# Carbon Nanotubes for Nanoelectronics

- Synthesis and Integration

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10/24/2008

# What is Carbon Nanotube?



graphene sheet

SWNT



- 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*).



### **Nanotube: Metal or Semiconductor?**



### Nanotube Structure vs Electronic Property





The interband transition energies  $E_{ii}$  are uniquely determined by the diameter and chiral angle

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

#### Chiral angle θ dependence:

The trigonal warping effects increases with decreasing chiral angle. This causes a deviation of  $E_{ii}$  from  $E_{ii} - d_t$  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**



Si tri-gate transistor

#### SWNT tri-gate transistor

#### 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 K, bright peak G ~ 4e<sup>2</sup>/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 Nanochips



Top-down method 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 energygap for high performance transistors and memory devices.

#### Patterning technology: precise registry and orientation control

Array with regular spacing.

Connection to electrodes.





SWNT tri-gate transistor

# 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



Y. Zhang et al., Phil. Mag. Lett. 79, 473 (1999)

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



Without NiCo catalyst

10 nm

100 nm

10 nm

With NiCo catalyst

## **Exploring Exotic Nanotube Properties**

Nanoelectromechanical System (NEMS) Optomechanical device Optoelectronics

Y. Zhang & S. lijima, *Phys. Rev. Lett.* 82, 3472 (1999)





### Novel Heterostructured Nanotubes - BCN & C composite nanotubes



### Novel Heterostructured Nanowires - Coaxial Nanocable

#### Y. Zhang et al., Science 281, 973 (1998)

3 µm







### **Controllable 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

# **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:  $C_2H_4$ , 700°C (Dai group)

5<u>00 nm</u>

SWNT: CH₄, 900°C



DWNT: CH<sub>4</sub>+H<sub>2</sub>, 900°C (Y. Zhang, unpublished data)

### **Controlling Nanotube Diameter**

#### - by controlling nanoparticle size

Y. Li et al., J. Phys. Chem. B 105, 11424 (2001)



Apoferritin

Ferritin

### Controlling Location – Catalyst Patterning







а

b

С

d

### Controlling Orientation - I - Self-directed Growth of Suspended SWNT

(Y. Zhang, unpublished data)



**Self-directed** 

Self-directed

Self-directed + E-field directed



# **Controlling Orientation – II**

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10 µm

0 𝔍 DC, 0 𝒴/μm

5 µm

### **Other Issues Regarding Nanotube IC**

Interconnection  $\checkmark$ **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

Y. Zhang & H. Dai, *Appl. Phys. Lett.* 77, 3015 (2000) Y. Zhang et al., *Chem. Phys. Lett.* 331, 35 (2000)





### Ideal Contact Solution - Nanotube-nanowire nanojunctions



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

Α 100 nm B B SiC  $\{111\}$ 0.25 nm 5 nm

Y. Zhang et al., Science 285, 1719 (1999)



**TiC-SWNT** 

#### SiC-SWNT

### Novel NT/NW Heterostructures - Hybrid nanotube-nanowire devices

Y. Zhang et al., Science 285, 1719 (1999)

Carbon Nanotube welded on a STM tip through TiC formation



### **Application: Probe-based data storage**



Y. Cho et al., Appl. Phys. Lett., 81, 4401 (2002).

PFM: http://www.home.agilent.com/upload/cmc\_upload/All/AN-PiezoRes\_103107F.pdf

# **PFM principles**



# Advantage of using CNT probe

Small diameter  $\rightarrow$  small recording bit size  $\rightarrow$  high data storage density

Good electrical conductivity  $\rightarrow$  electrical read/write

Good mechanical strength  $\rightarrow$  low wear rate

High aspect ration  $\rightarrow$  No degradation of resolution with wear  $\rightarrow$  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



N. Teyabi et al., Appl. Phys. Lett. 93, 103112 (2008)

# **Sharpening Nanopencil**



N. Teyabi et al., Appl. Phys. Lett. 93, 103112 (2008)

#### Application: OD-1D System : Ultra-Sensitive Charge Sensor – Biosensor and Single-Electron Memory Devices



Noncovalent sidewall functionalization of single-walled carbon nanotubes for protein immobilization R. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* 123, 3838 (2001).

# **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 SiO<sub>2</sub> Deposit Au thin film and form nanocrystals Cap the device with 30 nm **PECVD** oxide Etch (RIE) open the pads for electrical measurements

U. Ganguly et al., Appl. Phys. Lett. 87, 043108 (2005)





### 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 Cylinderical 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: $\Delta$ Vth / $\Delta$ Vcharge = 1.2V/3V=0.4

V for hysteresis for P
W f

 $I_D$  vs  $V_G$  for device without nanocrystals showing charge injection into traps in the evaporated SiO<sub>2</sub> Charging efficiency with QD:

#### $\Delta V$ th / $\Delta V$ charge = **2V / 3V=0.67**



I<sub>D</sub> vs V<sub>G</sub> 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

#### ∆Vth / ∆Vcharge < 0.2V / 2.5V=0.08



I<sub>D</sub> vs V<sub>G</sub> at T=10K for device WITHOUT NANOCRYSTALS showing MINIMAL charge injection

#### $\Delta V$ th / $\Delta V$ charge = **1.6V / 3.4V=0.5**



#### I<sub>D</sub> vs V<sub>G</sub> at T=10K for device WITH NANOCRYSTALS showing charge injection into NANOCRYSTALS only

# Coulomb blockade in nanocrystals: single-electron charging



#### Hysteresis Measurement and Coulomb Blockade



(a) Stepping the V<sub>CH</sub> in fine steps of 50mV shows aggregation of I<sub>D</sub>V<sub>G</sub> curves (b) Extraction of V<sub>G</sub> for arbitrary constant I<sub>D</sub>=0.95nA results in steps in V<sub>G</sub> due the combined effect of coulomb blockade in nanocrystals and single charge sensitivity of nanotube conductance.

# **NEGF Simulation of CNTFET Charge Sensor**



J. Guo et al., J. Appl. Phys. 99, 084301 (2006)

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0

40

60

t<sub>ox</sub> [nm]

80

100

-3

-2

Gate Voltage (V)

0∟ 20

0.5

0.4

0.2 0.3 V<sub>G</sub>[V]

10<sup>1</sup>

10<sup>0</sup>

 $10^{-2}$ 

10

0

0.1

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# Resonant Tunneling and Charge Position Dependence



# "Bottle-neck" Effect and Resonant Tunneling



# **Electrostatic Analysis**





nanocrystals diameter: 6 nm; the nanotube diameter 2 nm;
pitch: 12 nm; dt : 3 nm ( Si EEPROM) and 5 nm ( CNT-
nanocrystal memory); <i>dc</i> : 30 nm (Si EEPROM); <i>dc</i> is
used as a parameter to calculated capacitive-coupling of
CNT nanocrystal memory structure for different <i>dc</i> : 27
nm; 30 nm ; 100 nm; . <i>p</i> : 12 nm (for all structures)

Structural Parameters		Potential on NC (V)	
	<i>d<sub>c</sub></i> (nm )	Capacitive Coupling <i>V<sub>G</sub></i> =5 (Programming)	Self Capacitance $q_{NC}$ =5 $e$ (Retention)
1NC-CNT BG	27	2.52	-0.517
	30	2.35	-0.519
	100	1.77	-0.528
1NC-CNT TG	30	2.69	-0.509
3NC-CNT BG	30	2.33	-0.68
1 NC-Si		0.81	-0.46
3 3 NC -Si		0.74	-0.67

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.

## **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**







-20

-60

-40

0

Distance Z (nm)

20

40

60

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# **Major Challenges for HVM of CNT Devices**

Electronically pure material: precise property control

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#### Patterning technology: precise registry and orientation control

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SWNT tri-gate transistor

#### What in-growth control can do and cannot do...

# 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 tubetube 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 SWNT**

(Prior-arts)



polymer wrapping



micellular suspension



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**



# De-functionalization with small molecules

R. J. Chen and Y. Zhang, J. Phys. Chem. B 110, 54 (2006)

Poly T<sub>30</sub>-coated CNTs Molecule replacement initiates DNA desorption CNTs begin to rebundle Desolubilized CNTs precipitate out

3

# De-functionalization using complementary ss-DNA

R. J. Chen and Y. Zhang, J. Phys. Chem. B 110, 54 (2006)



#### De-functionalization: Selective Precipitation?



## 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.</li>
- 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** 

# Selectivity of Optical Trapping of Carbon Nanotubes



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...



#### **Experimental Setup**



#### 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"



## **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





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** 

## In-situ Raman / Optical Trapping - Theory

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

1064 nm 1.16eV



- The susceptibility (χ) 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<sup>-1</sup> has the highest χ 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 *x* 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



(Unpublished data)

# Other CNT Manipulation Method: - Dielectrophoresis

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





 $\vec{F}_{\text{DEP}} \alpha \epsilon_{\text{m}} \frac{\varepsilon_{\text{p}} - \varepsilon_{\text{m}}}{\varepsilon_{\text{p}} + 2\varepsilon_{\text{m}}} \nabla E^{2}_{\text{rms}}$ 



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### Future Direction: Controlling Length and End-functionalization



#### O<sub>2</sub> plasma etch CNTs



Endfunctionalization

Self-assembly



(Unpublished data)

#### Future Direction: Bottom-Up Assembly of Molecular Electronics



## What could controllable-synthesis and assembly enable?


## 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.

# **Acknowledgement**

#### **NEC Fundamental Research Labs:**

Summit lijima (NEC Corp., JST, Meijio Univ.), Toshinari Ichihashi (NEC), Kazu Suenaga (JST)

#### **Stanford University:**

Hongjie Dai, Qian Wang, Jing Kong, Robert Chen, Nathan Franklin, Jien Cao, Woong Kim, Yiming Li, Erhan Yenilmez, Aileen Chang, Nathan Morris

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