Fabrication Methods: Chapter 4

Often two methods are typical

**Top Down**
- Begins with bulk materials
- Reduced in size to nano
- By thermal, physical
  Chemical, electrochemical means

**Bottom Up**
- Begins with atoms or molecules
- React to form nanostructured materials
- Dots: wires, thin films (zero, one and two Dimensions)
Some “blurring” of methods (crossover between bulk and microscopic)
Can be argued during the synthesis

Example: formation of carbon nanotubes by laser ablation

Armchair, zig-zag and chiral nanotubes
Looks “top down”

Starts with lump of carbon

Hit with laser

Forms nanotubes

Laser ablation chamber
However: the nanotubes re-form from atoms and molecules knocked off
The bulk sample by the high energy laser beam.

This “catalytic” process is definitely “bottom up”

We have fabricated well-organized arrays
of self-assembled functional DNA
nanotubes on the sub-millimeter scale by
combining the bottom-up and top-down
methods. We have also demonstrated that
such DNA-nanotube arrays can efficiently
direct the assembly of arrays of quantum
dots, proteins, and DNA targets. The results
are published in Angewandte Chemie

C Lin, Y. Ke, Y. Liu, M. Mertig, J. Gu, H. Yan,
"Functional DNA nanotube arrays: bottom-up
meets top-down", Angewandte Chemie

Wednesday, 08 August 2007

Bottom-up meets top-down

Mixture of BU and TD often termed
hybrid technology

Converge around 30 nm: bulk/nano is not a sharp
transition
Top-Down Methods

Physical fabrication Methods are considered mostly as Top-Down

See: detailed Tables in Chapter 4: let’s look at some specifics

We need to reduce the size of bulk: Top-down methods are therefore considered to be *subtractive*

Reside within the domains of Engineering and Physics

We follow the book and look at some selected methods here

Others will come forward later in the nano program and in the book
Mechanical Methods

Important method

Tungsten ball bearings
Grind away material

Nanomaterials produced
Are full of defects

Wide range of sizes

Transmission electron micrograph for 5 hours dry milled zinc ferrite.
Thermal Methods

External source of heat is applied

1. Chill Block Melt Spinning

Simple idea: bulk material is melted

Formed into a stream which hits spinning target: rapid quenching

2. Gas Atomization

High Energy beam of inert gas is fired at molten metal stream

Knocks off atoms etc which solidify into nanoparticles
High Energy Methods

Arc Discharge, laser ablation and solar vaporization are important top-down Methods.

Arc Discharge

Developed in early 1980’s

Forms SWCNT as long
As catalyst is present

Rather dirty
Many unwanted products
Laser Ablation

We met this earlier: developed in mid-1990’s

Graphite targets at 1200K are exposed to laser pulses
Heat generated from furnace and laser

Vaporized carbon is condensed on a cold “finger”
Solar Furnaces

Solar Power used to make CNT’s by Top-Down Methods

Scale-up of laser ablation methods is difficult

The 10-kilowatt HFSF consists of a tracking heliostat and 25 hexagonal mirrors to concentrate solar radiation. The solar furnace can nominally provide flux at 2,500 suns, but, when required, can use specialized secondary optics to generate significantly higher concentrations (greater than 20,000 suns).

Goal is to get to 500kW
Plasma Methods

What is a Plasma?

Plasma is a partially ionized gas: some electrons are free. The ability of the positive and negative charges to move somewhat independently makes the plasma electrically conductive: responds strongly to electromagnetic fields.

Inside the Test Chamber
One way of growing nanotubes is in a hot plasma gas which consists of a whirling mixture of Hydrogen, carbon and metal particles. As this hot soup of elements cools, carbon condenses around the particles of metal catalyst, forming carbon nanotubes.
Apparatus

In reactive Ion etching the trajectory of the ions is mostly normal to the plane of the substrate, this gives anisotropic etching unlike Chemical etches which are isotropic.
Chemical Top Down Methods

**Combustion:** contaminants such as oils tend to preclude high purity products
Has been used for MgO (see book –very brief)

**Chemical Etches:**

Important process: For example in lithography (see later)

Chemical Etching of Silicon is an industrial process

The anisotropic etching of silicon is a ubiquitous process in micromachining.

\[
\text{Si (s) + 4 KOH (aq) } \rightarrow \quad [\text{SiO}_4]^{4-} + 4\text{K}^+ + 2\text{H}_2 (g)
\]

\text{Si\{100\} surface etches the quickest of the low (miller) index planes}
Anodizing and Electropolishing

Anode: recall CHEM 1050: Anode means oxidation

Anodizing creates an insulating porous layer on a conductive anode material

-usually Aluminum

Produces regular pore system

Template for synthesizing nano materials

Pore diameter and length are controllable

10 to 50 nm

i-pod nano
-anodized aluminum!
What’s it look like?

A top view of PAA with 50 nm pores that was created by anodizing aluminum in 0.3 M oxalic acid at 40 V and 40°C. More than 10 billion pores are present on a 1 cm² piece of anodized alumina.
Electrochemical Reactions

Anodic: $2\text{Al}^0 (s) \rightarrow 2\text{Al}^{3+} + 6\text{e}^-$

Oxide-electrolyte interface

$2\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+$

Cathodic Reaction

$6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2$

Overall: $2\text{Al}^0 (s) + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2$

-mixed method: top down and bottom up