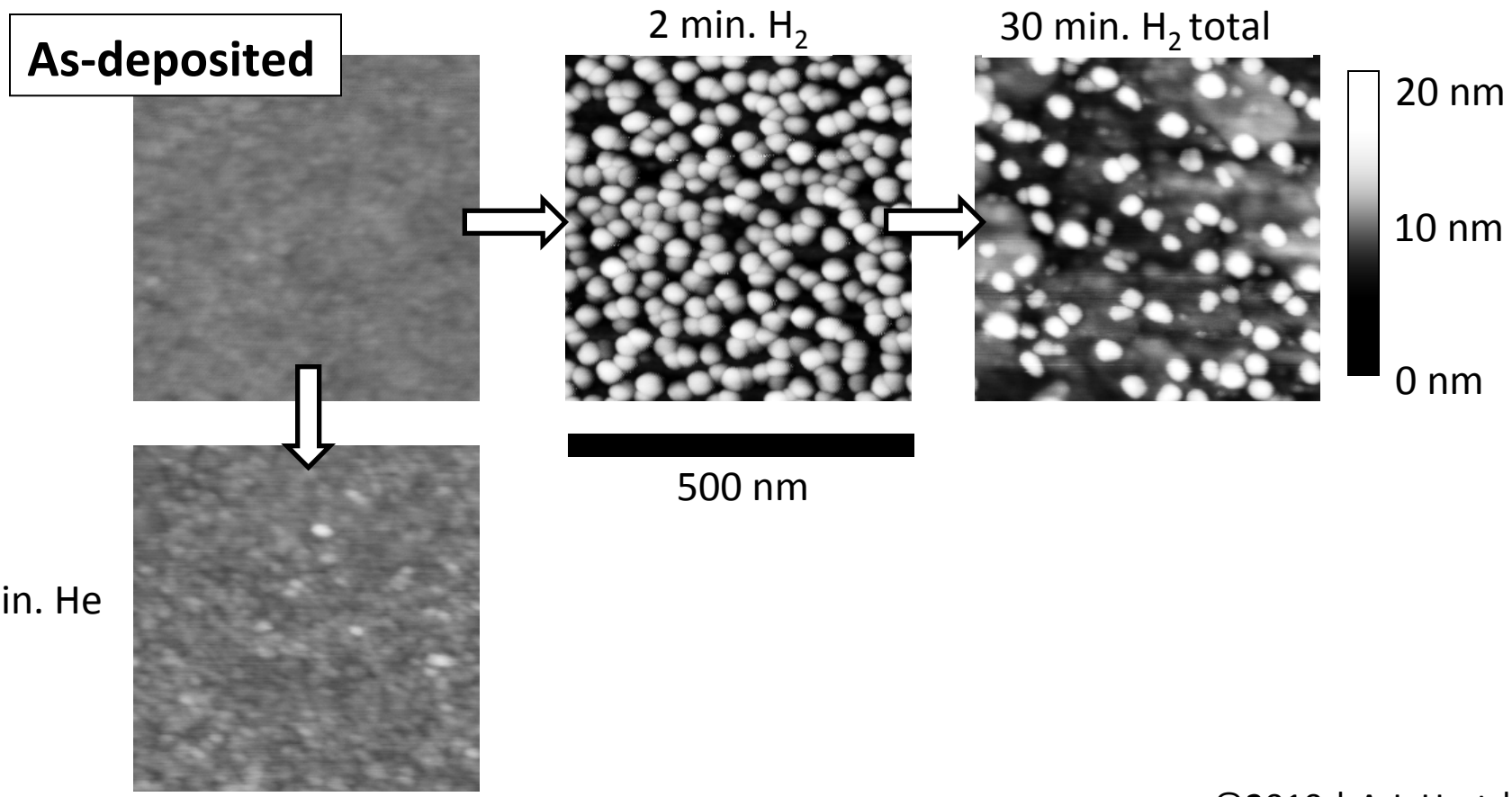
Catalytic growth of NWs/NTs and assemblies



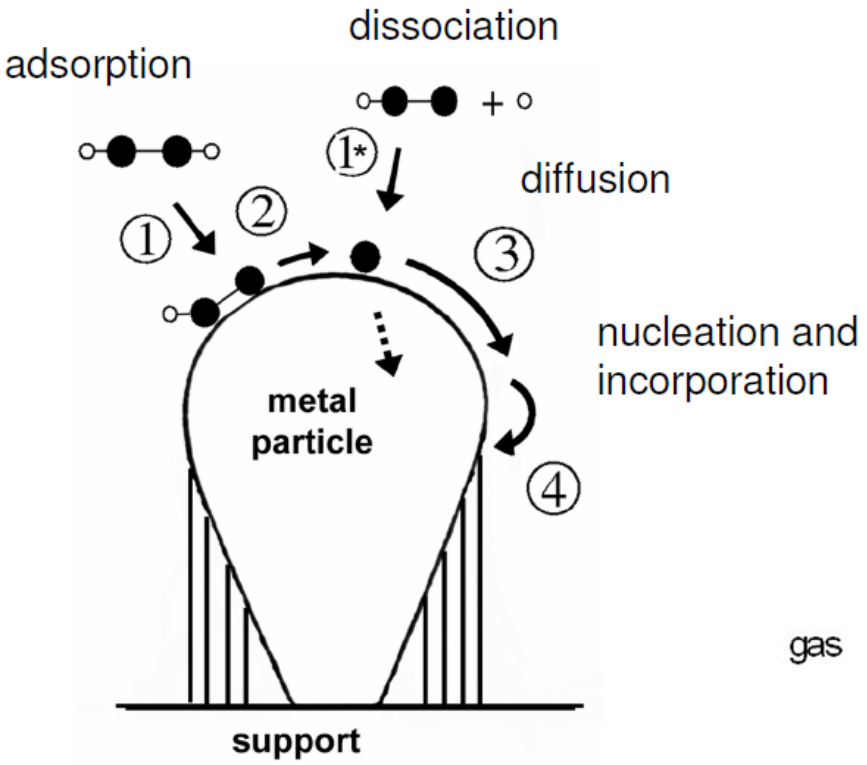
→ *can also spray catalyst in gas phase, etc …more examples later*

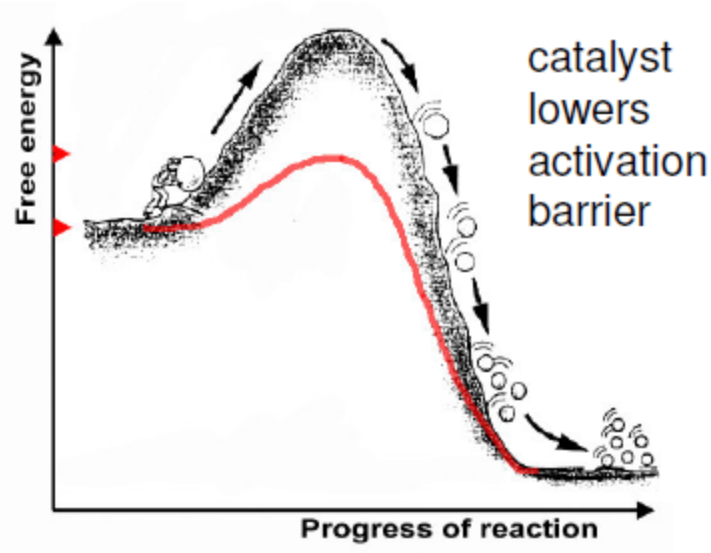
Making catalysts from thin films

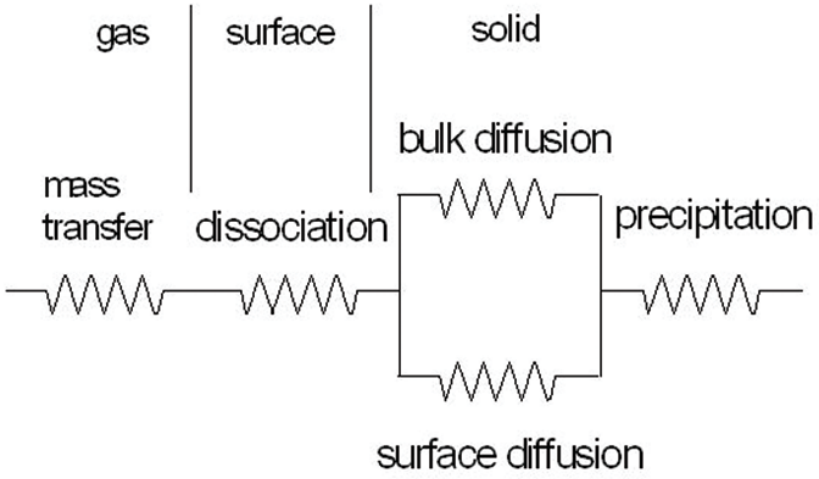
Deposit a catalyst film → **Anneal to form particles**

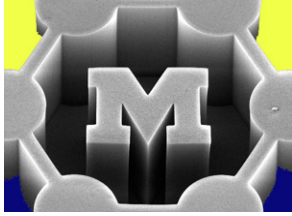


A catalyst particle is a small substrate and a small reactor

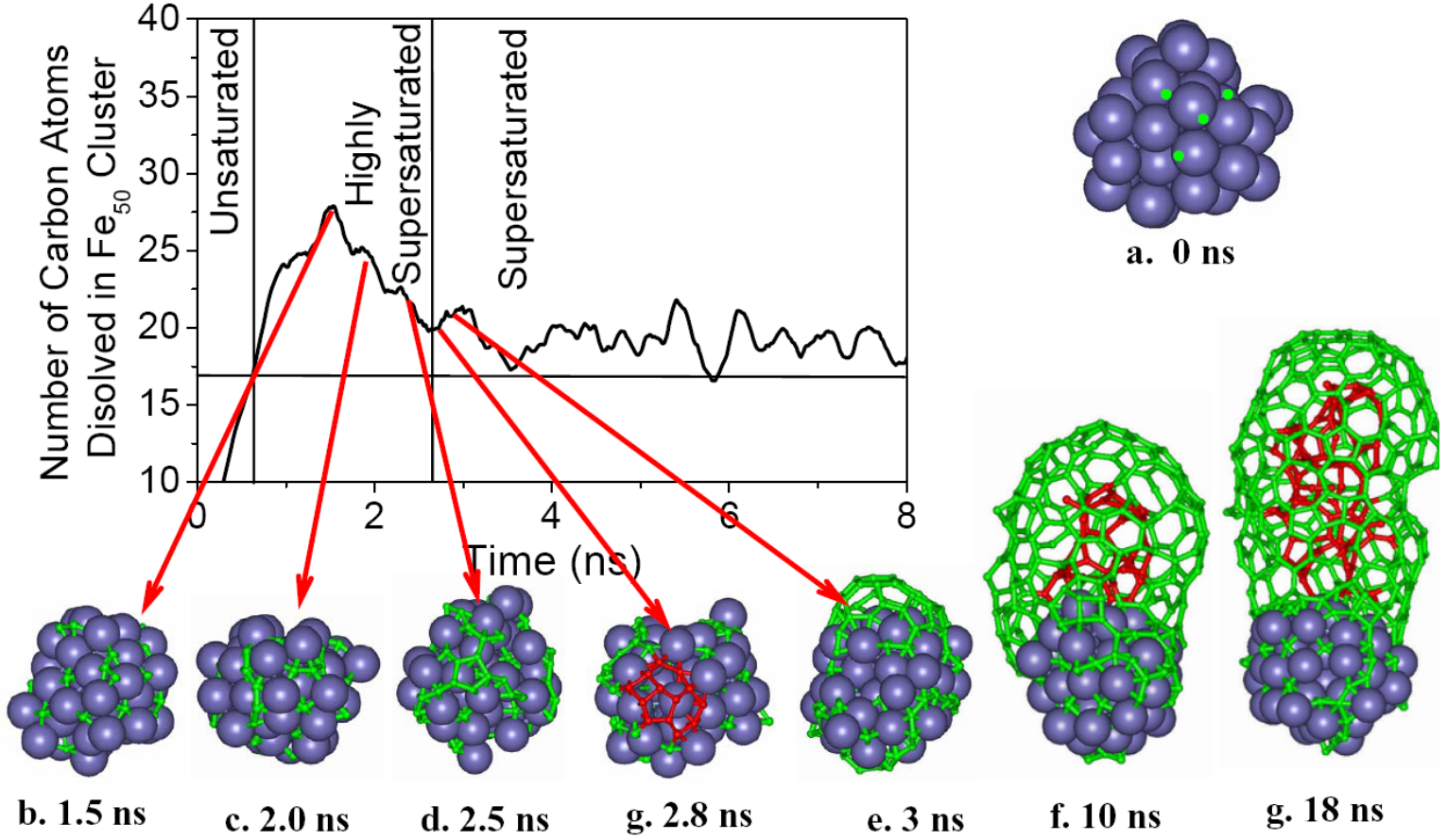








Zhu et al.


Number of Carbon Atoms Disolved in Fe_{50} Cluster
40
35
30
25
20
15
10
0
2
4
6
8
Time (ns)
Unsaturated
Highly Supersaturated
Supersaturated
a. 0 ns
b. 1.5 ns
c. 2.0 ns
d. 2.5 ns
g. 2.8 ns
e. 3 ns
f. 10 ns
g. 18 ns

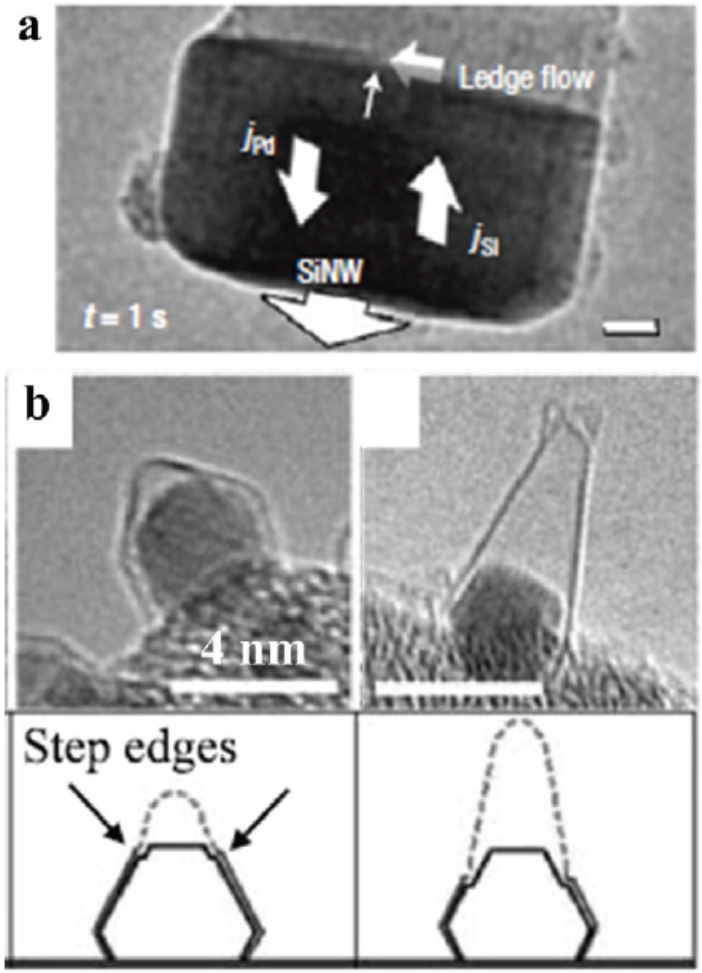


Figure 2. Observations of step edges on nanoscale particles during (a) SiNW growth (Hofmann et al.) and (b) CNT growth (Zhu et al.)

Many variables…

INPUTS

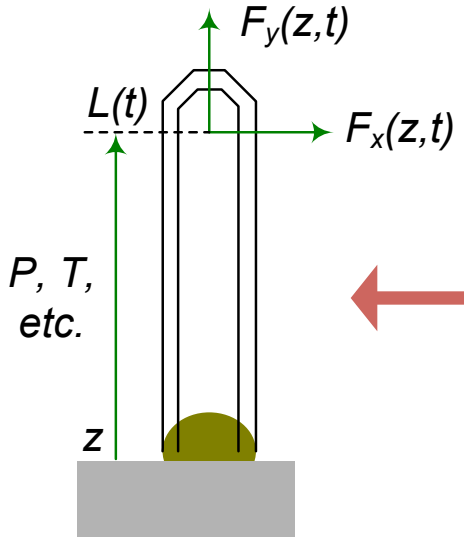
Catalyst and support:
- Material and composition
- Particle size
- Chemical state (annealing)
- Surface roughness

Reaction conditions:
- Substrate temperature
- Pressure
- Reactant composition
- Buffer/etchant composition
- Reactant pre-treatment
- Supply rates
- Flow profiles/dynamics
- Time and temporal adjustment
- Forces acting during growth

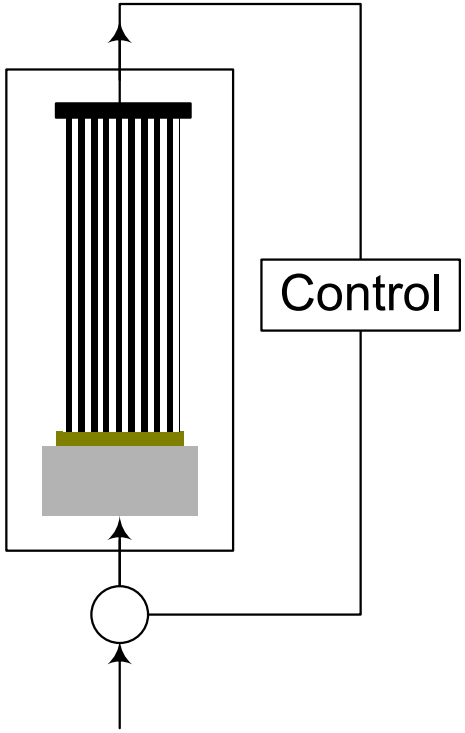
OUTPUTS

Properties:
- Diameter and structure
- Length, growth rate, lifetime
- Defect density

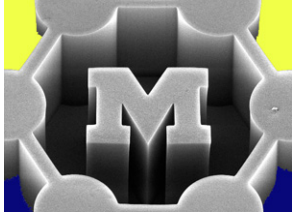
Model:
ONE nanostructure



Manufacturing:
MANY nanostructures

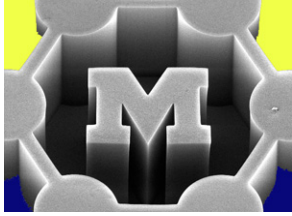


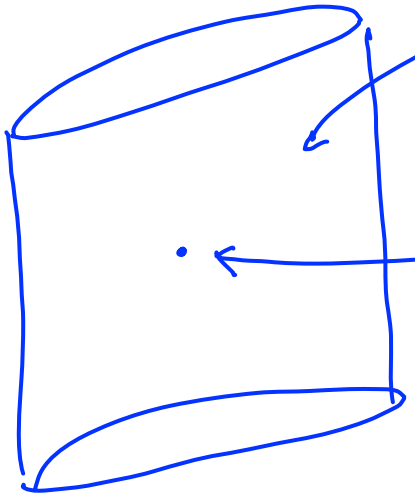
Types of nucleation



- **Homogeneous nucleation:** solute molecules within a liquid combine to produce nuclei; no solid interface present
- **Heterogeneous nucleation:** A nucleus forms on a pre-existing surface of another material (e.g., impurity, vessel wall)
- **Secondary nucleation:** Occurs at a pre-existing "seed" of the same material, or by aggregation of particles

Thermodynamic model of homogeneous nucleation





$$\Delta G_{tot} = \Delta G_{bulk} + \Delta G_{surface}$$

needed to form 1 particle

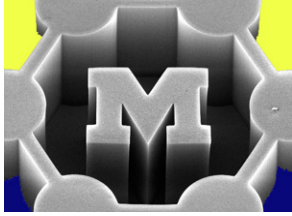
$$= \left(\frac{\frac{4}{3}\pi R^3}{a_v} \right) \Delta\mu + 4\pi R^2 \gamma$$

$V = \frac{4}{3}\pi R^3$

change in chemical pot per atom.

N_{atoms}

atomic volume



bulk term.

$$N\Delta\mu = N(\mu_l - \mu_v) = -Nk_bT \ln S$$

S: supersaturation

: P/P_e

↑ equilibrium vapor pressure

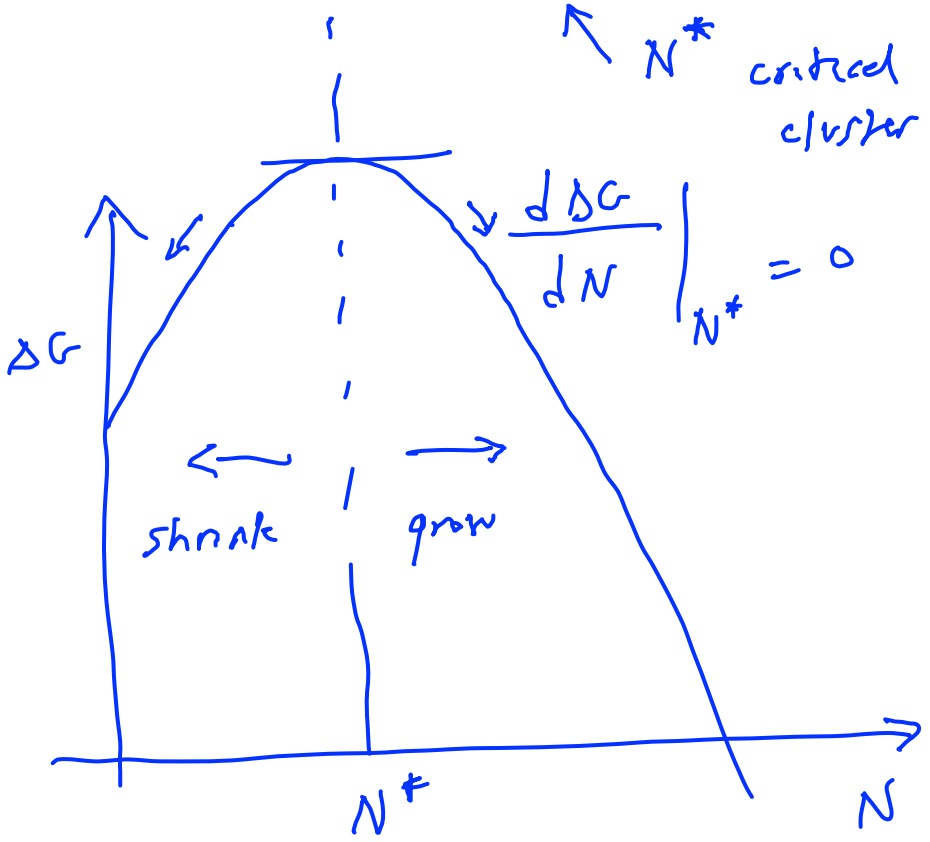
surface term

$4\pi R^2\gamma$, $\quad v = \frac{4}{3}\pi R^3 = a_v N$

$$4\pi R^2 = 4\pi \left(\frac{3a_v}{4\pi}\right)^{2/3} N^{2/3}$$

$$\Delta G_{for} = -NkT\ln S' + \gamma 4\pi\left(\frac{3a_v}{4\pi}\right)^{2/3} N^{2/3}$$

N^* critical cluster size



$$\left.\frac{d\Delta G}{dN}\right|_{N^*} = 0$$

$$\frac{d\Delta G}{dN} = 0:$$

$$-kT\ln S' + \frac{8}{3}\pi\gamma\left(\frac{3a_v}{4\pi}\right)^{2/3} N^{-1/3}$$

$$N^* = \frac{32\pi\gamma^3 a_v^2}{3(kT\ln S')^3}$$

$$N^+ \rightarrow R^* = \frac{2\gamma \Omega_v}{k_b T \ln(S)}$$

if $S \uparrow \Rightarrow N^* \downarrow, R^* \downarrow$

if $T \uparrow \Rightarrow N^* \downarrow, R^* \downarrow$

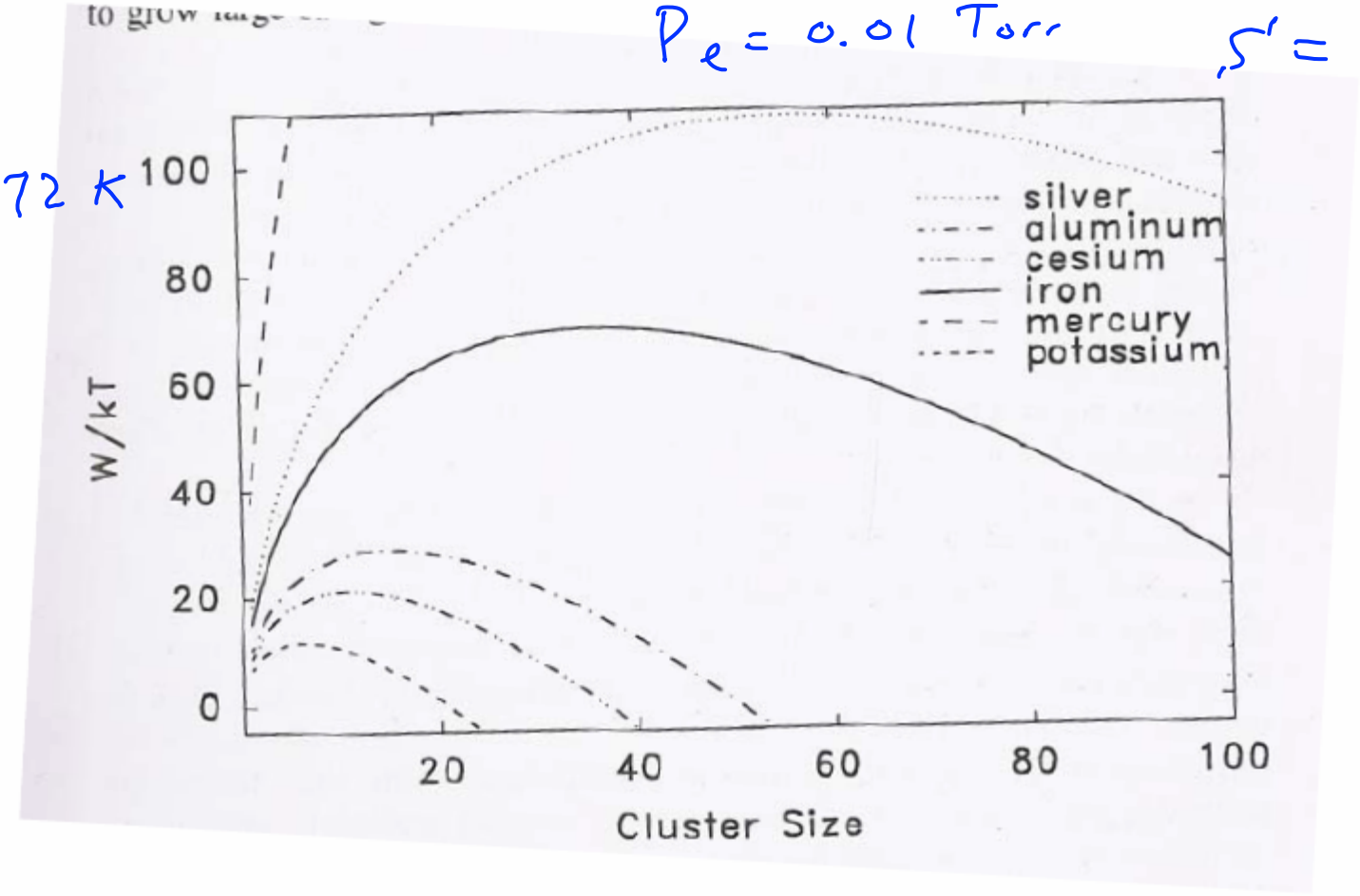
Critical cluster sizes for some metals

$P_e = 0.5$ Torr

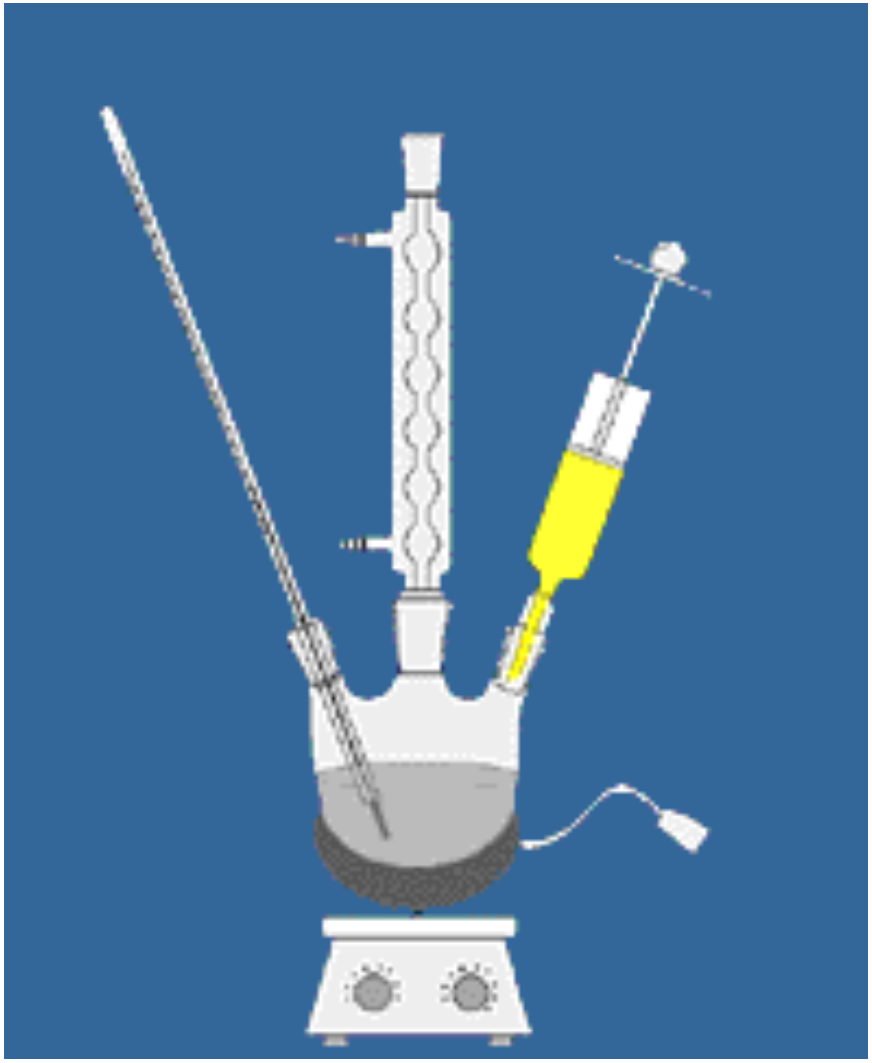
$P_e = 0.01$ Torr

$S' = 50$

$A_C = 1472\ K$



Example: size distributions of nanoparticles by chemical synthesis



Monodispere CdSe

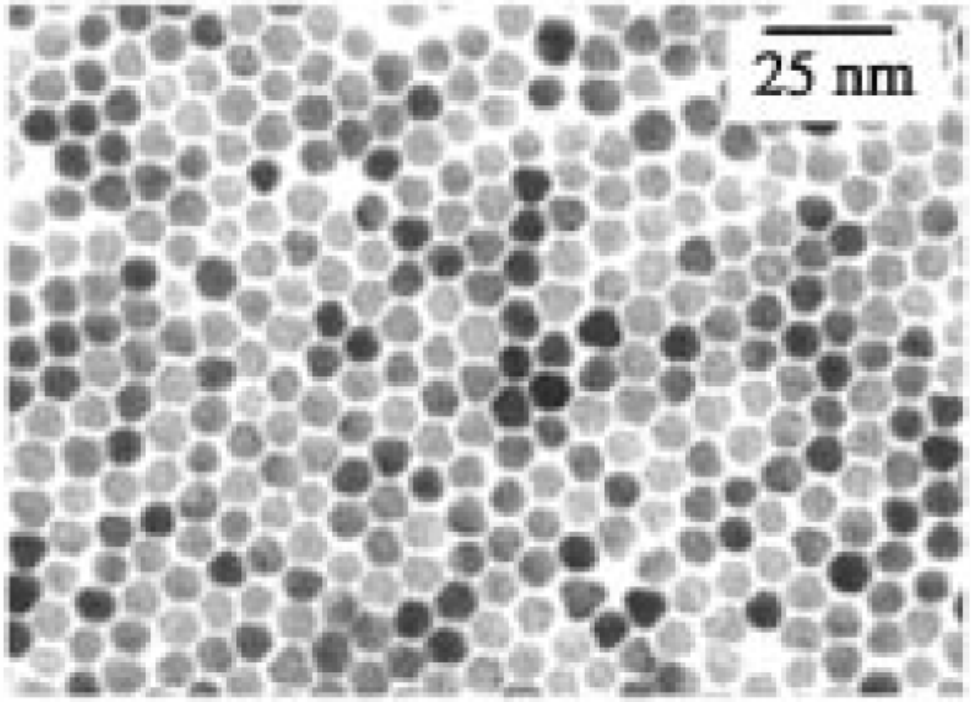


Figure 3. Transmission electron micrograph of 8.5 nm diameter CdSe nanocrystals prepared by the method of distribution focusing.

Peng et al., *Journal of the American Chemical Society* 120:5343, 1998.

Monitoring particle size by optical absorption and emission

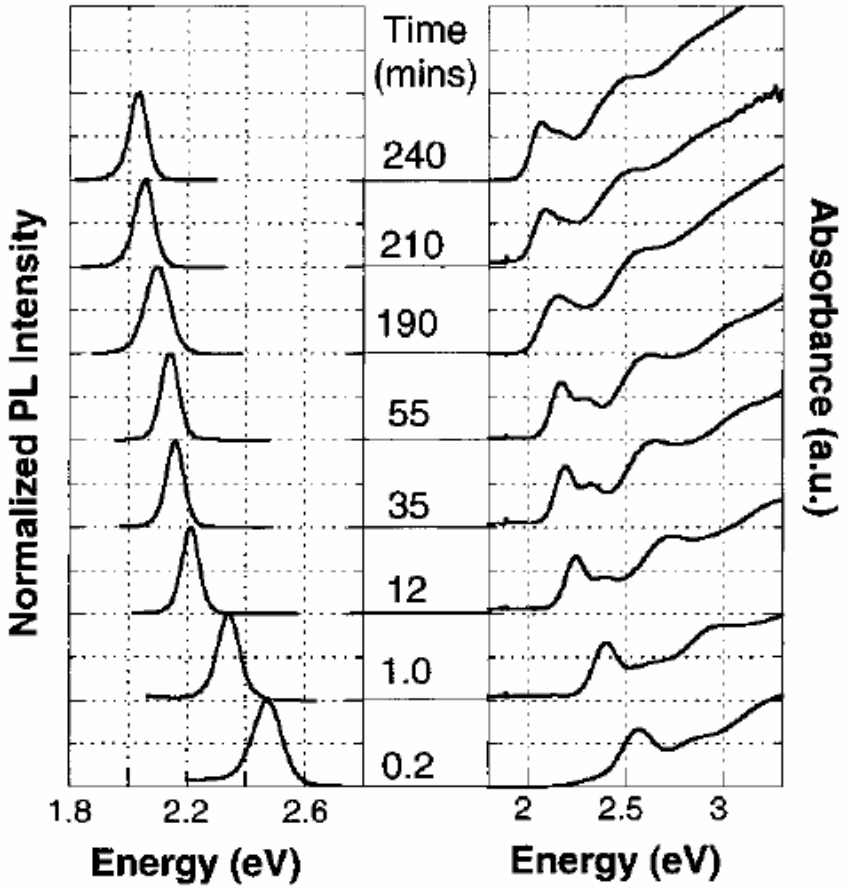


Figure 1. Room-temperature PL and absorption spectra from the sample of CdSe nanocrystals. Note that a secondary injection of monomer occurs at 190 min.

Peng et al., *Journal of the American Chemical Society* 120:5343, 1998.

Results: size broadening and focusing

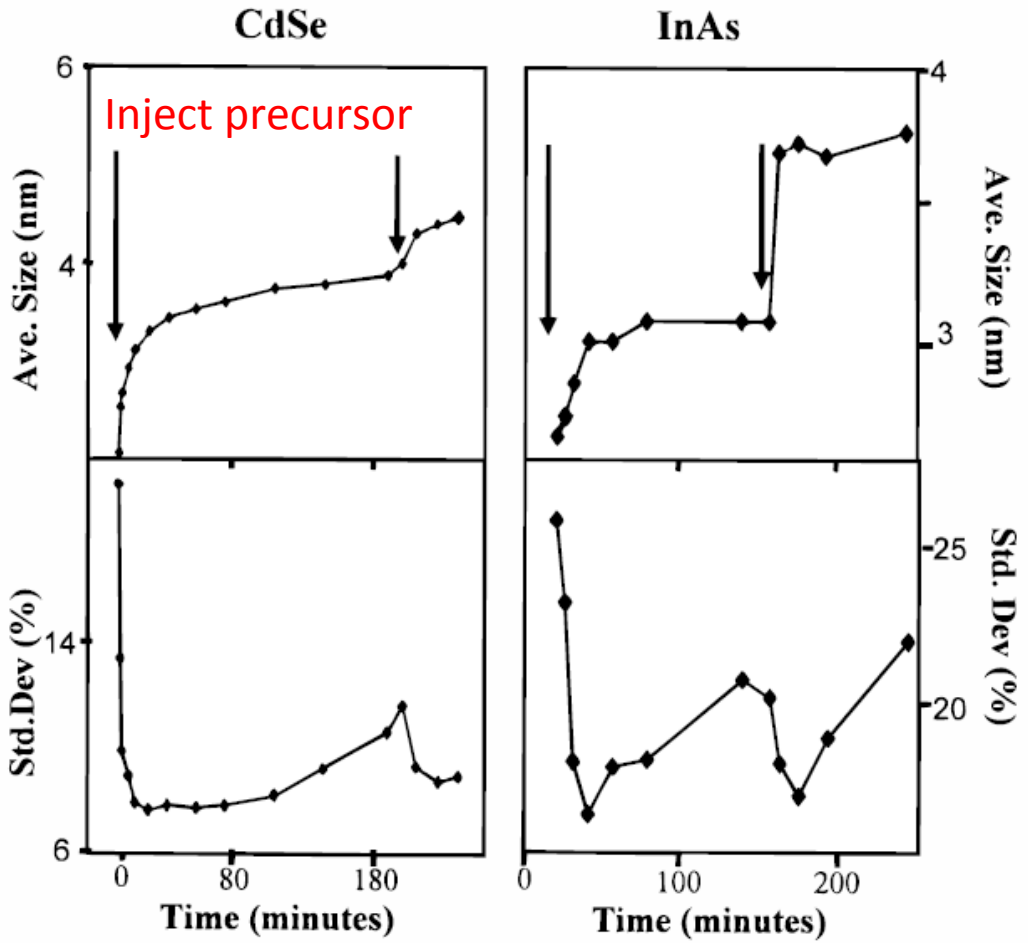
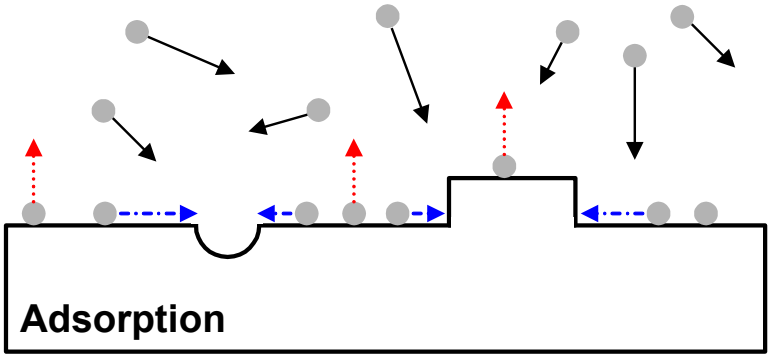
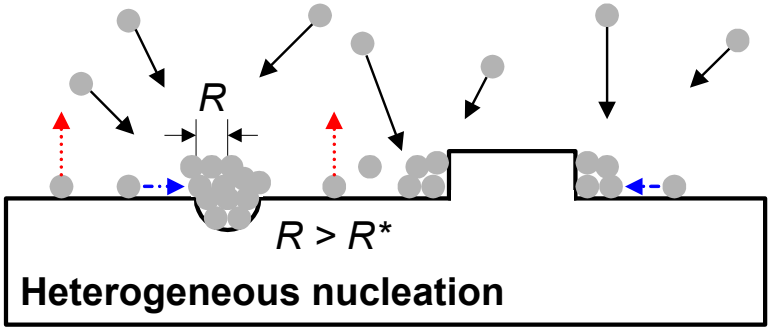


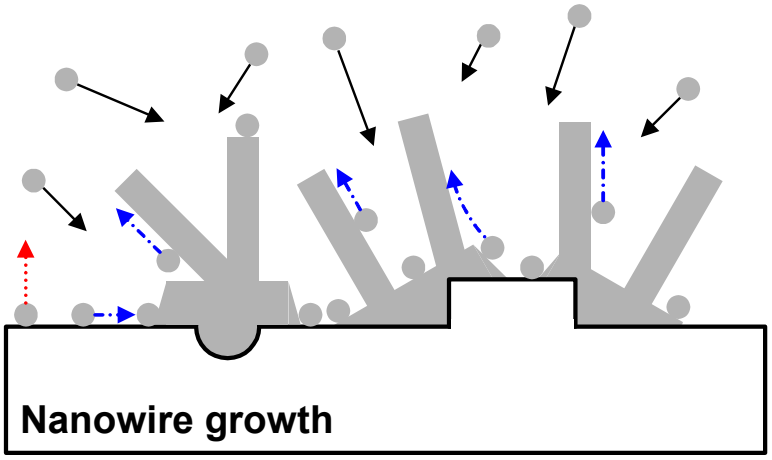
Figure 2. Left: The mean size and the size distribution extracted from the data in Figure 1. Right: The same data extracted from the PL for a synthesis of InAs. Arrows indicate injections.

Peng et al., *Journal of the American Chemical Society* 120:5343, 1998.

Similarities in NW growth

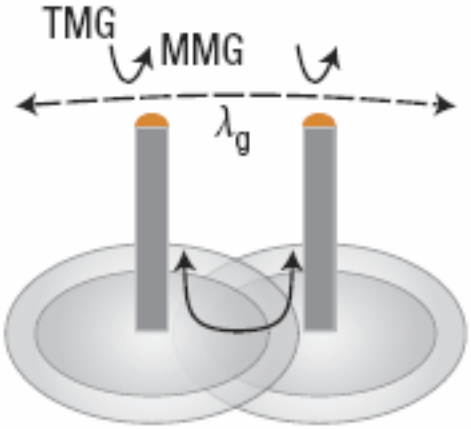




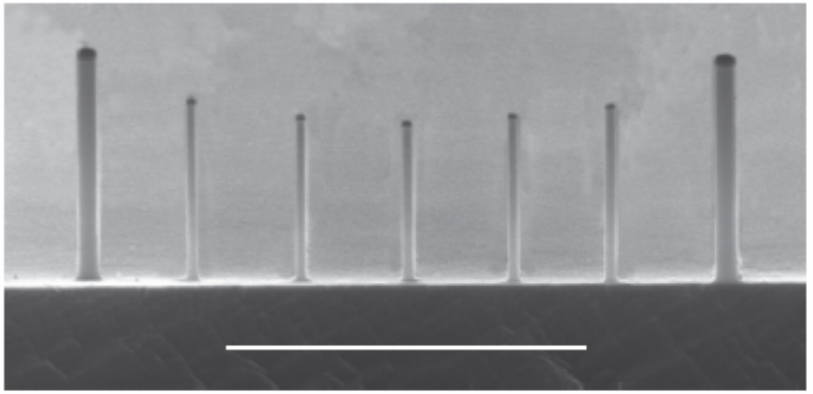


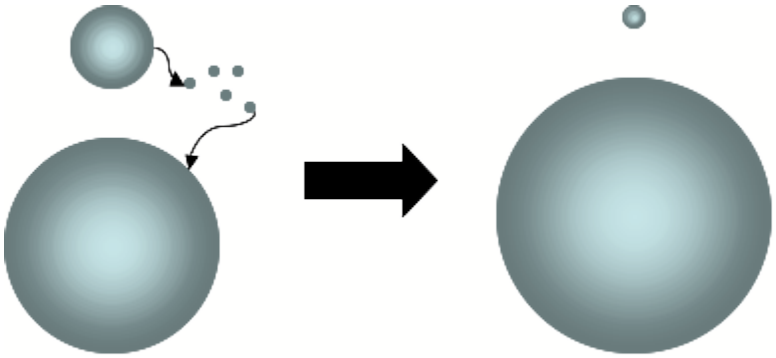
- How does the NW length change with time?
- How does the NW diameter change with time?

Competition and size evolution



Competition for material supply





Ostwald ripening

Borgstrom et al., *Nature Nanotechnology* 2:541, 2007.