Nanoparticle Synthesis

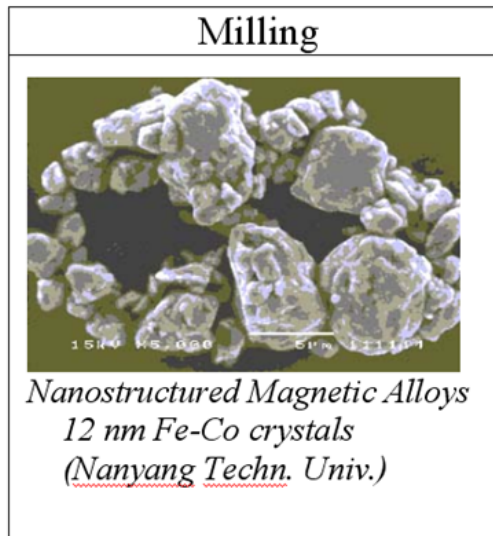## Top-Down

via Attrition / Milling

Involves mechanical thermal cycles
Yields
- broad size distribution
  (10-1000 nm)
- varied particle shape
  or geometry
- impurities
Application:
- Nanocomposites and
- Nano-grained
  bulk materials

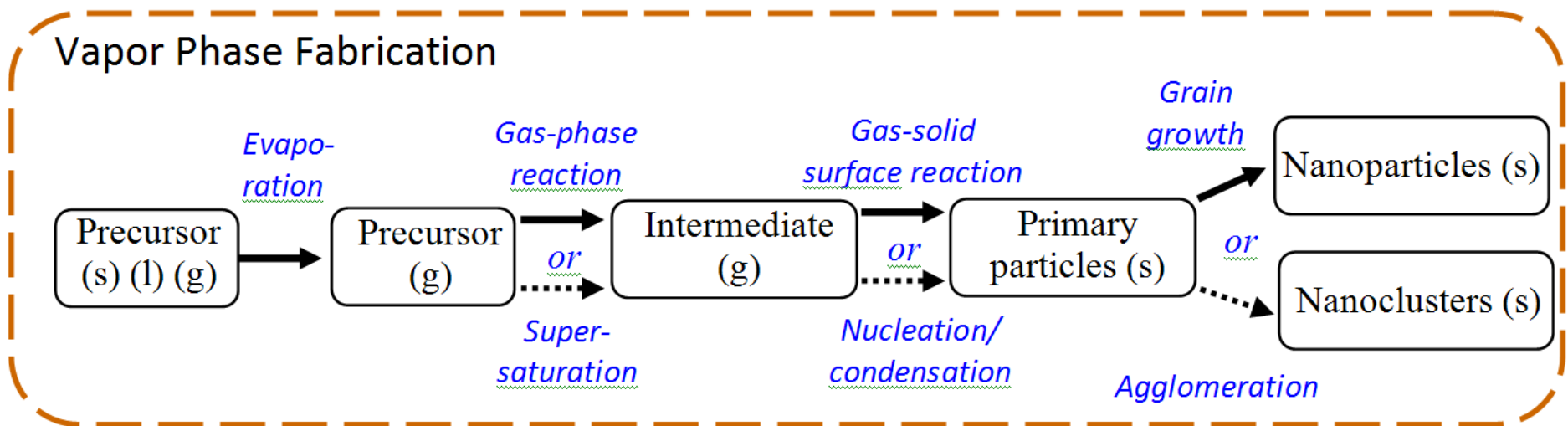Milling

Nanostructured Magnetic Alloys
12 nm Fe-Co crystals
(Nanyang Techn. Univ.)

Bottom-Up

Via
- Pyrolysis
- Inert gas condensation
- Solvothermal Reaction
- Sol-gel Fabrication
- Structured Media
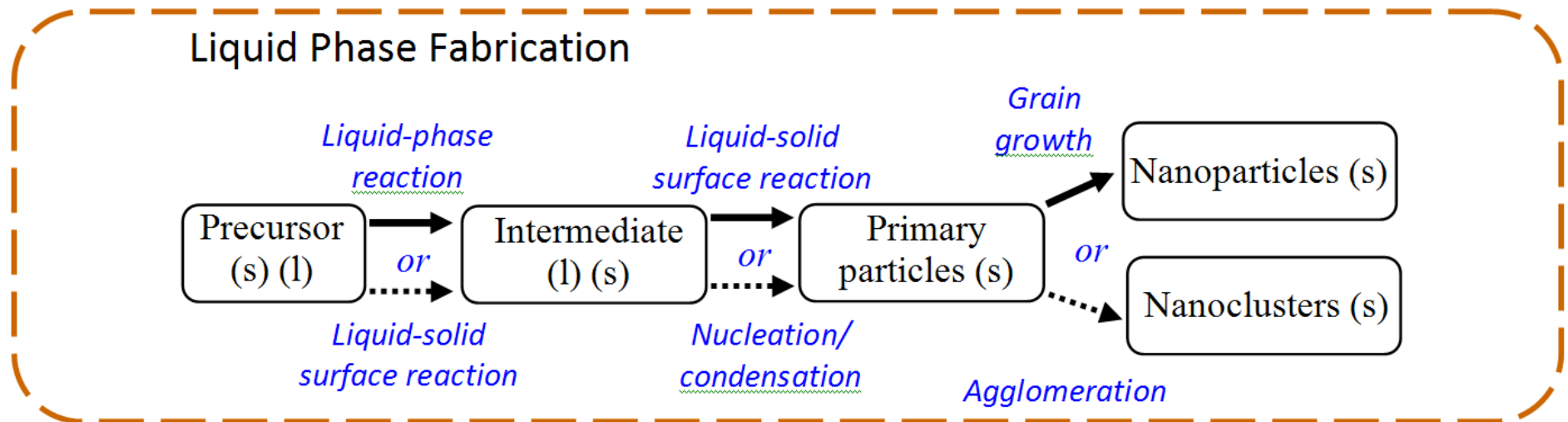
Bottom – Up Synthesis

Phase Classification:

I. Gas (Vapor) Phase Fabrication: Pyrolysis, Inert Gas Condensation, ….

II. Liquid Phase Fabrication: Solvothermal Reaction, Sol-gel, Micellar Structured Media

Vapor Phase Fabrication

| Precursor (s) (l) (g) | Evaporation → | Precursor (g) | Gas-phase reaction → or ⋯→ Super-saturation | Intermediate (g) | Gas-solid surface reaction → or ⋯→ Nucleation/ condensation | Primary particles (s) | Grain growth → Nanoparticles (s) or ⋯→ Nanoclusters (s) Agglomeration |

Bottom – Up Synthesis

Phase Classification:

I. Gas (Vapor) Phase Fabrication: Pyrolysis, Inert Gas Condensation, ….

II. Liquid Phase Fabrication: Solvothermal Reaction, Sol-gel, Micellar Structured Media

Liquid Phase Fabrication

Precursor (s) (l) → *Liquid-phase reaction* / *Liquid-solid surface reaction* (or) → Intermediate (l) (s) → *Liquid-solid surface reaction* / *Nucleation/condensation* (or) → Primary particles (s) → *Grain growth* → Nanoparticles (s) / *Agglomeration* (or) → Nanoclusters (s)
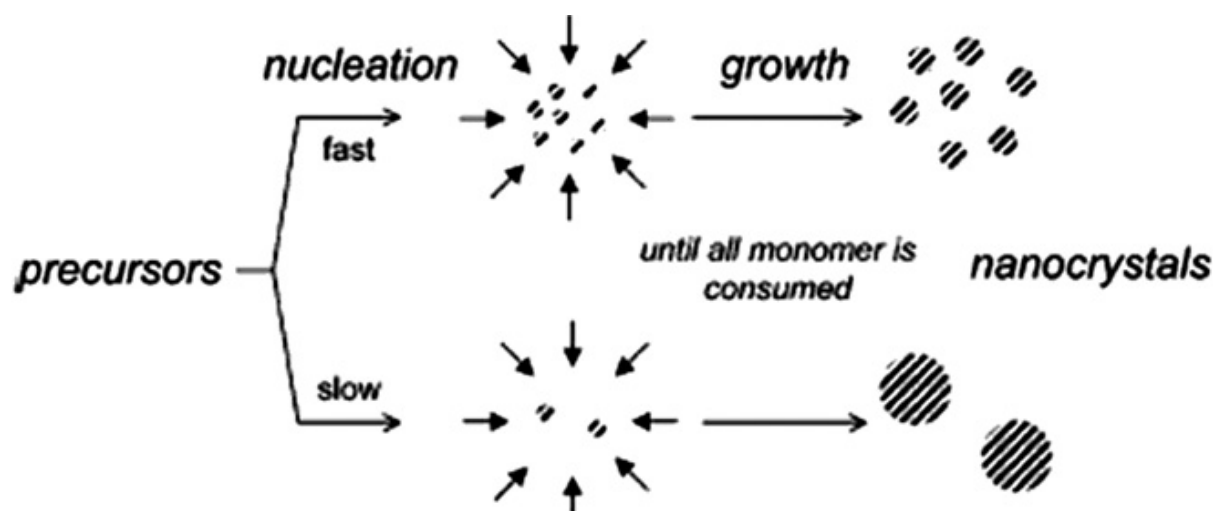
Homogeneous Condensation

Cluster free energy:

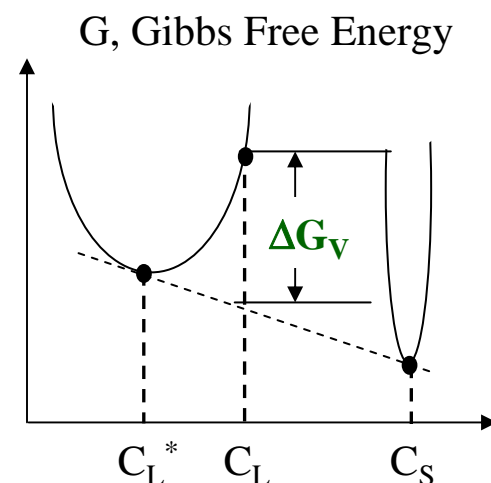*negative volume term*   *positive surface term*

$$\Delta G^* = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Driving Force: ΔG_V

Bulk free energy difference between old and new phase

G, Gibbs Free Energy

nucleation   growth

fast

precursors

until all monomer is consumed   nanocrystals

slow

*E.E. Finney, R.G. Finke / J. Coll. Inter. Sci. **317** (2008) 351–374*

ΔG_V

C_L^* C_L C_S

Concentration:
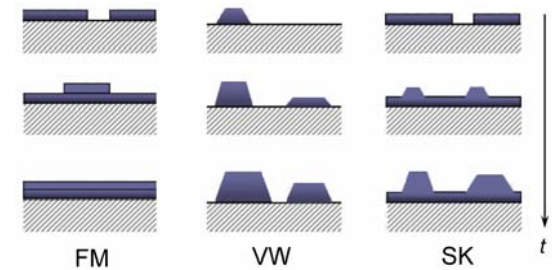C_L^* … Solution in Equilibrium
C_L … Supersaturated Solution
C_S … Solid phase

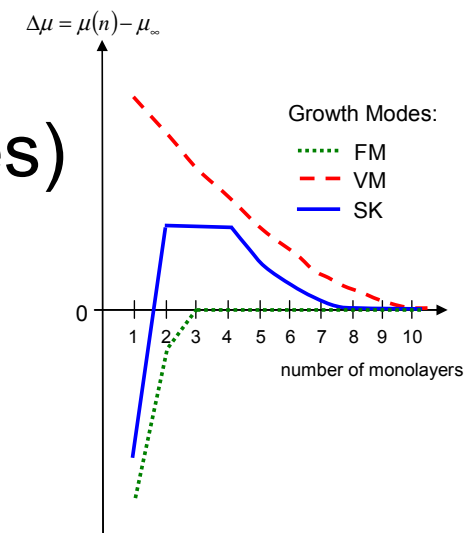# Growth Steps and Limitations

- ## Steps

  - Generation of growth species (e.g., reduction from minerals)

  - Diffusion from bulk to the growth surface

  - Adsorption

  - Surface growth ($\rightarrow$ growth modes)

- ## Limitation

  - Diffusion-limited growth

  - Size-limited (Oswald ripening)

  - Transport-limited growth

FM VW SK t

$\Delta\mu = \mu(n) - \mu_\infty$

Growth Modes:

········ FM

– – – VM

——— SK

0

1 2 3 4 5 6 7 8 9 10

number of monolayers

Vapor Phase Growth

Growth rate of vapor condensation:

Flux from gas kinetic theory

$$R = \xi A_{NP} \frac{\Delta p}{\sqrt{2\pi m k_B T}};$$

$$\Delta p = p_V - p_e$$

Spherical NP: $A_{NP} = 4\pi d_{NP}$

ξ... condensation coefficient (between 0 and 1)

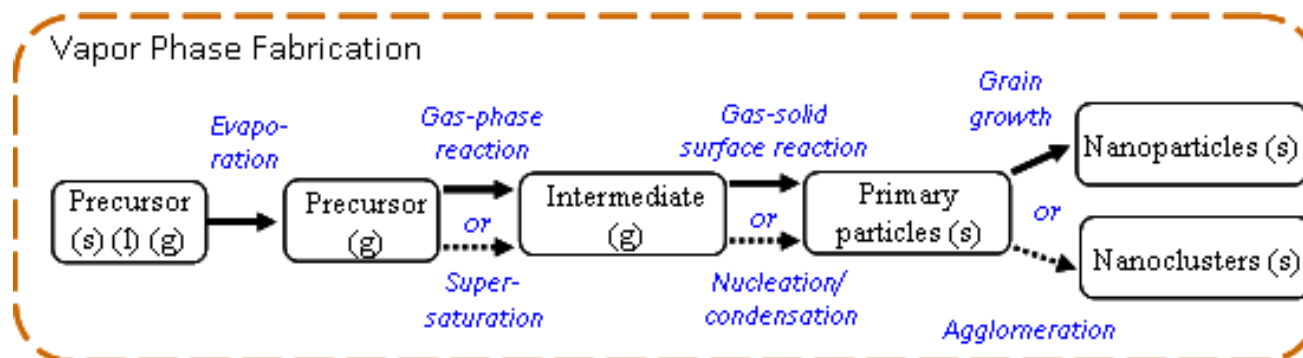A_{NP} ... surface area of condensate (nanoparticle NP)

m .... mass of gas molecule

k_B .... Boltzmann constant, and T … absolute temperature

Driving force: pressure difference Δp

p_V ….instantaneous vapor pressure

P_e …. local equilibrium pressure at the growing cluster

Mechanism and Effectiveness

(i) precursor vaporization (typically involves a catalyst)

(ii) nucleation, and

(iii) growth stage

Effectiveness demands:

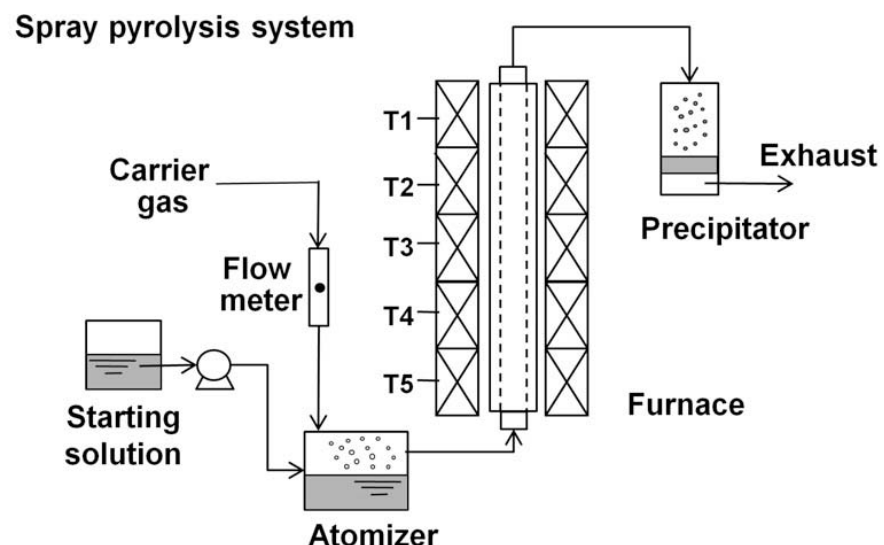- simple process

- low cost

- continuous operation

- high yield

Aerosol Spray Methods
(e.g., Spray Pyrolysis)
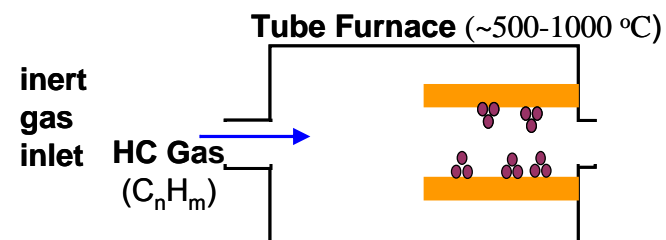
Vapor Phase Synthesis Methods

Discussed are:

- ## Pyrolysis
  ## (Spray Pyrolysis)

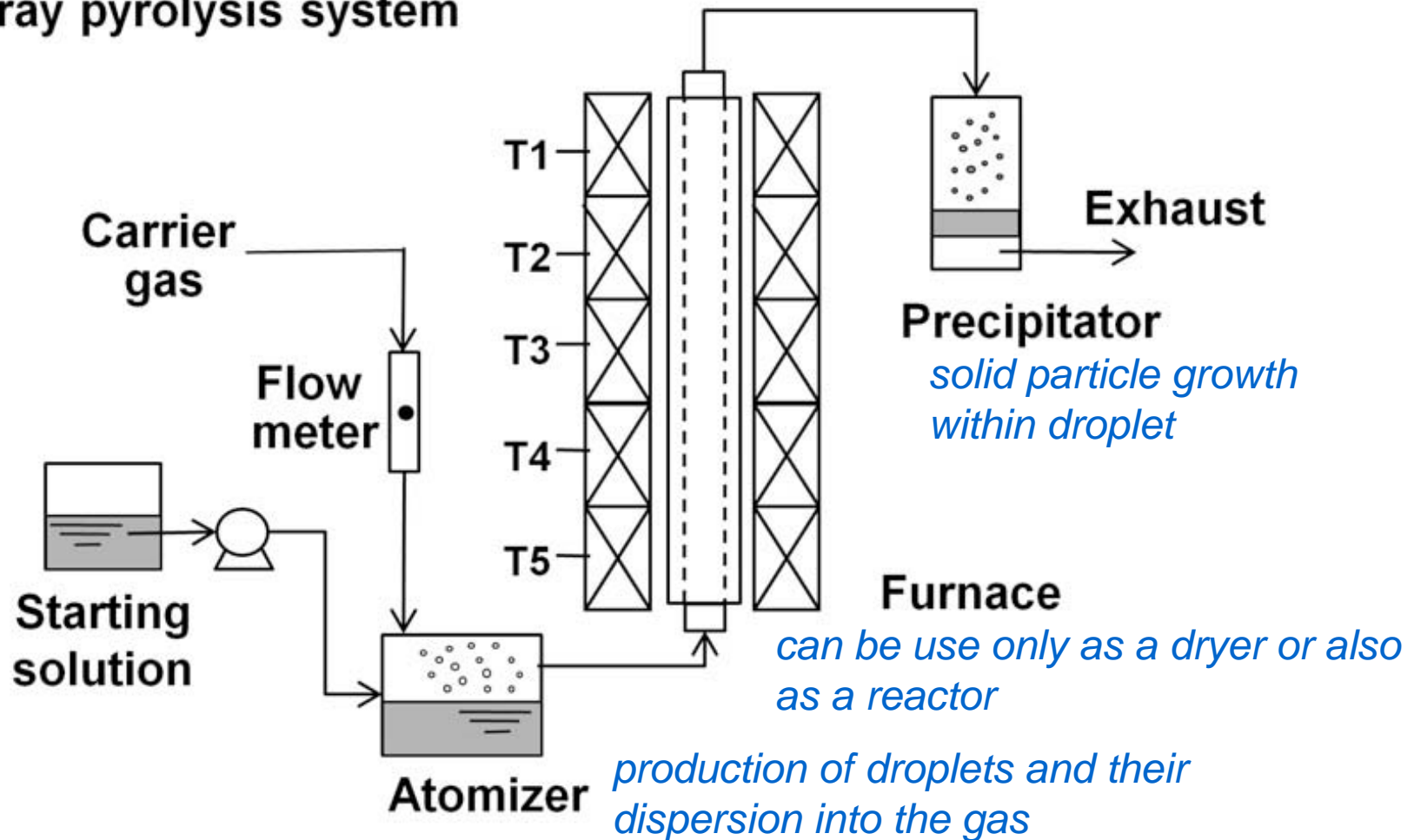 *Spray pyrolysis is the aerosol process that atomizes a solution and heats the droplets to produce solid particles*

Spray pyrolysis system

- ## Inert Gas Condensation
  ## (Chemical Vapor Deposition)

Tube Furnace (~500-1000 °C)

inert gas inlet   HC Gas (C_nH_m)

Spray Pyrolysis

Spray pyrolysis system

solid particle growth within droplet

can be use only as a dryer or also as a reactor

production of droplets and their dispersion into the gas

F. Iskandar, Adv. Powder Techn. **20** (2009) 283

Spray Pyrolysis

Atomizer Type	Furnace Type	Precipitator Type

Two fluid nozzle

Ultrasonic nebulizer

Flame

Electrical furnace

Electrical precipitator

Bag filter
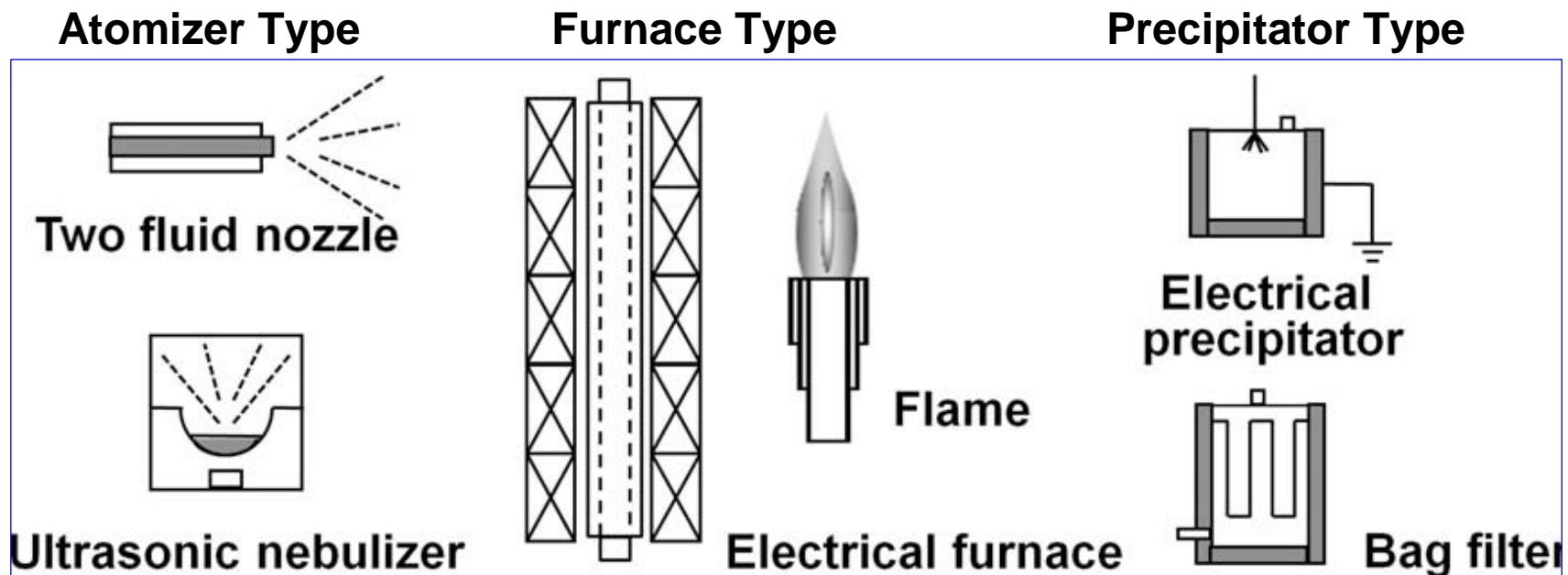
F. Iskandar, Adv. Powder Techn. **20** (2009) 283

Spray Pyrolysis

Droplet Evolution

Evaporation	Precipitation	Drying	Decomposition	Sintering

Solvent Vapor
Diffusion

D_v

D_s

R α_l

Precipitate   Solution

Solvent
Vapor α_g

Heat transfer
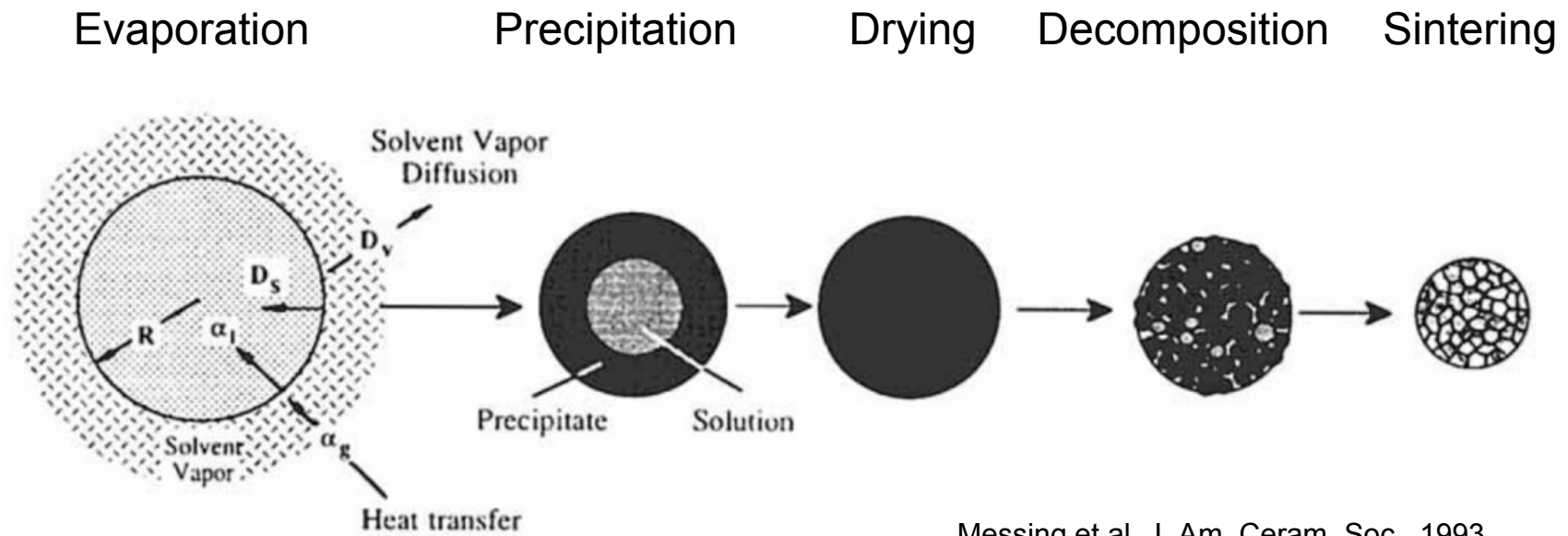
Messing et al, J. Am. Ceram. Soc., 1993

If the solute concentration at the center of the drop is less than the equilibrium saturation of the solute at the droplet temperature, then precipitation occurs only in that part of the drop where the concentration is higher than the equilibrium saturation, i.e., surface precipitation.

Spray Pyrolysis

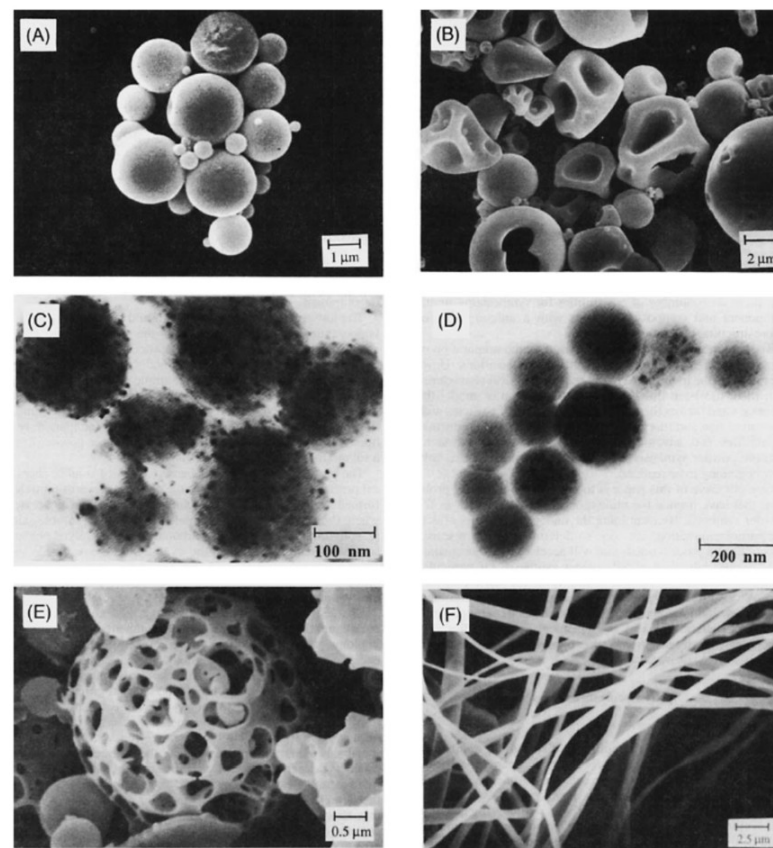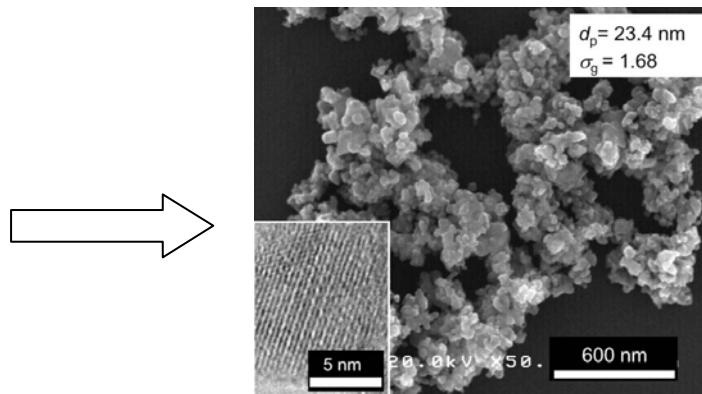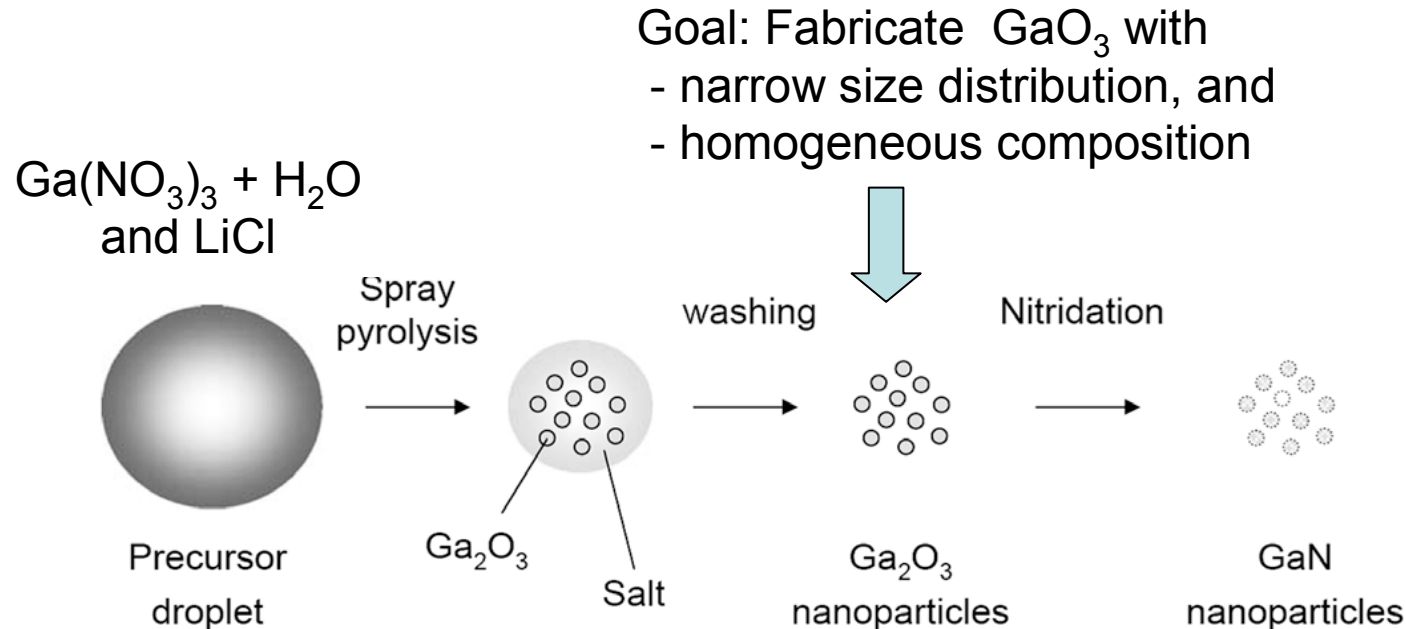## Precipitation Control
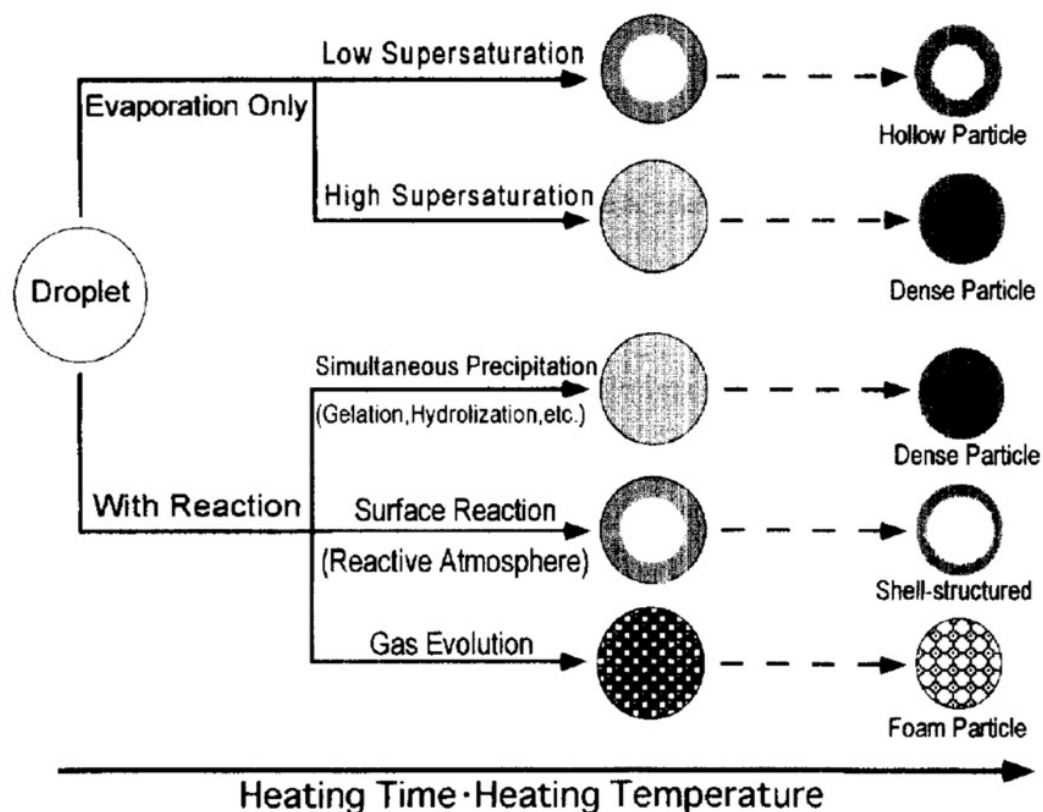
Messing et al, J. Am. Ceram. Soc., 1993

Fig. 3. Various morphologies of particles produced by SP processes: (A) solid ZrO₂ particles derived from 0.1M ZHC solution, (B) irregular ZrO₂ particles derived from 1M ZAC solution, (C) Al₂O₃/platinum nanocomposite particles derived from 0.5M Al₂(SO₄)₃–H₂PtCl₆ solution, (D) Al₂O₃/platinum nanocomposite particles derived from 0.5M Al(OBuⁱ)₃–H₂PtCl₆ solution, (E) catalyst particles derived from 0.1M NH₄VO₃–H₃PO₄–citric acid solution, and (F) Y₂O₃-stabilized ZrO₂ discontinuous fiber derived from ZAC–6 wt%–PVOH–surfactant solution.

Che et al, J. Aer. Sci., 1998

Spray Pyrolysis: $Ga(NO_3)_3$ and GaN

Goal: Fabricate GaO_3 with
- narrow size distribution, and
- homogeneous composition

$Ga(NO_3)_3 + H_2O$
and LiCl

Spray pyrolysis

washing

Nitridation

Precursor droplet

Ga_2O_3

Salt

Ga_2O_3 nanoparticles

GaN nanoparticles

d_p= 23.4 nm
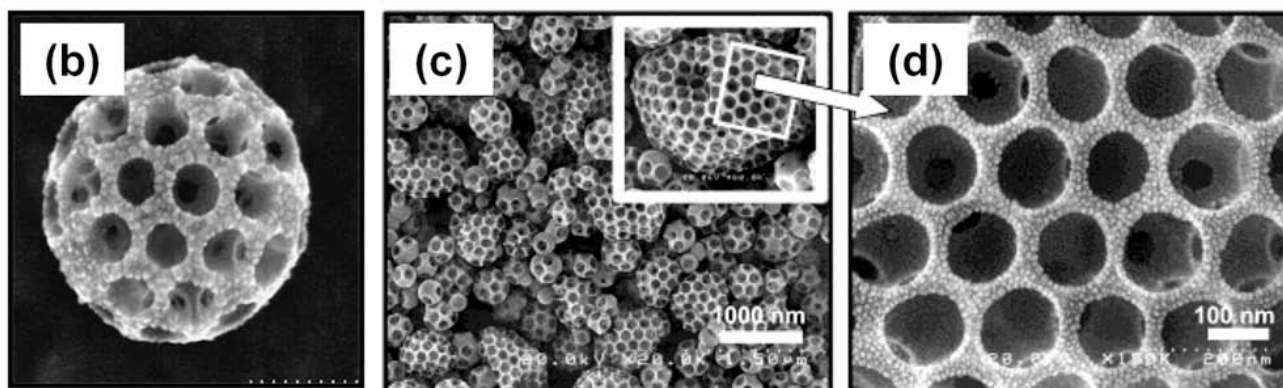σ_g = 1.68

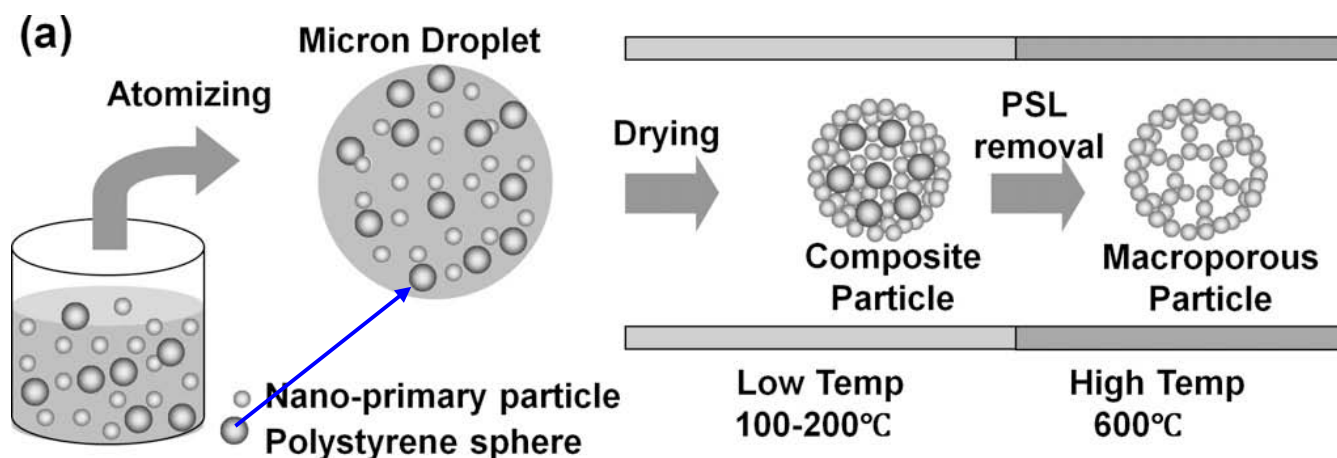5 nm   20.0kV X50.   600 nm

GaN nanoparticles of
23.4 ± 1.7 nm diameter

T. Ogi et al., Adv. Powder Technology 20 (2009) 29
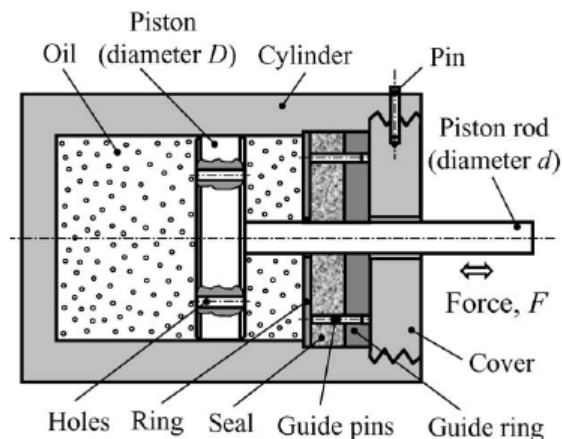
Spray Pyrolysis: Porous Silica NP

Pyrolysis: Generate droplet mixtures of "Primary Particles" with Polymer Particles

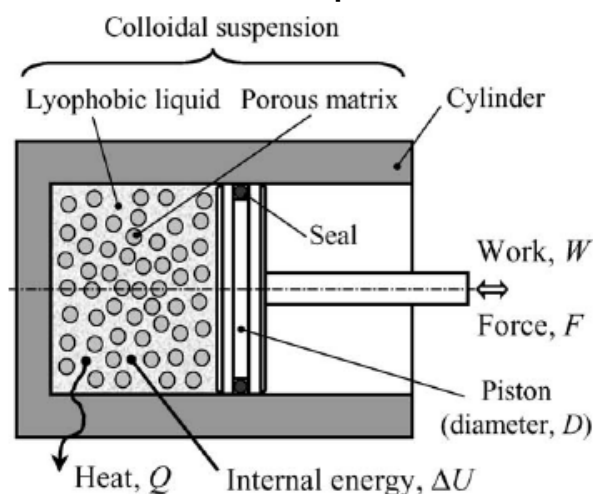F. Iskandar / Advanced Powder Technology 20 (2009) 283

Porous Silica NP Application: Colloidal Damper
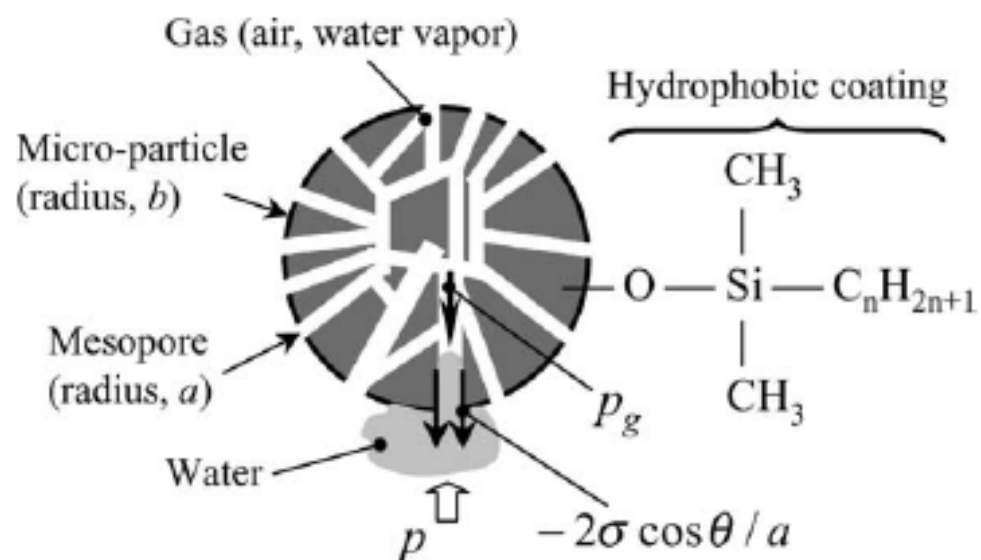
Hydraulic Damper (oil is working fluid, energy is dissipated via orifice flow)

Hydrophobized porous silica particle (outside and inside) suspended in water as the working fluid

Colloidal Damper

Advantage: Little heat generation in colloidal damper.

C.V. Suciu et al., J. Coll. Interf. Sci., 259 (2003) 62.

Inert Gas Condensation (IGC)

Entails the evaporation of a course substance in an inert gas atmosphere.

Methods:

Cold Finger

- Physical Vapor Deposition (PVD)
  (no catalytic interaction)

- Chemical Vapor Deposition (CVD)
  (with catalytic interaction)

Evaporation Sources

inert gas inlet

Tube Furnace (~500-1000 ^{o}C)

HC Gas (C_nH_m)
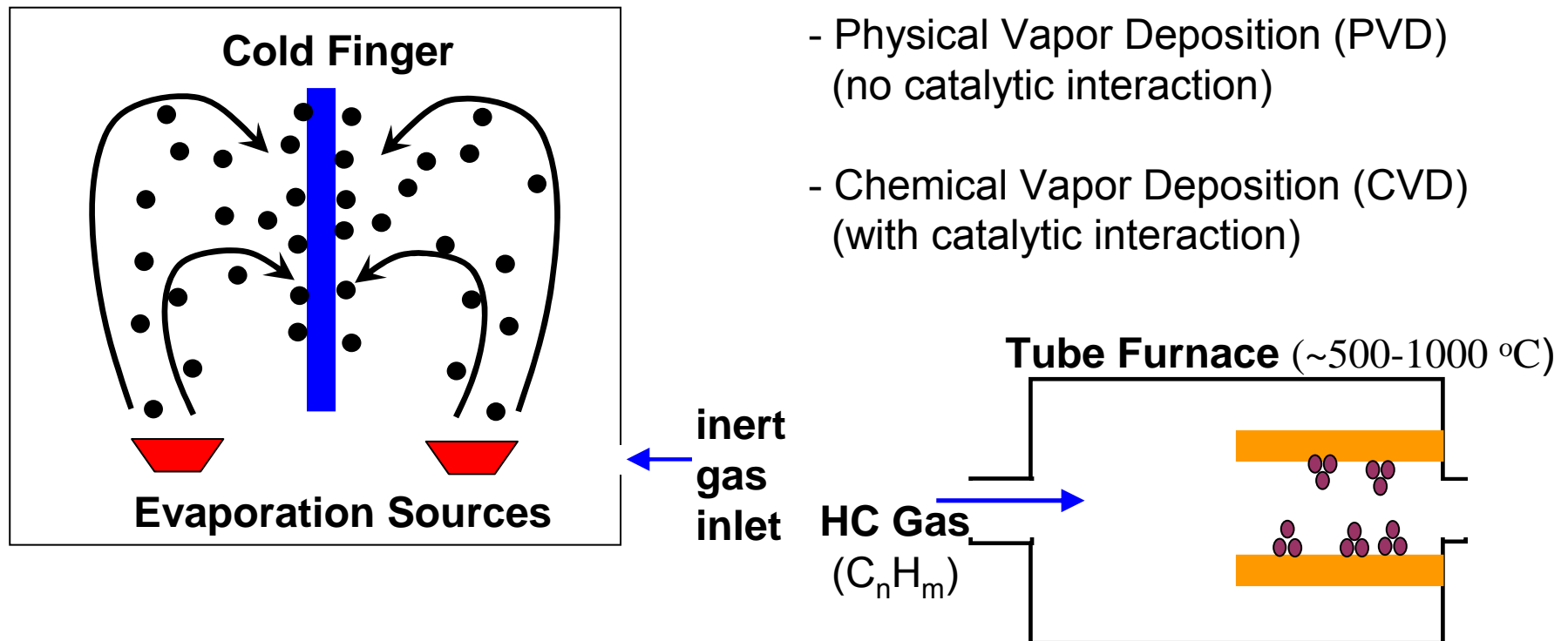
F. Iskandar, Adv. Powder Techn. **20** (2009) 283

Coalescence and Agglomeration

One of the big challenges in condensation growth is that the particles coalesce and agglomerate.

A solution proposed: **Use of a gas jet stream.** A jet stream of carrier gas positioned above the evaporation sites is used to carry away the metal vapor.
Utilize that carrier gas vapor mixture cools downstream

→**Continuous Particle growth**
   (nucleation, condensation and coagulation)

Carrier Gas Jet Stream

Continuous Particle Growth: Nucleation, Condensation and Coagulation

Evaporation Source
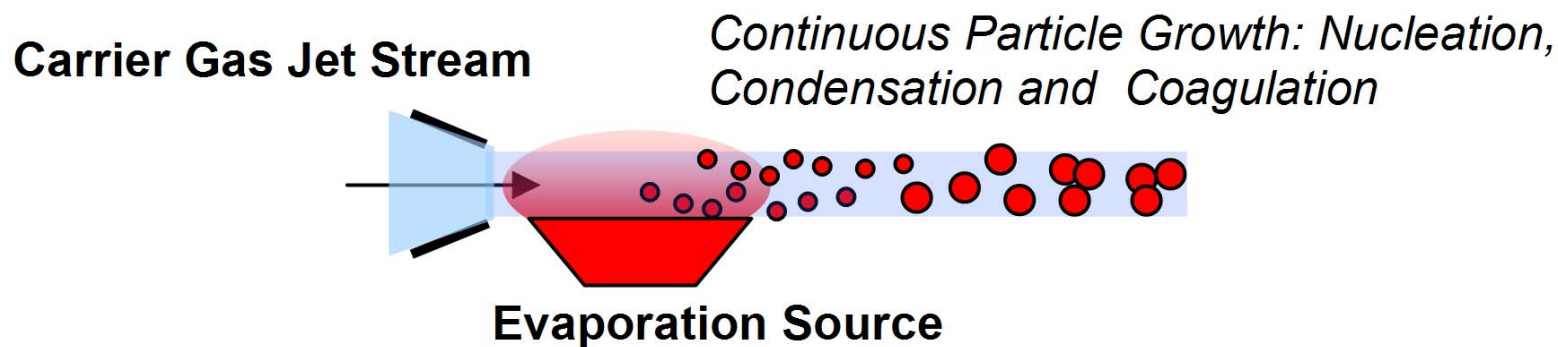
Liquid Phase Synthesis Methods

The liquid phase fabrication entails a wet chemistry route.
Methods:

- Solvothermal Methods
  (e.g. hydrothermal)

- Sol-Gel Methods

- Synthesis in Structure Media
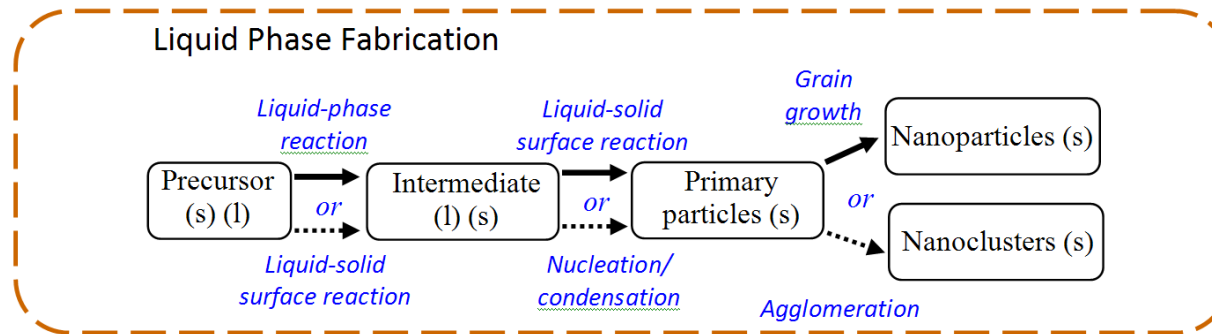 (e.g., microemulsion)

Mechanism and Effectiveness

Liquid Phase Fabrication

Precursor (s) (l) → *Liquid-phase reaction* → Intermediate (l) (s) → *Liquid-solid surface reaction* → Primary particles (s) → *Grain growth* → Nanoparticles (s)

or — *Liquid-solid surface reaction* — *or* — *Nucleation/ condensation* — *or* — *Agglomeration* → Nanoclusters (s)

(i) precursor solution (typically involves a catalyst)

(ii) nucleation, and

(iii) growth stage
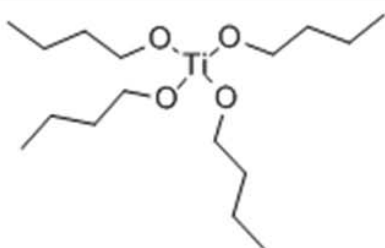
Effectiveness demands:

- simple process

- low cost

- continuous operation

- high yield

Sol-Gel and Solvothermal Synthsis

Solvothermal Synthesis

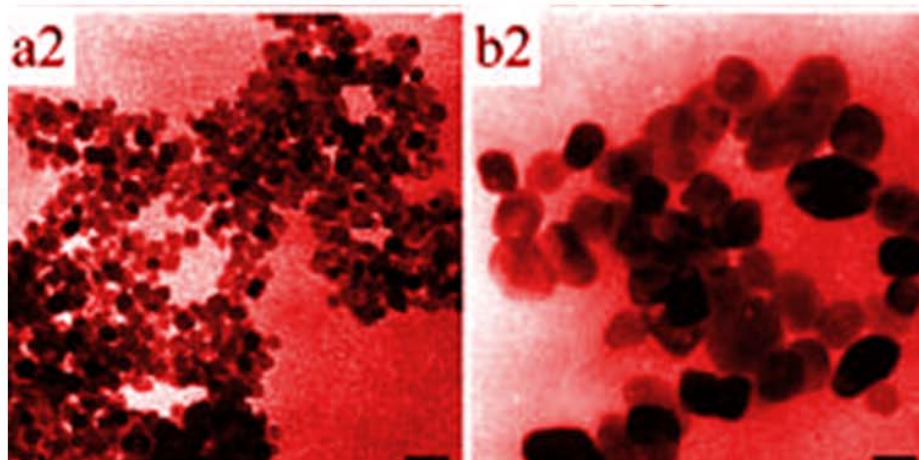- ## Precursors are dissolved in hot solvents (e.g., n-butyl alcohol)
  - Solvent other than water can provide milder and friendlier reaction conditions If the solvent is water then the process is referred to as hydrothermal method.
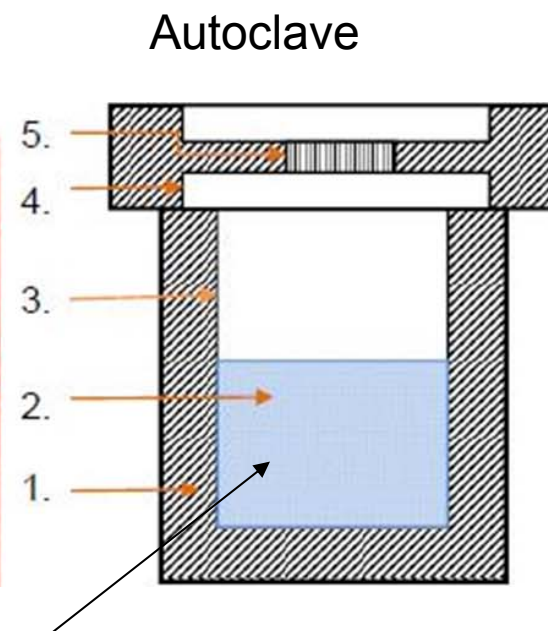
Autoclave

Example: TiO$_2$ Nanocrystallites

Precursor:
Titanium
n-butoxide

X.F. Yang et al., Euro. J. Inorganic Chem., 2229 (2006).

Precursor solution with butyl alcohol

Sol-Gel Processing

- Creation of Sol (solid particles in solution)
- Followed by the following two generic sol-gel processes (assuming as a precursor a metal alkoxide MOR):

hydrolysis: $-MOR + H2O \rightarrow -MOH + ROH$

Ex.: $Si(OR)_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ R\text{-}OH$

condensation: $-MOH + ROM- \rightarrow -MOM- + ROH$

$(OR)_3\text{–}Si\text{-}OH + HO\text{–}Si\text{-}(OR)_3 \rightarrow [(OR)_3Si\text{–}O\text{–}Si(OR)_3] + H\text{-}O\text{-}H$

or $-MOH + HOM- \rightarrow -MOM- + H2O$

$(OR)3\text{–}Si\text{-}OR + HO\text{–}Si\text{-}(OR)3 \rightarrow [(OR)3Si\text{–}O\text{–}Si(OR)3] + R\text{-}OH$

Condensation towards network of siloxanes
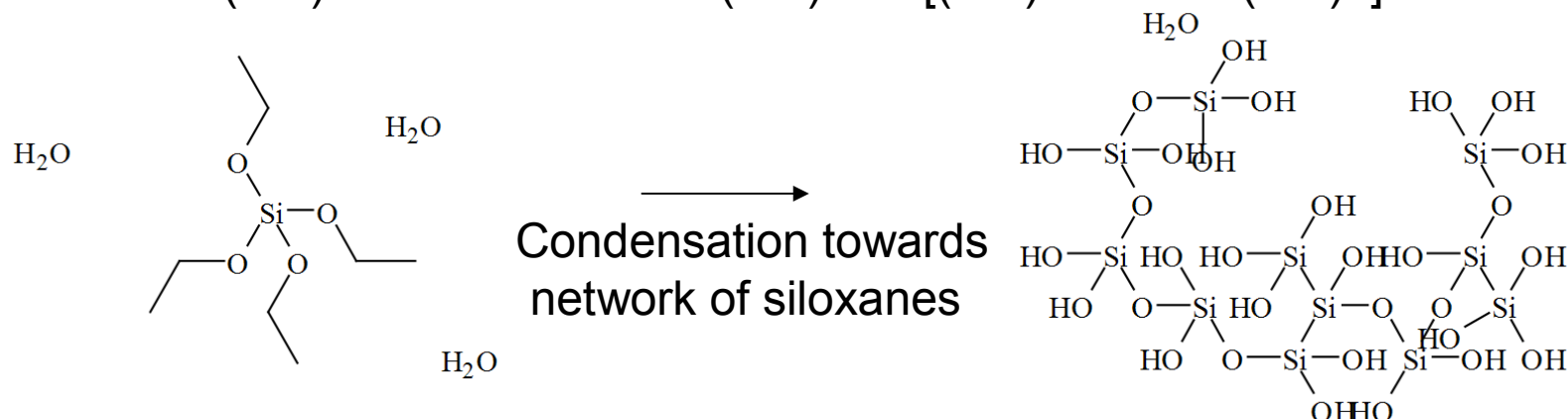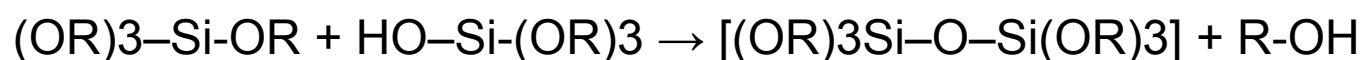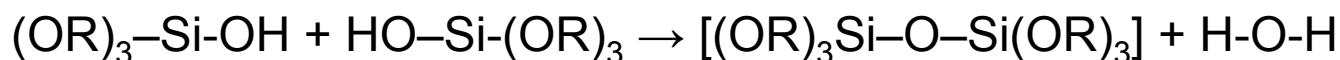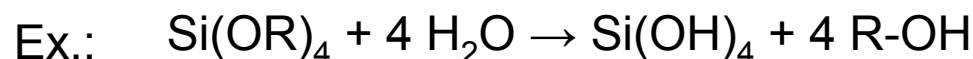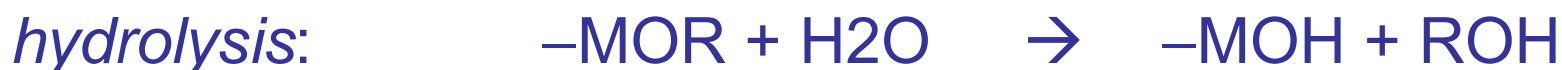
Sol-Gel Steps:

- Formation of stable sol solution
- Gelation via a polycondensation or polyesterification reaction
- Gel aging into a solid mass. → causes contraction of the gel network, also
  (i) phase transformations and
  (ii) Ostwald ripening.
- Drying of the gel to remove liquid phases. Can lead to fundamental changes in the structure of the gel.
- Dehydration at temperatures as high as 8000 °C, used to remove M-OH groups for stabilizing the gel, i.e., to protect it from rehydration.
- Densification and decomposition of the gels at high temperatures (T > 8000 oC), i.e., to collapse the pores in the gel network and to drive out remaining organic contaminants
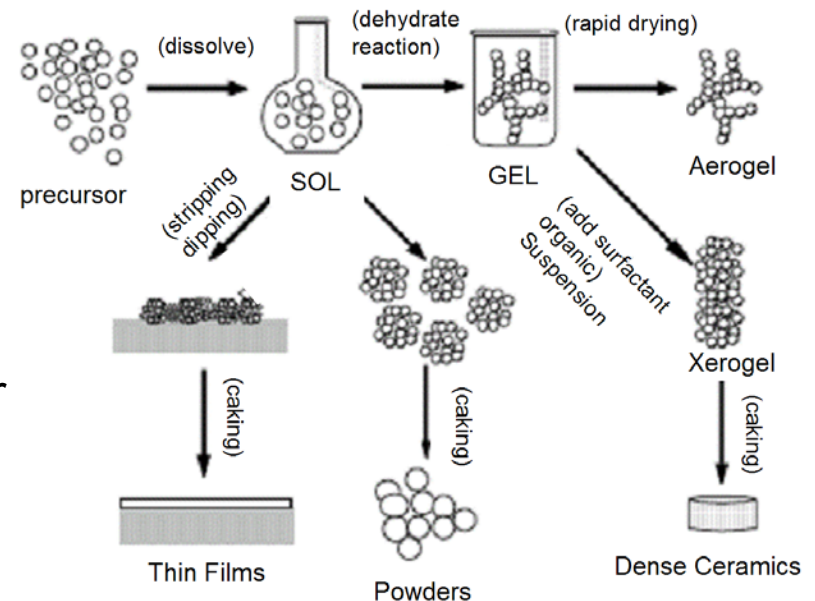
Synthesis in Structured Medium

Influence Growth Kinetics by Imposing Constraints
in Form of Matrices:

• Zeolites

• Layered Solids

• Molecular Sieves

• Micelles/Microemulsions

• Gels

• Polymers

• Glasses

Ex.: Mixing of two Microemulsion
carrying metal salt and reducing agent

→Intermicellar interchange process via coalescence (rate limiting)
    (much slower than diffusion: 10 μs and 1 ms

Microemulsion I   Microemulsion II

Aqueous Phase
Metal Salt
($FeCl_3$, $FeCl_2$,
$CuCl_2$, etc.)

Aqueous Phase
Reducing Agent
(NH_4OH, N_2H_4,
$NaBH_4$, etc.)

Oil Phase   Mix Microemulsions I and II   Oil Phase

Collision and
Coalescence of
Droplets   Percolation

Chemical Reaction Occurs   Precipitate
(Metal or Metal Oxide)

I. Capek, Adv. Coll. Interf. Sci. 110 (2004) 49

NP Systems: Unique Properties

Optics: High- or low refractive index

Electronics: Unique density of state

Catalysis: High reactivity

Drug Delivery: Controlled delivery

Sensors: High sensitivity

Coatings: Increased material strength
                     Ultralow and high adhesion
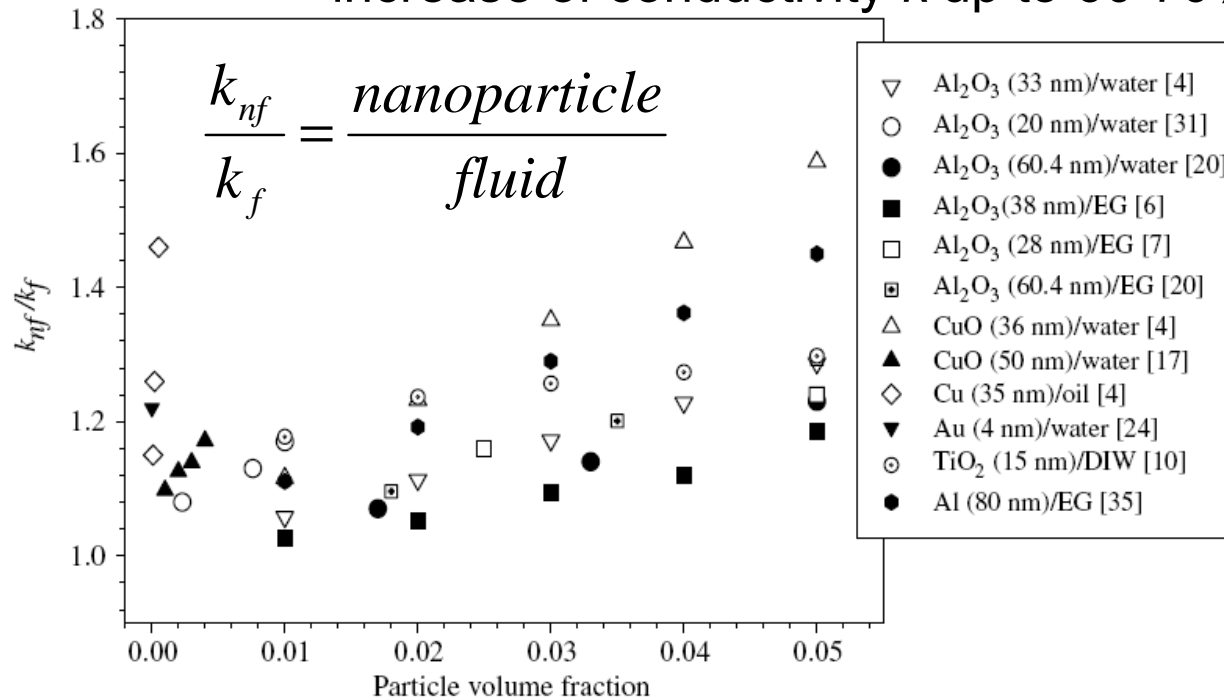
High impact on composite and fluidic systems.

Nanofluids: High Thermal Conductivity

Nanofluids: Nanoparticle suspension
increase of conductivity k up to 60-70%

$$\frac{k_{nf}}{k_f} = \frac{nanoparticle}{fluid}$$

▽	Al$_2$O$_3$ (33 nm)/water [4]
○	Al$_2$O$_3$ (20 nm)/water [31]
●	Al$_2$O$_3$ (60.4 nm)/water [20]
■	Al$_2$O$_3$(38 nm)/EG [6]
□	Al$_2$O$_3$ (28 nm)/EG [7]
⊡	Al$_2$O$_3$ (60.4 nm)/EG [20]
△	CuO (36 nm)/water [4]
▲	CuO (50 nm)/water [17]
◇	Cu (35 nm)/oil [4]
▼	Au (4 nm)/water [24]
⊙	TiO$_2$ (15 nm)/DIW [10]
⬢	Al (80 nm)/EG [35]

(y-axis: k_{nf}/k_f; x-axis: Particle volume fraction)

Maxwell Model : $k_{nf} = k_f \left(\dfrac{k_p + 2k_f + 2\phi\left(k_p - k_f\right)}{k_p + 2k_f - \phi\left(k_p - k_f\right)} \right)$

k_p , k_p ….particle and fluid
   thermal conductivity,
ϕ ….particle free volume
   fraction

Such classical models cannot account for increased conductivity in nanofluids.
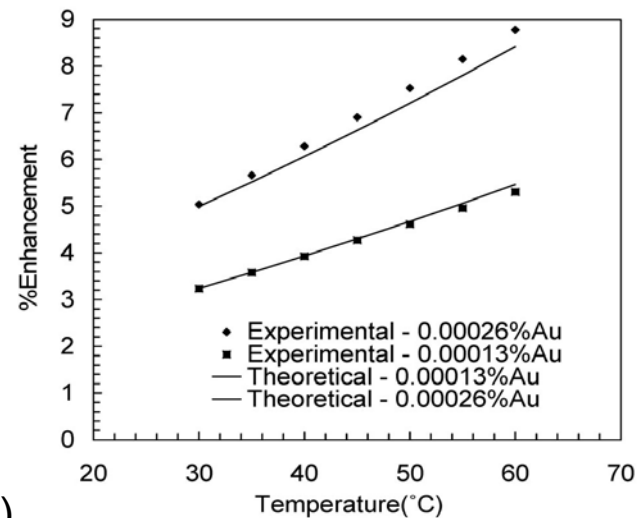
Nanofluids: High Thermal Conductivity

Classical models cannot account for increased conductivity in nanofluids as they lack information about:

- Particle size and surface energy
- Particle dispersion and clustering
- Brownian motion of the particles
- Liquid layering (entropy reduction)
- ….

Dynamic Model (based on kinetic theory and Fourier's Law) considers Brownian motion and particle size:

$$k_{nf} = k_f \left(1 + c \frac{2k_B T}{\pi \eta d_p^2} \frac{\phi r_f}{(1-\phi) r_p} \right)$$

D.H. Kumar et al., Phys. Rev. Lett. **93** (2004) 4301)

%Enhancement vs Temperature(°C)

- Experimental - 0.00026%Au
- Experimental - 0.00013%Au
- Theoretical - 0.00013%Au
- Theoretical - 0.00026%Au

Nanofluids: Conduction Models

Murshed argues:

- Most of the recently developed models only include one or two postulated mechanisms of nanofluids heat transfer.
- Moreover, these models were not validated with a wide range of experimental data.
- There is, therefore a need to develop more comprehensive models, which are based on the first principle, and can explicitly explain the enhanced thermal conductivity of nanofluids.
- Particles size, particle dispersions and clustering should be taken into account in the model development for nanofluids.

| Researchers	Models/Expressions for nanofluids
Wang et al. [17]	$\frac{k_{eff}}{k_f} = \frac{(1-\phi)+3\phi \int_0^\infty \frac{k_{cl}(r)n(r)}{k_{cl}(r)+2k_f}dr}{(1-\phi)+3\phi \int_0^\infty \frac{k_f n(r)}{k_{cl}(r)+2k_f}dr}$
Xue [60]	$9\left(1-\frac{v}{\lambda}\right)\frac{k_{eff}-k_f}{2k_{eff}+k_f} + \frac{v}{\lambda}\left[\frac{k_{eff}-k_{c,x}}{k_{eff}+B_{2,x}(k_{c,x}-k_{eff})} + 4\frac{k_{eff}-k_{c,y}}{2k_{eff}+(1-B_{2,x})(k_{c,y}-k_{eff})}\right] = 0$
Yu and Choi [38,61]	(1) $k_{eff}/k_f = \frac{k_{pe}+2k_f+2\phi(k_{pe}-k_f)(1+\beta)^3}{k_{pe}+2k_f-\phi(k_p-k_f)(1+\beta)^3}$
	(2) $k_{eff}/k_f = 1 + \frac{n\phi_{eff}A}{1-\phi_{eff}A}$, where $A = \frac{1}{3}\sum_{j=a,b,c}\frac{k_{pj}-k_f}{k_{pj}+(n-1)k_f}$
Xuan et al. [62]	$k_{eff}/k_f = \frac{k_p+2k_f-2\phi(k_f-k_p)}{k_p+2k_f+\phi(k_f-k_p)} + \frac{\phi\rho_p c_p}{2k_f}\sqrt{\frac{K_B T}{3\pi r_c \eta}}$
Kumar et al. [24]	$k_{eff}/k_f = 1 + c\frac{2K_B T}{\pi\eta d_p^2}\frac{\phi r_f}{k_f(1-\phi)r_p}$
Jang and Choi [40]	$k_{eff}/k_f = 1 + c\frac{d_f}{d_p}k_f\phi Re_{d_p}^2 Pr$
Prasher et al. [63]	$k_{eff}/k_f = (1 + A\phi Re^m Pr^{0.333})\frac{(1+2\alpha)+2\phi(1-\alpha)}{(1+2\alpha)-\phi(1-\alpha)}$ where $\alpha_f = 2R_b k_f/d_p$
Koo and Kleinstreuer [64]	$k_{eff}/k_f = \frac{k_{MG}}{k_f} + \frac{1}{k_f}5\times10^4\beta\phi\rho_p c_p\sqrt{\frac{K_B T}{\rho_p D}}f(T,\phi)$
Xie et al. [65]	$k_{eff}/k_f = 1 + 3\Theta\phi + \frac{2\Theta^2\phi^2}{1-\Theta\phi}$
Gao and Zhou [66]	$1 - \phi = \left(\frac{k_f}{k_{eff}}\right)^{3A}\left(\frac{k_f+B_1}{k_{df}+B_1}\right)^{3C_1}\left(\frac{k_f+B_2}{k_{eff}+B_2}\right)^{3C_2}$
Leong et al. [67]	$k_{eff} = \frac{(k_p-k_{lr})\phi_p k_{lr}[2\gamma_1^3-\gamma^3+1]+(k_p+2k_{lr})\gamma_1^3[\phi_p\gamma^3(k_{lr}-k_f)+k_f]}{\gamma_1^3(k_p+2k_{lr})-(k_p-k_{lr})\phi_p[\gamma_1^3+\gamma^3-1]}$
Murshed et al. [29]	$k_{eff} = \frac{k_f\left[1+0.27\phi_p^{4/3}\left(\frac{k_p}{k_f}-1\right)\right]\left[1+\frac{0.52\phi_p}{1-\phi_p^{1/3}}\left(\frac{k_p}{k_f}-1\right)\right]}{1+\phi_p^{4/3}\left(\frac{k_p}{k_f}-1\right)\left(\frac{0.52}{1-\phi_p^{1/3}}+0.27\phi_p^{1/3}+0.27\right)}$
Murshed et al. [35]	$k_{eff} = \frac{(k_p-k_{lr})\phi_p k_{lr}[\gamma_1^2-\gamma^2+1]+(k_p+k_{lr})\gamma_1^2[\phi_p\gamma^2(k_{lr}-k_f)+k_f]}{\gamma_1^2(k_p+k_{lr})-(k_p-k_{lr})\phi_p[\gamma_1^2+\gamma^2-1]}$

S.M.S. Murshed et al. / Applied Thermal Engineering 28 (2008) 2109–2125

Strain in Nanoparticles

High surface energy (tension) causes strain in the material
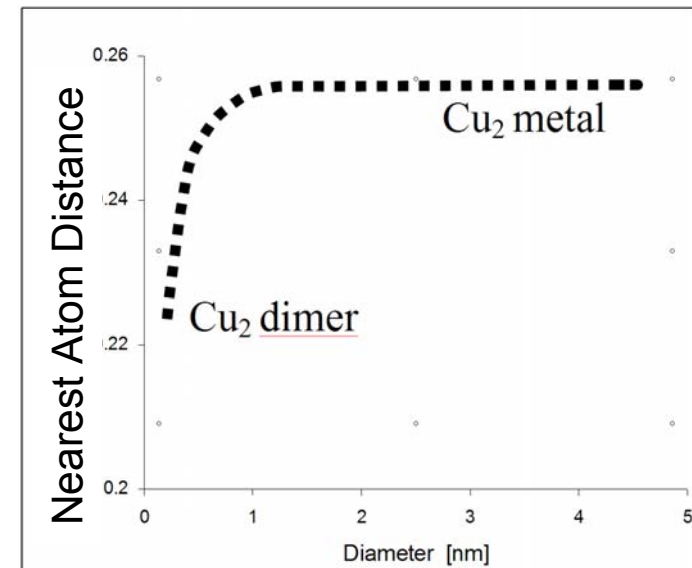
σ **stress** [GPa]

$$\varepsilon = \frac{\sigma}{E}$$

E (Young's Modulus)

ε **strain** []
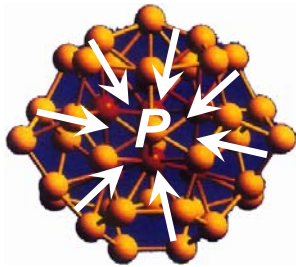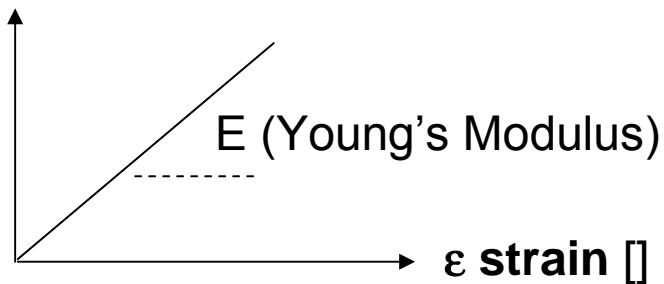
Isotropic stress: $\sigma = 1/3\ P$

Pressure caused by interfacial tension:

$$P = 2\gamma/r \ \ \dots. \text{ Laplace Pressure}$$

$\gamma\dots$ *Surface Tension, r* $\ \dots.$ *Particle Radius*

$$\varepsilon = \frac{1}{3}\frac{P}{E} = \frac{2}{3}\frac{\gamma}{Er} \propto \frac{1}{r}$$

Nearest Atom Distance

Cu$_2$ metal

Cu$_2$ dimer

Diameter [nm]

0.26

.24

.22

0.2

0 1 2 3 4 5

Bulk Crystal and Heterostructure Growth

Nanotechnology needs: Ultrahigh Quality and Purity

E.g., Crystalline Silicon: impurity levels < 0.1 ppb (1 in 10^{10})

Three Step Process to obtain Polycrystalline Silicon:

using amorphous carbon electrodes in submerged arc furnace and carbon in the form of mineral carbon, petroleum coke, charcoal, wood-chips

$$SiO_2 + 2C \rightarrow Si + 2CO$$
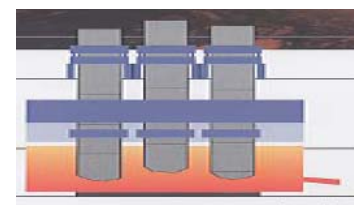
additional reduction reactions with dry hydrochloric acid to drive out impurities

$$Si + 3HCl \rightarrow HSiCl3 + H_2 + impurities$$

final step: hydrogen conversion reaction of trichlorosilane

$$HSiCl_3 + H_2 \rightarrow 2Si + 6HCl$$
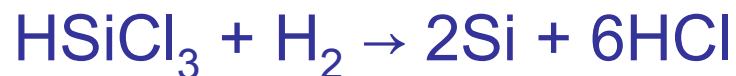
Fabrication of Silicon in Nanoelectronics

Polycrystalline silicon conversion into single crystal Si ingots:

Czochralski method: *Yields doped single crystal Si*

Beginning of crystal growth

seed

mm/s

Si crystal

silicon melt
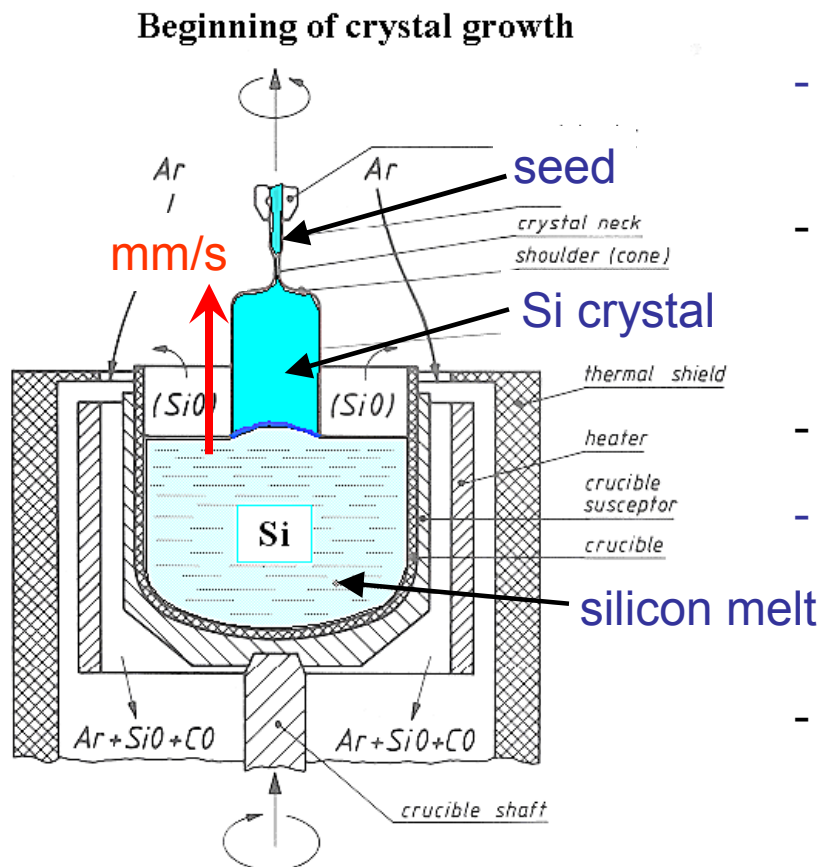
- poly-Si crushed in a crucible in clean room and melted

- Convective steams within the melt due to temperature gradients are suppressed by big magnetic fields.

- Dopants added to the melt at this point.

- A seed crystal is inserted and slowly withdrawn (mm/s) under rotational motion to assure homogeneity,

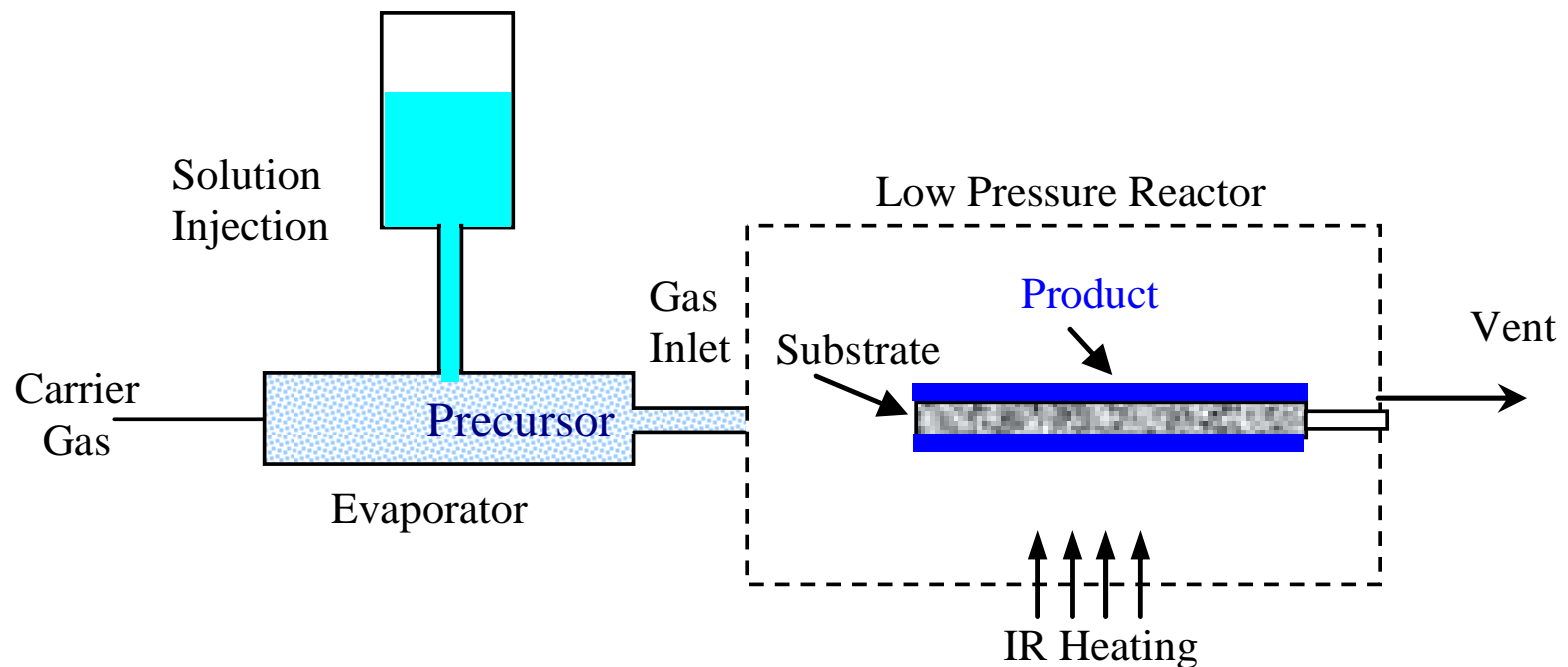- Via mechanical processes wafers are obtained from the single-crystal ingot.

Source: http://www.tf.uni-kiel.de/matwis/amat/elmat_en/kap_6/illustr/i6_1_1.html

Fabrication of Multilayered Crystals

Methods excellently suited for heterostructure growth:
- Chemical Vapor Deposition (CVD)
- Molecular beam epitaxy (MBE)

Schematic of one of many CVD setups

Solution
Injection

Low Pressure Reactor

Gas
Inlet

Product

Vent

Carrier
Gas

Substrate

Precursor

Evaporator

IR Heating

E.g. for silicon layer growth on silicon wafer with dopants: $SiCl_4 + 2H_2 \rightarrow Si + 4HCl$

Heteroepitaxial Crystal Growth Modes

Three Growth Modes for Heteroepitaxial Growth:

- Frank-van der Merwe (FM) ("layer-by-layer" growth)

- Volmer-Weber (VW) ("island" growth), and

- Stranski-Krastanow (SK) (combined "layer-by-layer and island" growth)

Surface Energies:

γ_1 … substrate
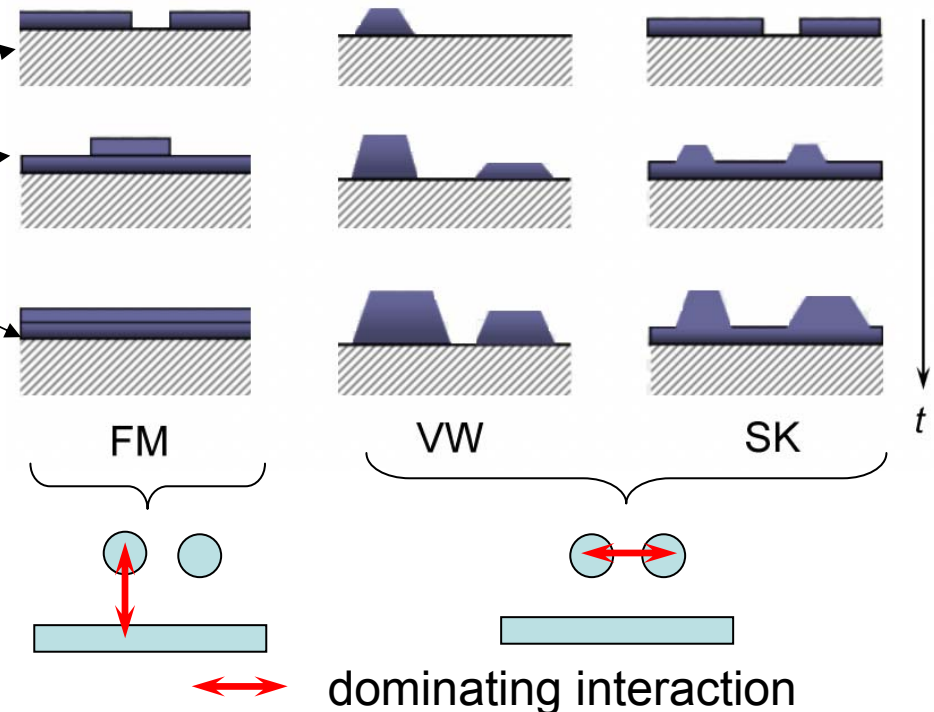
γ_2 … epilayer

γ_{12} … interfacial energy

Wetting: $\boxed{\gamma_1 \geq \gamma_2 + \gamma_{12} \longrightarrow \text{FM}}$

$\Delta\gamma \equiv \gamma_2 + \gamma_{12} - \gamma_1 \leq 0$

"Poor wetting" $\boxed{\gamma_1 < \gamma_2 + \gamma_{12} \longrightarrow \text{VW, SK}}$

$\Delta\gamma \equiv \gamma_2 + \gamma_{12} - \gamma_1 > 0$

FM   VW   SK t

dominating interaction

Epilayer (Film) Growth

Chemical Energy of nth monolayer:

$$\mu(n) = \mu_\infty + \mu_\Sigma = \mu_\infty + a^2 \left[\gamma_2 + \gamma_{12}(n) - \gamma_1 \right] = \mu_\infty + a^2 \Delta\gamma$$

μ_∞ bulk chemical potential of the adsorbate material

$\mu_\Sigma = a^2 \Delta\gamma$ surface chemical potential,

     a … area occupied by an atom

$$\Delta\gamma = \gamma_2 + \gamma_{12}(n) - \gamma_1 \begin{cases} \leq 0; & FM\ growth \\ > 0; & VM\ growth \end{cases}$$

equivalent to the chemical potential difference of the nth layer and bulk

$$\Delta\mu \equiv a^2 \Delta\gamma = \mu(n) - \mu_\infty \begin{cases} \leq 0; & FM\ growth \\ > 0; & VM\ growth \end{cases}$$

→ Surface energy increases for FM growth (and vice versa)

Epilayer Pseudomorphic Growth

Chemical Energy of nth monolayer with interfacial stress:

$$\mu(n) = \mu_\infty + \Delta E^* = \mu_\infty + a^2\left[\gamma_2 + \gamma_{12}^*(n) - \gamma_1\right] = \mu_\infty + a^2\Delta\gamma^*$$

$\gamma_{12}^*(n)$
$\Delta\gamma^*$ thickness dependent interfacial stress or difference

→ ΔE^*, "adhesion energy between misfitting crystals"

$$\Delta E^* = a^2\Delta\gamma^* = \mu(n) - \mu_\infty = \left[\varphi_{des} - \varphi'_{des}(n) + \varepsilon_d(n) + \varepsilon_e(n)\right]$$

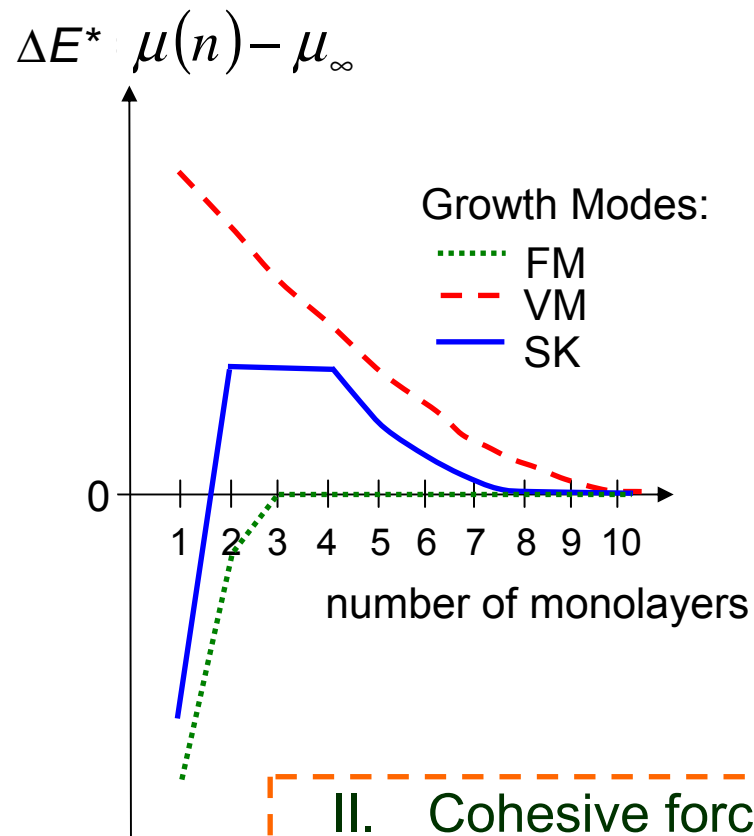φ_{des} desorption energy of an adsorbate atom from a wetting layer of the same material

φ'_{des} the desorption energy of an adsorbate atom from the substrate

ε_d the per atom misfit dislocation energy

ε_e the atom homogeneous strain energy, ε_e

$$\Delta E^* = \mu(n) - \mu_\infty \approx \begin{cases} \varphi_{des} - \varphi'_{des}(n) & \text{heteroepitaxial} \\ \varepsilon_d(n) + \varepsilon_e(n) & \text{homoepitaxial} \end{cases}$$

Chemical Potential and Growth Modes

$\Delta E^* \quad \mu(n) - \mu_\infty$

Growth Modes:
- .... FM
- --- VM
- ——— SK

0

1 2 3 4 5 6 7 8 9 10

number of monolayers

I. Adhesive forces exceed cohesive forces

$$\varphi'_{des} > \varphi_{des}$$

and **weak** interfacial mismatch:
➔ **Frank-van der Merwe Growth (FM)**
   (*Layer-by-layer growth*:
   chemical potential increases with
   increasing layer number)

for **larger** mismatch
➔ **Stranski-Krastanov Growth (SK)**
   (three growth regimes ➔ *Combined
   layer-by-layer and island" growth*)

II. Cohesive forces exceed adhesive forces

$$\varphi'_{des} < \varphi_{des}$$

➔ **Volmer-Weber Growth (VM)**; i.e., decreasing chemical
portential with layer number ➔ *Island growth*