Carbon Nanotubes for Nanoelectronics - Synthesis and Integration

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What is Carbon Nanotube?

✓ Single-walled nanotube (SWNT) consists of a single layer of graphene sheet.

✓ Multi-walled nanotube (MWNT) consists of a set of concentrically nested SWNTs. The inter-shell distance is about 0.34 nm, similar to that of turbostratic graphite.
Different Structures of Nanotubes

Theoretically, there are indefinite ways to roll-up a graphene sheet into nanotubes. Each nanotube can be uniquely denoted by an index \((n, m)\).

\[
\bar{C}_h = n\bar{a}_1 + m\bar{a}_2 \equiv (n, m)
\]

\[
\begin{align*}
d_i &= \frac{L}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \\
\theta &= \tan^{-1} \frac{\sqrt{3m}}{2n + m}
\end{align*}
\]

- **armchair**  \(\theta = 30^\circ\)  
  \((n, m) = (5, 5)\)

- **zigzag**  \(\theta = 0^\circ\)  
  \((n, m) = (6, 0)\)

- **chiral**  \(0 < \theta < 30^\circ\)  
  \((n, m) = (10, 5)\)

Example \((4, 2)\)
Nanotube: Metal or Semiconductor?

\[ n - m = \begin{cases} 
3p & \text{metal} \\
3p \pm 1 & \text{semiconductor} 
\end{cases} \]
Nanotube Structure vs Electronic Property

The interband transition energies $E_{ij}$ are uniquely determined by the diameter and chiral angle. The trigonal warping effects increase with decreasing chiral angle. This causes a deviation of $E_{ij}$ from $E_{ij} - d_t$ curves for chiral tubes (splitting or shifting of van Hove singularities).

**Diameter dependence:** $E_{ij} \propto 1/d_t$
- e.g. Metallic tubes: $E_{11}^M \approx 6 \gamma_0 a_{C-C} / d_t$
- Semicon. tubes: $E_{11}^S \approx 2 \gamma_0 a_{C-C} / d_t$
  $E_{22}^S \approx 4 \gamma_0 a_{C-C} / d_t$
  $E_{33}^S \approx 8 \gamma_0 a_{C-C} / d_t$

**Chiral angle $\theta$ dependence:**

The trigonal warping effects increase with decreasing chiral angle. This causes a deviation of $E_{ij}$ from $E_{ij} - d_t$ curves for chiral tubes (splitting or shifting of van Hove singularities).
Why Nanotubes?

**Perfect geometry**
- ~ 1 nm diameter
- 1-D nanowire with extremely high aspect ratio

**Perfect atomic structure**
- Single crystal & single molecule

**Perfect properties**
- Mechanical: resilience; tensile strength; Young’s modulus
- Thermal: stability; conductivity
- Chemical: stability
- Electrical: metallic & semiconducting, ballistic transport, high current density, low electromigration rate, high carrier mobility…
Nanotube Electronics

Advantages of nanotube transistor...

- No surface state.
- High carrier mobility or **ballistic transport**.
- Natural thin channel to minimize short channel effect.
- Unique geometry enabling better gate-channel capacitive coupling through “fringe field” of the surrounding dielectrics.

**Ballistic nanotube FET** (inset: Fabry-Perot-like interference pattern at $T = 1.5\, {\text{K}}$, bright peak $G \sim 4e^2/\text{h}$)
Nanotube Electronics

Other Nanotube Opportunities

- Room-temperature single-electron transistor
- Optoelectronics
- Nano-electro-mechanical devices
- Interconnect
- Thermal interface materials
- Nano-sensors
- High density memory devices
How to Build Nanotube Chips?

Microchips
Top-down method
Nanochips
Bottom-up?
Top-down?
Bottom-up + Top-down?

90nm process
2003 production

65nm process
2005 production

45nm process
2007 production

32nm process
2009 production

22nm process
2011 production
Major Challenges for HVM of CNT Devices

✓ Electronically pure material: precise property control
  – Pure metallic nanotubes for on-chip interconnection.
  – Pure semiconducting nanotubes with a well-defined energy-gap for high performance transistors and memory devices.

✓ Patterning technology: precise registry and orientation control
  – Array with regular spacing.
  – Connection to electrodes.
Synthesis of Carbon Nanotubes

- **Arc Discharge**
- **Laser Ablation**
- **Chemical Vapor Deposition (CVD)**

- Controllable process
- Direct growth on substrate
- Clean nanotubes
- Inexpensive

**Type of nanotube:**
- MWNT or SWNT
- Diameter
- Location
- Orientation
- Length
- Chirality
  - Metallic or semiconducting
Arc Discharge
- HREM of SWNT and peapod structure

Laser Ablation - in nitrogen atmosphere

Y. Zhang et al., Appl. Phys. Lett. 73, 3827 (1998)

With NiCo catalyst
Without NiCo catalyst
Exploring Exotic Nanotube Properties

Nanoelectromechanical System (NEMS)
Optomechanical device
Optoelectronics

Novel Heterostructured Nanotubes
- BCN & C composite nanotubes

Novel Heterostructured Nanowires
- Coaxial Nanocable

Controllable Synthesis of Carbon Nanotubes

Arc Discharge
Laser Ablation
Chemical Vapor Deposition (CVD)

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Type of nanotube:
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Controlling Nanotube Type

Type of catalyst
- Metal nanoparticle
  - Tube nucleation
Supporting materials
- Make/disperse, keep nanoparticles
Growth condition
- Feedstock gas
  - Provide carbon
- Carrier gas
  - Adjust reaction
- Temperature
  - Decompose hydrocarbon
  - Anneal out defects

MWNT: C₂H₄, 700°C (Dai group)
SWNT: CH₄, 900°C
DWNT: CH₄+H₂, 900°C (Y. Zhang, unpublished data)
Controlling Nanotube Diameter

- by controlling nanoparticle size

Controlling Location – Catalyst Patterning

1. **PDMS stamp with catalyst coating**
2. **Catalyst transfer**
3. **Remove stamp**
4. **Inked Si Substrate**
5. **1. Calcine 2. CVD**
6. **Directed nanotube bridges**
Controlling Orientation - I
- Self-directed Growth of Suspended SWNT

(Y. Zhang, unpublished data)
### Controlling Orientation – II

**Electric-field-directed Growth**


<table>
<thead>
<tr>
<th>Electrode</th>
<th>Carbon Nanotube</th>
<th>Catalyst</th>
<th>Poly-Si</th>
<th>Quartz</th>
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**Images:**

- **0 V DC, 0 V/μm**
  - Scale: 5 μm

- **20 V DC, 0.5 V/μm**
  - Scale: 10 μm
Other Issues Regarding Nanotube IC

- Interconnection ✓
- Ohmic Contact
- Doping
  - Intrinsic semiconducting nanotube?
- Environment
  - Why semiconducting nanotube is p-type?
- Device stability
- Dielectric materials and Gate materials
  - Compatibility with nanotube IC
Ohmic Contact
- SWNT/metal contact

Ideal Contact Solution
- Nanotube-nanowire nanojunctions

Novel NT/NW Heterostructures
- Nanowire and NW/NT Heterojunctions


SiC-SWNT

TiC-SWNT
Novel NT/NW Heterostructures
- Hybrid nanotube-nanowire devices


Carbon Nanotube welded on a STM tip through TiC formation

Ti tip
TiC nanorod
Carbon nanotube

TiC
Nanotube

100 nm
Application: Probe-based data storage


PFM: http://www.home.agilent.com/upload/cmc_upload/All/AN-PiezoRes_103107F.pdf
PFM principles

Piezoresponse Force Microscopy

AFM probe with initial deflection up

Ferroelectric domain with polarization \( \vec{P} \)

Electric field, \( \vec{E} \), parallel to \( \vec{P} \) applied to ferroelectric domain

Ferroelectric domain expands and bends the AFM cantilever up, more than the initial deflection

AFM probe with initial deflection up

Ferroelectric domain with polarization \( \vec{P} \)

Electric field, \( \vec{E} \), anti-parallel to \( \vec{P} \) applied to ferroelectric domain

Ferroelectric domain contracts, and reduces upward bending of AFM probe

Advantage of using CNT probe

- Small diameter $\to$ small recording bit size $\to$ high data storage density
- Good electrical conductivity $\to$ electrical read/write
- Good mechanical strength $\to$ low wear rate
- High aspect ration $\to$ No degradation of resolution with wear $\to$ wear tolerant

**Weak Point:** buckling for long tubes, especially for SWNTs, under contact mode operation

**Solution:** dielectric enhancement: keeping small electrical contact; much stronger for contact mode operation.
Nanopencil W/R on ferroelectric media

Sharpening Nanopencil


Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization
Prototype CNT-QD Device

Back gated carbon nanotube FET (CNTFET) – Prior art
Degenerately doped Si
100 nm thermal gate oxide
5nm Cr / 50 nm Au source/drain

NV-memory: Superstructure on CNFET containing innovation:
Deposit 5 nm evaporated SiO₂
Deposit Au thin film and form nanocrystals
Cap the device with 30 nm PECVD oxide
Etch (RIE) open the pads for electrical measurements

Nanotube (1D) vs Si (2D) for nano-floating gate memory

Electrostatics due to nanocrystals:
Charged nanocrystals produce an egg-crate like potential well structure on the plane below or above

Nanotube based FET
- Cylindrical approximation for capacitance calculation – improved electrostatic coupling with gate – low r/w voltage.
- 1D electron system
- Transport in 1D – no percolation
- Electron is confined to nanotube and cannot circum-navigate around barriers
- High charge sensitivity

Planar silicon-based structures
- Parallel plate approximation for capacitance calculation
- 2D electron gas under inversion
- Transport governed by percolation
- Charge feels minimal potential during transport
- Minimal charge sensitivity
CNT-QD Memory Device at RT

Charging efficiency with traps:
\[ \frac{\Delta V_{th}}{\Delta V_{charge}} = \frac{1.2V}{3V} = 0.4 \]

Charging efficiency with QD:
\[ \frac{\Delta V_{th}}{\Delta V_{charge}} = \frac{2V}{3V} = 0.67 \]

\( I_D \) vs \( V_G \) for device **without nanocrystals** showing charge injection into traps in the evaporated SiO\(_2\)

\( I_D \) vs \( V_G \) for device **with nanocrystals** showing charge injection into traps and nanocrystals
CNT-QD Memory Device at Low-Temperature

Separating trap contribution from nanocrystal charging @ T=10K

\[ \Delta V_{\text{th}} / \Delta V_{\text{charge}} < 0.2V / 2.5V = 0.08 \]

\[ \Delta V_{\text{th}} / \Delta V_{\text{charge}} = 1.6V / 3.4V = 0.5 \]

\( I_D \) vs \( V_G \) at \( T=10K \) for device WITHOUT NANOCRYSTALS showing MINIMAL charge injection

\( I_D \) vs \( V_G \) at \( T=10K \) for device WITH NANOCRYSTALS showing charge injection into NANOCRYSTALS only
Coulomb blockade in nanocrystals: single-electron charging

(a) Stepping the $V_{CH}$ in fine steps of 50mV shows aggregation of $I_DV_G$ curves (b) Extraction of $V_G$ for arbitrary constant $I_D=0.95\text{nA}$ results in steps in $V_G$ due the combined effect of coulomb blockade in nanocrystals and single charge sensitivity of nanotube conductance.
NEGF Simulation of CNTFET Charge Sensor

Point charge

φ_B = 0.1eV, d_CNT ~ 1.7nm, L_ch = 200nm, t_bot = 100nm, t_top = 5nm

V_D = 0V and V_G = 0.2V

Resonant Tunneling and Charge Position Dependence

(a) $G_D [\mu S]$

(b) $E_C [eV]$

(c) $E_C [eV]$

(d) $E_C [eV]$
“Bottle-neck” Effect and Resonant Tunneling

$\text{SiO}_2$
$p++ \text{ Si}$

$V_D=0 \text{V} \text{ and } V_G=0.2 \text{V}$

$Q_1 = 2 \text{e}, Q_2 = 0$

$Q_1 = 2 \text{e}, Q_2 = 2 \text{e}$
Electrostatic Analysis


### Structural Parameters

<table>
<thead>
<tr>
<th>Structural Parameters</th>
<th>Potential on NC (V)</th>
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<tbody>
<tr>
<td></td>
<td>$d_c$ (nm)</td>
</tr>
<tr>
<td>1NC-CNT BG</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>1NC-CNT TG</td>
<td>30</td>
</tr>
<tr>
<td>3NC-CNT BG</td>
<td>30</td>
</tr>
<tr>
<td>1 NC-Si</td>
<td>0.81</td>
</tr>
<tr>
<td>3 3 NC -Si</td>
<td>0.74</td>
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</tbody>
</table>

Enhancement of electric field asymmetry in the CNT-NC- memory makes it easy to be programmed while keeping similar retention capability compared to the NC planar memory.

nanocrystals diameter: 6 nm; the nanotube diameter 2 nm; pitch: 12 nm; $dt$: 3 nm (Si EEPROM) and 5 nm (CNT-nanocrystal memory); $dc$: 30 nm (Si EEPROM); $dc$ is used as a parameter to calculated capacitive-coupling of CNT nanocrystal memory structure for different $dc$: 27 nm; 30 nm; 100 nm; $p$: 12 nm (for all structures)
Energy Band Diagram - Charging Mechanism

Note: For 1D channel, the fringe field makes the electrostatic potential profile of the back gate geometry the same as top-gate geometry shown here.
Retention Measurements

- **Id vs t retention for device 14**
  - $V_{CH} = -5V; V_{G} = 0V$
  - $V_{CH} = -5.5V; V_{G} = -1V$
  - 900s at $T = 300K$

- **Id vs VG at time=0s and time=6200s**
  - $V_{CH} = -5V$
  - $V_{CH} = -5.4V$
  - 1V shift after t=6200s
  - Negligible shift after t=6200s

- **2D channel: with 20% NC fill ratio.**

- **Metal NC (5e)**

- **Nanotube at 0V**

- **Control gate at 0V (Read/Retention)**

- **Ez field (MV/m)**

- **Distance Z (nm)**

- **Yuegang Zhang**
Major Challenges for HVM of CNT Devices

- **Electronically pure material: precise property control**
  - Pure metallic nanotubes for on-chip interconnection.
  - Pure semiconducting nanotubes with a well-defined energy-gap for high performance transistors and memory devices.

- **Patterning technology: precise registry and orientation control**
  - Array with regular spacing.
  - Connection to electrodes.
Controlling diameter and orientation in CVD process...

- Tube diameter dependence on the size of catalyst nanoparticles
- Electrical-field-directed growth

However...

- The diameter difference of a metallic and a semiconducting nanotube can be as small as merely 0.03 angstroms.
- There is no method available (yet) to control the chirality by controlling catalyst.

- There is no reliable way to control tube-tube spacing (yet).
Alternative Approach: Post-growth Processing

Nanotube functionalization
To isolate individual tubes from mixed bundle

Sorting
Separate nanotube types & sizes

Assembly into functional array
Directed self-assembly
Solubilization of SWNTs

(Prior-arts)

To overcome their poor intrinsic solubility, SWNTs are ultrasonically dispersed as individuals and wrapped with water-soluble surfactants or polymers to make them compatible with microfluidics and self-assembly reactions.
Chondroitin derivatives for selective solubilization

R. Chen et al., to be submitted
Chondroitin derivatives for selective solubilization

UV-vis-NIR

AFM: Chondroitin-Adenine SWNT

R. Chen et al., to be submitted
De-functionalization with small molecules


Poly T$_{30}$-coated CNTs → Molecule replacement initiates DNA desorption → CNTs begin to re-bundle → Desolubilized CNTs precipitate out
De-functionalization using complementary ss-DNA

De-functionalization: Selective Precipitation?


633 nm Excitation

---

Initial SWNT solution
0.05 mM R6G added
0.1 mM R6G added
Optical Trapping: a new method for nanotube sorting

- Laser dipole trap is based on the interaction of electrical field with instantaneous dipole momentum induced in molecules (neutral particles).
- Trapping: Laser frequency < resonant frequency.
- By tuning the laser frequency, M- or S-tubes can be selectively trapped or released.
- Nanotubes can be sorted according to their band-gaps (diameters).
The Physics behind Optical Trapping of Carbon Nanotubes

Induced dipole momentum of a neutral particle in E-field
\[ P = \varepsilon_0 \chi E \]
Energy (isotropic medium)
\[ U = - \langle P \cdot E \rangle = - \varepsilon_0 \chi \langle E \rangle^2 \]
\[ \chi(\omega) = \chi'(\omega) + i \chi''(\omega) \]

When \( \omega < \omega_0 \), \( \chi'(\omega) > 0 \),
\[ \therefore E \uparrow \Rightarrow U \downarrow \]
The particle moves towards the center of a laser beam (assuming a Gaussian intensity distribution).

What is special for 1-D object?
- Dipole always parallel to the axis
  \[ P = P_\parallel + P_\perp \cong P_\parallel = \varepsilon_0 \chi E_\parallel \]
  \[ U = - \langle P \cdot E \rangle = - \varepsilon_0 \chi \langle E \rangle^2 \cos \theta \]
  \[ \therefore E \uparrow \Rightarrow U \downarrow \& \theta \downarrow \Rightarrow U \downarrow \]

Trapping & Alignment
The interband transition energies $E_{ii}$ (therefore, the optical resonance frequencies $\omega_0^{ii}$) are uniquely determined by the diameter and chirality.
If the sample is properly prepared...
If a trapping laser is properly chosen...

Carbon nanotubes

solubilization

Individual tubes

Optical trapping

Further manipulation
Experimental Setup

Lasers: Nd:YVO₄ 1064 nm
Ti:Sapphire 720-1000 nm
Millennia 532 nm

Video of optical trapping of polystyrene beads

Laser power: 100 mW.
Laser wavelength: 1064 nm.
Beads: polystyrene, 4 um in diameter.
Visualizing Nanotube Trapping: “Dark Cloud”

Samples:
- DNA-CNT and DNA-TAMRA mixture.
- DNA-TAMRA concentration (0.003 μM).
- SWNT concentration 0.083 mg/mL.

Laser: 1064 nm; 150 mW (max.)
CNT trapping video

Laser power: 300 mW
Laser wavelength: 1064 nm
CNT-DNA-TAMRA mixture
Optical Sorting in Microfluidic Device

Laser sweeps across the channel to trap CNTs and release them into the water side.
In-situ Raman / Optical Trapping

- Dual Beam -
  O.T. & Raman Spectroscopy

Proceedings of SPIE, Vol 5593, pp. 73-81, 2004
**In-situ Raman / Optical Trapping**

DNA-HiPco: 1064 nm trapping, 785 nm probing

Enrichment of d = 0.9 nm tubes

Reference
- OT ON – 150mW
- OT ON – 300mW

- Raman Shift (cm⁻¹)
  - d=0.9 nm
  - 268 cm⁻¹

- Intensity (a.u.)

- Normalized Intensity
  - Intensity 235 cm⁻¹
  - Intensity 268 cm⁻¹
In-situ Raman / Optical Trapping - Theory

Susceptibility of the carbon nanotubes resonant with 785 nm (1.58 eV) Raman laser

- The susceptibility ($\chi$) of the tubes which are in resonance with the 785 nm Raman excitation are plotted.

- At 1.16 eV (1064 nm), the tube at 268 cm$^{-1}$ has the highest $\chi$ compared to other tubes. This is in agreement with the experiment.
In-situ Raman / Optical Trapping

DNA-HiPco: 1064 nm trapping, 633 nm probing

S-tubes were repelled
**In-situ Raman / Optical Trapping - Theory**

Susceptibility of the carbon nanotubes resonant with 633nm (1.96 Ev) Raman laser

- According to the simulation, the \( \chi \) for the 0.99 nm tube is larger than the \( \chi \) for the 0.88 nm tube, which is somewhat in agreement with the experiment (less repelled).

- But the \( \chi \) for the metallic tubes is even lower than that of the semiconducting tubes. This contradicts with the theory.
Other CNT Manipulation Method:
- CNT Alignment by Molecular Combing

Capillary force: \[ F_{\text{capillary}} \approx \frac{\pi \lambda \theta_o^2}{\log L / D} \]

Hydrodynamic force: \[ F_{\text{hydrodynamic}} \approx \eta l V \]

\[ F_{\text{capillary}} > F_{\text{hydrodynamic}} \]

Elastic deformation of contact line

Liquid surface concedes

- Partial anchoring of linear molecules
- Surface tension stretching for alignment

(Unpublished data)
Other CNT Manipulation Method:
- Dielectrophoresis

- Polarization and associated motion induced in particles by non-uniform electric field

\[
F_{DEP} \propto \varepsilon_m \left( \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \right) \nabla E^2_{\text{rms}}
\]

(Unpublished data)
Future Direction: Controlling Length and End-functionalization

- Lithographically defined length
- Sidewalls protected
- $O_2$ plasma etch CNTs

End-functionalization

Self-assembly

(Unpublished data)
Future Direction: Bottom-Up Assembly of Molecular Electronics

- Molecules with recognition capabilities
- Molecular probes
- Molecules with recognition capabilities

Yuegang Zhang
What could controllable-synthesis and assembly enable?

- Nanotubes
- Nanowires
- Quantum Dots
- Memory device
- Quantum logic device
- Molecular device
- Energy conversion device
- Sensors
Summary

Various methods can be used for nanomaterial synthesis.
CVD provides great controllability for nanotube device integration using a hybrid approach.
Excellent performance demonstrated for nanotube based transistors and memory devices.
Great progress made in electrical contacts for nanotube devices.
Obtaining electronically pure (single chirality) nanotubes and regular array assembly remain to be two major challenges for high-volume manufacture.
Bio-inspired functionalization and self-assembly provides great opportunity in addressing these challenges.
No boundaries in nanoscience and nanotechnology for physicists, chemists, and biologists.
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