Nanomaterials
CNTs and Applications

2.674
Jeehwan Kim
Nanomaterials

• Growing, Touching and Observing

• For lab #7
  – CNT growth
  – Surface drop test
How small is small?

- Atomic radius of silicon = 0.1 nm
- Size of one unit cell of silicon = 0.542 nm
- Atomic radius of carbon = 0.07 nm
- Size of one unit cell of diamond = 0.357 nm
- Thickness of hair/paper = 100 um $\rightarrow 10^5$ nm
  $\rightarrow$ around million atoms

Size of transistors in your computer $\rightarrow 14$ nm
$\rightarrow$ In $14 \times 14$ nm$^2$ channel: 4900 atoms
Semiconductor Materials

Semiconductor: Materials that can be switched between conductors (1) and insulators (0)

→ Digital electrical signal is composed of 0 (off) and 1 (on) to form logics

IV semiconductor

III-V compound semiconductor

Transition metal Dichalcogenide (TMDC) semiconductors

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Emerging nanomaterials
(Low-dimensional materials)

- **2D**: Single-atom thickness films
  - Flexible electronics
  - Sensors

- **1D**: Nanowires
  - Quantum electronics
  - Biosensors
  - Solar cell, photodetector

- **0D**: Quantum dots
  - Single electron transistor

**Why small??**
Quantum confinement, high surface area, Flexibility

Peter Allen, UCSB
Appl. Phys. Lett. 100, 143108 (2012);
Intech "Lithography", Michael Wang

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Carbon-based nanomaterials

**Basic building block**

- **Graphite (3D)**: van der Waals stack of graphene. Conductor.
- **Carbon nanotube (1D)**: Rolled graphene. Semiconductor (2/3) or metal (1/3).
- **Diamond (3D)**: sp3 bonding of carbons. Wide band gap (5.5 eV).
- **Fullerene (0D)**: Wide band gap (5.5 eV).

Single element carbon shows different functionality depending on its dimension.
History of nanomaterials

• 1959: Richard Feynman’s famed talk. “There's Plenty of Room at the Bottom”

• 1981: Binnig and Rohrer created the STM to image individual atoms. (Nobel, Physics 1986)

• 1985: Curl, Kroto, Smalley discovered fullerene (Nobel, Physics 1996)


• 2010 A. Geim and K. Novoselov (Nobel physics on Graphene)
Graphene overall orbital structure
# Properties of graphene

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<tr>
<th>Property</th>
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<th>Si</th>
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The way of rolling up graphene to form CNT

Diameter determines band gap
Chirality determines semiconductor or metal

Armchair | Zigzag | Chiral
--|---|---
Metallic | Semiconducting | Intermediate

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Possible Chiral Vectors

\[
\text{Ch} = na_1 + ma_2
\]

\[
|Ch| = \sqrt{3}a_{cc} \sqrt{n^2 + nm + m^2}
\]

\[
d_{\text{tube}} = \frac{\sqrt{3}a_{cc}}{\pi} \sqrt{n^2 + nm + m^2}
\]

\[
\square = \tan \left[ \frac{\sqrt{3}m}{2n+m} \right]
\]

\[(n-m) = 3q \quad \text{metallic}
\]

\[(n-m) = 3q \pm 1 \quad \text{semiconducting}
\]
## Properties of Carbon Nanotubes

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Application of CNT: Electronics (CNT forest)
Application of CNT: Energy storage (CNT forest)
Application of CNT: Solar cell electrode (CNT network)


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Application of CNTs: Atomic Force Microscope tips

Reduced diameter – maximum atomic imaging resolution (Lab 10)
Application of CNT: Superhydrophobic surface (CNT forest)

Nano Letters, 2003, 3 (12), pp 1701–1705
Application of CNTs: Electronics (Single CNT)

- Transistor technology

**Past: Silicon**
- 130 nm (2001)
- 90 nm (2003)
- 65 nm (2005)
- 45 nm (2007)
- 32 nm (2009)
- 22 nm (2011)

**Past: Strained Silicon**

**Current: FIN Silicon**
- 14 nm (2016)

Introduction of strained silicon technology

**Future??**
- Ge pFETs/
- III-V nFETs
- CNT FETs
- Nanowire FETs

Single CNT transistor

Electron mobility of CNT is 2 orders of magnitude higher than that of silicon

Nano Lett., Vol. 4, No. 1, 2004
Chemical vapour deposition (CVD)

CNT Forest formed by metal nanosphere catalyst

Longest CNTs grown?

Class award

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Diameter: 150~250nm
Length: 3~10μm

(H.W. Lee, S. Kim, and S.G. Kim, MIT)
Understanding CNT growth
: Formation of metal nanoparticles

Metal cannot completely wet Al$_2$O$_3$

$\gamma_{\text{metal/Al}_2\text{O}_3} + \cos \theta \gamma_{\text{metal/vapor}} > \gamma_{\text{Al}_2\text{O}_3/vapor}$

Metal cannot completely wet Al$_2$O$_3$

$\Rightarrow$ Discontinuous metal islands are automatically formed at ultrathin thickness
Understanding CNT growth
: Catalytic reaction with metal particles

Catalytic metals: Fe, Ni, Co

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Growth modes

Tip-growth mode
(weak interaction at substrate/metal)

Base-growth mode
(strong interaction at substrate/metal)

- SWNT, single-walled nanotube (0.3 < d < 3 nm)
- MWNT, multi-walled nanotube (d > 10 nm)

Carbon Nanotube Synthesis and Growth Mechanism
By Mukul Kumar (intechopen.com)
Understanding CNT growth: Role of catalytic metals & Al$_2$O$_3$

Role of catalytic metals

CNT growth sequence
- C dissolution into the catalyst
- $\rightarrow$ C supersaturation
- $\rightarrow$ C precipitation on catalytic nanoparticles
- $\rightarrow$ CNT growth from the periphery of nanoparticles

Role of Al$_2$O$_3$

Al$_2$O$_3$ enhances CNT growth

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In-situ observation of CNT growth

• In-situ TEM

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Challenges for Carbon Nanotube Applications

• Process control to produce nanotubes with same diameter and chirality.
  - **Purification**/sorting methods required for uniform CNT
  - **Placement**/alignment methods required for long-range order

• Develop large-scale, high productivity synthesis methods.

• Develop large-scale, long range order assembly processes deterministically.

• **ASSEMBLY, ASSEMBLY, ASSEMBLY!!!**
• Graphene → Lab 11
Placement: Key issue to realized benefit of CNT

Requirement:
- High density of individual CNTs (transistor density x CNTs/transistor ~ $10^{10}$/cm$^2$)
- Alignment with a constant pitch (< 10 nm)
- Compatibility with wafer-scale CMOS process
- Compatibility with a process for high purity of semiconducting CNTs

By David Frank, IBM, 2013

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Aligned growth of CNTs

Lateral growth of CNT at the step edges of sapphire wafers

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Conventional placement options

**Dielectrophoresis**

- **Nano Lett. 7, 1556 (2007)**
- 4×10⁶ sites/cm²
- AC bias (~ MHz)

**Dip-pen Nanolithography**

- **Nature 425, 36 (2003)**
- 10⁶ sites/cm²
- **PNAS 103, 2026 (2006)**
- 10⁷ sites/cm²

**Challenges:**

- Biasing to billions of transistors
- Scaling: limitation of minimum pad size
- Density: interference between electrodes
Specific Surface Functionalization

Strong electrostatic interaction between CNTs and surface monolayer

- **Surface monolayer (NMPI):** self-assembled on HfO₂ → **Positively charged**
- **CNTs:** dispersed in a normal surfactant solution (1% SDS) → **Negatively charged**


NMPI: 4-(N-hydroxycarboxamido)-1-methylpyridinium iodide
Position control: excellent selectivity and high density

Ion-exchange chemistry enables high density and potential for scaling

- Coulombic bonding → high density in small dimensions

SAN FRANCISCO — I.B.M. scientists are reporting progress in a chip-making technology that is likely to ensure that the basic digital switch at the heart of modern microchips will continue to shrink for more than a decade.

The advance, first described in the journal Nature Nanotechnology on Sunday, is based on carbon nanotubes — exotic molecules that have long held out promise as an alternative to silicon from which to create the tiny logic gates now used by the billions to create microprocessors and memory chips.

The I.B.M. scientists at the T.J. Watson Research Center in Yorktown Heights, N.Y., have been able to pattern an array of carbon nanotubes on the surface of a silicon wafer and use them to build hybrid chips with more than 10,000 working transistors.
# CNT vs Graphene

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Why graphene?

Flat/Monolayer/Single-crystalline Uniform in a LARGE SCALE

First single-crystalline wafer-scale graphene

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Application of CNT: Superhydrophobic surface (CNT forest)

Nano Letters, 2003, 3 (12), pp 1701–1705

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Super hydrophobicity (Lab 7)

Hydrophobic, $\theta > 90^\circ$

Hydropilic, $\theta < 90^\circ$

Super hydrophobic, $\theta > 150^\circ$

- Chemical modification, coating
- Nanostructured surface

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Super hydrophobicity (Lab 7)

Wenzel’ s model
- If the surface has a high free energy, roughness promotes wetting.
- If it has low free energy, roughness promotes hydrophobicity.

\[
\cos\theta^* = r \cos \theta
\]

\[
r = \frac{\text{actual\_area}}{\text{projected\_area}}
\]

\[
\theta^* = \text{apparent\_contact\_angle}
\]

Cassie’ s model
- Wettability of heterogeneous (solid+air) surfaces
- Contact angle on air fraction is 180°.

\[
\cos\theta^* = -1 + \phi_s (\cos\theta + 1)
\]

\[
\phi_s = \text{solid\_fraction\_surface}
\]
Super hydrophobicity (Lab 7)

Bouncing a water drop

**Deposition**

**Splash**

**Breakup**

reboun ding
When kinetic energy is very high

Restitution ratio = $|v'/v|$

$= \frac{\text{Relative speed after collision}}{\text{Relative speed before collision}}$

$\text{We} = \frac{\rho V^2 R}{\gamma} = \text{kinetic energy/surface energy}$

$\rightarrow \text{Bouncing patterns determined by Weber number}$

Low We: No deformation/Mid We: Deformation/High We: Break off
Lotus Effect

- Some plant leaves have near $170^\circ$ contact angle, and show no accumulation of dirt. (Lotus Effect)
- Superhydrophobicity by nano patterned surface
- Self-cleaning surface (no car wash?)


Nanotech Lecture: ‘Self-Cleaning Surfaces’ by Dr. Vesselin Paunov

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Super hydrophobicity (Lab 7)

Bouncing a milk drop

H. Doc Edgerton, MIT

MIT TechTV