Fabrication Processes for Nanomaterials

**Week 2**

**Self Assembly**

**Self-assembly**

Nanotechnologists want to make macroscopic materials (and structures) by arranging nanoscale building blocks.

*Could do this using an STM to move each atom (or molecule) into the correct position*

- A handful of material contains about $10^{22}$ atoms
- A very slow process

**Photolithography**
- E-beam lithography: 3000 Years - 3 billion years
- AFM lithography: 30 Years - 1/100 sec

Processing time for 5x5 mm

<table>
<thead>
<tr>
<th>Technique</th>
<th>Throughput (μm/hr)</th>
<th>Resolution (Å/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-beam lithography</td>
<td>10^4</td>
<td>10^7</td>
</tr>
<tr>
<td>AFM lithography</td>
<td>10^5</td>
<td>10^6</td>
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</tbody>
</table>

Need a way to assemble more efficiently

- Some useful reference books:
  - 1. Zhang et al, Self-Assembled Nanostructures
  - 2. Evans and Wennerstrom, The Colloidal Domain
  - 3. Ulman, Ultrathin Organic Films
Self-assembly - *Biology is very good at this*

Exploit this ability in nanotechnology to make materials from nano-building blocks

Biomimetics - materials that copy nature's abilities

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**Self assembly?**

*Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well defined aggregates joined by non-covalent bonds.*

*Whitesides et al. Science 254 1312 (1991).*

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As you view the following images you should consider the question:

*What drives and governs self assembly?*

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**Gecko feet**
Self-assembly
What drives this self assembly

Forces between individual particles - chemical bonds

Better to think in terms of energy

System self assembles because this is the lowest energy (most stable) structure

What drives self assembly?

Static Assembly
Thermodynamic free energy minimum
Once formed-stable

Dynamic Assembly
Kinetically formed, not necessarily free energy minimum
Not necessarily stable
What drives self assembly?

1. What forces do we have available?
   - covalent, ionic, van der Waals, hydrogen
2. Other forces
   - magnetic, electrostatic, fluidic, ...
   - Polar/Nonpolar (hydrophobicity)
3. Shape (configurational)
4. Templates (guided self assembly)
5. Kinetic conditions (e.g., diffusion limited)

Nanoscale self-assembly has been going on for BILLIONS of years

Challenges are to figure:
WHERE it has been going on (can't SEE it directly)
Which forms of self-assembly might be useful
Takes a HUGE number of forms (harder we look, more we find!!)

Common denominator = Nature → lower energy through organisation

Large Scale Self-Assembly (Geological)

Giant's Causeway (Northern Ireland)

Volcanic basalt cooled rapidly to form these (mostly) hexagonally shaped columns

With solid matter, most common form = CRYSTAL GROWTH

Atoms or molecules
Flying through gas or drifting through solution
With solid matter, most common form = CRYSTAL GROWTH

Atoms or molecules
Flying through gas or drifting through solution

Guy with red arrow has REALLY good idea:
If reaches corner will be bound to three atoms → really low energy

Real-life demonstrations of crystal growth:
Crystal growth / self-assembly of glass spheres (a.k.a marbles):

Note (centre top) the flaws in the crystal at boundary of two “substrate” grains

Source: Interdisciplinary Education Group, NSF MRSEC project of the University of Wisconsin.

Real-life demonstrations of crystal growth:
Crystal growth / self-assembly of floating plastic magnets:

• Note how it takes many tries to find the ideal / lowest-energy configuration
• Facilitated by agitation (background energy) to knock it out of less desirable states

Source: Interdisciplinary Education Group, NSF MRSEC project of the University of Wisconsin.
"Molecular Beam Epitaxy" (MBE)

**Nearest nano equivalent**

Throw individual atoms across vacuum chamber (by evaporating them)

They land on mildly heated substrate (which allows them to still move around)

Process is just like earlier diagram:

Except it takes 10x$ plus worth of vacuum equipment to make it this "simple"

John Bean’s homepage view:
Full two growth chamber system:

**OK, but where's the nano?**

Sure, involves nano atoms, but how does this produce nano structures?

Flip upside down, install TWO evaporation sources, then alternate atoms:

*Viola! Single atom layers!*

**Or more realistically:**

FROM "UVA VIRTUAL LAB"
**But what if want 3D nano-structures?**

Try with atoms of different sizes: Smaller Si atoms and larger Ge atoms

Alternative #1: Larger Ge atoms squeeze to fit ("strained layer epitaxy"): 

Alternative #2: Arriving atoms exploit their surface mobility to segregate / island:

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**Really does occur this way:**

**AFM image of slightly organized MBE Germanium islands on Silicon**

(from work of Max Lagally and John C. Bean)

**TEM cross-section of MBE Germanium island embedded in Silicon**

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**And can be extended to produce 3D nanostructures:**

**TEM Cross-section of MANY layers of self organizing Ge dots embedded in Si:**

**Analysis of the 3D relationship of Ge quantum dots in a Si matrix using focused ion beam tomography**


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**Self Assembly By Crystal Growth**

“Vapour Deposition”

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NANO EXAMPLES
Nanostructured Materials - Fabrication Processes

CVD

Grow nanotubes like trees
- Put iron nanopowder crystals on a silicon surface
- Put in a chamber
- Add natural gas with carbon (vapor deposition)
- Carbon reacts with iron and forms a precipitate of carbon that grows up and out

- Because of the large number of structures you can create quickly, self-assembly is the most important fabrication technique

Source: http://www.chemistry.nmsu.edu/~etrnsfer/nanowires/

Carbon Nanotubes

Growing a forest of nanotubes!

2. Any other crystal growth tricks?

Heat metal dot on Si until melts.
Immerse in vapors of SiH₄.

Si dissolves into molten metal (forming eutectic)

Then precipitates onto Si surface

Now switch from SiH₄ to GeH₄ vapor:

Are you pulling our leg? No:

Lorelle Mansfield - NIST:

U. Helsinki:
www.micronova.fi/units/ntq/research/nanowires.php

Switch back and forth between gases:

Switch gases after metal removed:

Or do both:
Self Assembly By Crystal Growth “nano particles”

What exactly did he do?

Basic Process:
- Put gold chloride (HAuCl₄) into solution liberating Au⁺ ions
- Added sodium citrate “reducing agent” that de-ionizes the gold: Au⁺ → Au
- Some Au atoms then start to clump together into sub nanometer nuclei
- Remaining Au atoms then pile on → almost uniform Au nanoparticles

Size = 5 to 100 nm depending on gold chloride to sodium citrate ratio

OR can controllably enlarge nanoparticles in second process:
- Put above particles into fresh HAuCl₄ solution (creating new supply of Au⁺ ions)
  - “Reduce” driving those ions to coat old nanoparticles, enlarging them

Is self-assembly ALL about crystal growth?

Or how about self-assembly of gold nano particles:
From CytImmune Inc:

Supporting webpage with embedded animation:
Lecture 6 - Supporting Materials - CytImmune
ABSOLUTELY NOT! In fact I am running out of crystal growth examples

There are more numerous and more powerful examples in the wet world

A small sampler:

Consider the peculiar properties of water:

Oxygen wants electrons much more than hydrogen

So charge distribution in water is not uniform - Molecule is “polarized”

Which means that water molecules like to organize (sort of):

As liquid water jostles about, molecules tend to place (+) hydrogens next to (-) oxygens on neighbor

Energy reduced as opposite charges snuggle closer

“HYDROGEN BONDING”

When solidifies, REALLY gets organized - Why it expands

Screwed up if big non-polarized molecules (e.g. oils) inserted into mix:

Oils hold water molecules apart So oil and water tend to segregate

But what if add polarized end group to oil?

Then water IS attracted to ends.

Or even better:

Long molecules organize:

Hydrophillic (water loving) ends aligned in same direction

Becomes the low energy interface with the water

Excerpt from Letter of Benjamin Franklin to William Brownrigg (Nov. 7, 1773)

...At length being at Clapham, where there is, on the Common, a large Pond ... I fetched out a Cruet of Oil, and dropt a little of it on the Water. I saw it spread itself with surprising Swiftness upon the Surface ... the Oil tho’ not more than a Tea Spoonful ... which spread amazingly, and extended itself gradually till it reached the Lee Side, making all that Quarter of the Pond, perhaps half an Acre, as smooth as a Looking Glass....

A nanofilm!
Use in complex self-assembly?

**FLOAT LAYER OF OILY MOLECULES ON TOP OF WATER BATH**

Move surface barrier inward to compress oil layer

Monitor surface tension by the pull on a sheet partially immersed in bath to sense when oils “self-assemble” side to side

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**Langmuir Film**

- hydrophobic end
- e.g., steric acid
- pressure

- hydrophilic end
- monolayer film
- water

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

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**Langmuir-Blodgett Film**

Must control movable barrier to keep constant pressure

Solid

Liquid

Multiple dips - multiple layers

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**SAM: Self Assembled Monolayer**

alkanethiol on gold (Au) \( HS(CH_2)_nX \) where \( X \) is the end group of the chain –CH\(_3\), –OH, or –COOH

- Organic Interface: Determines surface properties
- Terminal Functional Group: Presents chemical functional groups
- Organic Interphase (1-3 nm): Provides well-defined thickness
- Spacer (Alkane Chain): Acts as a physical barrier
- Spacer (Alkane Chain): Affects electronic conductivity and local optical properties
- Metal-Sulfur Interface: Stabilizes surface atoms
- Metal Substrate: Modifies electronic states

Longer alkanethiol molecules have greater thermodynamic stability.

SAM: Self Assembled Monolayer

- Chemisorbed molecules
- Stabilized by intermolecular van der Waals interaction

Creating Nano Structures, Continued

**Dip-Pen Nanolithography (DPN)**
- Coated AFM tip is scanned across a surface, depositing chemical “ink” in its wake.

**Figure 3.14:** A very different application of chemically prepared systems in nanoscience is shown here. Northwestern University, International Institute for Nanotechnology, Chad Mirkin Group.

Creating Nano Structures, Continued

**Figure 3.15:** Ultra-high resolution pattern of mercaptohexadecanoic acid on atomically-flat gold surface. Northwestern University, International Institute for Nanotechnology, Chad Mirkin Group.
But there is an even better molecular arrangement!

Organize oils with special polarized ends so that they are tail to tail:

Called a “lipid bilayer” - Ring a bell?

Both sides of film now “hydrophilic” so sheet is happy if it is immersed in water:

OK, so I’m tired of orienting dozens of tiny water molecules!

“We’re not in Kansas anymore!” - A hands-on introduction to nanoscience

Which gives . . . a cell membrane!

Which is constructed out of exactly such a “lipid bilayer” layer

And does not actually involve atomic bonding BETWEEN the lipid molecules:


via computer animation:

FROM THE “AUTO CELL PROJECT”

Nanoparticle Monolayer Formation

Requirements:
- rapid evaporation
- excess dodecane present
- attractive interaction to liq-air interface and between particles

via computer animation:

FROM THE “AUTO CELL PROJECT”

SELF ASSEMBLY with DIBLOCK COPOLYMERS

Block “A”
PMMA
Block “B”
PS

~10 nm
Ordered Phases

10% A
30% A
50% A
70% A
90% A

Scale set by molecular size

CORE CONCEPT FOR NANOFABRICATION

Deposition Template
(physical or electrochemical)

Etching Mask

Nanoporous Membrane

Versatile, self-assembling, nanoscale lithographic system

Remove polymer block within cylinders (expose and develop)

TEMPLATE CHARACTERIZATION

SAXS
PS/PMMA
MW = 42,000

SEM

Array Period = 24 nm
Pore Diameter = 14 nm

Nanomagnets in a Self-Assembled Polymer Mask

nanoporous template

1x10^{12} magnets/in^2

Data Storage...
...and More
**Programmed Assembly**

**NANO EXAMPLES**


“Programmed” Assembly

(A) Diagram of Preparation of Nanoparticle-Lipid Composite Films by Electrostatically Controlled Entrapment from Solution

(B) Diagram Illustrating the Generation of Spatially Separate, Patterned Hetero-colloidal Particle Assemblies in Thermally Evaporated Octadecylamine Films

“Programmed” Assembly

But there is much more than mere atomic/molecular self-assembly!

TO REALLY GET INTO PROGRAMMED SELF-ASSEMBLY WE NEED TO LEARN ABOUT:

ORGANIC CHEMISTRY \rightarrow DNA REPICATION \rightarrow ET CETERA

Programmed DNA Folding to Make "DNA Origami"


Using Synthetic DNA for Designer Structures

Designer DNA molecules can be synthesized chemically, and allowed to assemble into a specific configuration of lowest energy.

Ned Seeman, NYU

“Programmed” Self-Assembly

How do we get to these levels of complexity?
For every product, the structure of the parts must encode the structure of the whole. This requires that components be more complex, which tends to make design and fabrication more difficult. Partitioned by complex internal interfaces that have no operational function. Unless they are strengthened after assembly, these interfaces will weak. These are major constraints.

Self-assembly has a fundamental advantage over mechanically directed assembly: It requires no machinery to move and orient components, letting random, Brownian motion do the job instead. Molecular synthesis methods and self-assembly can be used to produce atomically precise nanosystems by the billions, and even by the ton, thereby establishing a technology base with wide-ranging applications that can drive development forward.

The architecture of biomolecular fabrication is based on the use of programmable machines to produce the complex parts necessary for self-assembly of complex systems. The same fundamental architecture can be extended to use artificial biomolecular machines (and then non-biomolecular machines), resulting in products made of better and more diverse engineering materials.
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