Carbon Nanotube Electronics

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Nanoelectronics FFF160
Outline

• Basics of graphene and CNTs
  – Structural
  – Electronic
  – Production of CNTs

• Advantages of CNTs for FETs
  – Gate length scaling
  – Coaxial gate
  – High-k compatibility
  – Band-to-band tunneling

• Challenges of CNT integration
  – Contacts
  – Doping
  – Positioning
  – Chirality control

• Towards integration
  – Flexible electronics
  – High frequency performance
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Hybridisation of carbon orbitals

- 4 valence electrons
- 1 s-electron can "mix" with 1-3 p-electrons
- \textit{sp}^2 have three \(\sigma\)-bonds in a plane + \(\pi\)-bond
- \textit{sp}^3 have four \(\sigma\)-bonds

\begin{itemize}
  \item \textit{sp}^2
  \begin{align*}
    &1 \text{ s-orbital} \quad 3 \text{ p-orbitals} \\
    \rightarrow &3 \text{ sp}^2\text{-orbitals} \quad 1 \text{ unchanged p-orbital}
  \end{align*}
  \begin{center}
    \textit{sp}^2 \quad \text{Trigonal Planar geometry}
  \end{center}

  \item \textit{sp}^3
  \begin{align*}
    &1 \text{ s-orbital} \quad 3 \text{ p-orbitals} \\
    \rightarrow &4 \text{ sp}^3\text{-orbitals}
  \end{align*}
  \begin{center}
    \textit{sp}^3 \quad \text{Tetrahedral geometry}
  \end{center}
\end{itemize}
Carbon allotropes

Figure 2.1: a-d) Crystal structure of a few carbon allotropes a) Diamond b) Graphite c) C60 d) CNT. e) sp³ hybridised orbitals forming σ bonds. f) sp² hybridised orbitals forming σ bonds and the remaining pz orbital giving rise to π bonds.
Graphene is mother of all $sp^2$-carbon
Graphene band structure

- Semimetal: no gap and zero DOS at $E_f$
- Only $\pi$-bands are interesting
- Linear dispersion near $E_f$
- Conduction and valence bands meet at the K-points
Rolling graphene

- Cut graphene into narrow strip and roll into tube
- Different structure depending on direction of cut
- Armchair, zigzag, chiral CNTs
- Chirality defined by index \( (n,m) \)

\[
\vec{C} = n\vec{a}_1 + m\vec{a}_2
\]

- Armchair, zigzag, chiral CNTs
- Chirality defined by index \( (n,m) \)
Confinement of electron wavefunctions

- Have to have continuous wavefunction around circumference
- Periodic boundary conditions
- Only some wavevectors \( k_\perp = \frac{2n\pi}{C} \) with \( n=1,2,3... \) allowed
Diameter dependence of confinement

large diameter = small energy difference

small diameter = large energy difference
Confinement of electron wavefunctions

- Slices in graphene dispersion relation of allowed wavevectors around circumference
- Position of slices depends on chirality
- Small diameter CNT have larger distance between slices
Allowed wavevectors

- $n-m = 3i$ with $i=1,2,3...$ -> slice goes through K-point -> metallic CNT
- $n-m \neq 3i$ -> slice does not go through K-point -> semiconducting CNT with parabolic bands

$$E(k) = \pm \left( (\hbar v_F k)^2 + (E_g/2)^2 \right)^{1/2}$$
Subbands

- $\pi$-bands split into 1D subbands of increasing energy
- Mainly important at high gate voltages or for optical transitions
- Wavefunctions just schematic, need TB calculation
Band gap vs diameter

- Linear dispersion of graphene gives $E_g$ inversely proportional to diameter for CNTs
- Curvature induced gap of 10’s of meV in most of the “metallic” CNTs
- Only armchair CNTs truly metallic
All CNTs are different

- 1/3 metallic or small gap
- 2/3 semiconducting with different gap
Density of states

- Van Hove singularities with high DOS at band edges
- Can be seen in scanning tunneling microscope or capacitance measurements
- Strong influence on optical properties

\[ g_i(E) = \frac{4}{\pi \hbar v_F} \left[ 1 - \left( \frac{E_g^i}{2E} \right)^2 \right]^{-1/2} \]
Electrical characteristics

- semiconducting: strong gating effect
- metallic: no gating effect
- small gap semiconducting: some gating effect
- Can withstand $10^9$ A/cm$^2$
Transport through Schottky barriers

- Schottky barriers at metal contacts
- Tunneling through SB determines transport
- Negative gate voltages -> hole transport
- Positive gate voltages -> electron transport
- Similar SB heights -> ambipolar characteristics

\[ \Phi_{SBh} \]

\[ \Phi_{SBe} \]

p branch

\[ E_c \]

\[ E_v \]

source

hole

drain

\[ V_d \]

n branch

off state

\[ \Phi_{SBe} \]

increasing gate voltage

electron

voltage

source
Mobility vs diameter

- Lower curvature of bands for smaller diameter -> mobility proportional to $d^2$
- $\mu > 100000 \text{ cm}^2/\text{Vs at 50 K}$
Scattering

- Elastic scattering have to reverse direction of electron

- Acoustic phonon scattering dominates at low bias and gives \( \text{mfp} > 300 \text{ nm} \) -> ballistic transport possible

- Optical phonons scattering dominates at high bias and gives \( \text{mfp} = 15 \text{ nm} \)

- Potential variations or phonons in substrate under CNT can also scatter electrons

Acoustic phonon
\[ q \sim 0, \ \hbar \Omega \ll k_B T \]

Optical phonon
\[ q \sim 0, \ \hbar \Omega > k_B T \]

Zone boundary phonon
\[ q > 0, \ \hbar \Omega > k_B T \]
Ballistic transport

- Channel length $\ll$ mfp -> no scattering in channel
- Mobility not relevant but injection velocity is
- $R_{\text{min}} = \hbar/4e^2 = 6.5$ kOhm in ballistic 1D system with 4 modes

\[ v_T = \sqrt{\frac{2kT}{\pi m^*}} \]
Production of CNTs

- Arc discharge: high voltage creates spark between graphite rods
- Laser ablation: laser vaporises graphite target
- Chemical vapor deposition: metal catalyst particles decompose hydrocarbon gas
Grown CNTs

- d=1-4 nm, L>10 cm
- Tangled web of CNTs
- Can be imaged using SEM, TEM, AFM, STM
- Deposit from suspension or grow on device substrate
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Gate length scaling

+ Increased speed  ->  lower gate delay \((CV/I)\), higher \(g_m\) and \(f_T\)

+ Reduced power consumption  ->  energy delay product \((CV/I \cdot CV^2)\)

+ Enables higher packing density

- Short channel effects when source and drain influence potential in the channel

Need to reduce gate dielectric thickness, increase dielectric constant or change geometry.
Different gating geometries

- $\lambda = $ screening length, reduced by higher gate dielectric constant or thinner channel

- $L_g > 5 \lambda$ to avoid short channel effects

- More wrapping of the channel reduces $\lambda \rightarrow$ enables $L_g$ scaling

- CNTs and graphene allows for very good gate length scaling

\[
\lambda_1 \approx \sqrt{\frac{\varepsilon_{ch}}{\varepsilon_{ox}} t_{ox} t_{ch}} \quad > \quad \lambda \approx \sqrt{\frac{\varepsilon_{ch} t_{ch} t_{ox}}{2\varepsilon_{ox}} \left(1 + \frac{\varepsilon_{ox} t_{ch}}{4\varepsilon_{ch} t_{ox}}\right)} \quad > \quad \lambda \approx \sqrt{\frac{\varepsilon_{ch} t_{ch} t_{ox}}{4\varepsilon_{ox}} \left(1 + \frac{\varepsilon_{ox} t_{ch}}{4\varepsilon_{ch} t_{ox}}\right)}
\]
Gate length scaling

- No short channel effects down to $L_g=15$ nm
- $I_{on} = 10 \, \mu A$
- on/off ratio = $10^5$
- $SS = 90$ mV/dec also for short devices

High k gate dielectrics

- No dangling bonds give nice interface
- Difficult to use ALD directly without dangling bonds to react with precursors
- Overgrow from surface or functionalize CNT

Coaxially gated CNTFET

- Wrap CNT in Al2O3 and WN using ALD
- Poor subthreshold swing due to interface charge and short channel effects
Coaxially gated CNTFET

- Control p or n-type by different high-k

Franklin et al. *Nano Lett.* 13 (6), (2013)
Surface scattering

- Need to reduce channel thickness to be able to reduce $L_g$
- Mobility of SOI MOSFETs is lowered with $t_{SOI}$ due to surface scattering
- Not a problem for CNTs – no unsaturated bonds / no roughness

K. Uchida et al., IEDM2002, p.47
Improving the inverse subthreshold slope

- "conventional" FETs rely on thermionic emission over a barrier

- $SS \geq \ln(10)k_B T = 60 \text{ mV/dec at RT}$

- A decreased SS enables a lower $V_{dd}$ while keeping the same on/off ratio -> increased speed and reduced power consumption

\[
S = \left( \frac{d \log_{10}(I_d)}{dV_g} \right)^{-1}
\]
Band-to-band tunneling

- $\lambda$ is a few nm in CNT -> sharp band bending
- Low effective mass
- Long mfp
- Same effective mass of electrons and holes
- Direct band gap

Electrical characteristics

- Back gate to form p-type regions
- Al gate to switch FET
- Ambipolar characteristics
- SS=40 mV/dec for the n-branch
- Band-to-band tunneling at the border between the gates
Mechanism of SS reduction

- Only high energy tail of Fermi-Dirac distribution is transferred in thermionic emission or in tunneling through Schottky barrier

- Band-to-band tunneling "filters" the Fermi-Dirac distribution

- For BTB tunneling, small movement of bands give large change in current i.e. small SS
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Schottky barrier basics

- Potential barrier between metal and semiconductor
- Gives rectifying behaviour
- Change metal work function -> change SB height
- Too simple !!!

\[
\Phi_{SB \text{e}} = \phi_m - \chi \\
\Phi_{SB \text{h}} = \chi + E_g - \phi_m = I_s - \Phi_m
\]
Fermi level pinning

- Interface states form dipoles that shift bands
- SB height often independent on metal work function

\[ \Phi_{SBe} = \gamma(\Phi_m - \chi) + (1 - \gamma)(E_g - \Phi_0) \]
\[ \gamma = \frac{1}{1 + \frac{q D_{it} \delta}{\epsilon_i}} \]
Schottky barrier to CNTs

- Theoretically predicted that interface states have no influence on CNT-metal contacts
- Increasing CNT diameter gives lower barriers
- Increasing metal work function gives lower hole barriers
Different contact metals

- Increasing $I_{on}$ with larger CNT diameter
- Increasing $I_{on}$ with higher work function
- No or small effect of Fermi level pinning

Metal work function impact

- Can form n or p-type devices using different metals
- Pd best for p-type
- Sc best for n-type

Imaging Schottky barriers

- Laser generates e-h pairs
- Pair separated by electric field -> photocurrent
- Scan laser spot and change gate voltage
- Obtains size of depletion width

End bonded contacts

- Mo contacts heated to 800°C forms Mo$_2$C
- Sidecontact transformed to end contact
- Contact only 2 nm$^2$

Doping

- Important for CMOS and good contacts
- Substitutional doping is difficult without destroying CNTs.
CNTFETs in air

- Physisorbed oxygen p-dopes CNT
  OR
- Increases metal work function of contact

Contact metal work function change

p-doping -> thinner Schottky barrier for holes
Potassium doping

- O exposure -> p-branch is lowered, n-branch is increased, no $V_{th}$ shift
- K physisorbed on CNT n-dopes by charge transfer -> $V_{th}$ shift
- K not stable in air
- O: changes work function / K: dopes CNT

Doping of thin film CNTFETs

- Organic molecules are deposited on CNT network
- n-doping lower Schottky barrier for holes and shifts $V_{th}$

Doped contacts

- n-dope outer CNT segments using K
- Removes influence from Schottky barrier at metal contact

Logic gates

- Inverter from p and n CNTFET on the same CNT
- Use K doping or annealing to form n-CNTFET

Positioning

- Multiple parallel CNTs in each FET increases $I_{on}$, $g_m$
- Dense packing reduces parasitic capacitances
- Need to control position and orientation of CNTs pre- or postgrowth
Electric field alignment

- Apply voltage to electrodes during CVD
- Dipole in CNTs align them with field lines
- Difficult to implement for large scale circuits
"epitaxial" alignment

- CNTs align in certain crystal orientations of sapphire (Al$_2$O$_3$) or quartz substrates
- CNTs align at atomic steps
- Strong attractive interaction between CNTs and Al atoms
- 99.9% are aligned within 0.01°
- 10 CNTs / µm
Chirality control

- Metallic CNTs in FETs -> leakage currents - > poor on/off ratio

- Need chirality control or at least control of CNT type

- Need to either:
  - Selectively grow only metallic or semiconducting
  - Separate the two types
  - Selectively destroy one type
Selective growth

- Anneal metal catalyst in Ar, He or H₂
- Increased metallic CNT part from 33% to 91%
- Strong facets when annealed in He
- Steps in particle important for chirality control?
- Not well understood!

Templated growth

- Molecule defines cap
- Only (6,6) CNTs i.e. "real" metallic

Separation by dielectrophoresis

- AC voltage between electrodes
- Drop with CNTs
- Metallic CNTs attracted to electrodes and removed from suspension
- Only small scale (nanograms)

Separation by centrifugation

- Centrifuge CNT suspension at 64000 rpm -> 200000 g
- CNTs are sorted according to density
- Pick up some part of vial and repeat
- 97% of CNTs are within 0.2 Å of mean diameter

Selective destruction

- Apply gate voltage to switch off semiconducting CNTs
- Apply high S/D voltage
- Metallic CNTs are heated and destroyed
- Difficult for large scale circuits
- May destroy nearby CNTs
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Thin film transistors

- Printed / flexible / transparent / biomedical electronics
- Lower requirements on size and speed
- More sensitive to cost and fabrication complexity
- Amorphous-Si, Poly-Si, InGaZnO, organic molecules

Thin film transistors

A. printable

B. flexible

C. transparent

D. biocompatible
Flexible electronics

- Graphene for electrodes
- CNTs for channel
- No degradation when bent

Thin film transistors comparison

Requirements for RF applications

- Need high $g_m$ and low $g_d$ -> only semiconducting CNTs

- Minimize parasitic capacitance / CNT -> dense array of CNTs

$$f_T = \frac{g_m}{2\pi} \frac{1}{(C_{gs} + C_{p,gs} + C_{p,gd})( (R_{p,s} + R_{p,d})g_d + 1 ) + C_{p,gd}g_m(R_{p,s} + R_{p,d})}$$

Table 1 | Ideal parameter values for making a high-frequency field-effect transistor from single-walled nanotubes.

<table>
<thead>
<tr>
<th>Property/parameter</th>
<th>Target value or range</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>1.5–2.0 nm</td>
<td>Current is largest in this range$^{54-55}$.</td>
</tr>
<tr>
<td>Chirality</td>
<td>Semiconducting and same $(n,m)$</td>
<td>To obtain identical transport properties.</td>
</tr>
<tr>
<td>Purity</td>
<td>&gt;99% semiconducting nanotubes</td>
<td>No metallic nanotubes for high gain and high $f_{\text{max}}$.</td>
</tr>
<tr>
<td>Length</td>
<td>&gt;1 μm</td>
<td>Nanotube length must be longer than the intended channel length.</td>
</tr>
<tr>
<td>Density</td>
<td>&gt;10 nanotubes μm$^{-1}$</td>
<td>Reduces the parasitic capacitance per nanotube; increases current carrying capacity; improves impedance matching.</td>
</tr>
<tr>
<td>Alignment</td>
<td>All parallel</td>
<td>Results in higher transconductance and denser nanotube packing.</td>
</tr>
<tr>
<td>Uniformity</td>
<td>Wafer scale</td>
<td>Essential for large-scale processing.</td>
</tr>
</tbody>
</table>

RF performance

- Difficult to measure single CNT due to impedance mismatch
- Use separated semiconducting CNTs
- $f_T = 80$ GHz
- Much better than "original" CNT material

CNT computer

- 178 p-type CNTFETs. Aliged growth -> transfer -> burn-off
- Not CMOS, only p-type.
- Counting and number sorting.
- 1980’s level.

Large scale integration

- p-type CNTFETs (from centrifuged CNTs)
- n-type InGaZnO (sputtered)
- Flexible substrate
- 501 stage ring oscillators
- >1000 transistors

Summary

• **Individual CNTs have great electronic properties**
  – High mobility
  – Coaxial gate + thin -> good scaling
  – Compatible with high-k dielectrics
  – No surface scattering

• **CNTs are difficult to integrate in large scale circuits**
  – Schottky barriers at contacts
  – Unstable doping
  – Poor position control
  – Semiconducting / metallic mix