Carbon-Based Electronics:
Will there be a carbon age to follow the silicon age?

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Solid State Seminar
9-13-13
Outline

• Review of development of Carbon Nanotube (CNT) transistors (for logic)
  – Issues, progress, prospects

• Advent of graphene
  – Recognition of promise of graphene nanoribbons (GNRs) for logic transistors
  – Issues, progress, prospects

• Summary of prospects for carbon transistors
C60: Birth of carbon Nanotech era

C_{60}: Buckminsterfullerene


Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.
Main properties of carbon nanotubes predicted before discovery!

Electronic structure of chiral graphene tubes

R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 27 January 1992; accepted for publication 4 March 1992)
Applied Physics Letters
Single-wall carbon nanotubes discovered in carbon ‘soot’ by TEM

CNT Transistor

Laser vaporization method for CNT synthesis

Catalytic CVD growth of CNTs on a surface

Catalyst: Fe(NO3)3·9H2O/alumina/methanol suspension
CVD at 1000°C with methane

Self-Aligned Ballistic FETs w/High-k

High Performance p- and n-FETS

- Doping by adsorption
- Lg = 80nm

CNT-CMOS Integration Chip

- NMOS binary tree 11-bit decoder
- 2048 back-gated CNT transistors
- >4000 Si NMOS transistors, 1 μm Microlab baseline process

[UCB/Stanford, Bokor/Dai groups]
Carbon Nanotube + Silicon MOS Integrated Circuit

Direct correlation to diameter variation

- Ion, Vgs-Vt=-7v
- Measurement Limit

[UCB, Bokor group]
Parallel Tube CNTs

- To get large drive, need to stack multiple tubes in parallel with common contacts, gate

- Do parallel array currents add?
- How close can tubes be stacked?

- Important for ultimate circuit application
Parallel Array of Self-Aligned Ballistic FETs

- First demonstration of a parallel array
- ~200 µA of current for the array of 8 tubes.

CNT Array Density Limited by Screening

Wang, et al. SISPAD (2003) [IBM]
CNT Array Transistor Circuit Performance

Jie, et al., ISSSC (2007)
[Stanford/USC, Wong/Mitra/Zhou groups]
Vision for CNT channel array MOSFETs

- Array of 1D channels, densely packed
- Density 200-250 per µm
- No metallic tubes
- Narrow diameter distribution
A Multiple Growth Strategy to High Densities

- Single-crystal quartz growth substrate
- “Epitaxial” CNT growth
- Layer transfer to Si wafer

Density Scaling by Multiple Transfers

Selective Removal of m-tubess From Aligned Arrays

Coat with small molecule film

Induce Joule heating selectively in m-SWNTs to form trenches by thermocapillarity

O₂ plasma etch exposed m-SWNTs

Remove film and electrodes; build circuits on remaining s-SWNTs

J. Rogers group, UIUC
**Dynamics of Thermocapillary Flow**

**Joule Heating by a SWNT ($\Delta T \sim 5-15°C$)**

Heating options:
- Gated electrical Joule heating
- Selective laser absorption
- Selective microwave absorption

[UIUC, Rogers group]
Solution phase nanotube ‘sorting’/purification


“Density gradient” centrifugation
Electrical results on sorted CNTs

Percolating network transistor

Sorted tube transistor high on/off ratio

[Northwestern, Hersam group]
DNA sequence specific wrapping for sorting

Table 1 | DNA sequence versus SWNT chirality

<table>
<thead>
<tr>
<th>Chirality (n,m)</th>
<th>Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9,1)</td>
<td>(TCC)$<em>{10}$, (TGA)$</em>{10}$, (CCA)$_{10}$</td>
</tr>
<tr>
<td>(8,3)</td>
<td>(TTA)$<em>{3}$TT, (TTA)$</em>{3}$TGGT, (TTA)$_{5}$TT</td>
</tr>
<tr>
<td>(6,5)</td>
<td>(TAT)$<em>{4}$, (CGT)$</em>{3}$C</td>
</tr>
<tr>
<td>(7,5)</td>
<td>(ATT)$<em>{4}$, (ATT)$</em>{4}$AT</td>
</tr>
<tr>
<td>(10,2)</td>
<td>(TATT)$_{2}$TAT</td>
</tr>
<tr>
<td>(8,4)</td>
<td>(ATTT)$_{3}$</td>
</tr>
<tr>
<td>(9,4)</td>
<td>(GTC)$<em>{2}$GT, (CCG)$</em>{4}$</td>
</tr>
<tr>
<td>(7,6)</td>
<td>(GTT)$<em>{3}$G, (TGT)$</em>{3}$T</td>
</tr>
<tr>
<td>(8,6)</td>
<td>(GT)$<em>{6}$, (TATT)$</em>{3}$T, (TCG)$<em>{3}$TC, (GTC)$</em>{3}$TC, (TCG)$<em>{2}$TC, (GTC)$</em>{2}$TC, (GTC)$_{2}$T</td>
</tr>
<tr>
<td>(9,5)</td>
<td>(TGTT)$_{2}$TGT</td>
</tr>
<tr>
<td>(10,5)</td>
<td>(TTTA)$_{3}$T</td>
</tr>
<tr>
<td>(8,7)</td>
<td>(CCG)$_{2}$CC</td>
</tr>
</tbody>
</table>

DNA sequences enabling chromatographic purification of single chirality semiconducting SWNTs.

Purified Single Chirality (10,5) SWNTs

Zhang, et al, JACS (2009), [Stanford/Dupont, Dai/Zheng groups]

DNA used: (TTTA)3T
FETS with 99% Semiconducting Tubes

Mostly (10,5) SWNTs

Average 15 tubes per device
Ion/Ioff >10² : 88%
semiconducting tubes:
99% (0.99¹⁵ ~ 88%)

Zhang, et al, JACS (2009),
[Stanford/Dupont, Dai/Zheng groups]
Solution phase array assembly by Langmuir-Blodgett technique

Li, et al. JACS (2007) [Stanford, Dai group]
Solution processed CNTs are as good as CVD tubes at nanoscale Lg

Choi, et al., ACS Nano (2013) [UCB, Bokor/Javey groups]

Ultimate scaling study

M. Luisier (Purdue)

Also
DG AGNR

Graphene Nanoribbon

GAA CNT
GAA NW

DG UTB
Simulation parameters and assumptions

Device Characteristics:

- **All**: $L_g=5\text{nm}$, $V_{DD}=0.5\text{ V}$, $EOT=0.64\text{nm}$ (3.3nm of HfO$_2$ with $\varepsilon_R=20$)
- **SG and DG AGNR**: width=2.2nm, normalization by width
- **GAA CNT**: diameter=1.58, 1.0, and 0.6 nm, normalization by diameter
- **GAA and Ω-NW**: Si, diameter=3nm, transport=$<110>$, 1% uniaxial strain
- **DG UTB**: Si, body=3nm,, transport=$<110>$, 1% uniaxial strain

Simulation Approach:

- Same quantum transport simulator for all devices based on Non-equilibrium Green’s Functions (NEGF) formalism with atomistic resolution of simulation domain and finite element method for Poisson equation
- Bandstructure model: single-$p_z$ for carbon and $sp^3d^5s^*$ for silicon (tight-binding)
- Ballistic limit of transport (no electron-phonon scattering nor interface roughness taken into account)
- Intrinsic device performances (no contact series resistances included)
- No gate leakage currents included
- No structure optimization for any of the selected devices
Id-Vgs at Vds=0.5V in carbon-based Devices

AGNR width: 2.2nm / CNT diameter: 1.58nm / Band Gap Eg=0.56 eV

- Same EOT gives very different electrostatic gate-channel coupling

M. Luisier (Purdue)
Gate Dielectric Effect In Carbon-Based Devices

Comparison of Conduction Band Edge and Spectral Current in Single-Gate AGNR with 0.64nm SiO$_2$ ($\epsilon_R=3.9$) and 3.3nm HfO$_2$ ($\epsilon_R=20$) => same EOT=0.64nm

- Effective channel length is longer for the thicker HfO$_2$
- Barrier widens and tunneling current drops
Extreme (sub-10 nm S-D Tunneling regime) d=1.58 nm CNT FETs

Transfer Characteristics

Sub-threshold swing

- Bandgap 0.56 eV GAA- CNT (d=1.58 nm) scales poorly

M. Luisier, et al., IEDM (2011)
[Purdue/MIT/UCB, Lundstrom/Antoniadis/Bokor groups]
Gate-length trend for 1 nm CNTs

Transfer Characteristics

Sub-threshold Slope

- Bandgap 0.8 eV GAA- CNT (d=1.0 nm) scales better

M. Luisier, et al., IEDM (2011)
[Purdue/MIT/UCB, Lundstrom/Antoniadis/Bokor groups]
Gate-length trend for 0.6 nm CNTs

Transfer Characteristics

\[ I_d-V_{gs} \text{ at } V_{ds}=0.5V \text{ in CNT FETs with } d=0.6\text{nm and } 5\leq L_g \leq 12 \text{ nm} \]

Sub-threshold Slope

- Bandgap 1.4 eV GAA- CNT (d=0.6 nm) scales well

M. Luisier, et al., IEDM (2011)  
[Purdue/MIT/UCB, Lundstrom/Antoniadis/Bokor groups]
Comparison of different channel materials

\[ I_d-V_{gs} \text{ at } V_{ds}=0.5V \text{ in CNT, NW, and UTB Devices} \]

- CNT with \( d=0.6 \text{nm} \) and NW with \( d=3 \text{nm} \) have same band gap \( E_g=1.4 \text{eV} \)
- CNT with \( d=1.0 \text{nm} \) has band gap \( E_g=0.817 \text{eV} \)

- Bandgap 0.8 eV GAA-CNT (\( d=1.0 \text{ nm} \)) scales poorly
- Bandgap 1.4 eV GAA-CNT (\( d=0.6 \text{ nm} \)) scales well
- Si NW (\( d=3 \text{ nm} \)) scales very well due to high-mass and band-gap
Sub-10 nm Carbon Nanotube Transistor

Aaron D. Franklin, Mathieu Luisset, Shu-Jen Han, George Tulevski, Chris M. Breslin, Lynne Gignac, Mark S. Lundstrom, and Wilfried Haensch

1IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, United States
2Integrated Systems Laboratory, ETH Zurich, 8092 Zurich, Switzerland
3School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907, United States

Table 1. Comparison of Performance Metrics between This Work and the Best-Reported Sub-10 nm Si-Based Transistors

<table>
<thead>
<tr>
<th>ref</th>
<th>channel</th>
<th>L_{ch} (nm)</th>
<th>EOT (Å)</th>
<th>V_{th} (V)</th>
<th>V_{p} (V)</th>
<th>I_{on} (μA/μm)</th>
<th>I_{on}/I_{off}</th>
<th>L_{ch} (nm)</th>
<th>pitch (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>CNT</td>
<td>9</td>
<td>6.5</td>
<td>0.4</td>
<td>0.5</td>
<td>1760</td>
<td>10^4</td>
<td>9</td>
<td>5</td>
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<tr>
<td>15</td>
<td>Si nanowire</td>
<td>10</td>
<td>25</td>
<td>0.5</td>
<td>0.6</td>
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<td>469</td>
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<tr>
<td>16</td>
<td>Si Fin</td>
<td>10</td>
<td>17</td>
<td>0.5</td>
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<td>41</td>
<td>138</td>
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<td></td>
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<tr>
<td>17</td>
<td>ETSOI</td>
<td>8</td>
<td>15</td>
<td>0.5</td>
<td>0.6</td>
<td>55</td>
<td>41</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>
Monolithic 3D CNT Circuits!

Hai, et al., IEDM (2010) [Stanford, Mitra/Wong groups]
Graphene

Forms of graphene

Graphene resistivity

Geim and Novoselov, Nat. Mat. (2007) [Manchester]
Bandgap Prediction for Graphene Nanoribbons

[UCB, Louie group]
Bandgap Measurements of Etched GNRs

Han, et al., PRL (2007) [Columbia, Kim group]
GNR formation by unzipping CNTs

All sub-10nm GNRs are semiconducting
Ion currents few uA

[Dai group]
Bottom-up Synthesized GNRs

- Atomically perfect edges!
- 7 C atoms wide
- W = 0.74 nm!

Cai et al. Nature (2010) [EMPA (Switzerland), Fasel group]
Aligned Growth – Bandstructure Measured

~2 nm pitch!

$m^* = 0.21 \, m_e$

$E_g = 2.3 \, eV$

Synthesized GNR Transferred to SiO2

Bennett, et al., unpublished [UCB, Bokor/Crommie/Fischer groups]
Synthesized GNR Transistor Results

Bennett, et al., unpublished
[UCB, Bokor/Crommie/Fischer groups]
Wider GNRs Synthesized with 1.4 eV Gap

Chen, et al., ACS Nano (2013) [UCB, Fischer/Crommie groups]
Single-Molecule Heterostructures

a) pn ribbon

b) pn diode

CMOS inverter

Heterojunction TFET

source

undoped, small Eg

drain
Summary/Outlook

• CNT and GNR both promising candidates for CMOS channel material for $\leq 8$ nm gate length

• Why?
  • High drive at low V
  • Good scalability
  • 3D layer stacking:
    10 layers = 3 nodes on roadmap!

• More work needed:
  • Purified chirality for tubes
  • Longer, wider GNRs
  • Dense aligned arrays
  • Low resistance contacts

• GSR opportunities in my group