# Nano Materials Synthesis

#### Length scale



are indicated by arrows

R Strobel et al, J Catal 222, 296,

on titanium dioxide)

2003

Almaden Research Center.

Unauthorized use not permitted

hundred million times larger than a football, which is in turn one hundred million times larger than a buckyball. The section from 10-7m (100 nm) to 10-9m (1 nm) is expanded below. The lengthscale of interest for nanoscience and nanotechnologies is from 100 nm down to the atomic scale - approximately 0.2 nm.

### Fundamental Length Scales in Physics



#### Scattering Lengths



#### Consequences:

- Ballistic electrons at small distances (extra speed gain in small transistors)
- Recombination of electron-hole pairs at defects (energy loss in a solar cell)
- Loss of spin information (optimum thickness of a magnetic hard disk sensor)

#### Screening Lengths







Exponential cutoff of the Coulomb potential (dotted) at the screening length *l*.

### Length Scales in Polymers (including Biopolymers, such as DNA and Proteins)

Random Walk, Entropy

Radius of Gyration (overall size, N straight segments)



 $R_{\rm G} \propto l_{\rm P} \sqrt{\rm N}$ 

Stiffness a vs.  $k_{\rm p}T$ Persistence Length (straight segment)



 $l_{\rm p} = \alpha / k_{\rm B} T$ 

nm

DNA (double) Polystyrene Copolymers  $R_{\rm C} \approx 20-50$  nm  $l_{\rm p} \approx 50 \text{ nm}$   $l_{\rm p} \approx 1$ 



#### **Bottom-up**

#### Assemble from Nano-building blocks

- Powder/aerosol compaction
- Chemical synthesis

#### **Top-down**

#### Sculpt from Bulk

- Mechanical attrition
- Lithography
- Etching

# Nucleation and Growth of Crystals

Typical precipitation reaction:



# Nucleation and Growth Rates Control R<sub>c</sub>

- Nucleation, the first step...
- First process is for microscopic clusters (nuclei) of atoms or ions to form
  - Nuclei possess the beginnings of the structure of the crystal
  - Only limited diffusion is necessary
  - Thermodynamic driving force for crystallization must be present



Nucleation Rate – Thermodynamic barrier W<sup>\*</sup>



 $W_{tot} = W_{S} + W_{B}$ 

- At r<sup>\*</sup>,  $(\partial W(r) / \partial r)_{r=r^*} = 0$
- $r^* = -2\sigma / \Delta G_{cryst}(T)$ •  $W(r^*) \equiv W^* = 16\pi \sigma^3 / 3(\Delta G_{cryst}(T))$

### Bottom-up Approaches

- Two approaches
  - thermodynamic equilibrium approach
    - $\cdot$  generation of supersaturation
    - nucleation
    - subsequent growth
  - kinetic approach
    - · limiting the amount of precursors for the growth
    - confining in a limited space

# Homogeneous nucleation

- · Liquid, vapor or solid
- supersaturation
  - temperature reduction
  - metal quantum dots in glass matrix by annealing
  - *in situ* chemical reactions (converting highly soluble chemicals into less soluble chemicals)

### Homogeneous nucleation

### Driving force



**Fig. 3.1.** Schematic showing the reduction of the overall Gibbs free energy of a supersaturated solution by forming a solid phase and maintaining an equilibrium concentration in the solution.

### Homogeneous nucleation



Fig. 3.2. Schematic illustrating the change of volume free energy,  $\Delta \mu_{\nu}$ , surface free energy,  $\Delta \mu_s$ , and total free energy,  $\Delta G$ , as functions of nucleus' radius.

# Nuclei

- formation favor:
  - high initial concentration or supersaturation
  - low viscosity
  - low critical energy barrier
- uniform nanoparticle size:
  - same time formation
  - abruptly high supersaturation -> quickly brought below the minimum nucleation concentration

# Nuclei growth

- Steps
  - growth species generation
  - diffusion from bulk to the growth surface
  - adsorption
  - surface growth
- size distribution
  - A diffusion-limited growth VS. a growth-limited processes

### **Ostwald ripening**

 Many small crystals form in a system initially but slowly disappear except for a few that grow larger, at the expense of the small crystals. The smaller crystals act as "nutrients" for the bigger crystals. As the larger crystals grow, the area around them is depleted of smaller crystals. "LEEM (Low-energy electron microscopy) images of ripening of single atomic layer height islands on Si(001) at various times after the temperature was increased to 670° C: (a) 10 s, (b) 50 s, (c) 400

s, and (d) 1300 s.



### Metallic nanoparticles

- Reduction of metal complexes in dilute solution
  - Diffusion-limited process maintaining
  - Example: nano-gold particles
    - $\cdot$  chlorauric acid (2.5 x 10<sup>-4</sup> M) 20 ml boiling solution+ sodium citrate (0.5%) 1 ml
    - 100°C till color change + water to maintain volume
    - uniform and stable 20 nm particles

# Semiconductor nanoparticles

 Pyrolysis of organometallic precursor(s) dissolved in anhydrate solvents at elevated temperatures in an airless environment in the presence of polymer stabilizer (i.e., capping material)

### Coordinating solvent

- Solvent + capping material
- phosphine + phosphine oxide (good candidate)
- controlling growth process, stabilizing the colloidal dispersion, electronically passivating the surface

### Oxide nanoparticles

- Several methods
  - principles: burst of homogeneous nucleation + diffusion controlled growth
  - most commonly: sol-gel processing
  - most studied: silica colloids

#### Sol-gel process



### SOL-GEL SCIENCE

#### Mix the reactives





Gel

Gelification

Aerogel

### Gelification



# Sol-gel process

- Hydrolysis
  - -e.g.  $M(OEt)_4 + xH_2O \leftrightarrow M(OEt)_{4-x}(OH)_x + xEtOH$
- Condensation of precursors

-e.g.  $M(OEt)_{4-x}(OH)_{x} + M(OEt)_{4-x}(OH)_{x} \leftrightarrow$  $(OEt)_{4-x}(OH)_{x-1}MOM(OEt)_{4-x}(OH)_{x-1} + H_2O$ 

 typical precursors: metal alkoxides or inorganic and organic salts

# Sol-gel example: silica

- Precursors:
  - silicone alkoxides with different alkyl ligand sizes
- catalyst:
  - ammonia
- solvent:
  - various alcohols



#### Vigorous stirring



# Heterogeneous nucleation

- A new phase forms on a surface of another material
  - thermal oxidation, sputtering and thermal oxidation, Ar plasma and ulterior thermal oxidation
  - associate with surface defects (or edges)

### Heterogeneous nucleation



**Fig. 3.24.** Scanning force microscopy images of silver nanoparticles on HOPG-298 graphite substrates: (a) growth occurs only at the edge defects in the original substrate and (b) growth occurs wherever surface defects are present. [A. Stabel, K. Eichhorst-Gerner, J.P. Rabe, and A.R. González-Elipe, *Langmuir* 14, 7324 (1998).].

### **Solvothermal Synthesis**

#### **Solvothermal Synthesis**

Solvothermal synthesis utilizes a solvent under pressures and temperatures above its critical point to increase the solubility of solid and to speed up reaction between solids



- Most materials can be made soluble in **proper solvent** by heating and pressuring the system close to its critical point
- Easily control a solubility of solute
  - $\rightarrow$  Lower supersaturation state



#### **1 Dimensional Nanostructure !**

# Hydrothermal Synthesis

- The reactants are dissolved (or placed) in water or another solvent (solvothermal) in a closed vessel
- $\cdot$  Bomb is heated above BP
- Conventional or MW oven
- Commercially:
  - Tons of zeolites daily



• Semiconductor nanoparticles (CdE (E = S, Se, Te))

$$CdC_{2}O_{4} + E \xrightarrow{\text{solvent}} CdE + 2CO_{2} \uparrow E \text{ ; Chalcogenide (S, Se, Te)}$$

$$\stackrel{\text{ethylenediamine}}{\stackrel{\text{$$

100 nm

200 nm

# **Reduction in solution**

### **Synthesis of Ni nanoparticles**

- Average size :  $80nm \pm 20nm$
- Particle shape : monodisperse sphere
- Maximum size : 150nm
- Surface roughness : Smooth
- Impurity < 100ppm</li>

#### <Reduction in Solution>

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + 4H_2O + N_{2(g)}$$
Reducing agent



- Random shape
- Random size
- Broad size distribution



- Heterogeneous Nucleation
- Additive (dispersant, complex agent)

#### **Reduction in solution - How to control the particles**

#### Processing parameter

Temperature, Concentration , pH, Chemical composition ... etc.

Seed (Heterogeneous Nucleation)

#### Complex agent

Table 2 Changes in the redox potential of Ag<sup>+</sup> ion as a result of complex formation

Redox system	$-\log K_{\beta}$	$E_0/\mathbf{V}$
$Ag^+ + e^- \rightarrow Ag^0$		+0.799
$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag^0$	7.2	+0.38
$[Ag(SO_3)_2]^{3-} + e^- \rightarrow Ag^0 + 2 SO_3^{2-}$	8.7	+0.29
$[Ag(S_2O_3)_2]^{3-} + e^- \rightarrow Ag^0 + 2S_2O_3^{2-}$	13.4	+0.01
$[AgI_4]^{3-} + e^- \rightarrow Ag^0 + 4 I^-$	15.0	-0.09
$[Ag(CN)_3]^{2-} + e^- \rightarrow Ag^0 + 3 CN^-$	22.2	-0.51

#### **Reduction in solution - How to control the particles**

Seed-mediated growth

#### Formation mechanism

Seed-mediated growth for gold and silver



- Citrate ; capping agent (inhibit particle growth)
- Ascorbic acid ; Weak reducing agent
- CTAB ; Rod like template

### One dimensional nanostructures Nanowires Nanotubes

"They represent the smallest dimension for efficient transport of electrons and excitons, and thus will be used as interconnects and critical devices in nanoelectronics and nano-optoelectronics."

General attributes & desired properties

- Diameter 10s of nanometers
- Single crystal formation -- common crystallographic orientation along the nanowire axis
- □ Minimal defects within wire/tube
- □ Minimal irregularities within nanowire/nanotube arrays

# Synthesis Methods

#### (1) Spontaneous growth:

- (a) Evaporation (or dissolution)-condensation
- (b) Vapor (or solution)-liquid-solid (VLS or SLS) growth
- (c) Stress-induced recrystallization
- (2) Template-based synthesis:
  - (a) Electroplating and electrophoretic deposition
  - (b) Colloid dispersion, melt, or solution filling
  - (c) Conversion with chemical reaction
- (3) Electrospinning

### Spontaneous Growth

- A growth driven by reduction of Gibbs free energy or chemical potential. This can be from either recrystallization or a decrease in supersaturation.
- Growth along a certain orientation faster than other direction – anisotropic growth.
- For nanowire/nanowire, growth occurs only along one direction, but no growth along other directions.

# Growth of Single Crystal Nanobelts of Semiconducting or metal oxides

- Evaporating the metal oxides (ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, CdO) at high temperatures under a vacuum of 300 torr and condensing on an alumina substrate, placed inside the same alumina tube furnace, at relatively low temperature.
- Or heating the metal oxide or metal nanoparticles at T=780 – 820°C in air, Nanorods can be obtained depending upon annealing T and time. Nanowires such as ZnO, Ga<sub>2</sub>O<sub>3</sub>, MgO, CuO or Si<sub>3</sub>N<sub>4</sub> and SiC can be made by this method.



Fig. 4.6. SEM and TEM pictures of ZnO nanobelts [Z.W. Pan, Z.R. Dai, and Z.L. Wang, Science 291, 1947 (2001).]



Still mat

By controlling growth kinetics, a consequence of minimizing the total energy attributed by spontaneous polarization and elasticity, left-handed helical nanostructures and nano-rings can be formed.

Fig. 4.7. SEM images of the synthesized single crystal ZnO nanobelt helical nanostructures. The typical width of the nanobelts is ~30 nm, and pitch distance is rather uniform. The helixes are left-handed. [X.Y. Kong and Z.L. Wang, *Nano Lett.* 3, 1625 (2003).]

### Dissolution and Condensation Growth

 The growth species first dissolve into a solvent or a solution, and then diffuse through the solvent and deposit onto the surface resulting growth of nanowires.

### Growth of Ag Nanowire Using Pt Nanoparticles as Growth Seeds

- Precursor:  $AgNO_3$
- Reduction agent: ethylene glycol
- Surfactant: polyvinyl pyrrolidone (PVP)
- The surfactant absorbed on some growth surfaces and blocks the growth, resulting in the formation of uniform crystalline silver nanowires.



Fig. 4.9. SEM images of silver nanowires grown in solution using Pt nanoparticles as growth seeds. [Y. Sun, B. Gates, B. Mayers, and Y. Xia, *Nano Lett.* 2, 165 (2002).]



Fig. 4.10. (a) TEM images of BaTiO<sub>3</sub> nanowires, showing that the reaction produces mainly nanowires and small quantities ( $\sim 10\%$ ) of nanoparticle aggregates. (b) TEM image of a BaTiO<sub>3</sub> nanowire along with two convergent beam electron diffraction patterns. [J.J. Urban, J.E. Spanier, L. Ouyang, W.S. Yun, and H. Park, *Adv. Mater.* 15, 423 (2003).]

### Vapor (or solution)-Liquid-solid (VLS) Growth

In the VLS growth, a second phase material, commonly referred to as either impurity or catalyst, is purposely introduced to direct and confine the crystal growth on to a specific orientation and within a confined area. A catalyst forms a liquid droplet by itself or by alloying with growth material during the growth, which acts as a trap of growth species. Enriched growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in the one-directional growth. Wagner *et al.*<sup>42,43</sup>

It is noted that the surface of liquid has a large accommodation coefficient, and is therefore a preferred site for deposition.

### VLS Growth Process



Fig. 4.11. Schematic showing the principal steps of the vapor-liquid-solid growth technique: (a) initial nucleation and (b) continued growth.



Fig. 4.12. Phase diagram of the gold-silicon binary system.



Fig. 4.14. (a) Field-emission scanning electron micrograph of silicon nanowires produced by VLS method and (b) High-resolution TEM image of the end of a 15 nm diameter wire exhibiting Si lattice planes and a gold nanocluster. [J. Hu, T.W. Odom, and C.M. Lieber, *Acc. Chem. Res.* 32, 435 (1999).]

### Compound Semiconductor Nanowires

 Nanowires of binary group III-V materials (GaAs, GaP, InAs, and InP), ternary III-V materials (GaAs/P, InAs/P), binary II-VI compounds (ZnS, ZnSe, CdS, and CdSe), and binary IV-IV SiGe alloys have been made in bulk quantities as high purity (>90%) single crystals.



Fig. 1. Pseudobinary phase diagram for Au and GaAs. The liquid Au–Ga–As component is represented as L.

Table 1. Summary of single crystal nanowires synthesized. The growth temperatures correspond to ranges explored in these studies. The minimum and average nanowire diameters were determined from TEM and FESEM images. Structures were determined using electron diffraction and lattice resolved TEM imaging: ZB, zinc blende; W, wurtzite; and D, diamond structure types. Compositions were determined from EDX measurements made on individual nanowires. <u>All of the nanowires were synthesized using Au as the catalyst</u>, except GaAs, for which Ag and Cu were also used. The GaAs nanowires obtained with Ag and Cu catalysts <u>have the same size</u> <u>distribution, structure, and composition as those obtained with the Au catalyst</u>.

Material	Growth Temperature [°C]	Minimum Diameter [nm]	Average Diameter [nm]	Structure	Growth Direction	Ratio of Components
GaAs	800-1030	3	19	ZB	<111>	1.00 : 0.97
GaP	870900	3-5	26	ZB	<111>	1.00:0.98
GaAs <sub>0.6</sub> P <sub>0.4</sub>	800-900	4	18	ZB	<111>	1.00:0.58:0.41
InP	790-830	3-5	25	ZB	<111>	1.00:0.98
InAs	700-800	3-5	11	ZB	<111>	1.00:1.19
$InAs_{0.5}P_{0.5}$	780-900	35	20	ZB	<111>	1.00: 0.51: 0.51
ZnS	990-1050	4-6	30	ZB	<111>	1.00:1.08
ZnSe	900-950	35	19	ZB	<111>	1.00:1.01
CdS	790-870	3-5	20	W	<100>, <002>	1.00:1.04
CdSe	680-1000	3-5	16	W	<110>	1.00:0.99
$Si_{1-s}Ge_{s}$	820-1150	3–5	18	D	<111>	$\mathrm{Si}_{\mathrm{t-s}}\mathrm{Ge}_{\mathrm{s}}$



Fig. 4.15. Field-emission SEM images of compound semiconductor nanowires grown by VLS method: (a) GaAs, (b) GaP, and (c)  $GaAs_{0.6}P_{0.4}$ . The scale bars are 2  $\mu$ m. [X. Duan and C.M. Lieber, *Adv. Mater.* 12, 298 (2000).]



Fig. 4.16. Schematic illustrating the general concepts of control of the diameters and length of nanowires grown by growth time and the size of catalyst colloids. [M.S. Gudiksen, J. Wang, and C.M. Lieber, J. Phys. Chem. B105, 4062 (2001).]



Fig. 4.17. Radial size instability in nanowires grown by VLS. [E.I. Givargizov, *Highly Anisotropic Crystals*, D. Reidel, Dordrecht, 1986.]

#### **Oxide-assisted Growth**

#### Metal-Catalyzed Growth

![](_page_57_Figure_2.jpeg)

Fig. 7. A schematic diagram contrasting the OAG (left-hand side) and VLS growth (right-hand side).

# Methods for Growth of CNTs

![](_page_58_Figure_1.jpeg)

### CVD Growth of graphene

![](_page_59_Figure_1.jpeg)

### Template assisted nanowire growth

![](_page_60_Picture_1.jpeg)

- □ Create a template for nanowires to grow within
- Based on aluminum's unique property of self
   organized pore arrays as a result of anodization to
   form alumina (Al<sub>2</sub>O<sub>3</sub>)
- Very high aspect ratios may be achieved
- Pore diameter and pore packing densities are a function of acid strength and voltage in anodization step
- Pore filling nanowire formation via various physical and chemical deposition methods

# Al<sub>2</sub>O<sub>3</sub> template preparation

- Anodization of aluminum
- □ Start with uniform layer of ~1mm Al
- Al serves as the anode, Pt may serve as the cathode, and 0.3M oxalic acid is the electrolytic solution
- $\Box$  Low temperature process (2–5°C)
- □ 40V is applied

![](_page_61_Figure_6.jpeg)

- Anodization time is a function of sample size and distance between anode and cathode
- □ Key Attributes of the process (per M. Sander)
  - Pore ordering increases with template thickness pores are more ordered on bottom of template
  - Process always results in nearly uniform diameter pore, but not always ordered pore arrangement
- Aspect ratios are reduced when process is performed when in contact with substrate (template is -0.3-3 mm thick)

# The alumina $(Al_2O_3)$ template

![](_page_62_Figure_1.jpeg)

(T. Sands/ HEMI group http://www.mse.berkeley.edu/groups/Sands/HEMI/nanoTE.html)

![](_page_62_Figure_3.jpeg)

<sup>(</sup>M. Sander)

### **Electrochemical deposition**

- Over Works well with thermoelectric materials and metals
- Process allows to remove/dissolve oxide barrier layer so that pores are in contact with substrate
- □ Filling rates of up to 90% have been achieved

![](_page_63_Figure_4.jpeg)

### Template-assisted, Au nucleated Si

### nanowires

- Gold evaporated (Au nanodots) into thin -200nm alumina template on silicon substrate
- Ideally reaction with silane will yield desired results
- Need to identify equipment that will support this process contamination, temp and press issues
- Additional concerns include Au thickness, Au on alumina surface, template intact vs removed

(M. Sander)

![](_page_64_Picture_6.jpeg)

![](_page_64_Figure_7.jpeg)