Fabrication Processes for Nanomaterials

Week 2

Two approaches

Nanomaterials

Nanofabrication
Top-Down approach

**ADVANTAGES**
- Large scale production: deposition over a large substrate is possible
- Chemical purification is not required

**DISADVANTAGES**
Yields:
- Broad size distribution (10-1000 nm)
- Varied particle shapes or geometry
- Control over deposition parameters is difficult to achieve
- Impurities: stresses, defects and imperfections get introduced
- Expensive technique

Bottom-Up approach

**ADVANTAGES**
- Ultra-fine nanoparticles, nanoshells, nanotubes can be prepared
- Deposition parameters can be controlled
- Narrow size distribution is possible (1-20 nm)
- Cheaper technique

**DISADVANTAGES**
- Large scale production is difficult
- Chemical purification of nanoparticles is required

Bottom Up

Chemical Synthesis

Self Assembly

Positional Assembly

Particles, Molecules

Crystals, Films, Tubes

Cosmetics, Fuel Additives

Displays

Experimental, atomic or molecular devices
How could we cause attrition of a bulk material?

Mechanical Attrition

Imposing an extremely high deformation onto the material, structural refinement occurs by shearing and breaking down of existing structures and phases.

Ball Milling — not quite good enough
Mechanical Attrition – Ball Milling

Three common types of attrition devices

1. High shear and impact forces developed
   - Shaker Mills
     - Shaken at several thousand cycles per minute
   - Planetary Mills
     - Movement of a vial within the device
     - Vials rotated on their axis in opposite direction to device
     - Several thousand rpm
   - Attrition Mills
     - Vertical drum with carefully positioned impellers
     - High speeds

Mechanical Attrition

Control Factors:

- Composition of particles/powders
- Size of particles/powders
- Milling speed (energy of impact)
- Milling temperature
- Milling atmosphere

Arc Discharge

Nanomaterials are produced from bulk materials due to arc assisted breakdown of the bulk material

Most of the metallic nanoparticles, nanostructures and metal oxide nanoparticles are produced in this way.

As are carbon nanotubes
Arc Discharge - CNT in water

Laser Ablation

Advantages
- Possible high purity of the nanomaterial,
- Material variety, and the
- In-situ dispersion of the nanoparticles in a variety of liquids
- Allowing safe and stable handling of the colloids.

Set up

High energy, pulsed laser (femtoseconds to nanoseconds)
Focused beam
Can do in air/inert gas
Demonstration of material variety by laser ablation in liquids:
High energy laser is focused on to a target in a solvent.

- Short pulses of energy which is enough to vaporize small spots of the metal target which condenses as nanoparticle in the solvent.
- Usually this method is used to generate noble metallic nanoparticles such as gold, silver and platinum.
- Advantage is that many materials can be used, particularly alloys, a unique advantage of this method.
- Another advantage is no expensive chemicals needed.

**Fig 1. Schematic of pulsed laser ablation on a rotating target**

Focused Ion Beam (FIB) Milling/Sputtering

Sputtering rate depends on ion energy, mass, crystal orientation, substrate nature.
Ag Nanoparticles

UV-visible absorption spectrum: The absorption band at ~398 nm is due to SPR of Ag nanoparticles, confirms the formation of pure Ag nanoparticles.

TEM image of Ag sample synthesized at 40 mJ/pulse laser energy confirms formation of nanoparticles with average particle size 2-3 nm. The inset shows SAED pattern, indicates formation of crystalline nanoparticles.

Nanostructured metals

GRAIN SIZE < 100 NANOMETERS

Processing

(a) Severe Plastic Deformation: Starting materials have a bulk form.

(b) Mechanical Attrition: Starting materials have powders or fine pieces

(c) Electrodeposition: Anode – metal bar

(d) Amorphous Metals Route: Devitrify amorphous metal into fine crystalline precipitates

(1) Severe Plastic Deformation

HIGH PRESSURE TORSION

EQUAL CHANNEL ANGULAR PRESSING
Severe plastic deformation & Grain refinement

1). SPD at/below 0.4 T_m produces dislocation density as high as 10^{12} / mm^2 under hydrostatic pressure.

2). A portion of high density dislocations transform into grain boundaries under the proper heat treatment. Thus, this creates very fine grains of 100 nm – 500 nm in diameter.

Rapid Condensation & Solidification
- Liquid Solidification

Instead of phase transformation from vapour to solid, the process involve phase transformation from liquid (melted material) to solid

Control Factors:
- Temperature of melted material
- Flow rate of melted material
- Cooling conditions

Supercooling

- The driving force to nucleate increases as ΔT increases
- Small supercooling → slow nucleation rate - few nuclei – large crystals
- Large supercooling → rapid nucleation rate - many nuclei – small crystals
Phase Classification:

1. Wet chemical synthesis
   - Liquid Phase Fabrication:
     - Sol-gel,
     - Self assembled Monolayer (SAM)
     - Microemulsion method
     - Spray Pyrolysis
   - Processes use surface forces to create nanoscale particles and structures.

2. Gas (Vapor) Phase Fabrication:
   - PVD: - Inert Gas Condensation, -
   - Evaporation (Thermal, e-beam) –
   - Plasma Arcing, -
   - Laser ablation, -
   - Sputtering CVD: (PECVD and Microwave-PECVD) -

Chemical Synthesis

Processes involving molecular assembly by interactive forces between atoms and molecules, chemical bonds and Van der Waals forces to form aggregates of atomic and/or molecular units

Major processes: sol-gel process and chemical vapour deposition process

The sol-gel process

versatile solution process for making ceramics and glass materials. Applying the sol-gel process,
- ultra-fine or spherical shaped powders,
- thin film coatings,
- ceramic fibers,
- microporous inorganic membranes, monolithic ceramics and glasses, or
- extremely porous aerogel materials.
The sol gel process

Possibilities

"sol" is cast into a mould,
◦ a wet "gel" will form.

With further drying and heat-treatment,
◦ the "gel" is converted into dense ceramic or glass articles.

If the liquid in a wet "gel" is removed under a supercritical condition,
◦ a highly porous and extremely low density material called "aerogel" is obtained.

Possibilities, cont.

Adjust viscosity of a "sol"
◦ ceramic fibres can be drawn from the "sol".

Ultra-fine and uniform ceramic powders
◦ precipitation,
◦ spray pyrolysis, or
◦ emulsion techniques

Aerogel properties can be changed by adding different precursor molecules.
(a) an aluminum oxide foam prepared from aluminum nitrate has a cluster morphology that results in
(b) an opaque aerogel.
(c) Using aluminum chloride as the precursor produces an aerogel with fibrous morphology, resulting in
(d) a stronger foam that is also translucent.
Limitations of sol gel synthesis

**Presursors**
- often expensive
- sensitive to moisture

**Process**
- Time consuming

**Dimensional change**
- shrinkage

Advantages of sol gel synthesis

**Precursors**
- Volatile

Densification T’s low
Chemical conditions mild
Highly porous and nanocrystalline materials

Easily purified – high purity products

Silica particles produced by sol gel
Colloids

- Have small particles (ions or molecules)
- Are transparent
- Do not separate
- Cannot be filtered
- Do not scatter light.

A mixture of water H₂O and ethanol CH₃CH₂OH is homogeneous.

Solutions

- Cannot be filtered
- Do not "settle"
- Have medium size particles
- Separated with semipermeable membranes
- Scatter light (Tyndall effect)
- Dispersion of matter in size from about 1-1000nm

The Tyndall Effect
Colloid Examples

Natural aerosols - fog, clouds

Solid aerosols, smoke, dust

Foam, whipped cream, shaving cream

Natural aerosols - ink, paint, clouds

Stability of colloids

**Stable** - Freely dispersed

Flocculation:
- Particles are loosely aggregated in an open structure
- Reversible & temporary

Coagulation:
- Particles are closely aggregated & difficult to redisperse
- Destructive and permanent

Stability of disperse systems

Large area to volume ratio (Large interface)

High free energy

Unstable system

Aggregation of particles

So why are colloids stable?
Colloidal dispersions are more stable than suspensions and emulsions, due to:

- Smaller particle size
- Brownian movement

In 1889 G.L. Gouy found that the "Brownian" movement was more rapid for smaller particles (we do not notice Brownian movement of cars, bricks, or people).

Properties of colloids

**Kinetic Properties:** Motion of the particles with respect to the dispersion medium

- Thermal motion
- Brownian movement
- Diffusion
- Osmosis
- Gravity or centrifugal field
  - Sedimentation
  - Viscous flow
Stability of colloids

Stabilization factors:
- Electric double layer interactions
- Solvation
- Thermodynamically stable systems
DLVO Theory

... SURFACE CHEMISTRY!

Amphophiles

A colloid in which dispersed phase consists of micelles.
Example surfactant (surface active agent).

Some surfactants:
Micelles

- aggregates of amphiphilic molecules
- Critical micelle concentration
  - Concentration at which micelle is formed

At low concentration: amphiphiles exist separately (subcolloidal size)

Non-polar Region (hydrophobic)

Polar Region (hydrophilic)

Water

At high concentration: form aggregates or micelles (50 or more monomers) (colloidal size)

CMC - Critical Micelle Concentration
Micelles

Can get fancy

Colloidal Synthesis of CdSe (semiconducting) Quantum Dots:

TEM Studies

Nearly monodispersed and highly crystalline CdSe quantum dots can be synthesized by colloidal synthesis

Advantages:
- Greener technique (environment friendly)
- Cheaper and effective
- Narrow size particles (2-10 nm) can be synthesized

Disadvantage:
- Controlling time and precursor is critical

Gold Colloids
Summary of film

- Number of nucleation sites formed initially determines number of particles produced
  - Determined by amount of citrate added
- If initial AuCl₄⁻ is kept the same more nucleation sites means final particles will be smaller
- For monodisperse sol need to form nucleation sites quickly and simultaneously
  - Hard to do!
- Gold particles are neutral cores surrounded by AuCl₂⁻ ions
  - Colloid stabilised by electric double layer

How can we make nanoparticles?

Mixing hexadecyltrimethylammoniumbromide pentanol micelles of CdCl₂ with similar micelles containing Na₂S produces nanoparticle CdS

since the aqueous solution serves as a nanoreactor the particles cannot grow bigger than the micelle

Parameters

PARAMETERS AFFECTING PARTICLE SIZE, PARTICLE SIZE DISTRIBUTION, AND PHASES OF THE FINAL PARTICLES FORMED

- concentration of the reactive precursor in the micelle
  - weight percentage of the aqueous phase in the microemulsion

ADVANTAGES

- the preparation of very small particles
  - the ability to control the particle size.

DISADVANTAGES

- include low production yields and
  - the need to use large amount of liquids

Electrodeposition

Long-established way to deposit metal layers on a conducting substrate.

Ions in solution are deposited onto the negatively charged cathode, carrying charge at a rate that is measured as a current in the external circuit
Examples

Icosahedral microparticles, pentagonal microtubes and whiskers obtained in the process of copper electrodeposition (after A.A. Vikarchuk)

Vapour Deposition Techniques

Processes generally involving

- Creation of vapour phase,
- Vapour transport from a source to substrate and
- Deposition of the vapour phase on the substrate

Physical Methods

The actual active species are directly evaporated or injected into the gas phase;

A precursor is used that, on transporting into the vapor space, is chemically decomposed into the required species.

PVD ⇒ Chemical Vapour Deposition (CVD)

Physical Vapour Deposition (PVD)

Molecular Beam Epitaxy

Vapour Deposition

CVD ⇒ Evaporation

Precursor (g) or (l)

Primary particles (s) or (l)

Nanoparticles (s)

Nanoclusters (s)

(i) precursor vaporization (typically involves a catalyst)

(ii) nucleation, and

(iii) growth stage

Vapour Phase Technologies

Grain growth

Nucleation/condensation

Intermediate (g)

Super saturation (g)

Gas-solid surface reaction

Gas-phase reaction

Vapor Phase Fabrication

(iii) growth stage

(i) precursor vaporization (typically involves a catalyst)

(ii) nucleation, and
PHYSICAL VAPOUR DEPOSITION

Involves generation and condensation of vapor phase species via thermal evaporation, sputtering or laser ablation.

PVD processes are carried out under vacuum conditions.

The process involves four steps:
1. Evaporation
2. Transportation
3. Reaction
4. Deposition

Evaporation Techniques
Physical Vapor Deposition: PVD

2 types: evaporation and sputtering

ADVANTAGES:
- Versatile – deposits almost any material
- Very few chemical reactions
- Little wafer damage
- sputtering

LIMITATIONS:
- Line-of-sight
- Shadowing
- Thickness uniformity
- Difficult to evaporate materials with low vapor pressures

Inert Gas Condensation

A process involving evaporation of materials and rapid condensation of the vapour phases under very low gas pressure or high vacuum

Evaporated atoms or molecules undergo a homogeneous condensation to form powders or clusters on a cold-powder collection surface

Condensed powders are quickly removed from the cold surface to avoid coalescence of clusters and collected via a funnel

If required, the powders are compacted through a compaction unit

Example of nanoparticles obtained by IGC

Icosahedral gold nanoparticles generated from an inert gas aggregation source using helium and deposited on amorphous carbon film


Physical Vapour Deposition

Control Factors:

- Energies of emitted atoms/molecules
- Target-to-substrate separation and arrangement
- Chamber pressure and partial pressure of reactive gas
- Substrate bias voltage and temperature
CVD
CHEMICAL VAPOUR DEPOSITION

COLORLESS
GEM CUT
FROM
DIAMOND
GROWN BY
CHEMICAL
VAPOR
DEPOSITION

Working Concept

Variables: temperature, pressure, and concentrations

Metal deposition
metal halide (g) → metal(s) + byproduct (g)

Ceramic deposition
metal halide (g) + oxygen/carbon/nitrogen/boron source (g) → ceramic(s) + byproduct (g)

Chemical Vapour Deposition

- Precursor gases are used in the process
- A reactive gas/gas mixture is often impinged on the substrate
- Process is conducted at a high temperature such that molecular fragments and free atoms are formed and react with reactive gases to form a desired coating on the substrate

Chemical vapor deposition (CVD) results from the chemical reaction of gaseous precursor(s) at a heated substrate to yield a fully dense deposit.
Example

Thermal CVD system

Precursor Gas
For growing Carbon Nanotubes

http://www.iljinnanotech.co.kr/en/material/r-4-4.htm
Various types of CVD:

Atmospheric pressure – APCVD
Low pressure – LPCVD
Plasma enhanced – PECVD
High density plasma - HDPCVD

IN SUMMARY:

**CVD**
- Reactive gases interact with substrate
- Used to deposit Si and dielectrics
- Good film quality
- Good step coverage

**PVD**
- Used to deposit metals
- High purity
- Line of sight

Note: BOTH PVD AND CVD TECHNIQUES CAN FORM NANO (OR EVEN THICKER) FILMS ON SUBSTRATES