Chapter 10:
Nanostructures and Solids with Low-Dimensional Properties

**Nanoscience**: the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties differ significantly from those at larger scale.

**Nanotechnology**: the production and application of structures, devices, and systems for controlling shape and size at the nanometer scale.
How big is a nanometer?

- Consider a human hand

10 centimeters, 1 centimeter, 1 millimeter, 100 microns, 10 microns, 1 micron, 100 nanometers, 10 nanometers, 1 nanometer.
Using Light to See

- The naked eye can see to about 20 microns
  - A human hair is about 50-100 microns thick
- Light microscopes let us see to about 1 micron
  - Bounce light off of surfaces to create images

Using Electrons to See

- Scanning electron microscopes (SEMs), invented in the 1930s, let us see objects as small as 10 nanometers
  - Bounce electrons off of surfaces to create images
  - Higher resolution due to small size of electrons

Greater resolution to see things like blood cells in greater detail
**Touching the surface**

- **Scanning probe microscopes**, developed in the 1980s, give us a new way to “see” at the nanoscale.
- We can now see really small things, like atoms, and move them too!

This is about how big atoms are compared with the tip of the microscope.

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**Nanoparticle morphology**

www.nature.com/nmat/journal/v6/n9/fig_tab/nmat1957_F1.html
Electronic Structure

Density of states

Semiconducting nanotube

Optical Properties
Nanoparticles

Smallest nanoparticles resemble molecular absorptions

Larger nanoparticles have featureless absorptions resemble bulk solid

Nanogold

• **Well... strange things happen at the small scale**
  – If you keep cutting until the gold pieces are in the nanoscale range, they don't look gold anymore... They look RED!
  – In fact, depending on size, they can turn red, blue, yellow, and other colors

• **Why?**
  – Different thicknesses of materials reflect and absorb light differently
Optical properties

Zinc oxide

- **Large ZnO particles**
  - Block UV light
  - Scatter visible light
  - Appear white
- **Nanosized ZnO particles**
  - Block UV light
  - So small compared to the wavelength of visible light that they don’t scatter it
  - Appear clear

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Magnetic properties

<table>
<thead>
<tr>
<th>Solid</th>
<th>$D_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>14</td>
</tr>
<tr>
<td>Co</td>
<td>70</td>
</tr>
<tr>
<td>Ni</td>
<td>55</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>55</td>
</tr>
</tbody>
</table>
Physical Properties:

Melting Point

- **Melting Point (Microscopic Definition)**
  - Temperature at which the atoms, ions, or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a “fixed” position in a solid.
  - Surface atoms require *less* energy to move because they are in contact with *fewer* atoms of the substance.
  - In contact with 3 atoms
  - In contact with 7 atoms

<table>
<thead>
<tr>
<th>Majority of atoms are:</th>
<th><strong>macroscale</strong></th>
<th><strong>nanoscale</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>almost all inside the object</td>
<td>split between the inside and the surface</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Changing an object’s size:</th>
<th><strong>macroscale</strong></th>
<th><strong>nanoscale</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>has minimal effect on the % of atoms on the surface</td>
<td>has a substantial effect on the % of atoms on the surface</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The melting point:</th>
<th><strong>macroscale</strong></th>
<th><strong>nanoscale</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>doesn’t depend on size</td>
<td>is lower for smaller particles</td>
</tr>
</tbody>
</table>
Fabrication Methods

- **Atom-by-atom assembly**
  - Like bricklaying, move atoms into place one at a time using tools like the AFM and STM

- **Chisel away atoms**
  - Like a sculptor, chisel out material from a surface until the desired structure emerges

- **Self assembly**
  - Set up an environment so atoms assemble automatically. Nature uses self assembly (e.g., cell membranes)

Self Assembly by Crystal Growth

- **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**
Graphite

Intercalation Compounds of Graphite

KC₈

CaC₈

N(E)

E
“Each Volt’s battery cell contains a carbon anode (the negative electrode), a manganese-based cathode (the positive electrode) and a safety reinforced separator, which provides the medium for the transfer of electrical charge ions between the anode and the cathode inside the battery cell.”

Buckminster Fullerene

The Nobel Prize in Chemistry 1996

Robert F. Curl Jr.  
USA
Rice University, Houston, TX, USA

Sir Harold W. Kroto  
United Kingdom
University of Sussex, Brighton, United Kingdom

Richard E. Smalley  
USA
Rice University, Houston, TX, USA

“for their discovery of fullerenes”
Carbon Nanotubes

- Using new techniques, we’ve created amazing structures like carbon nanotubes
  - 100 time stronger than steel and very flexible
  - If added to materials like car bumpers, increases strength and flexibility

Armchair nanotubes are metallic. Zig-zag and chiral nanotubes can be either metallic or semiconducting.
Arc-discharge Laser Furnace
• Hydrocarbon vapor passed through a tube furnace.
• SWNTs or MWNTs depends on size and temperature of catalyst (Fe, Ni with NH₃).
• Low-temperature (600-900°C) yields MWNTs, higher temperature (900-1200°C) favors SWNTs.
Problems with CNT production
• Mixture of metallic and semiconducting
• Alignment and positioning

A breakthrough?
• ST-cut single crystal quartz substrates
• Ethanol/methanol as carbon source
• Cu nanoparticles as catalysts

Results
• 1.55 to 1.78 nm diameter SWNT
• 95% semiconducting
• CNT aligned
Space Elevator

Space Elevator Cable

![Graph showing comparison of density and strength for Steel, Kevlar, and Carbon nanotubes.](image)

- **Density, kg/m³**
  - Steel: 7500
  - Kevlar: 1500
  - Carbon nanotubes: 950

- **Required Strength, GPa**
  - Steel: 350
  - Kevlar: 100
  - Carbon nanotubes: 150

- **Actual Strength, GPa**
  - Steel: 330
  - Kevlar: 90
  - Carbon nanotubes: 140
Photolithography
The Nobel Prize in Chemistry 2000

"for the discovery and development of conductive polymers"

Alan J. Heeger

1/3 of the prize
USA
University of California
Santa Barbara, CA, USA
b. 1936

Alan G. MacDiarmid

1/3 of the prize
USA and New Zealand
University of Pennsylvania
Philadelphia, PA, USA
b. 1937
(Leicester, New Zealand)
d. 2007

Hideki Shirakawa

1/3 of the prize
Japan
University of Tsukuba
Tokyo, Japan
b. 1936

Polyacetylene

Conjugated polymers

insulators
semiconductors
metals

Conductivity
quartz
diamond
glass
silicon
germanium
copper iron silver
Conducting polymers: Repeating units

Polymer structures:
- Polypyrrole
- Polythiophene
- Polyaniline
- Polyphenylenevinylene

Bonding in Polyacetylene

[Diagram showing bonding energy (E) for polyacetylene with Peierls' Theorem]
<table>
<thead>
<tr>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conjugated polymer</td>
</tr>
<tr>
<td>ITO</td>
</tr>
<tr>
<td>Glass</td>
</tr>
</tbody>
</table>

**Organic Polymer LED**

**OLED Structure**

- Cathode
- Emissive Layer (Organic Molecules or Polymers)
- Conductive Layer (Organic Molecules or Polymers)
- Anode
- Substrate

**OLED Creating Light**

1. Electrical current flows from the cathode to the anode through the organic layers, giving electrons to the emissive layer and removing electrons from the conductive layer.

2. Electrons flow from the cathode and holes flow from the anode.

3. The holes jump to the emissive layer and recombine with the electrons. As the electrons drop into the hole, they release their extra energy as light.

**Light Photon**

www.mrsec.wisc.edu/Edetc/SlideShow/slides/oLED/oLEDspin_mov.html
www.mrsec.wisc.edu/Edetc/SlideShow/slides/oLED/oLEDevap_mov.html
OLED vs. LCD

**Advantages**
- no backlight or polarizer
- wider viewing angle
- lower power consumption
- easier processing
- thinner and lighter
- faster response time

**Disadvantages**
- lifetime and color stability
- newer technology

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**OLED TV**
Sony 11-inch OLED TV is 3 mm thick with a 1,000,000:1 contrast ratio.

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**OLED MP3/Video Player**
Cowon S9 16 GB
iriver Clix Rhapsody

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**OLED Phone**
Nokia 7500 Prism Tri-Band GSM Phone

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**Keyboard Extender**
Flexible OLED and Roll-to-Roll Manufactured OLEDs

Molecular metals – 1D

molecular nanowires
Molecular metals – 2D

Polymers and Ionic Conduction
Rechargeable Lithium Batteries

\[
\text{Li(s)} \rightleftharpoons \text{Li}^+ \text{(solv)} + \text{e}^- \quad \text{and} \quad x\text{Li}^+\text{(solv)} + \text{TiS}_2(s) + xe^- \rightleftharpoons \text{Li}_x\text{TiS}_2(s)
\]

Overall: \[x\text{Li(s)} + \text{TiS}_2(s) \rightleftharpoons \text{Li}_x\text{TiS}_2(s)\]
**TABLE 6.1**

Conductivities of polymer-metal salt complexes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular mass</th>
<th>Salt</th>
<th>Conductivity/Sm$^{-1}$</th>
<th>Temperature range/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>400</td>
<td>LiBF$_4$</td>
<td>$3.1 \times 10^{-4} - 3.1 \times 10^{-5}$</td>
<td>298 – 450</td>
</tr>
<tr>
<td>PEO</td>
<td>$5 \times 10^6$</td>
<td>LiBF$_4$</td>
<td>$10^{-5} - 10^{-7}$</td>
<td>298 – 450</td>
</tr>
<tr>
<td>PEO</td>
<td>$4 \times 10^6$</td>
<td>CH$_2$COOLi (O/Li = 4)</td>
<td>$3.16 \times 10^{-5} - 10^{-6}$</td>
<td>298 – 420</td>
</tr>
<tr>
<td>PEO</td>
<td>$4 \times 10^6$</td>
<td>CH$_2$COOLi (O/Li = 9)</td>
<td>$10^{-4} - 10^{-5}$</td>
<td>298 – 420</td>
</tr>
<tr>
<td>PEO</td>
<td>$4 \times 10^6$</td>
<td>CH$_2$COOLi (O/Li = 18)</td>
<td>$10^{-4} - 10^{-5}$</td>
<td>298 – 420</td>
</tr>
<tr>
<td>PEO (cross-linked)</td>
<td>3000</td>
<td>LiClO$_4$</td>
<td>$10^{-3} - 10^{-9}$</td>
<td>253 – 273</td>
</tr>
<tr>
<td>PEO (linear)</td>
<td>3000</td>
<td>LiClO$_4$</td>
<td>$10^{-8} - 10^{-11}$</td>
<td>253 – 273</td>
</tr>
</tbody>
</table>
AFM Probe Tip

600 nm deep trenches; 250 nm wide

image using conventional tip