Carbon Nanotube Electronics

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Nanoelectronics EITP05

Outline

- Basics of graphene and CNTs
  - Structural
  - Electronic
  - Production of CNTs
- Advantages of CNTs for FETs
  - Electrostatics -> length scaling
  - 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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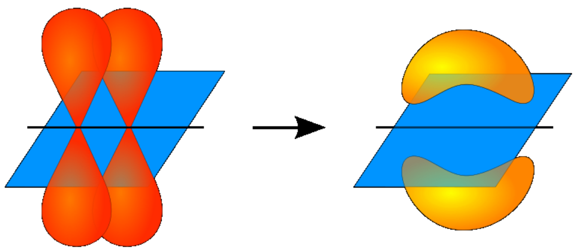
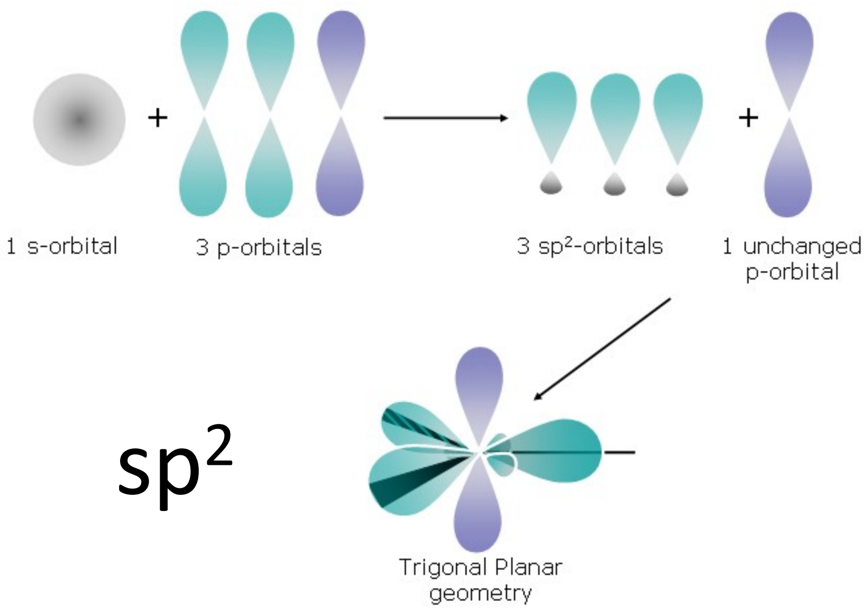
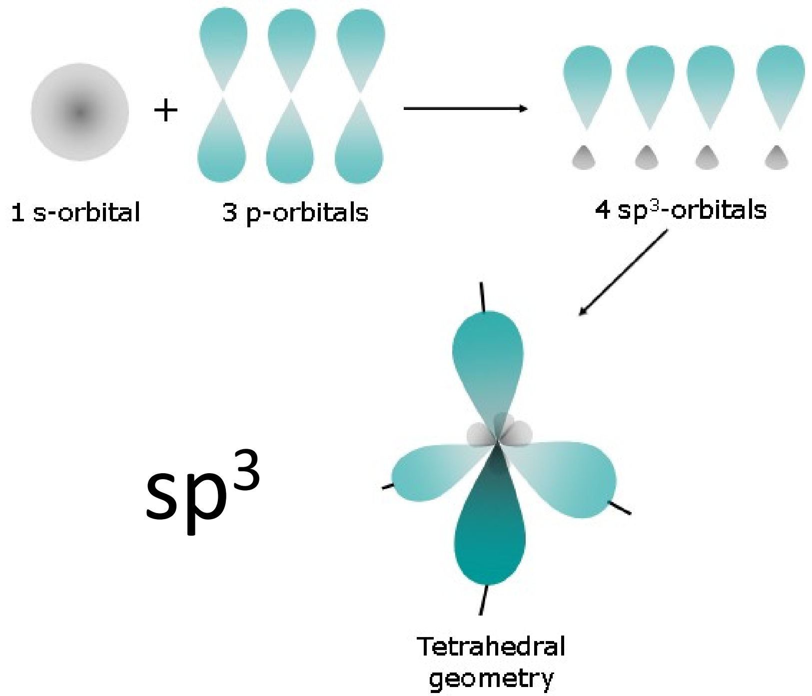
Hybridisation of carbon orbitals

- 4 valence electrons
- 1 s-electron can ”mix” with 1-3 p-electrons
- sp^2 have three σ-bonds in a plane + π-bond
- sp^3 have four σ-bonds





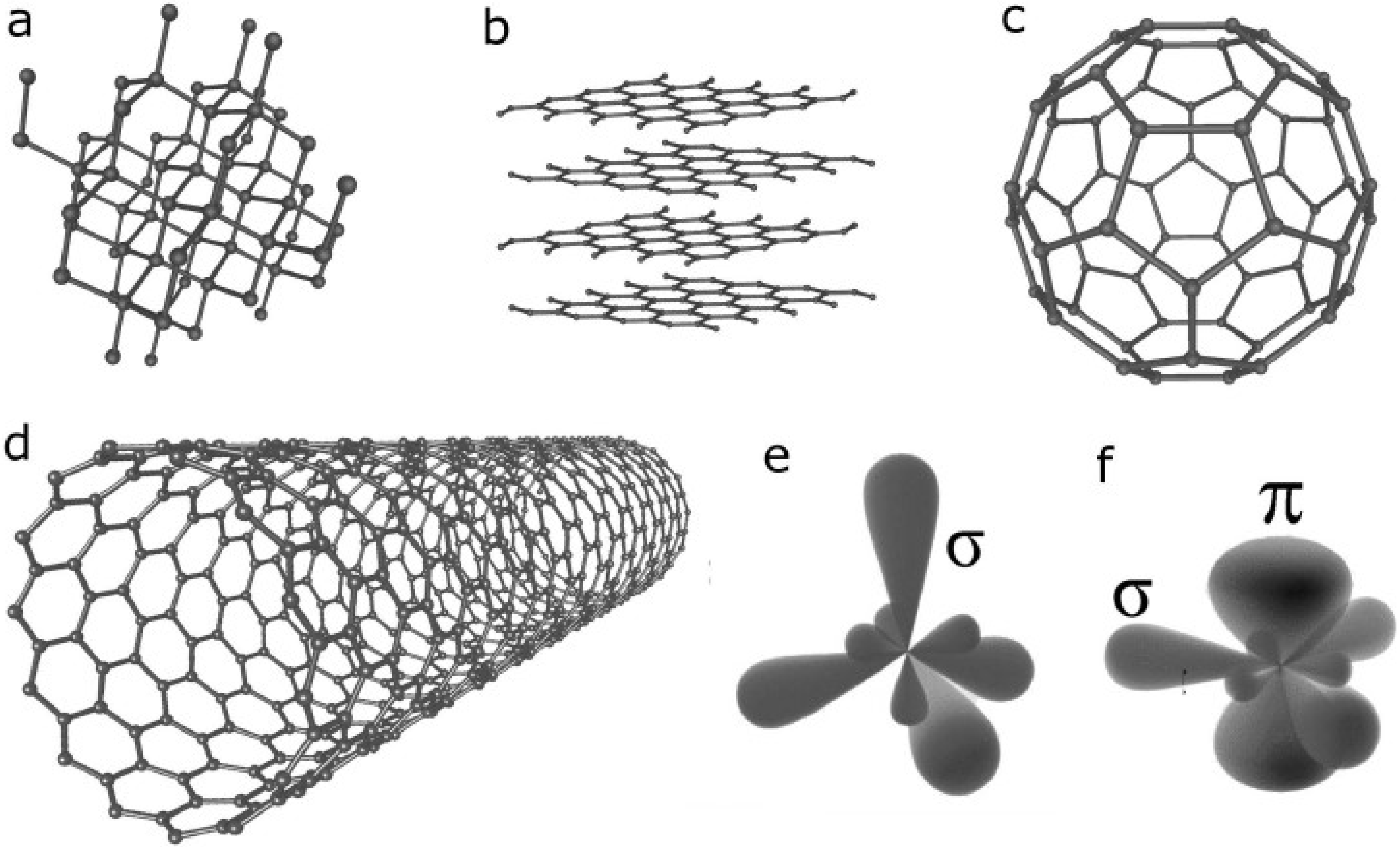
sp^2



sp^3

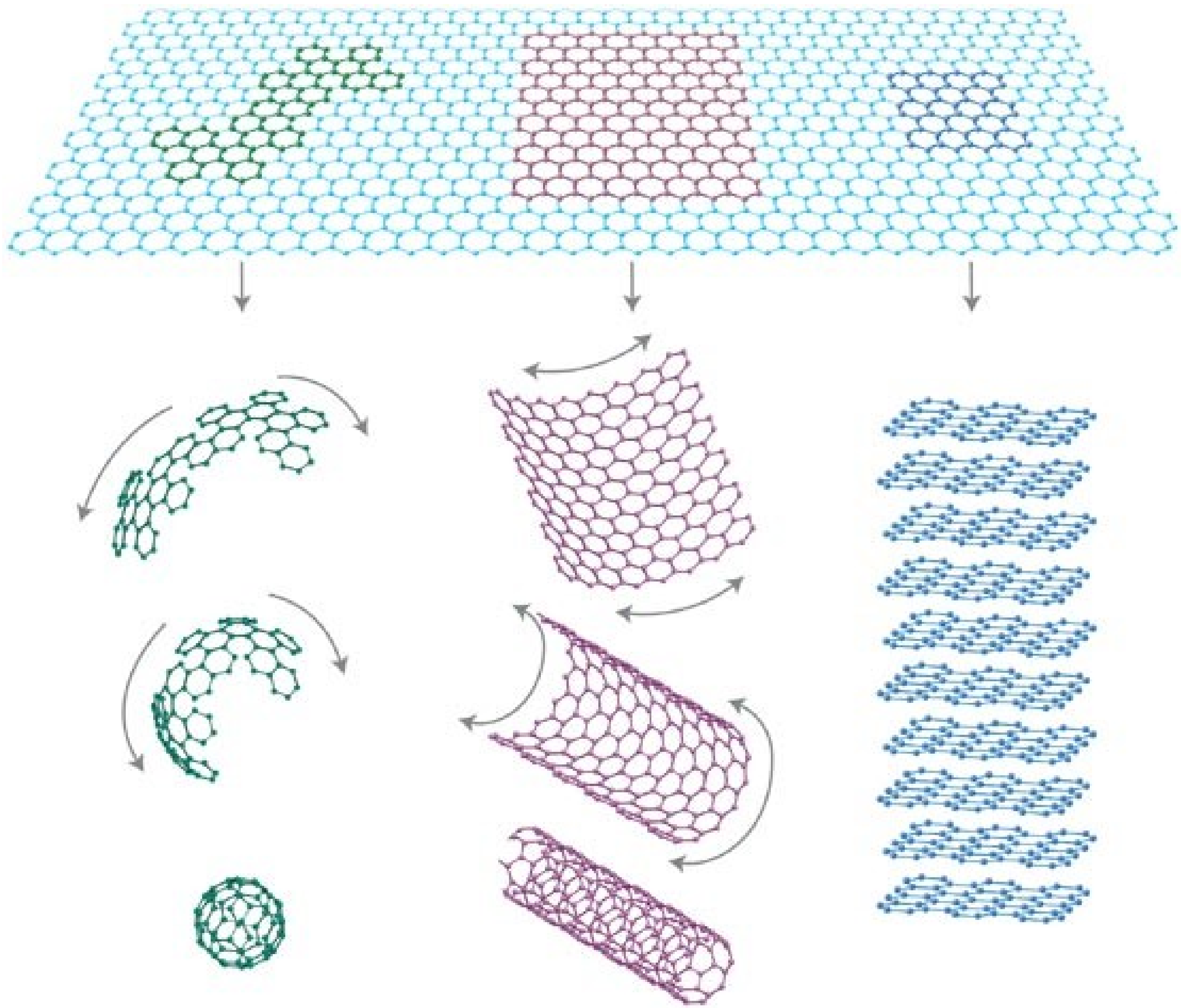
Carbon allotropes

diamond **graphite** **C_{60} (fullerene)**



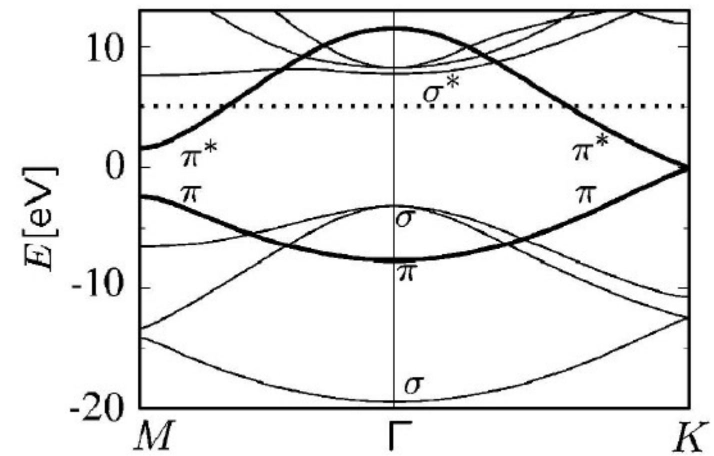
Carbon nanotube **sp^3** **sp^2**

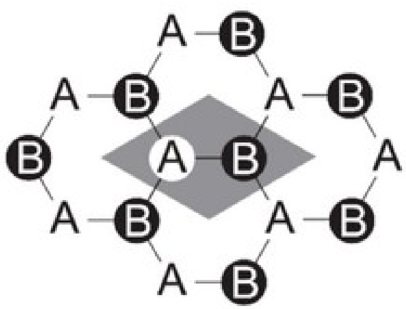
Graphene is mother of all sp^2-carbon

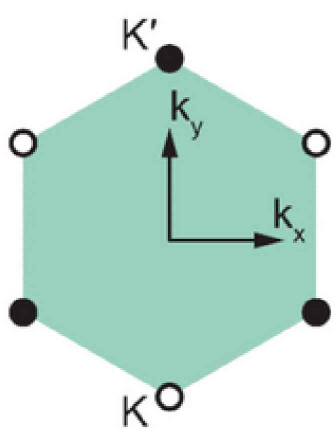


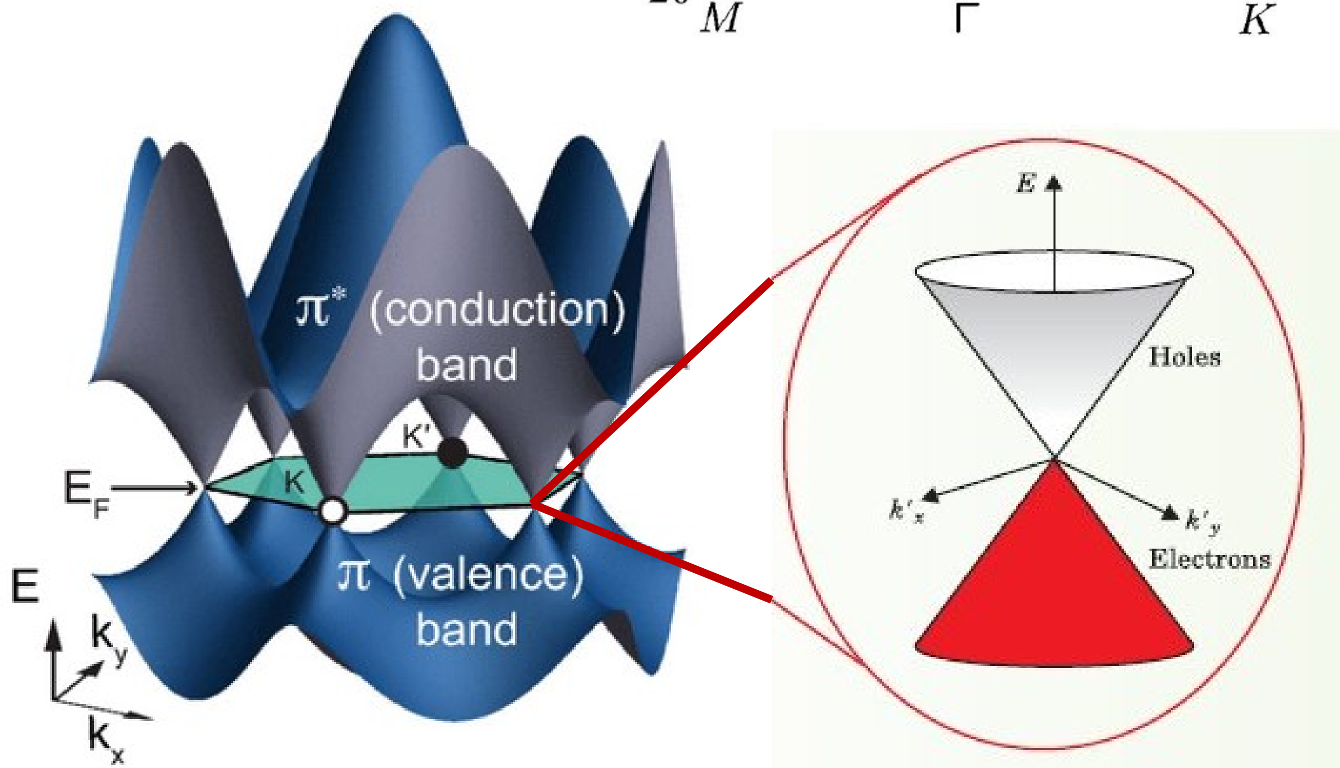
Graphene band structure

- Semimetal: no band gap and zero DOS at E_f
- Only π-bands are relevant for transport
- Conduction and valence bands meet at the K/K'-points
- Linear dispersion near E_f







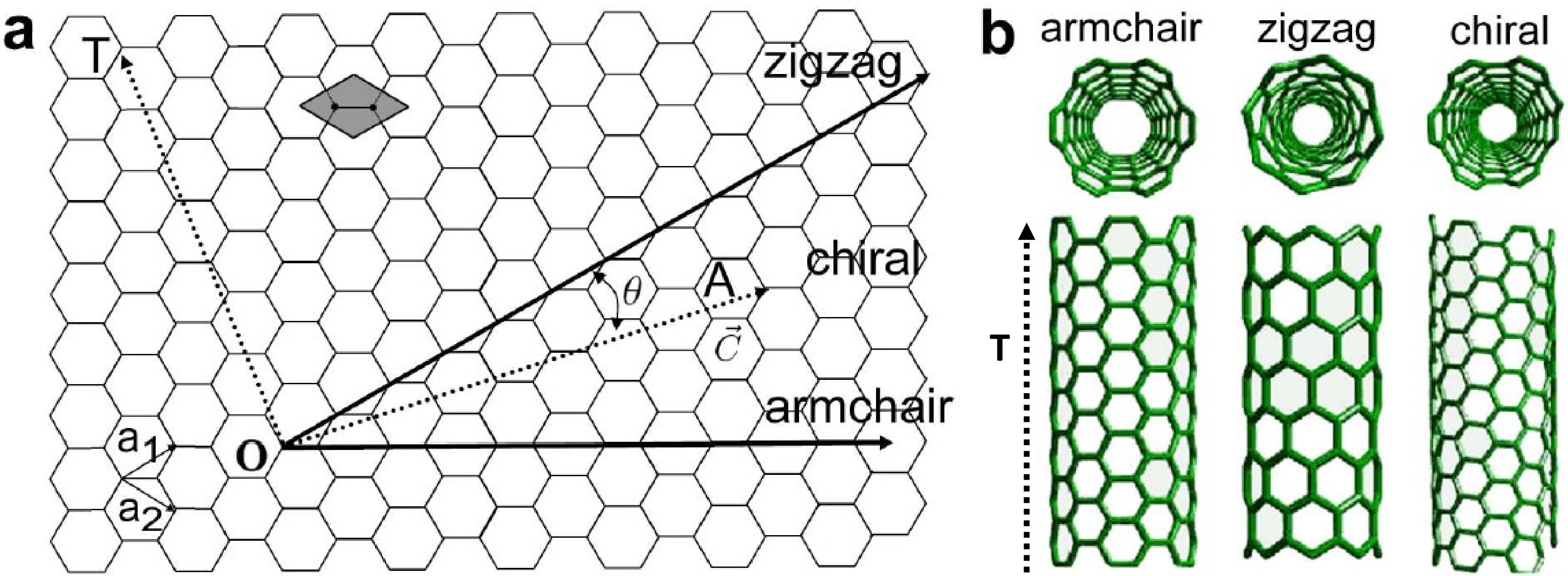


Rolling graphene into CNT

- 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)

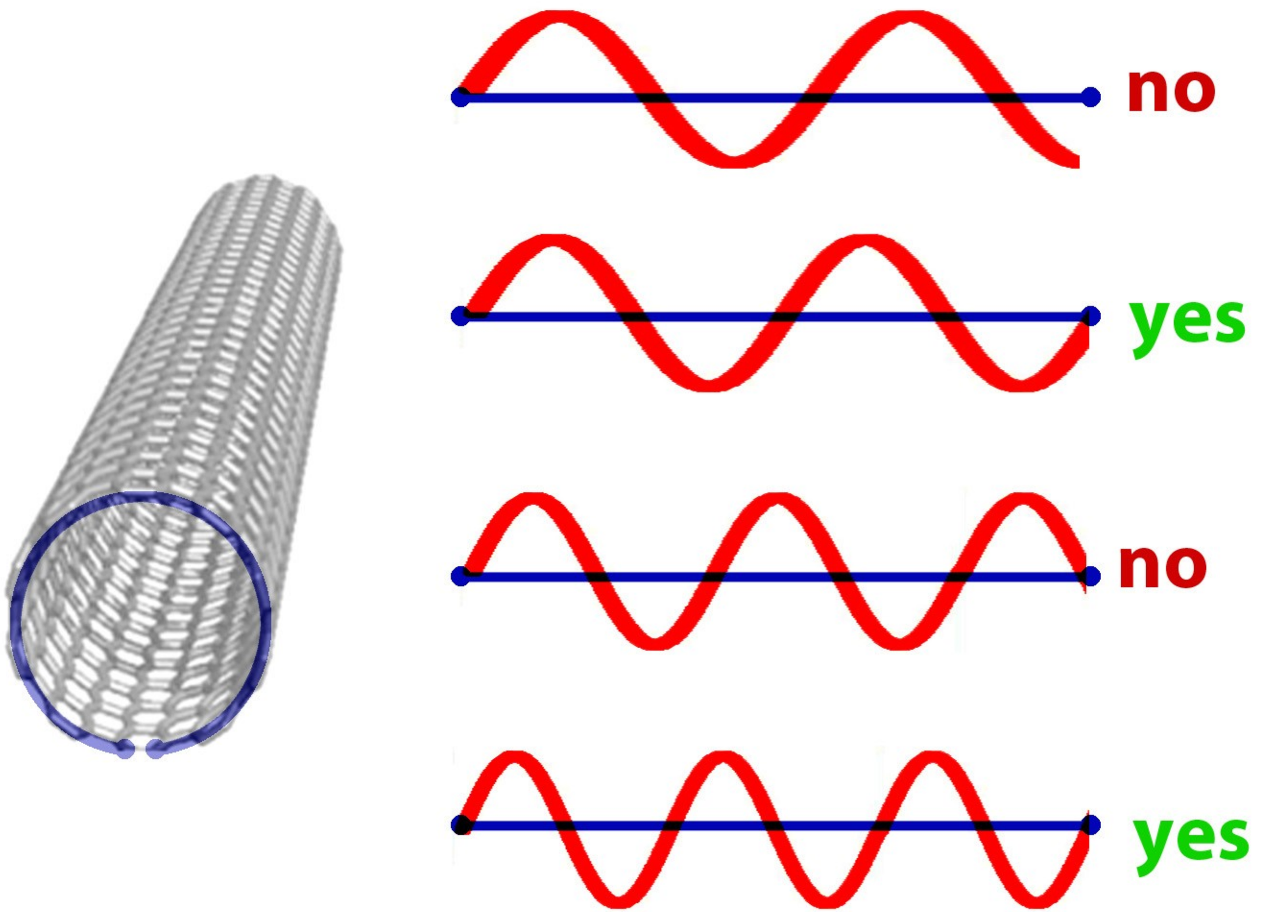
$$\vec{C} = n\vec{a}_1 + m\vec{a}_2$$

$n = m$ $\quad$ $n = 0$



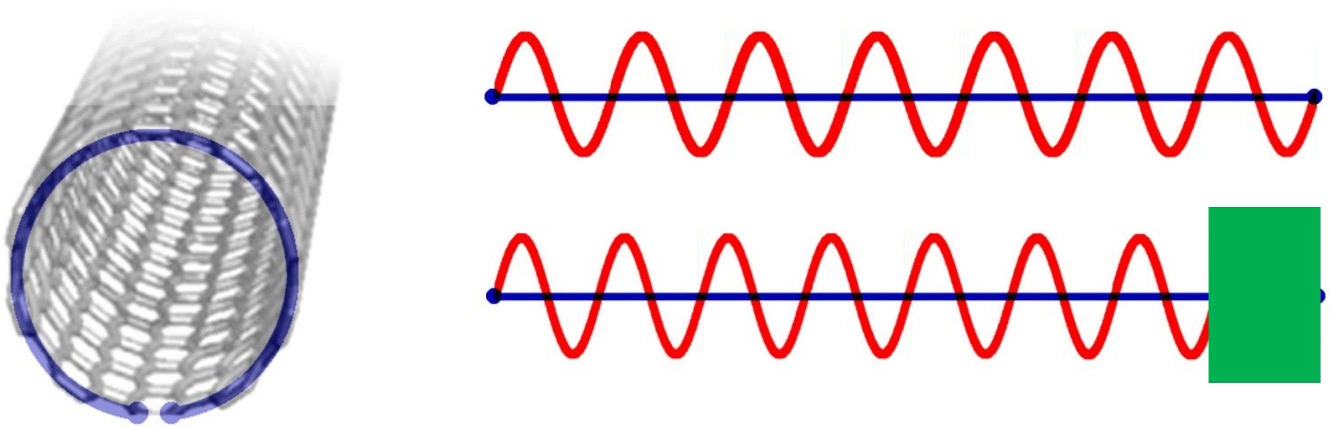
Confinement of electron wavefunctions

- Have to have continous wavefunction around circumference
- Periodic boundary conditions
- Only some wavevectors $k_{\perp} = 2n\pi/C$ with n=1,2,3... allowed



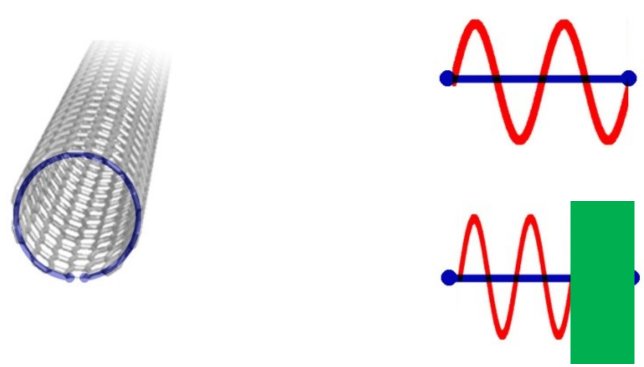
Diameter dependence of confinement

large diameter = small energy difference



Next allowed $k_{\perp}$

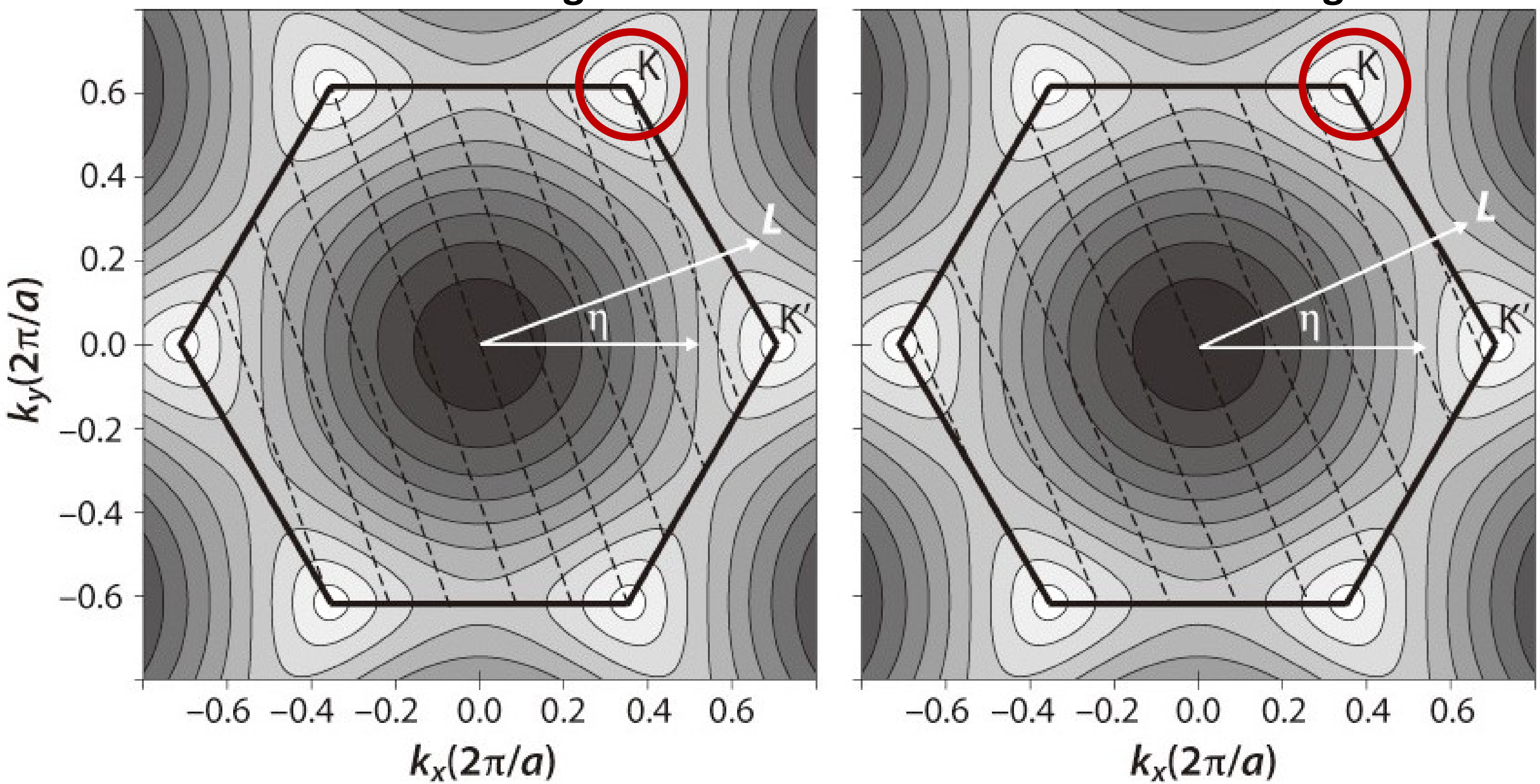
small diameter = large energy difference



Confinement of electron wavefunctions

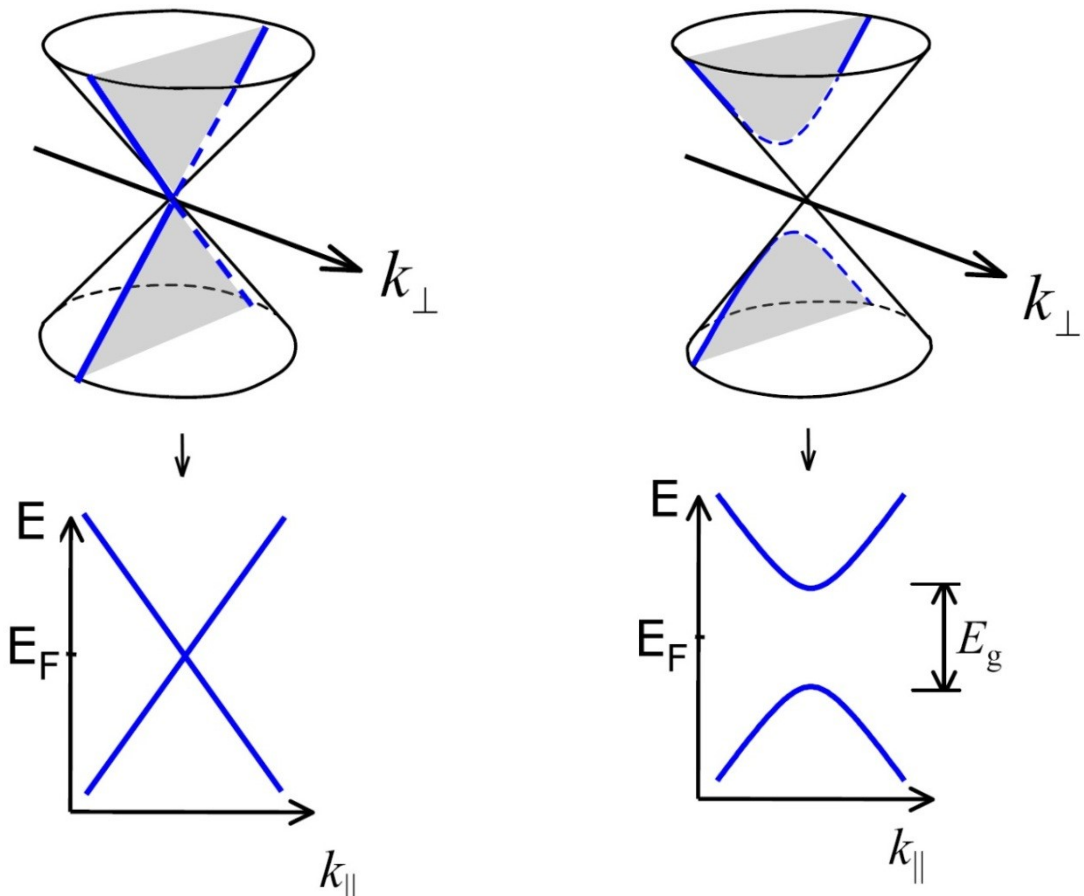
- Slices in graphene dispersion relation of allowed wavevectors around circumference
- Position of slices depends on chirality
- Small diameter CNT have larger distance between slices

Slice through K **Slice not through K**



Allowed wavevectors

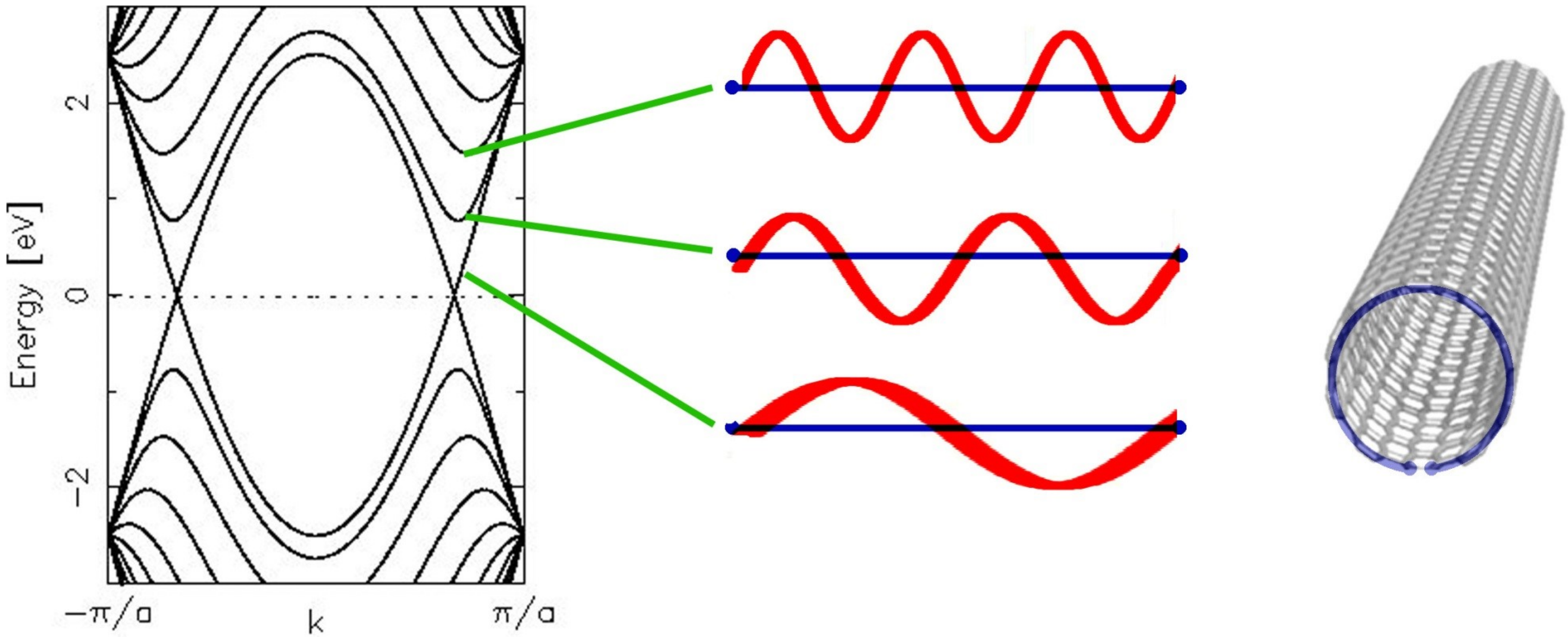
- n-m = 3i with i=1,2,3... -> slice goes through K-point -> metallic CNT
- n-m ≠ 3i -> slice does not go through K-point -> semiconducting CNT with parabolic bands



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

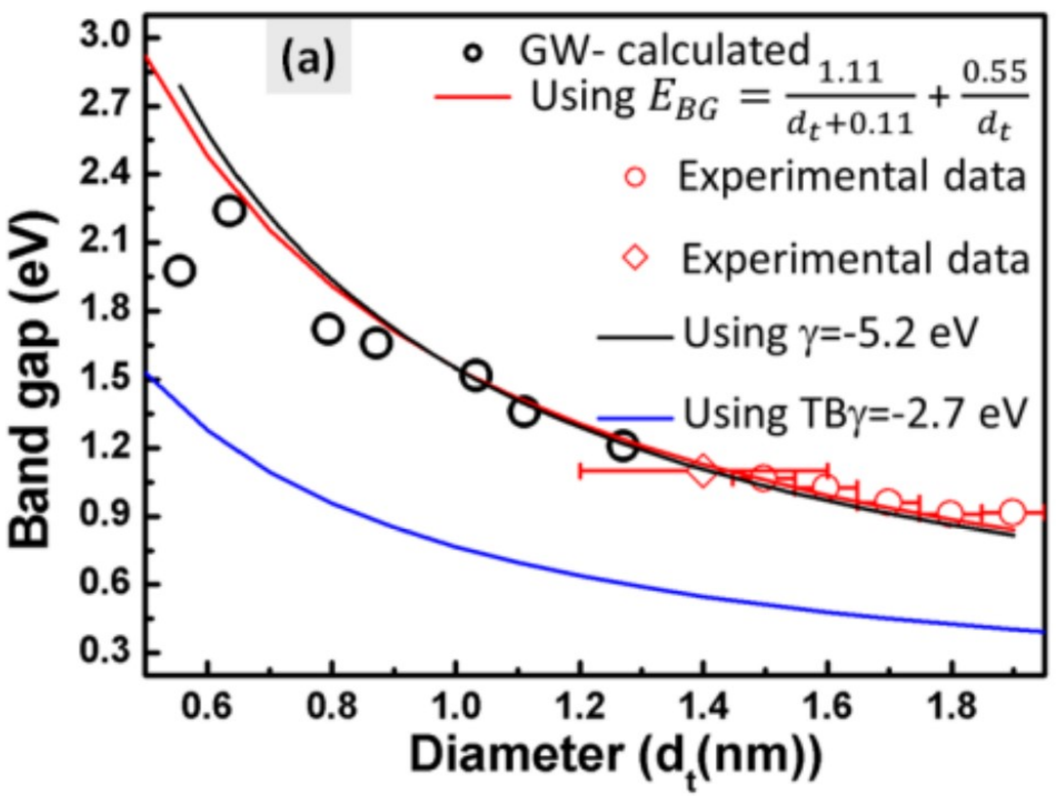
Subbands

- π-bands split into 1D subbands of increasing energy
- Mainly important at high gate voltages or for optical transistions
- Wavefunctions just schematic, need TB calculation



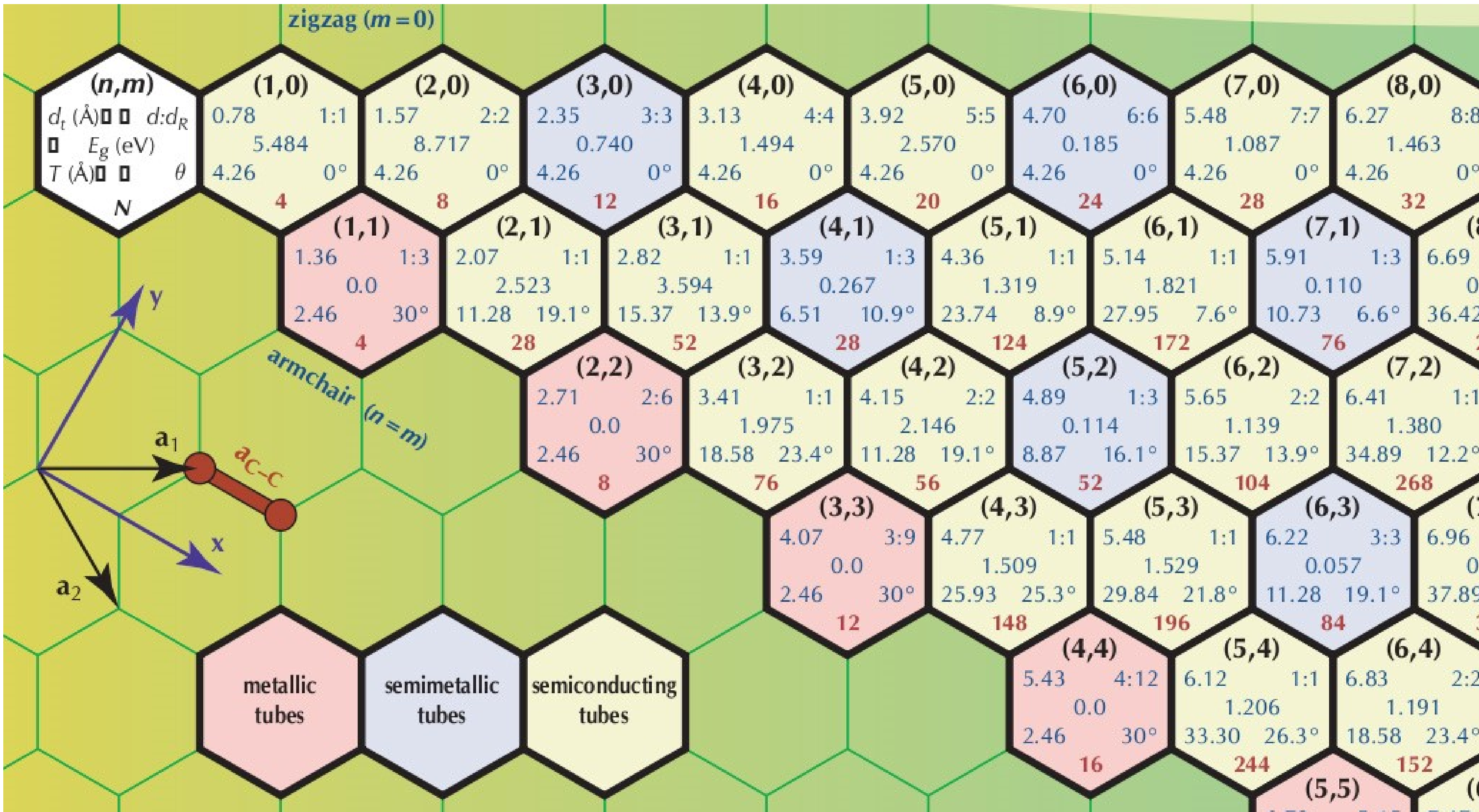
Band gap vs diameter

- 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

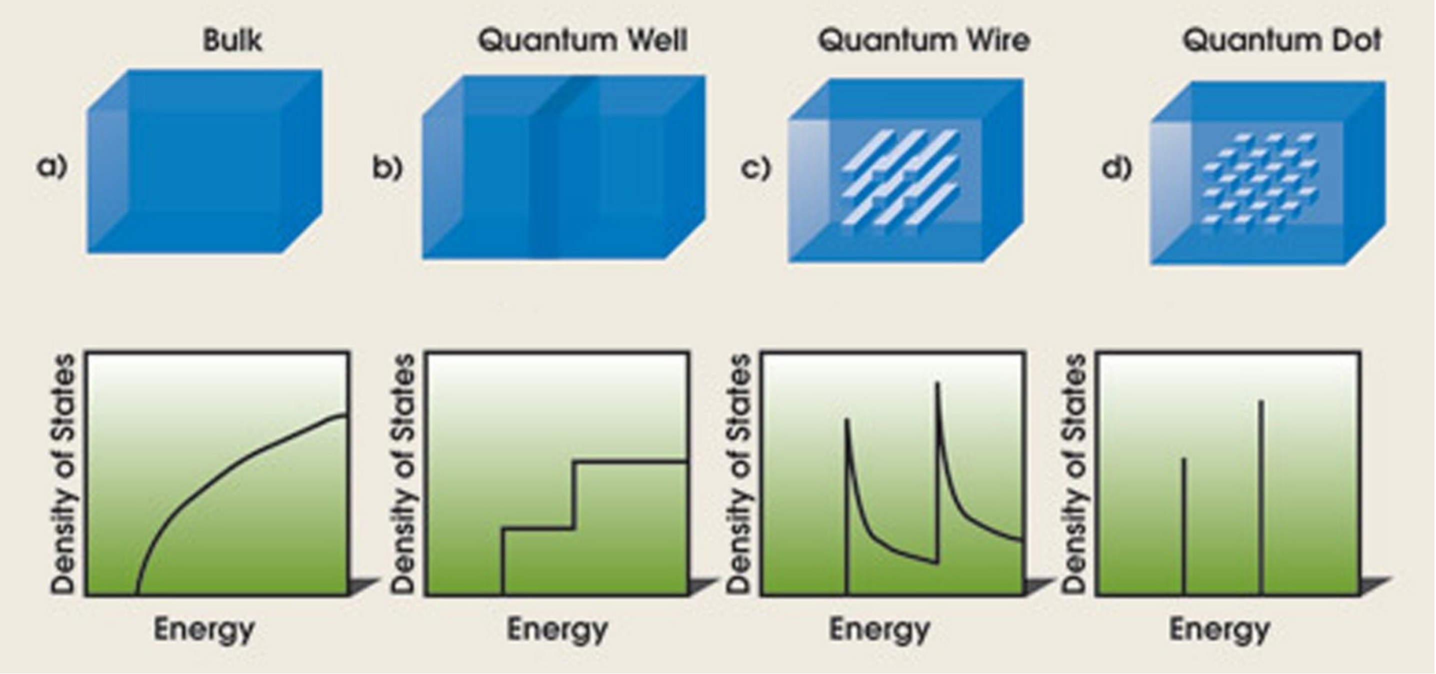
- 1/3 metallic or small gap
- 2/3 semiconducting with different gap

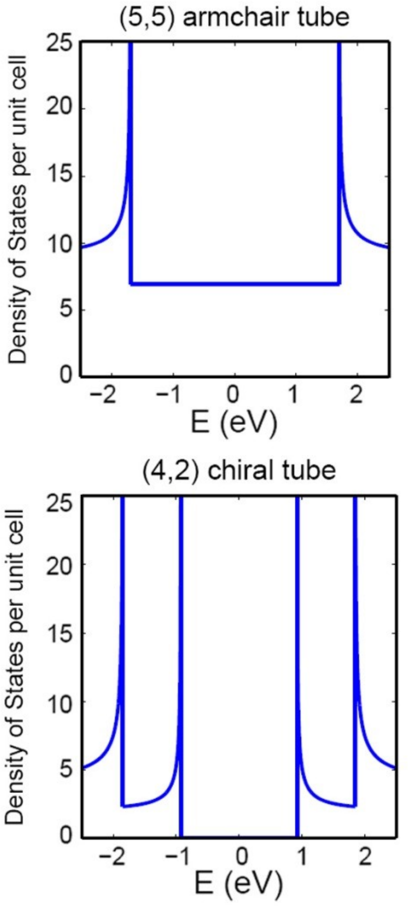


Density of states

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

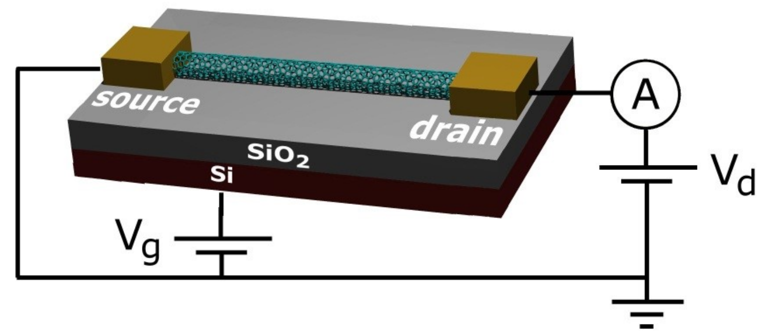
$$g_i(E) = \frac{4}{\pi \hbar v_{\mathrm{F}}} \left[1 - (E_{\mathrm{g}}^i / 2E)^2\right]^{-1/2}$$





Electrical characteristics

- Three types
  1. Semiconducting: strong gating effect
  2. Metallic: no gating effect
  3. Small gap semiconducting: some gating effect

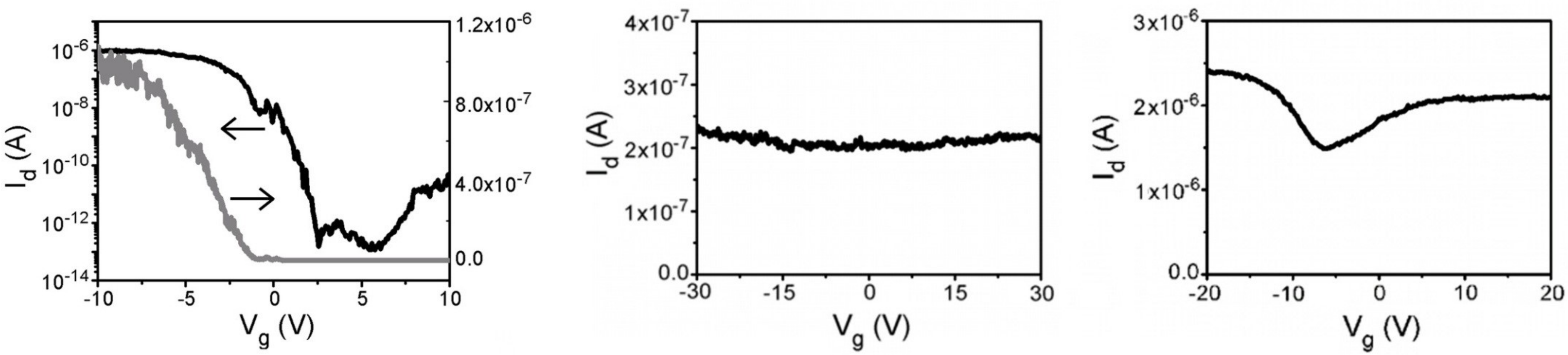


- Can withstand 10^9 A/cm^2

semiconducting

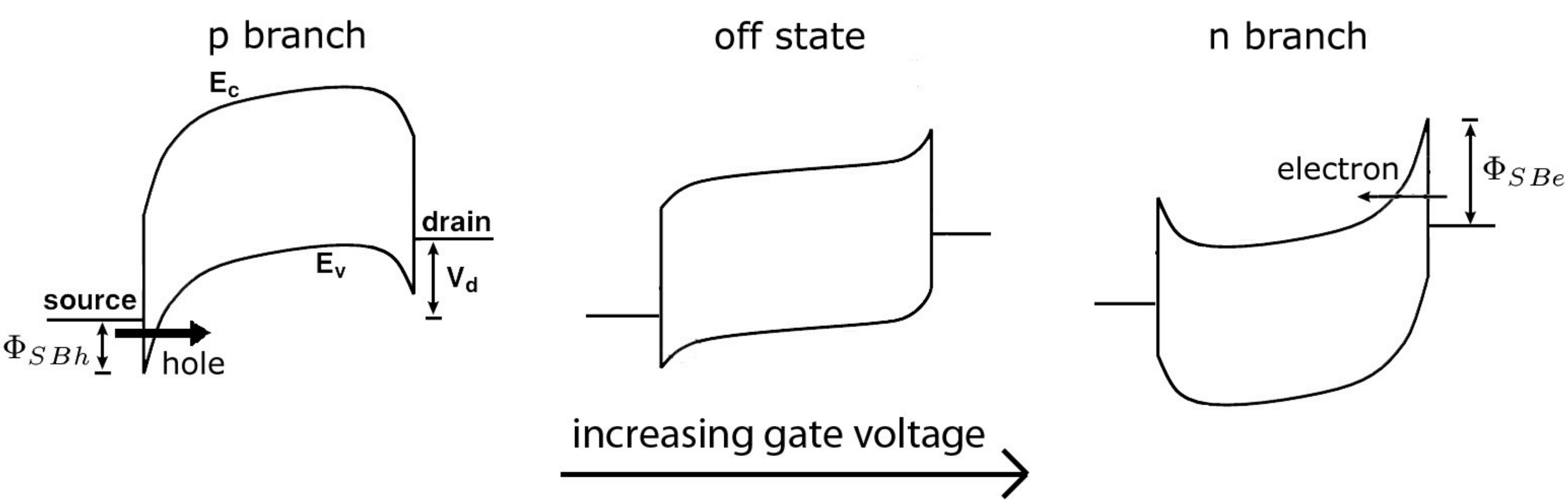
metallic

small band gap



Transport through Schottky barriers

- First CNTFETs had 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

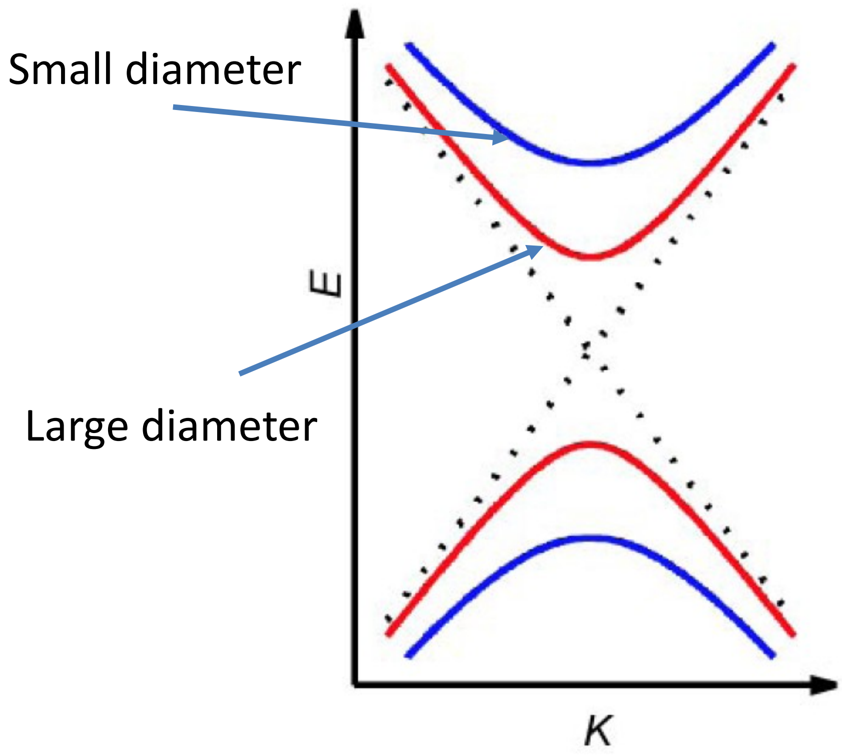


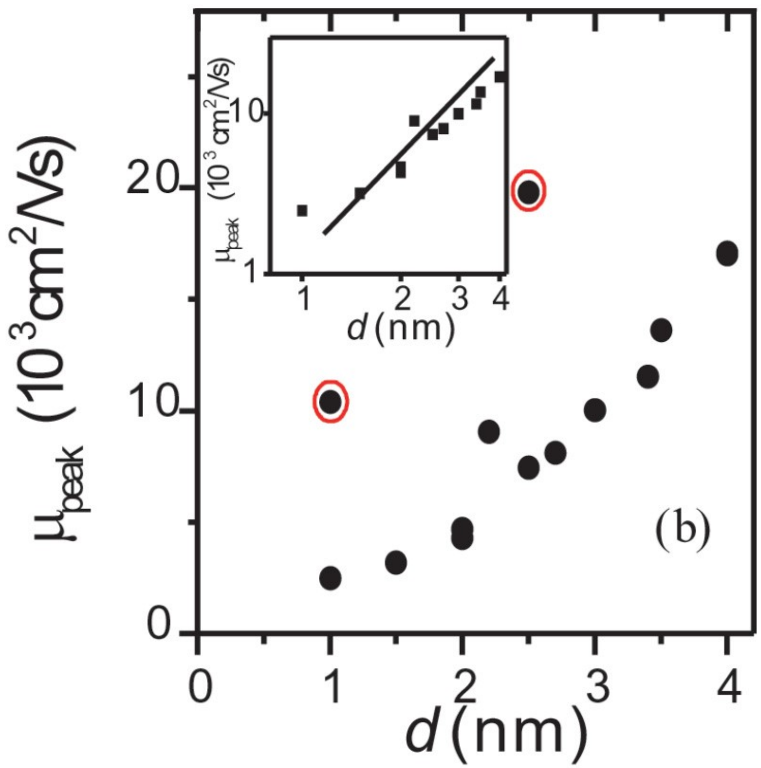
Mobility vs diameter

- Lower curvature of bands for smaller diameter -> mobility proportional to d^2
- $\mu > 100\,000\ cm^2/Vs$ at 50 K

$$m^* = \hbar^2 \cdot \left[\frac{d^2\varepsilon}{dk^2}\right]^{-1} .$$

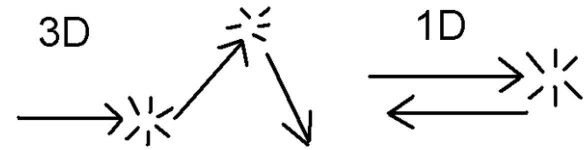
$$\mu_{FE} = \frac{L^2}{C_g}\frac{\partial G}{\partial V_g}$$



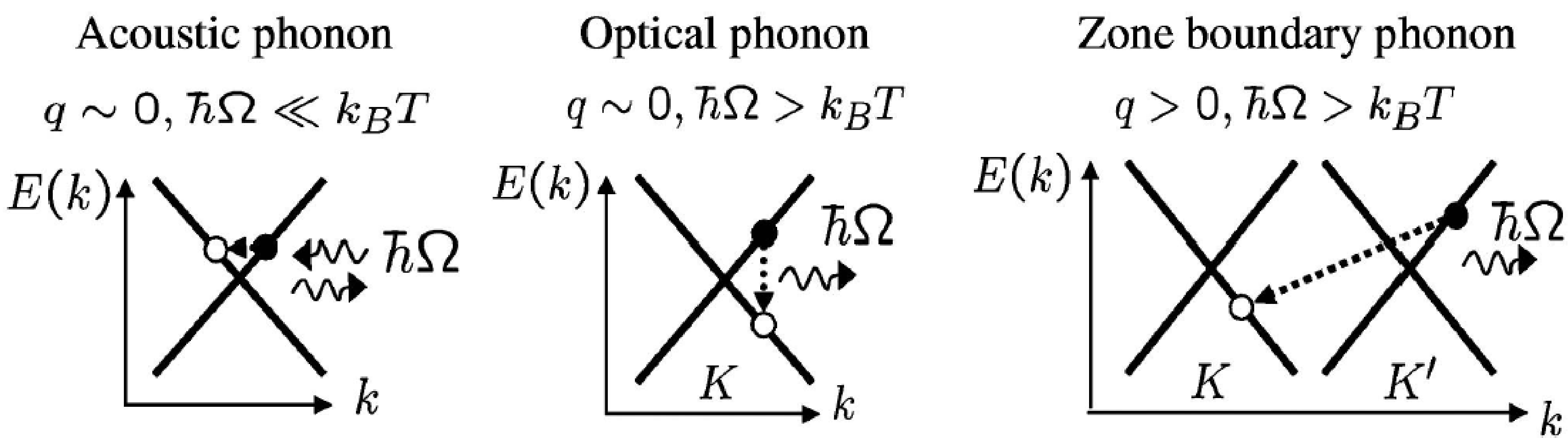


Scattering

- Elastic scattering has to reverse direction of electron

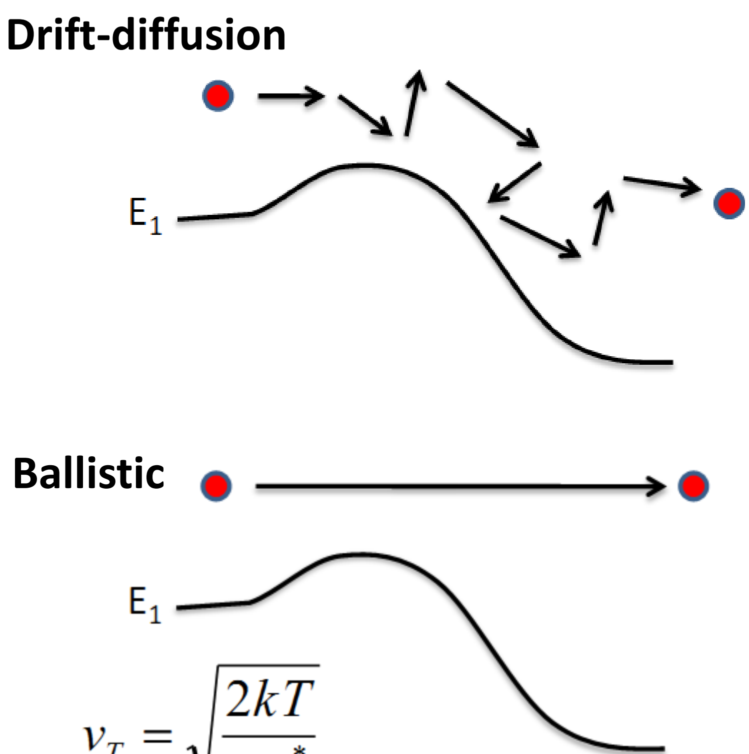


- Acoustic phonon scattering dominates at low bias and gives mfp > 300 nm -> ballistic transport possible
- Optical phonons scattering dominates only at high bias and gives mfp = 15 nm
- Potential variations or phonons in substrate under CNT can also scatter electrons

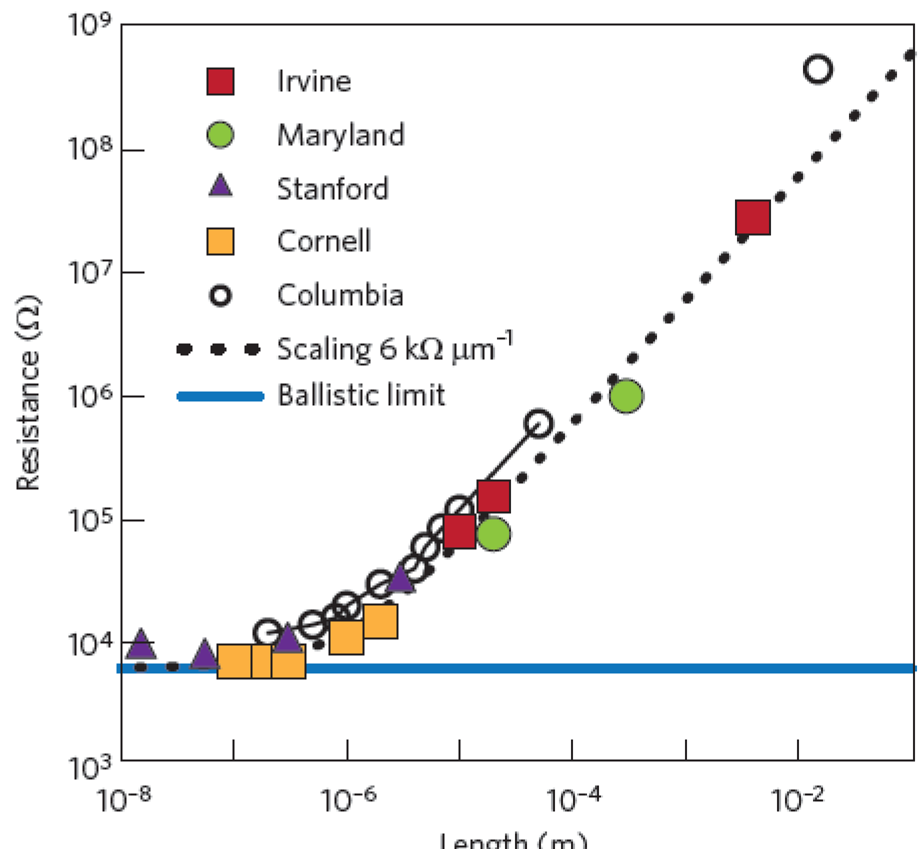


Ballistic transport

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

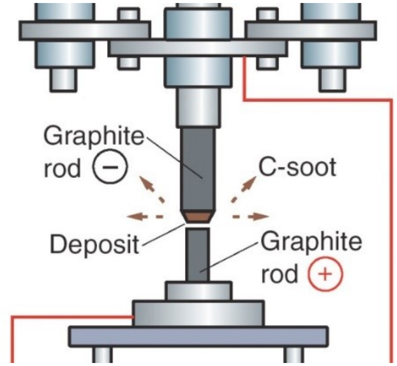


$$v_T = \sqrt{\frac{2kT}{\pi m^*}}$$

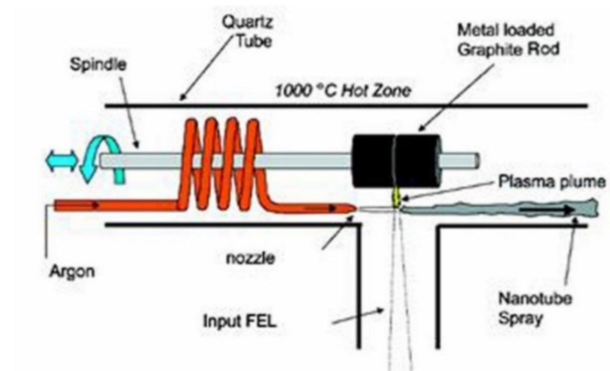


Production of CNTs

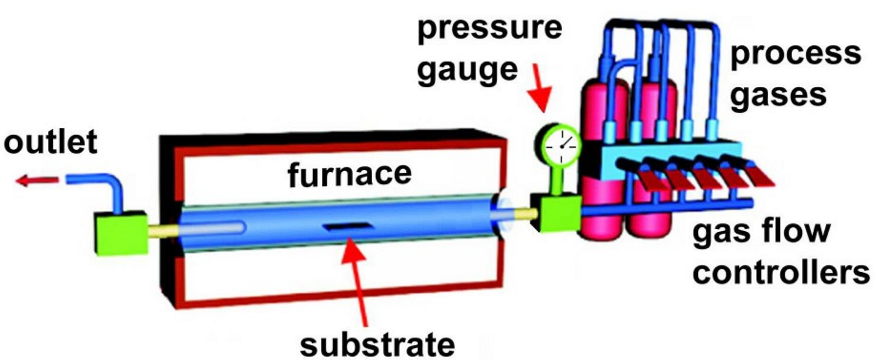
- Arc discharge: high voltage creates spark between graphite rods

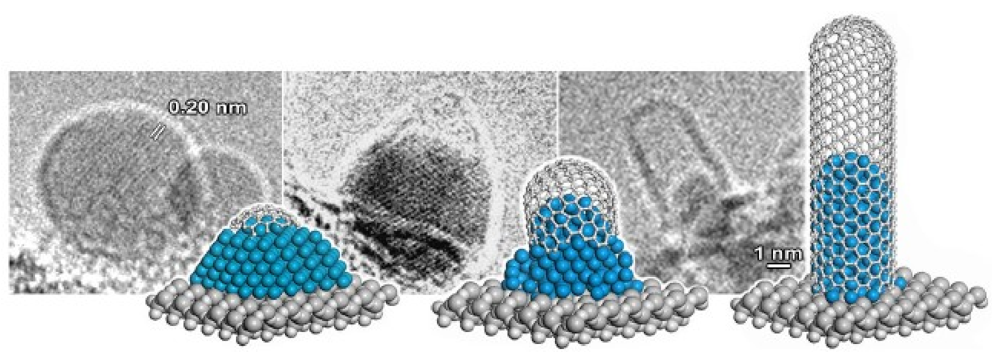


- Laser ablation: laser vaporises graphite target



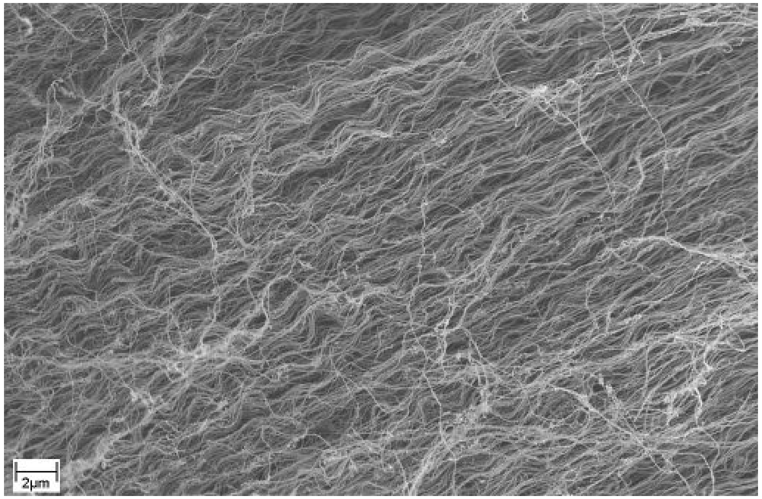
- Chemical vapor deposition: metal catalyst particles decompose hydrocarbon gas

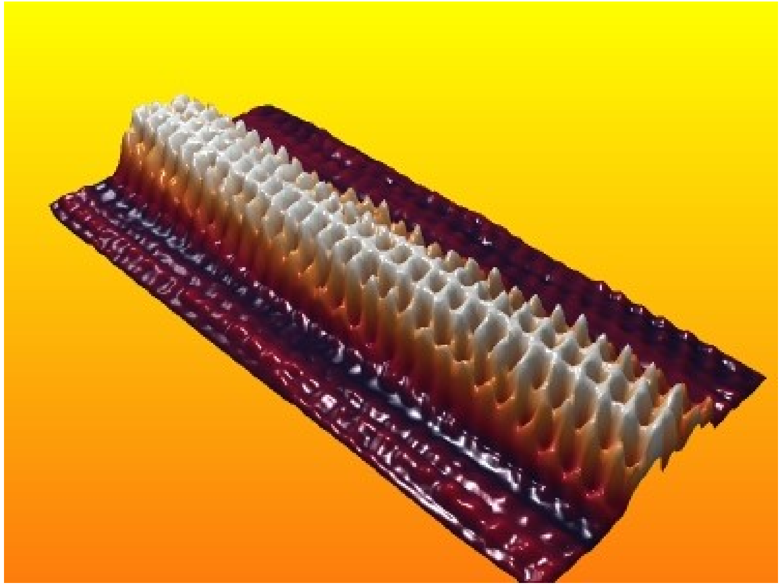


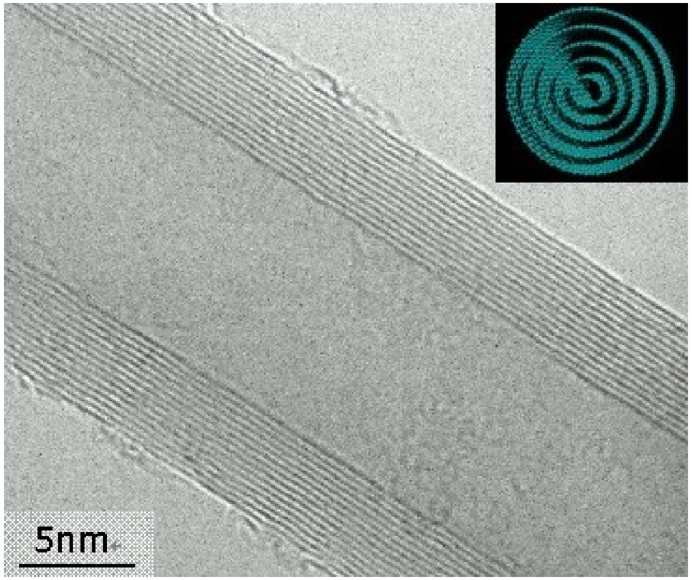


Grown CNTs

- d=1-4 nm, L > 30 cm
- Can be imaged using SEM, TEM, AFM, STM
- Deposit from suspension or grow on device substrate
- Mix of metallic, semiconducting and small band gap semiconducting

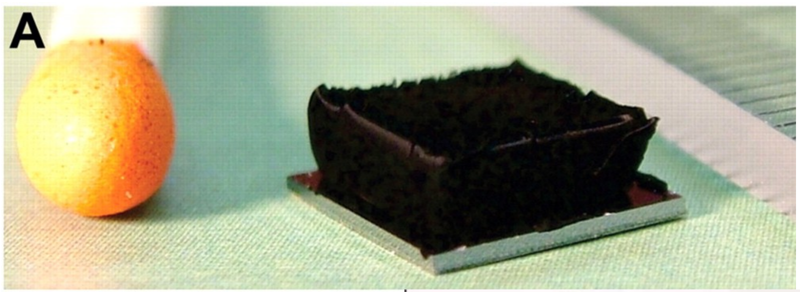


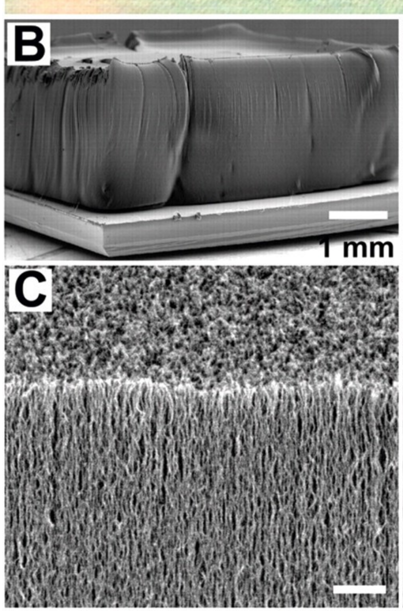




VANTA black

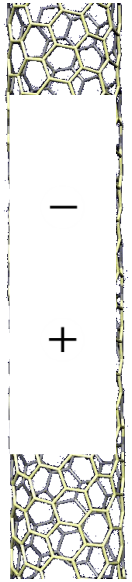
- **V**ertically **A**ligned **N**ano**T**ube **A**rray
- Absorbs 99.965% of visible light

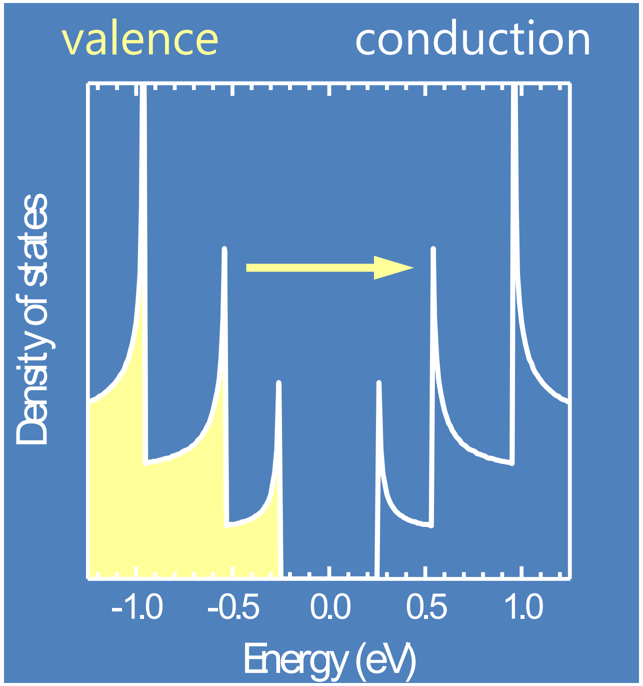


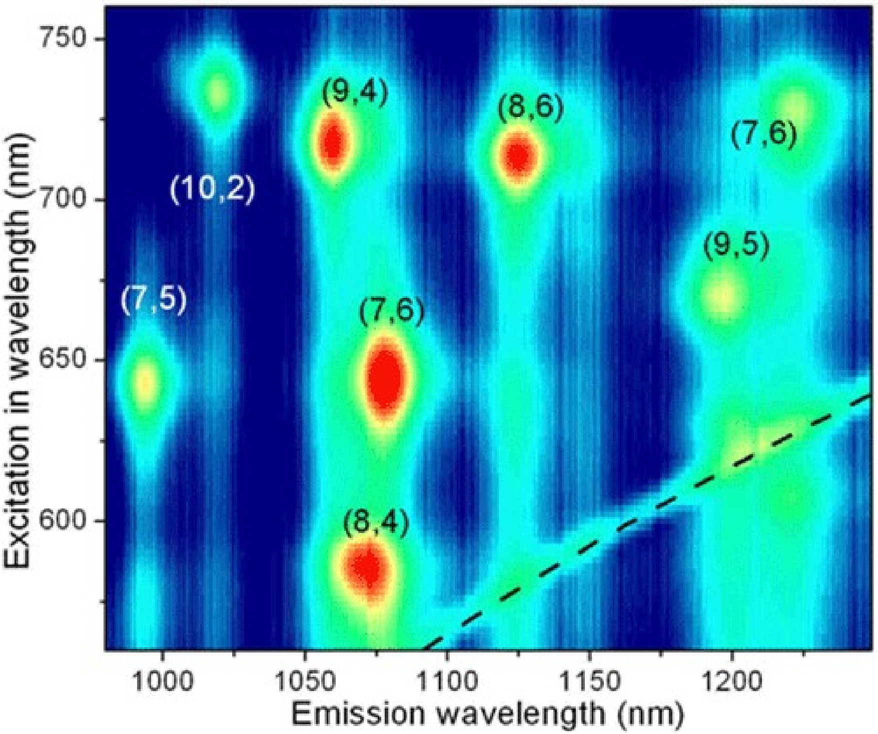


Determination of type

- Photoluminescence with varying excitation λ
- Every (*n*,*m*) nanotube has specific pairs of transition energy







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Gate length scaling

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

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

\+ Higher packing density -> less interconnect delay, cheaper

\- Short channel effects (drain potential influence the channel) -> poor subthreshold slope, DIBL, high output conductance (g_d).

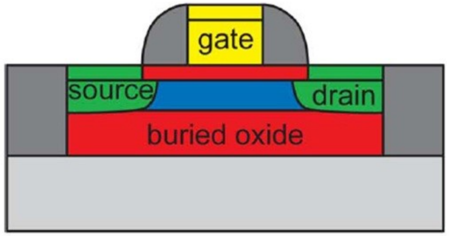
ITRS 2015 - 3 nm node: L_g=10 nm, L_c=11 nm, spacer=4 nm -> footprint =40 nm

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

Different gate geometries

- λ = 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 λ -> enables L_g scaling
- CNTs and graphene allows for very good gate length scaling

planar



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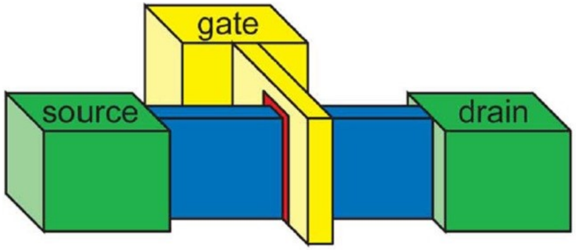
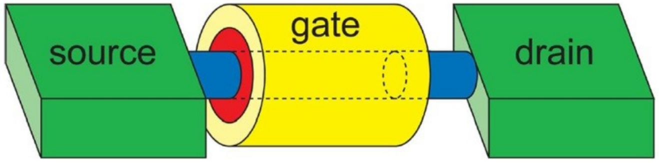


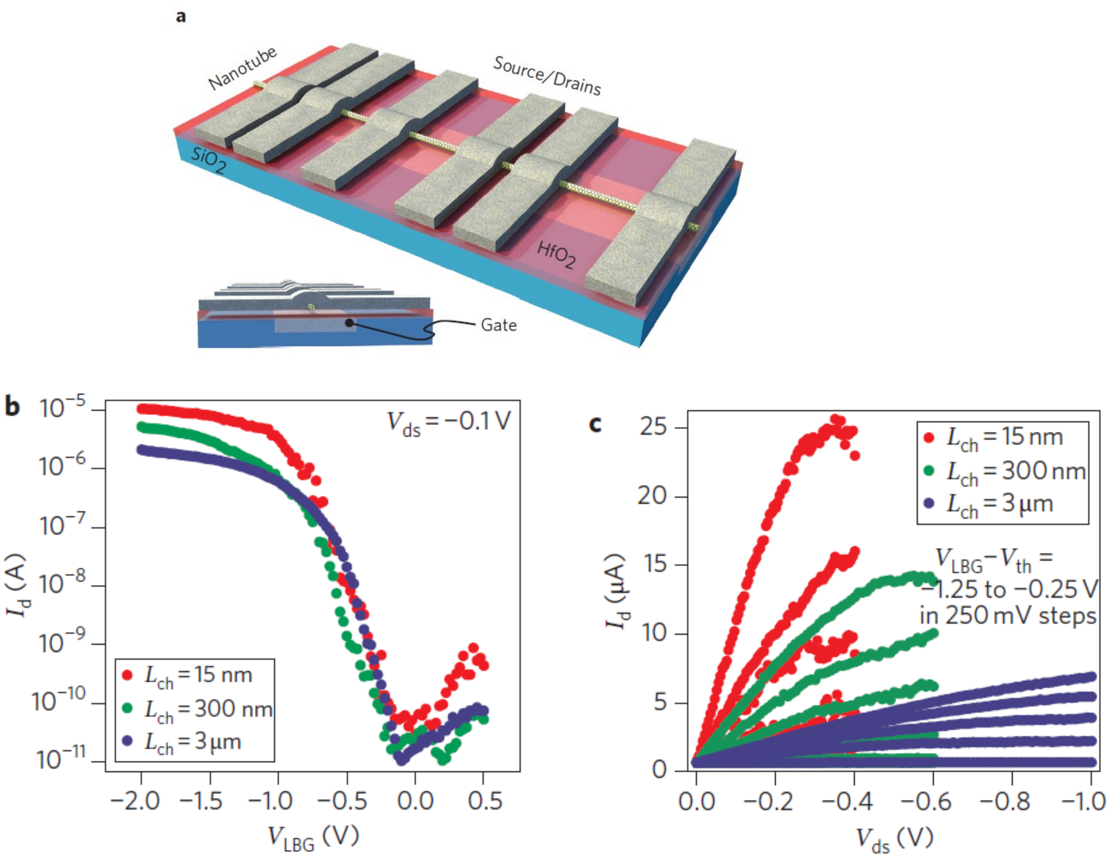
gate-all-around

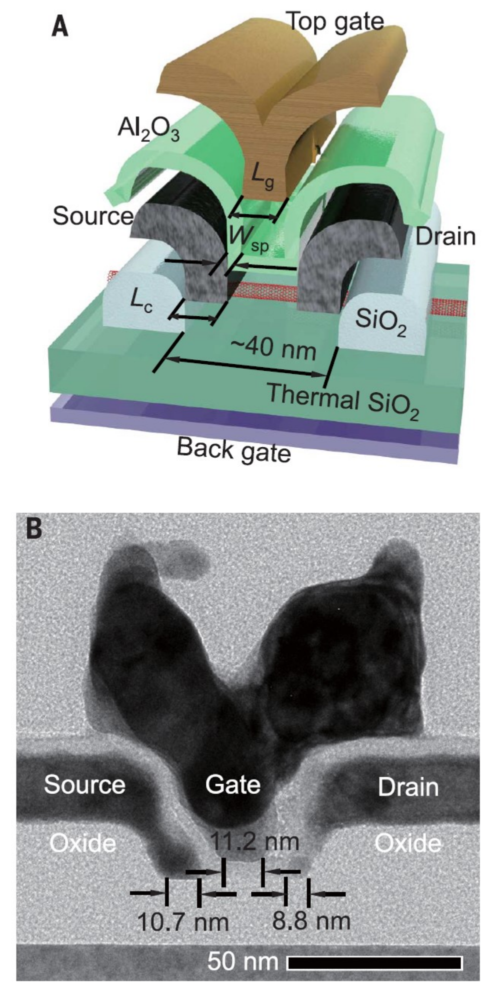


$$\lambda_1 \approx \sqrt{\frac{\varepsilon_{ch}}{\varepsilon_{ox}} t_{ox} t_{ch}} \quad > \quad \lambda \approx \sqrt{\frac{\varepsilon_{ch}}{2\varepsilon_{ox}} t_{ch} t_{ox} \left(1 + \frac{\varepsilon_{ox}}{4\varepsilon_{ch}} \frac{t_{ch}}{t_{ox}}\right)} \quad > \quad \lambda \approx \sqrt{\frac{\varepsilon_{ch}}{4\varepsilon_{ox}} t_{ch} t_{ox} \left(1 + \frac{\varepsilon_{ox}}{4\varepsilon_{ch}} \frac{t_{ch}}{t_{ox}}\right)}$$

Gate length scaling

- No short channel effects (DIBL, SS degradation) down to L_g=15 nm
- I_{on} = 0.9 mA/µm -> normalisation ?
- on/off ratio = 10^5
- SS = 90 mV/dec also for short devices



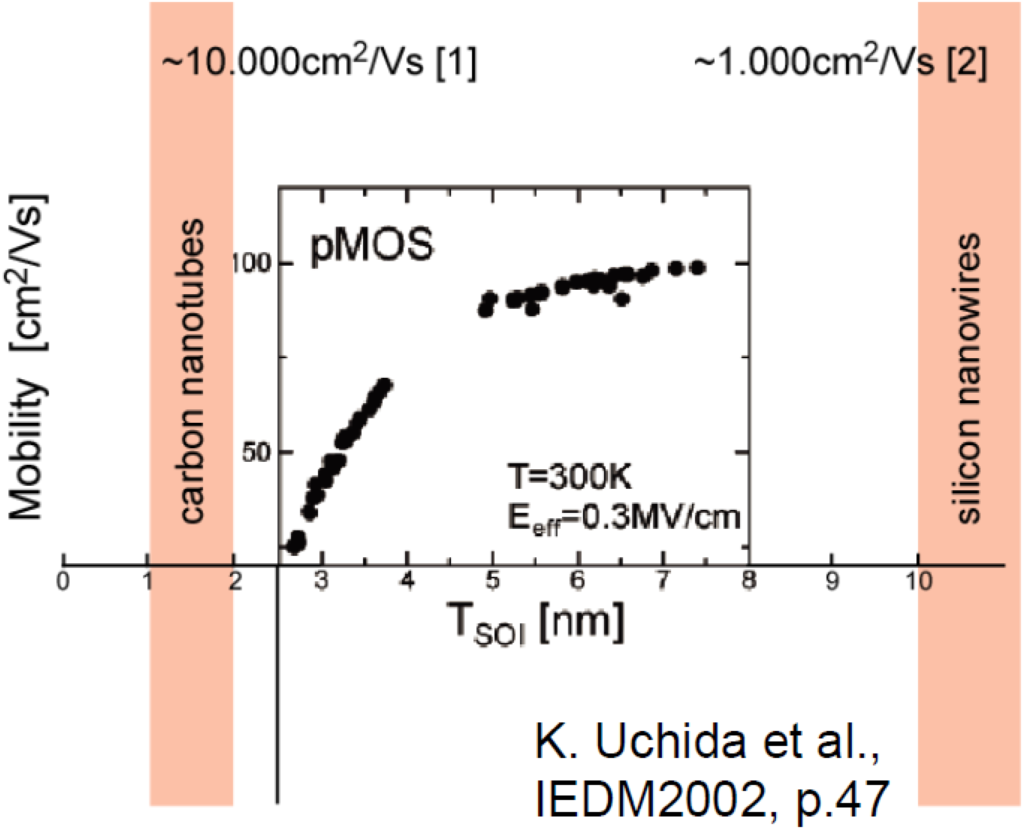


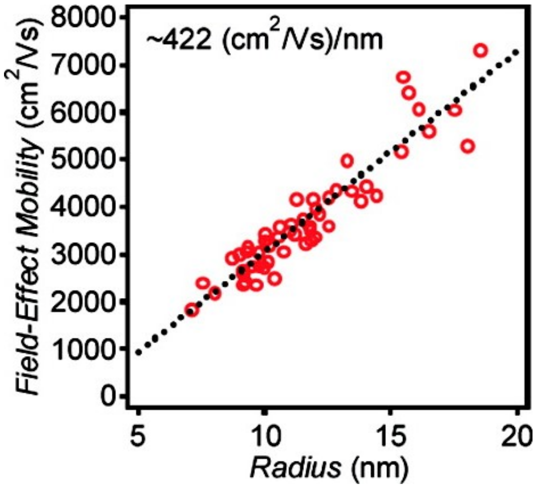
Franklin et al. *Nature Nanotechnol.* **5**, 858–862 (2010)

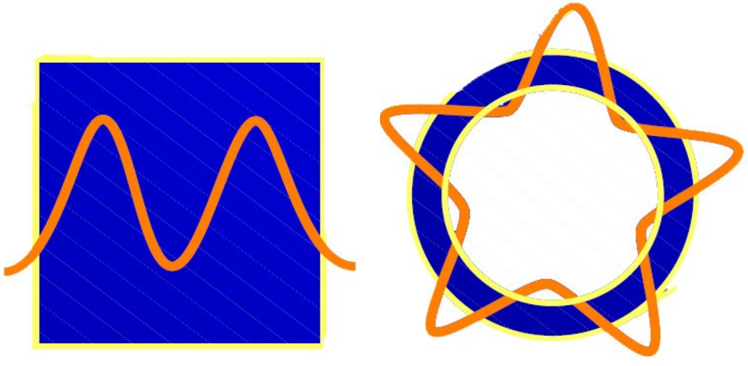
Cao et al., *Science* 356, 1369–1372 (2017)

Surface scattering

- Need to reduce channel thickness to be able to reduce L_g
- Surface roughness scattering gives $\mu \sim t^6$ for SOI MOSFETs
- Not a problem for CNTs – no unsaturated bonds / no roughness

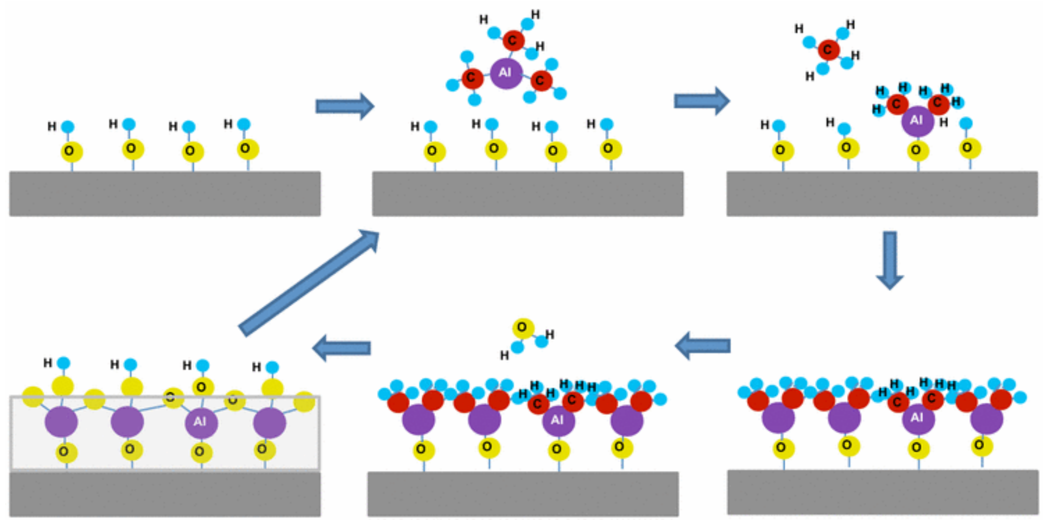


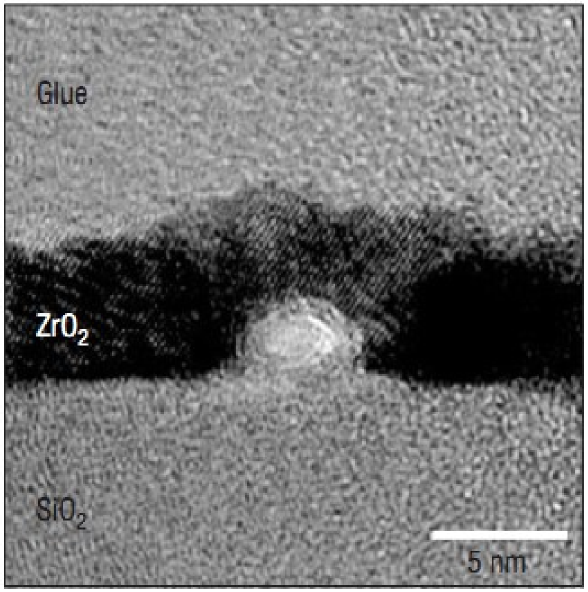


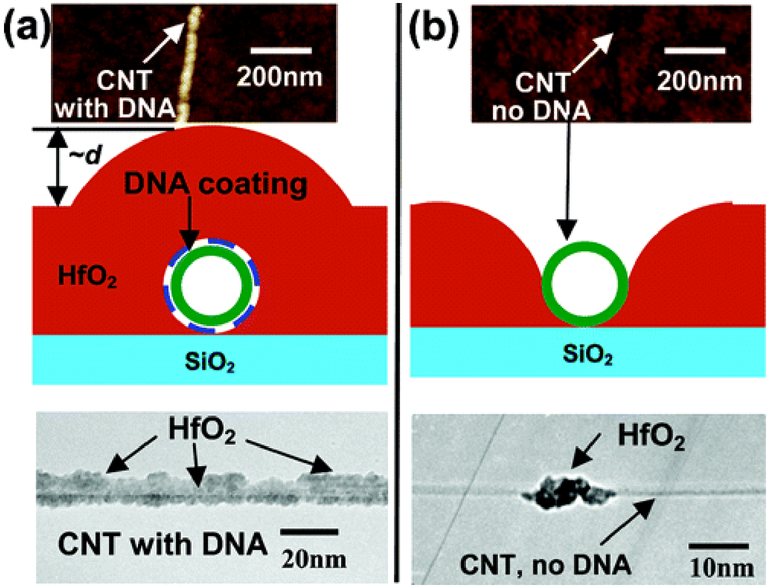


High k gate dielectrics

- Need OH groups for ALD.
- Overgrow from surface or functionalize CNT.
- No dangling bonds give nice interface? Traps in oxide?





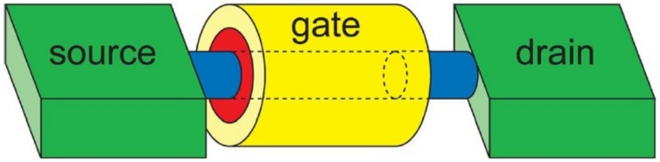


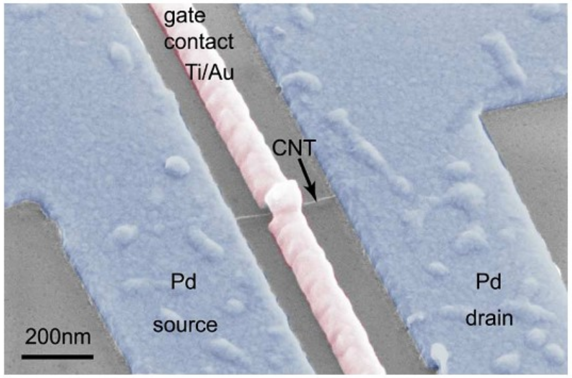
Javey et al. *Nature Materials,* 1 (4), 241-246, 2002

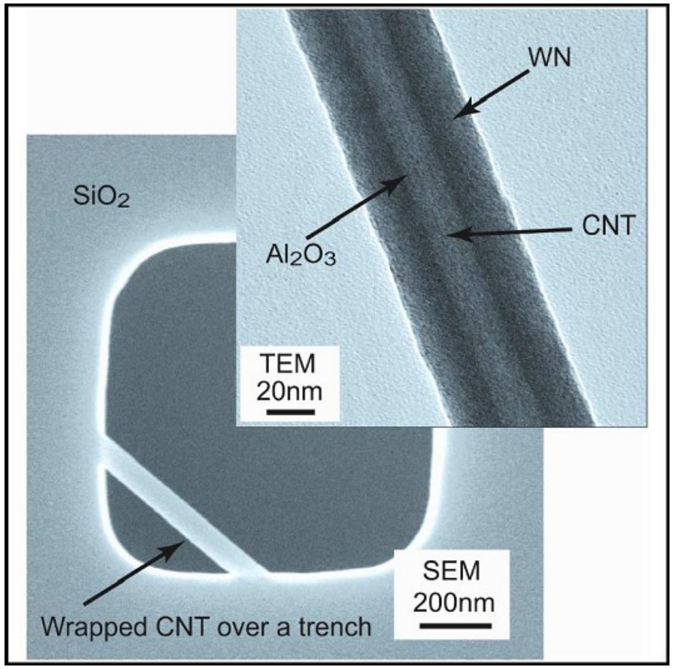
Lu et al. *J. Am. Chem. Soc.*, 128, 3518–3519, 2006

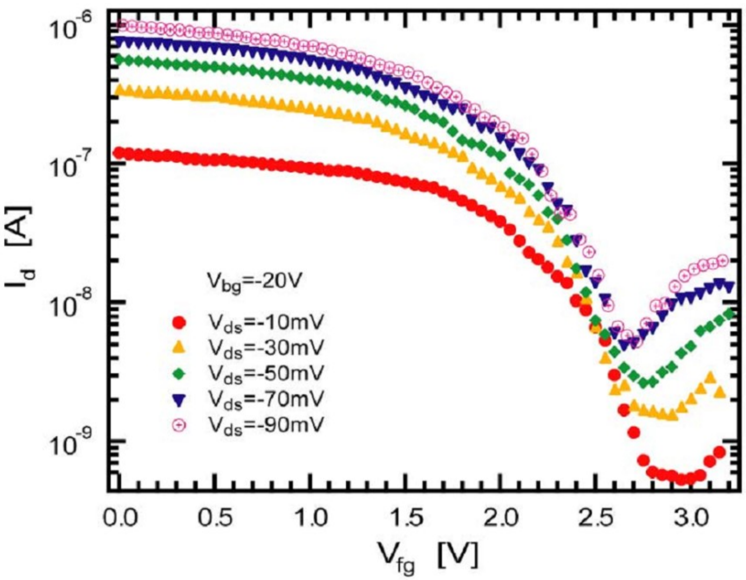
Gate-all-around CNTFET

- Wrap CNT in Al2O3 and WN using ALD
- Poor subthreshold swing due to interface traps and short channel effects





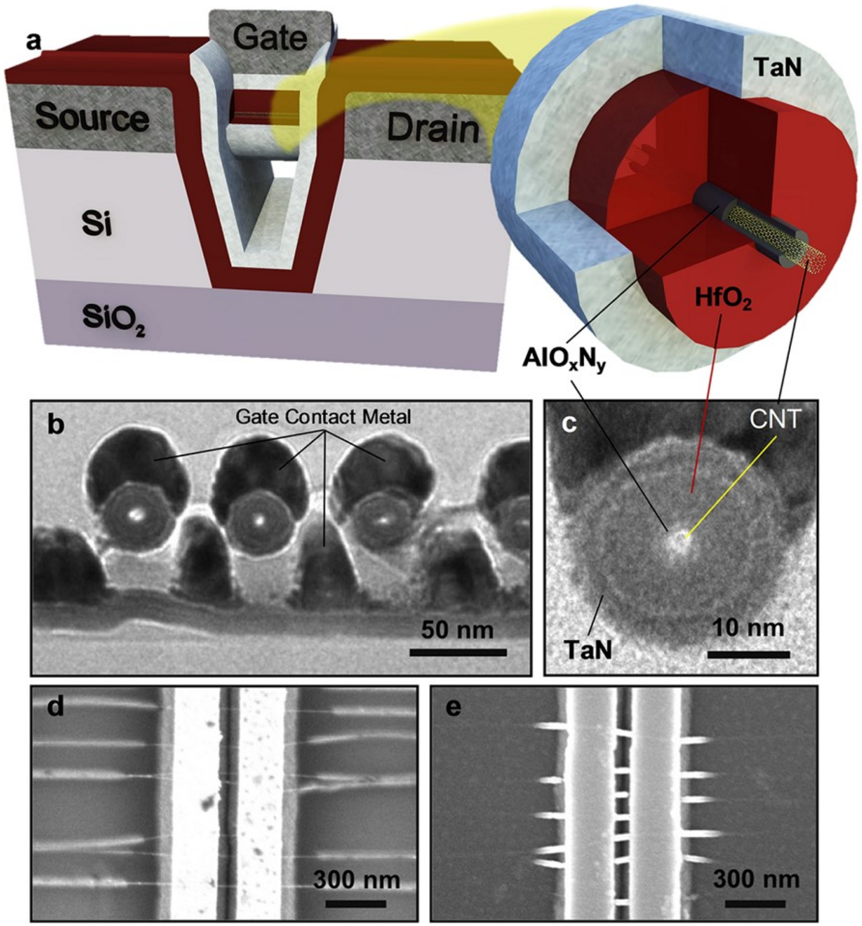


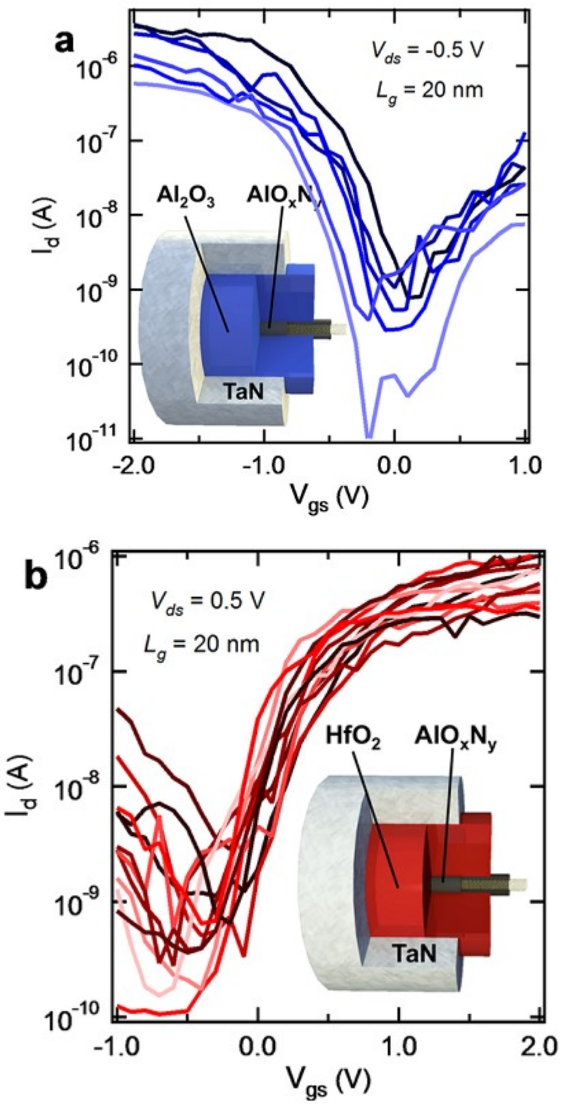


Chen et al. *IEEE Electron. Dev. Lett*. **29**, 2 (2008)

Different high-k

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

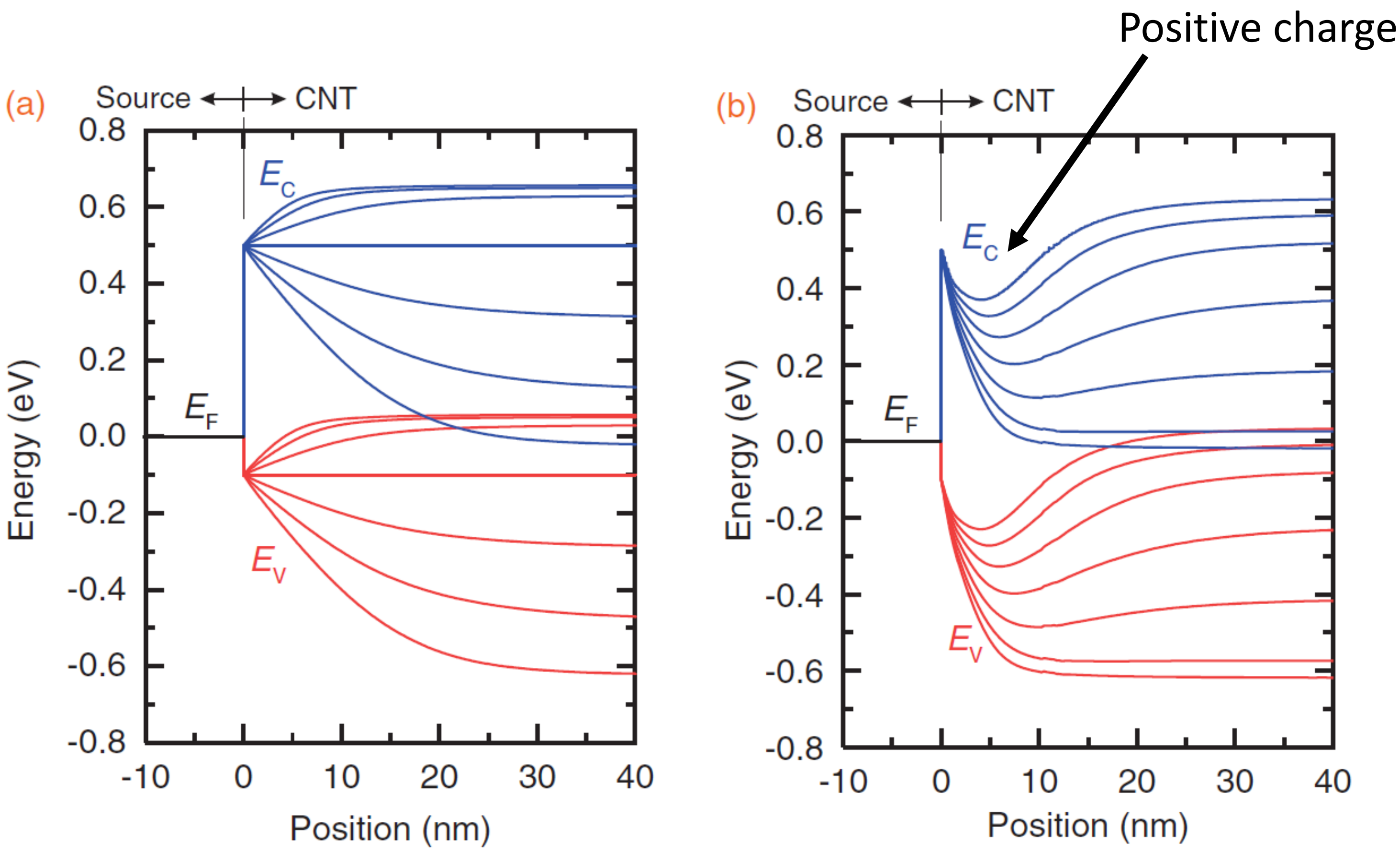




Franklin et al. *Nano Lett.* 13 (6), (2013)

Conversion from p- to n-type

- High work function metal -> low Schottky barrier to valence band
- Positive charge (in e.g. oxide) close to contact increases barrier to valence band and thins down barrier to conduction band.

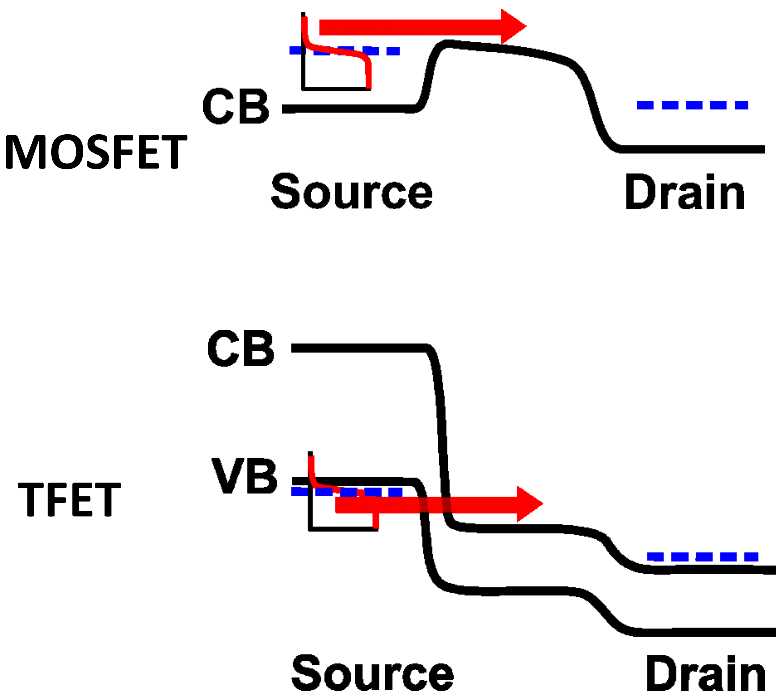


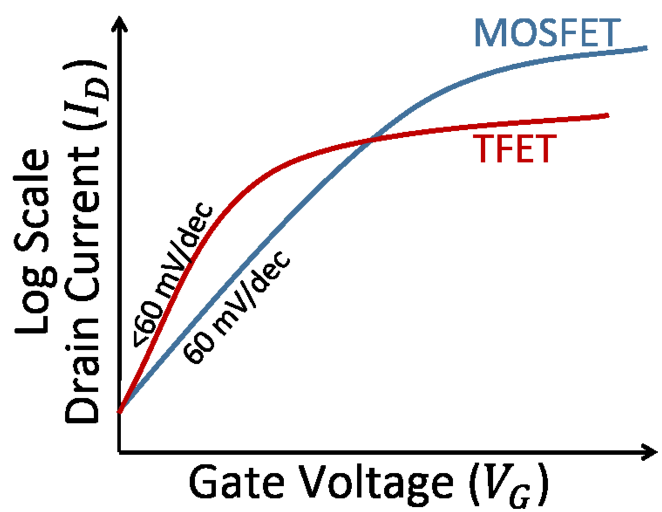
Suzuki, Appl. Phys. Express 6 (2013)

Improving the inverse subthreshold slope

- ”conventional” FETs rely on thermionic emission over a barrier
- SS ≥ ln(10) $k_B T$ = 60 mV/dec at room temperature
- A decreased SS enables a lower V_{dd} while keeping the same on/off ratio -> increased speed and reduced power consumption

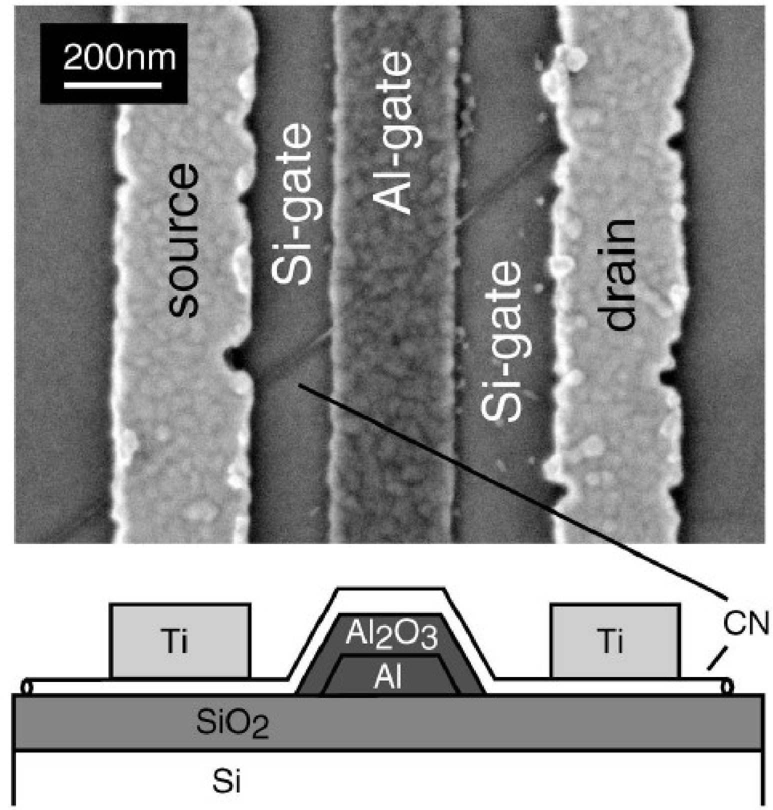
$$S = \left(\frac{d log_{10}(I_d)}{dV_g} \right)^{-1}$$





Band-to-band tunneling transistor

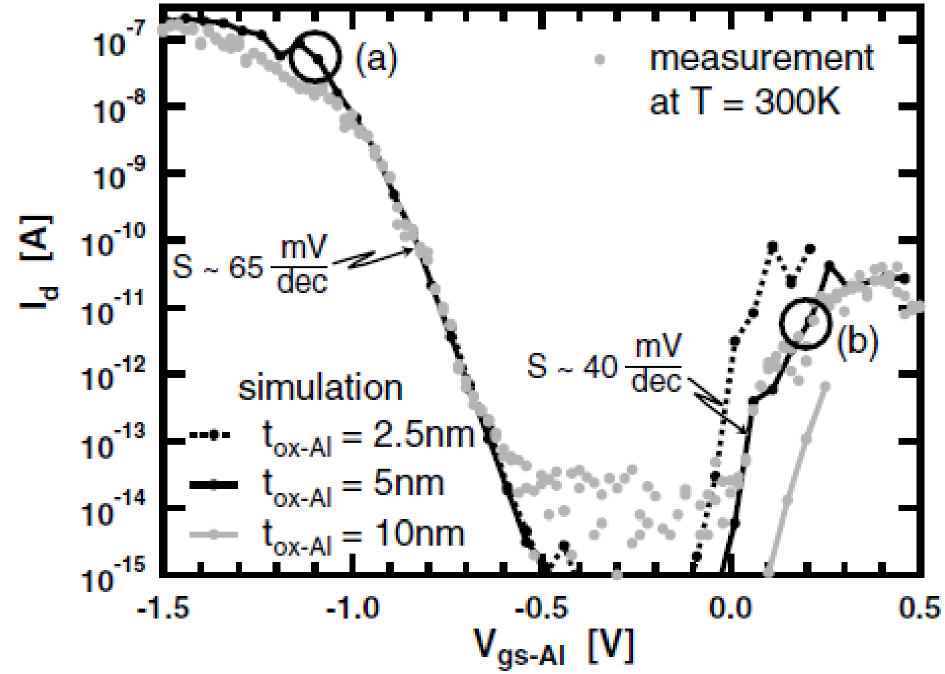
+ λ is a few nm in CNT - > sharp band bending
+ Low effective mass
+ Long mfp
+ Same effective mass of electrons and holes
+ Direct band gap

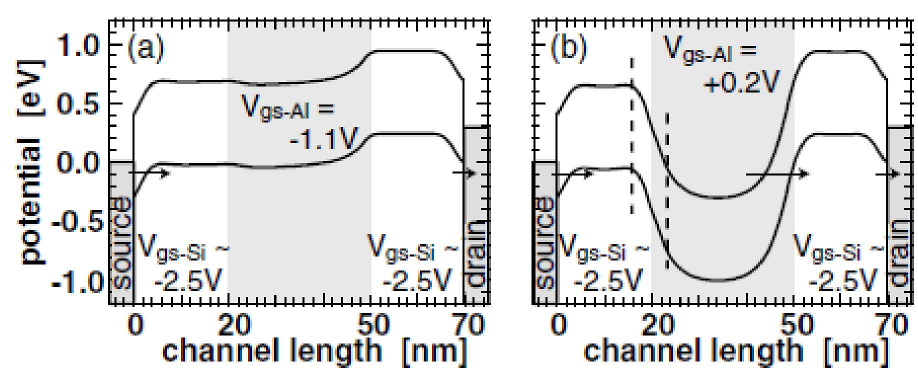


Appenzeller et al. *PRL*. **93**, 196805 (2004)

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





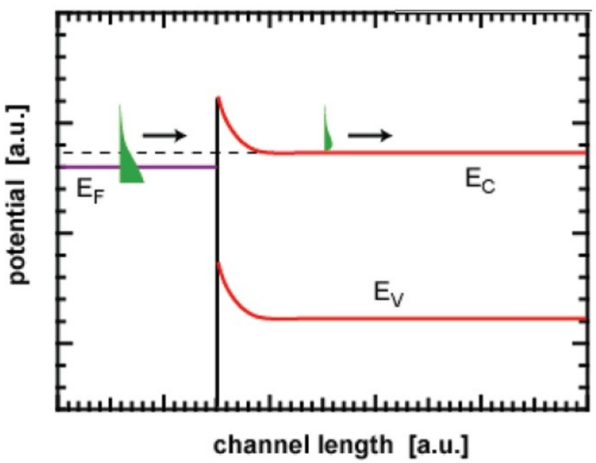
Mechanism of SS reduction

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

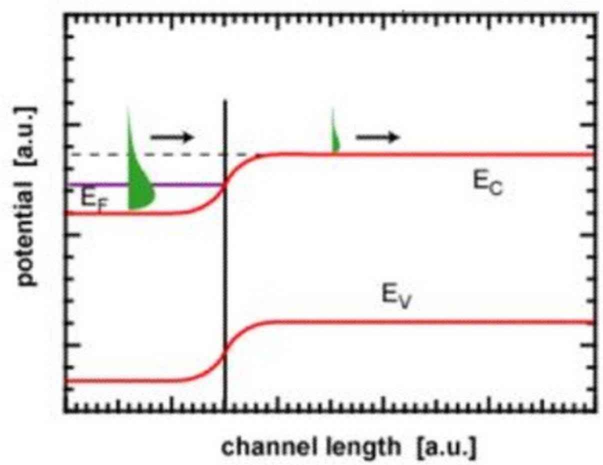
- Band-to-band tunneling ”filters” the Fermi-Dirac distribution

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

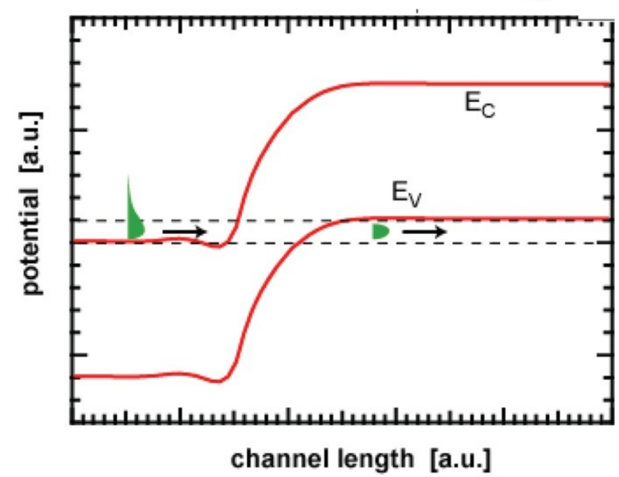
tunneling at Schottky barrier



thermionic emission



band-to-band tunneling



Outline

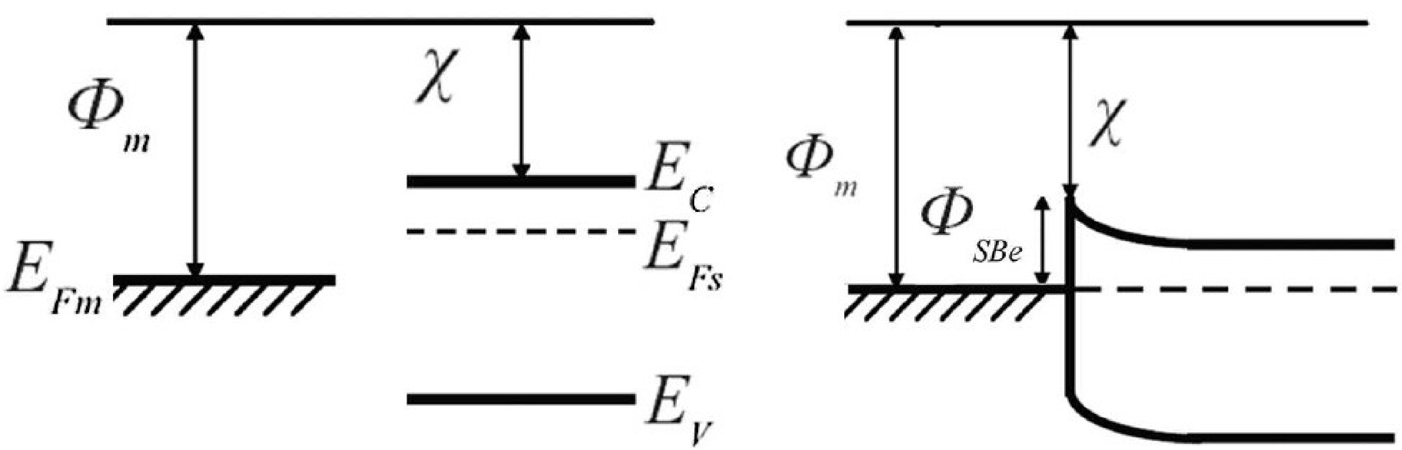
- Basics of graphene and CNTs
  - Structural
  - Electronic
  - Production of CNTs
- Advantages of CNTs for FETs
  - Electrostatics -> length scaling
  - High-k compatibility
  - Band-to-band tunneling
- Challenges of CNT integration
  - Contacts
  - Doping
  - Positioning
  - Chirality control
- Towards integration
  - Flexible electronics
  - High frequency performance

Schottky barrier basics

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

$$\Phi_{SBe} = \phi_m - \chi$$

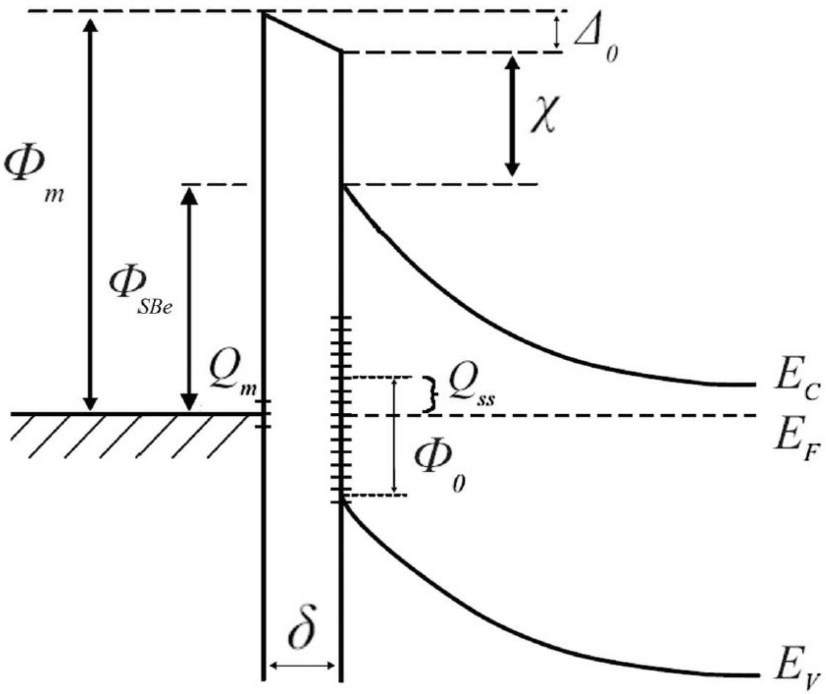
$$\Phi_{SBh} = \chi + E_g - \phi_m = I_s - \Phi_m$$

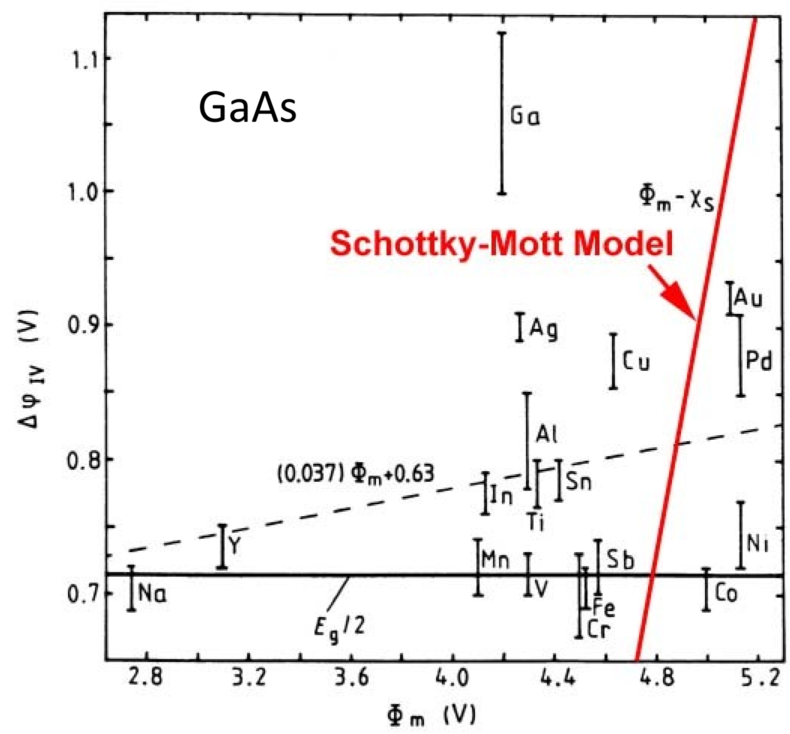


Fermi level pinning

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

$$\Phi_{SBe} = \gamma(\Phi_m - \chi) + (1-\gamma)(E_g - \Phi_0) \qquad \gamma = \frac{1}{1 + \frac{qD_{it}\delta}{\epsilon_i}}$$

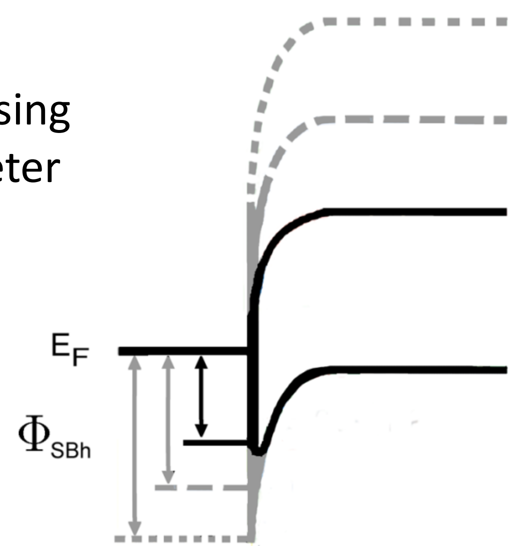




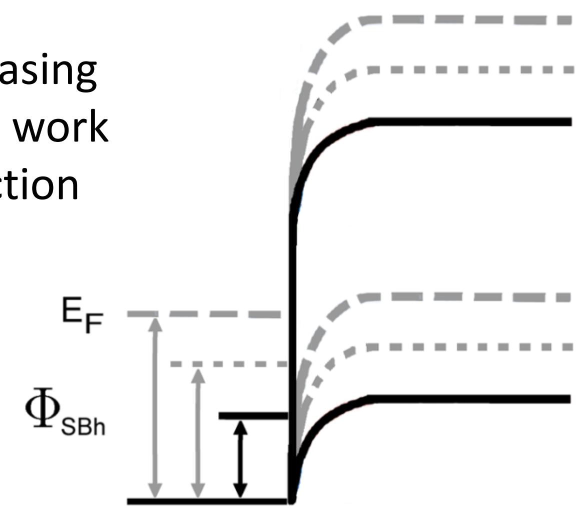
Schottky barrier to CNTs

- 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

Increasing diameter

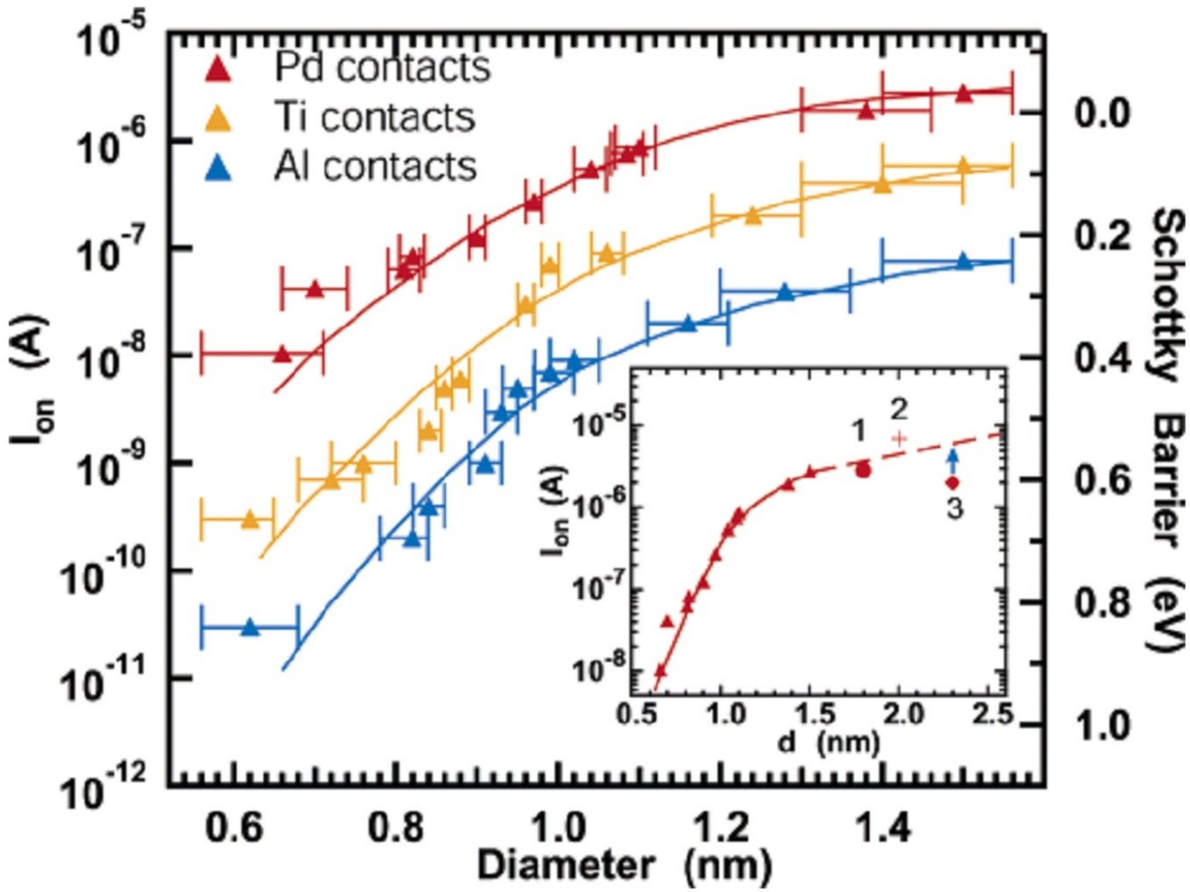


Increasing metal work function



Different contact metals

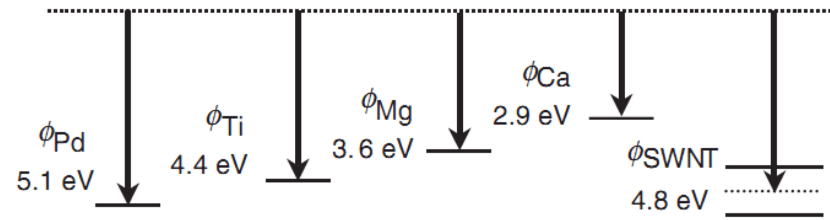
- Increasing I_{on} with larger CNT diameter
- Increasing I_{on} with higher work function
- No or small effect of Fermi level pinning

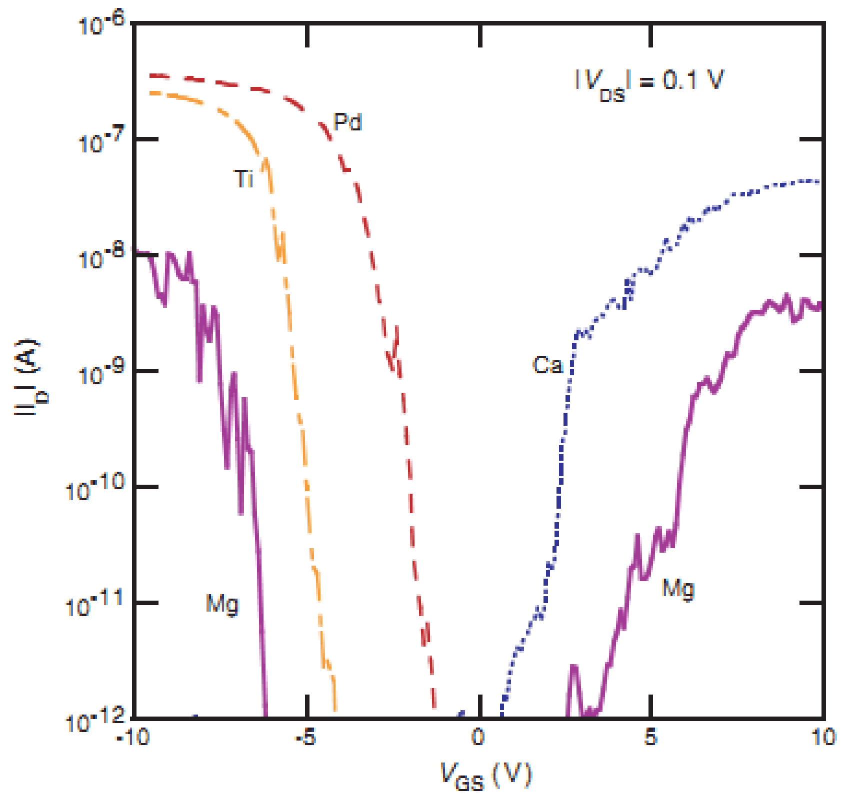


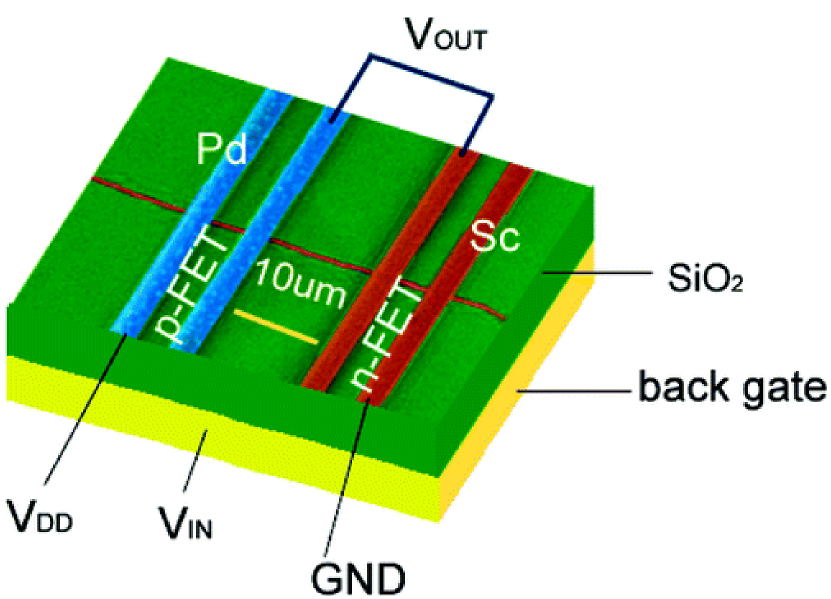
Chen et al. *Nano Lett.* **5,** 1497–1502 (2005)

Impact of metal work function

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





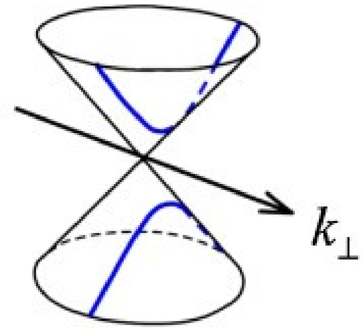


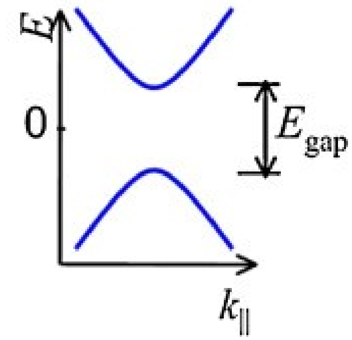
Nosho et al. *Nanotechnology* **17** , 3412 (2006)

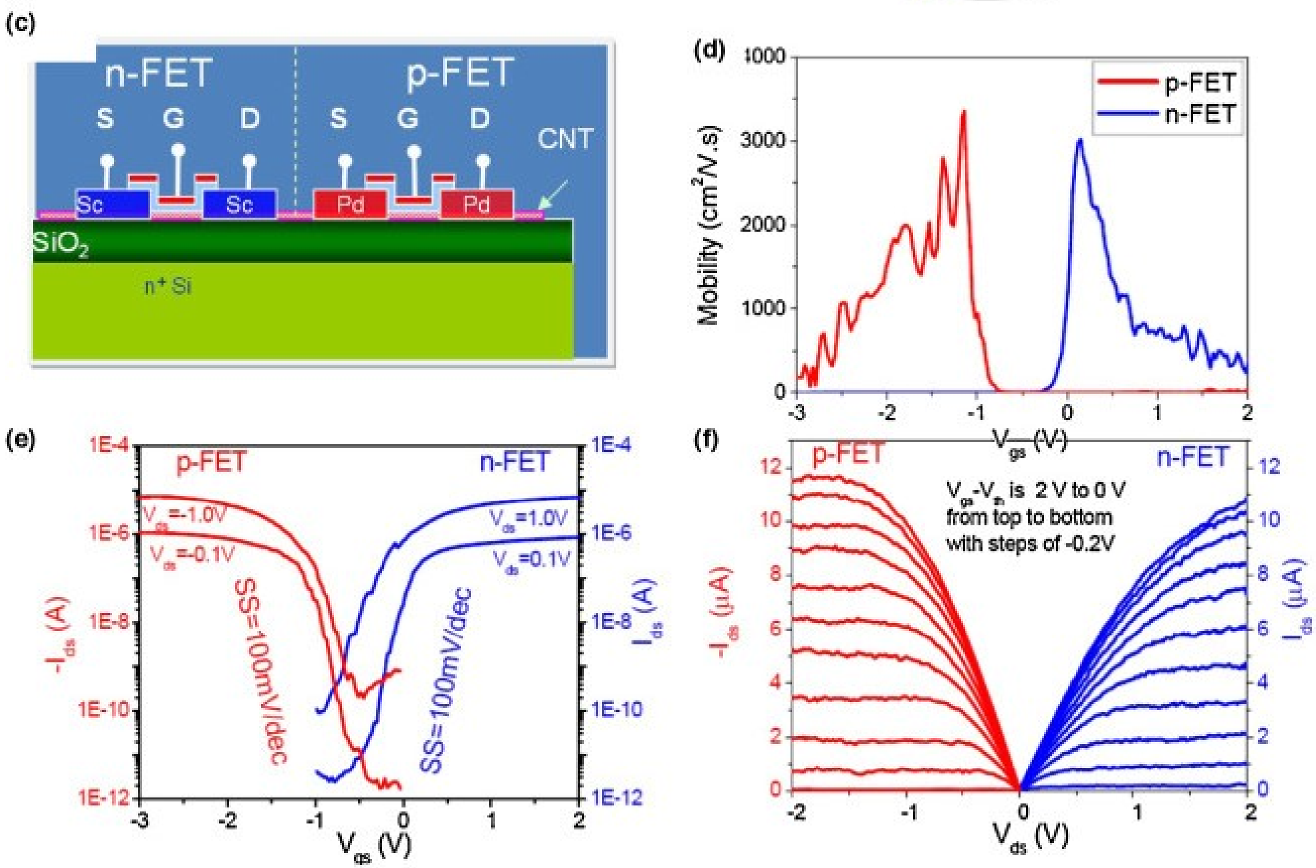
CNTFETs for CMOS

- For most semiconductors $\mu_e > \mu_h$

- Symmetric valence and conduction bands give similar PMOS and NMOS performance for CNTFETs

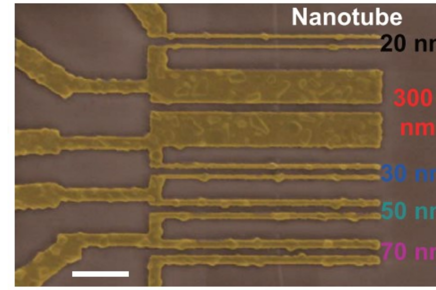


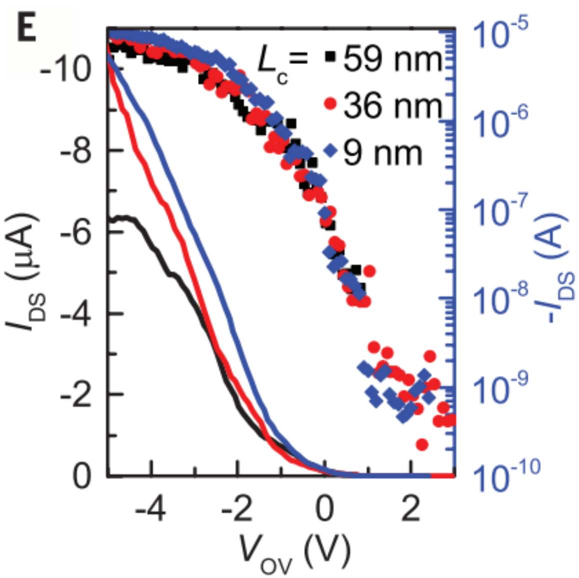


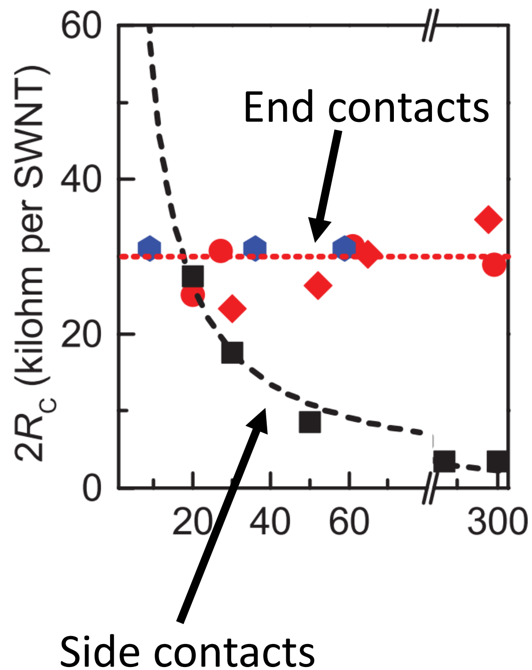


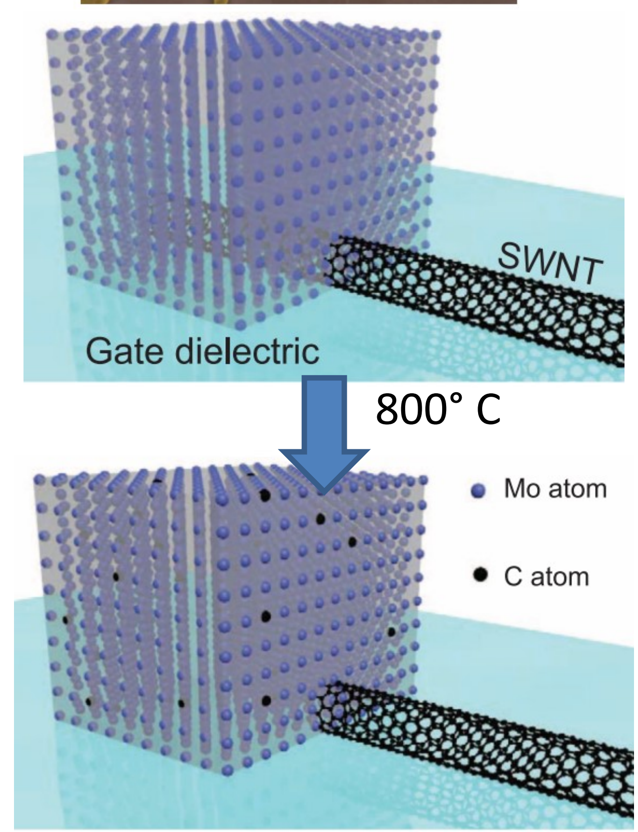
End bonded contacts

- Mo contacts heated to 800°C forms Mo_2C
- Sidecontact transformed to end contact
- Contact only 2 nm^2
- Useful for very dense circuits





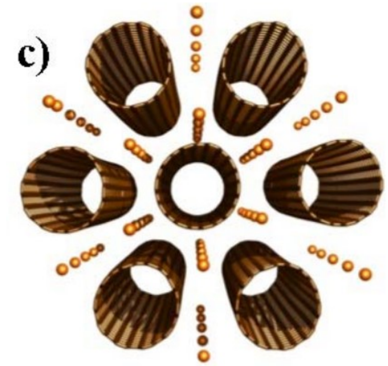


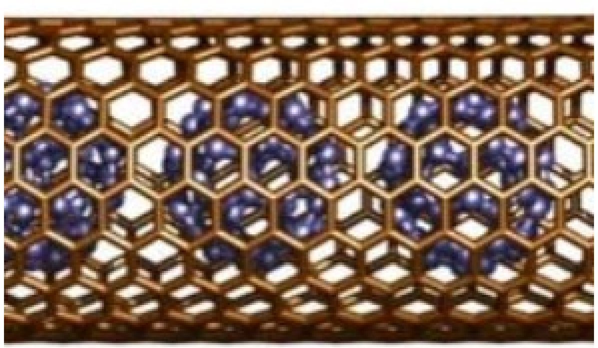


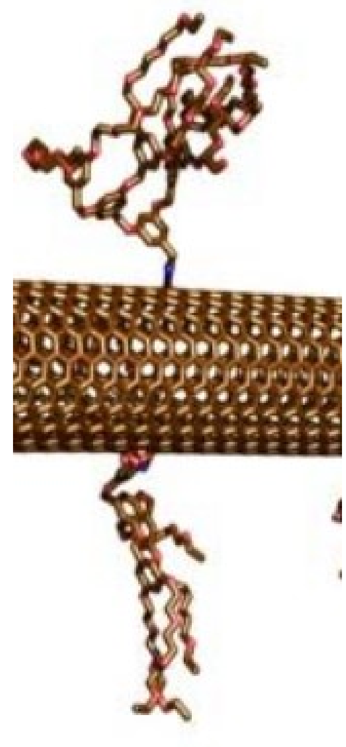
Cao et al. *Science* **350**, 68-72 (2015)

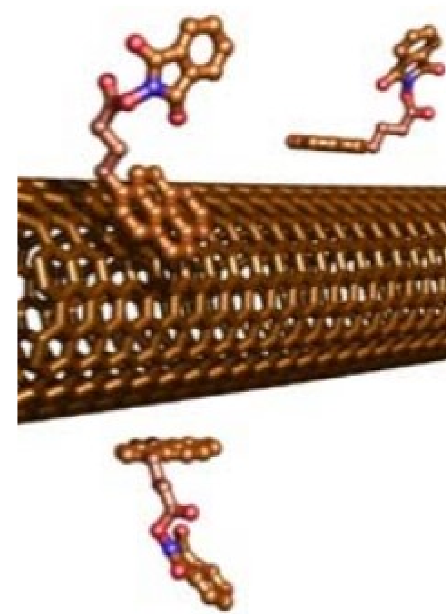
Doping

- Important for CMOS, pn-junctions and good contacts.
- Substitutional doping is difficult without destroying CNTs.





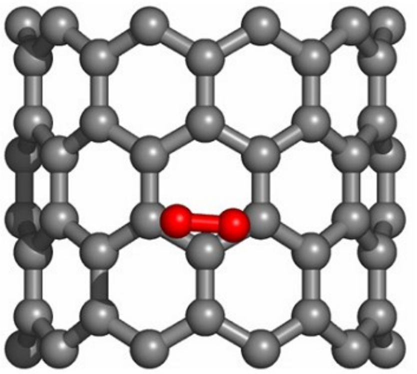


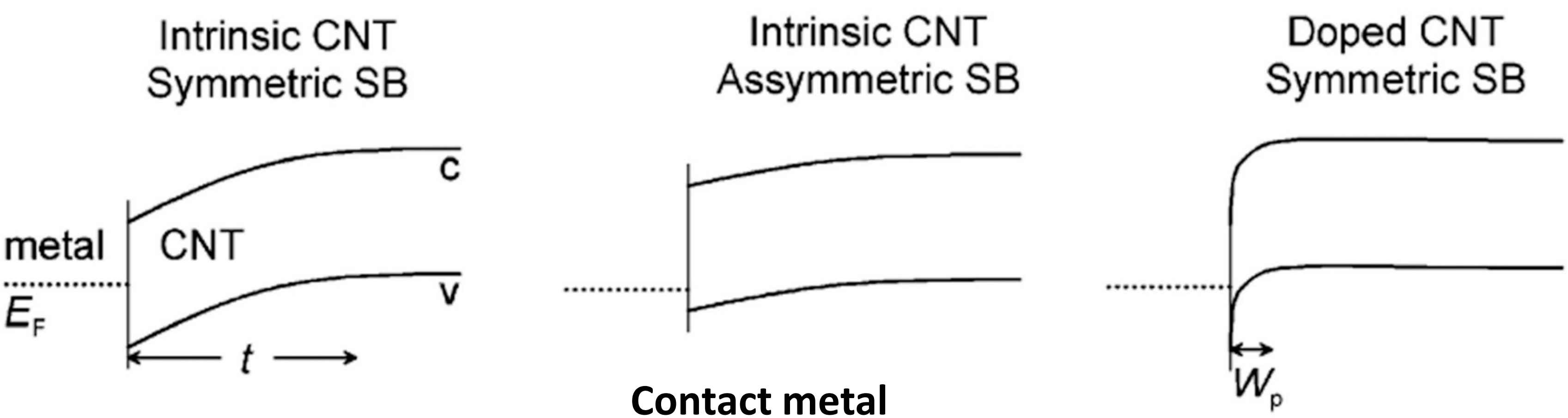


CNTFETs in air

- Physisorbed oxygen p-dopes CNT

  OR
- Increases metal work function of contact



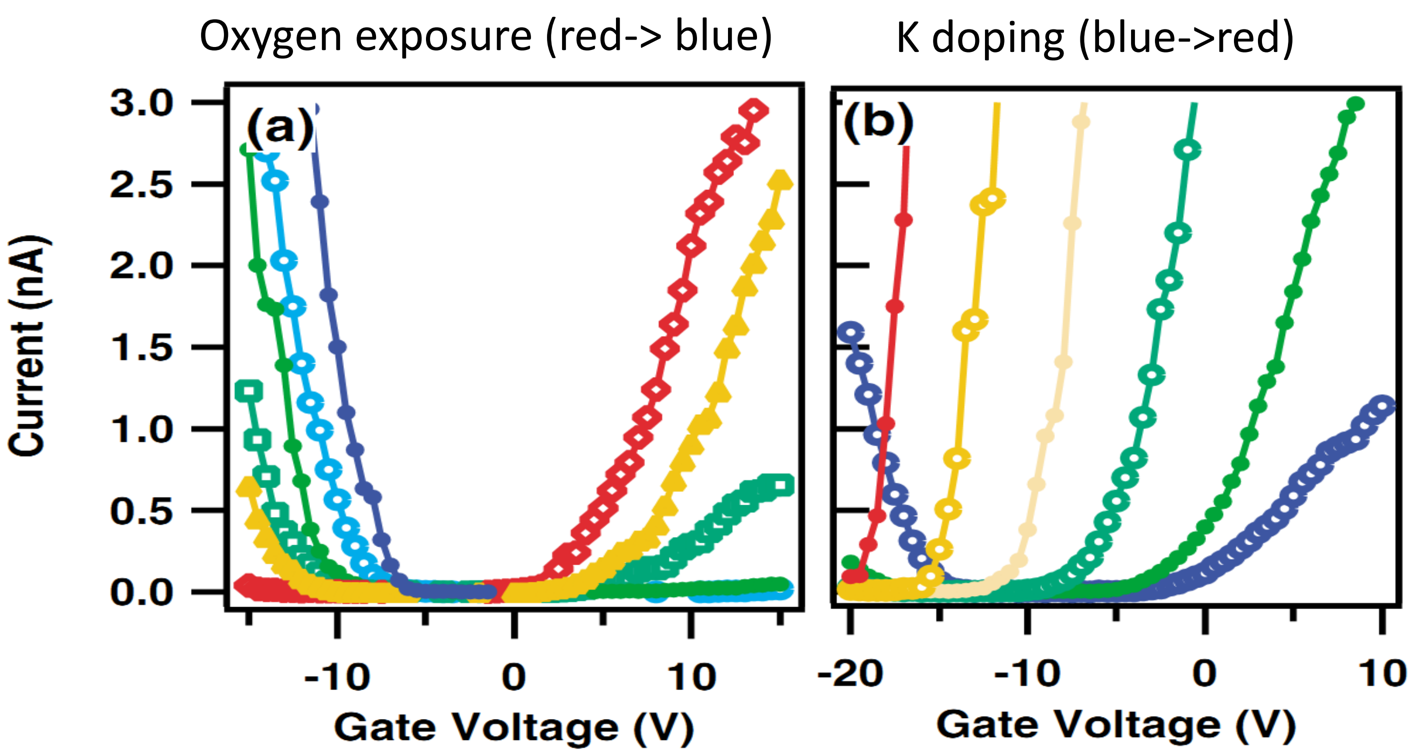


Contact metal work function change

p-doping -> thinner Schottky barrier for holes

Potassium doping

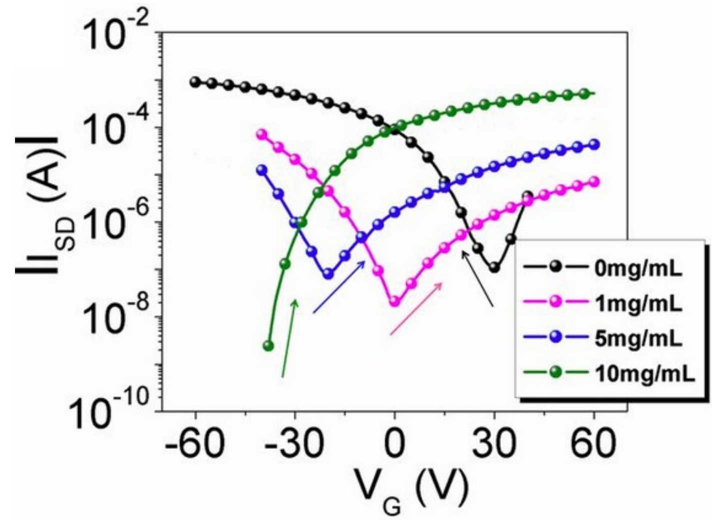
- O exposure -> p-branch is lowered, n-branch is increased, no V_{th} shift
- K physisorbed on CNT n-dopes by charge transfer -> V_{th} shift
- O: changes work function // K: dopes CNT

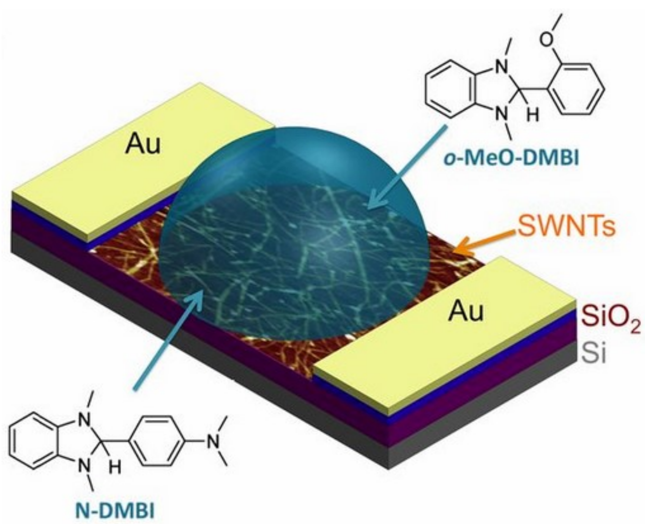


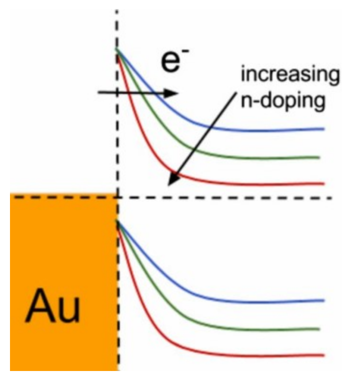
Heinze et al. *PRL*, **89**, 10 (2002)

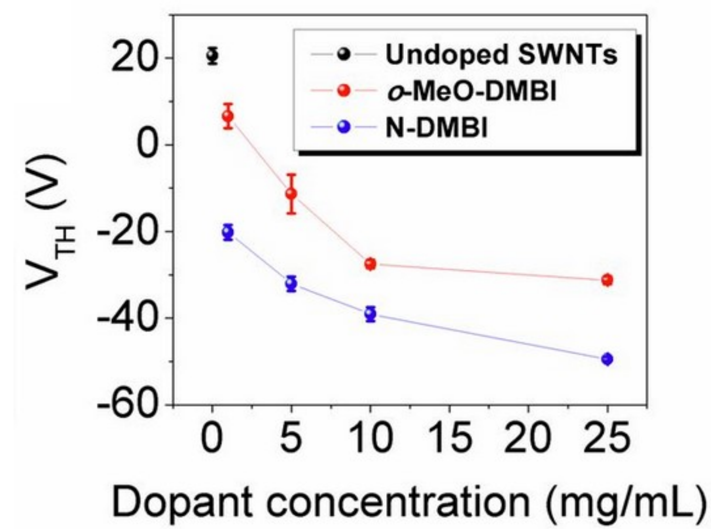
Doping of thin film CNTFETs

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





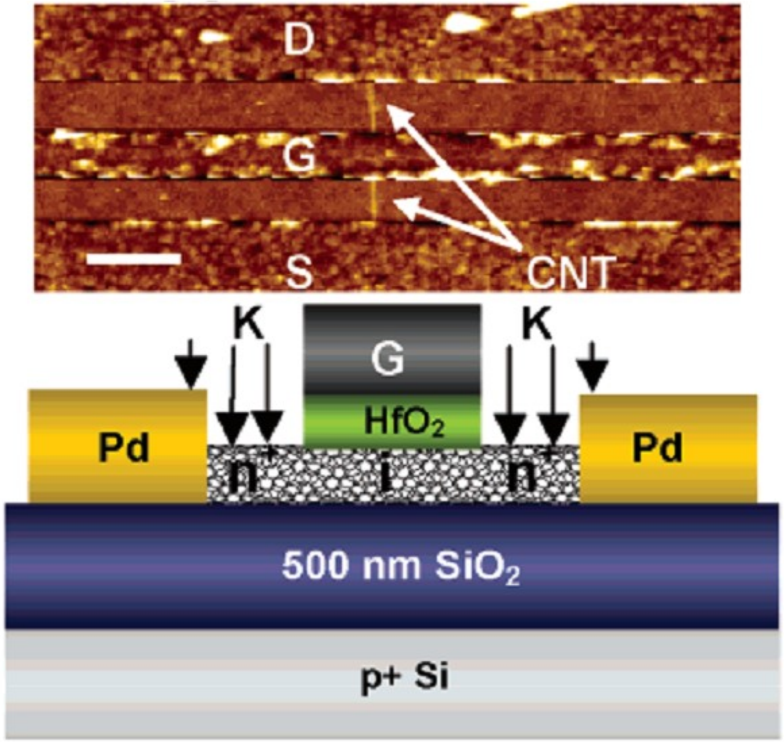


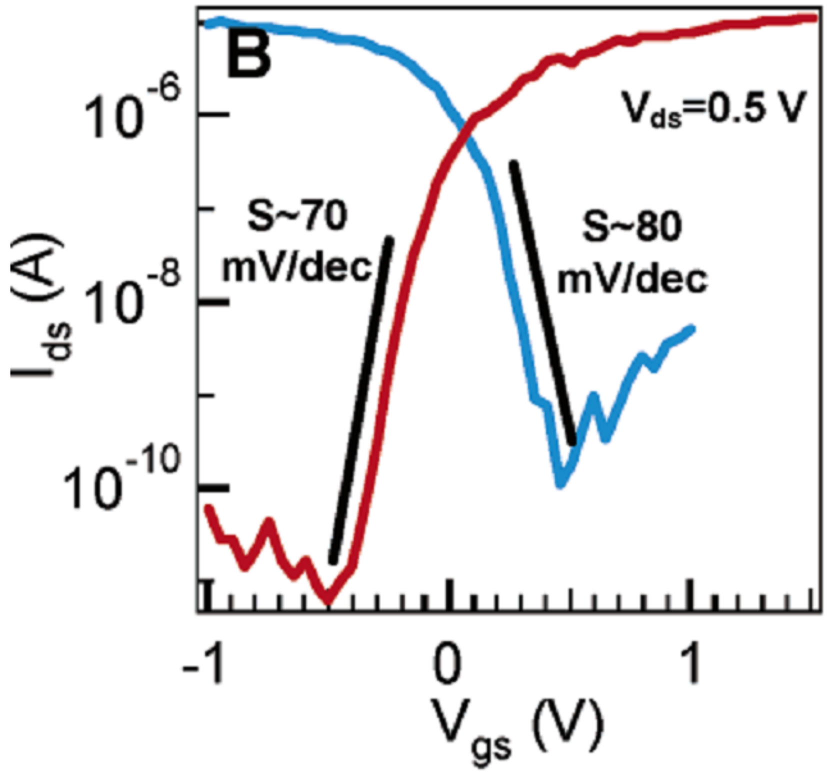


Wang et al. *PNAS*, **111**, 4776–4781 (2014)

Doped contacts

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

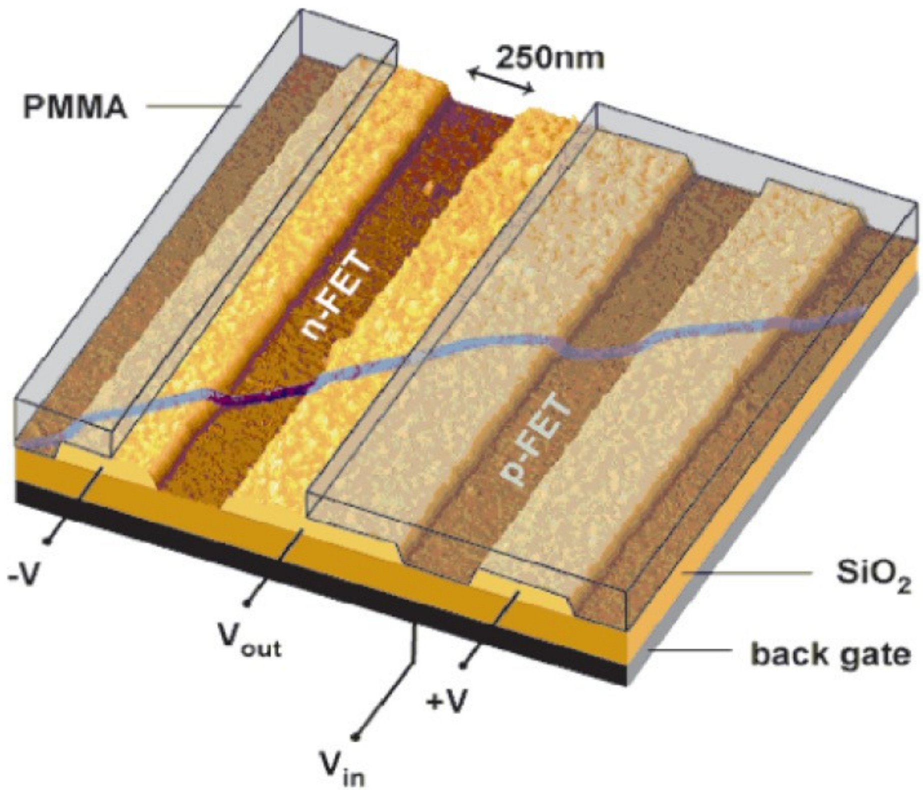


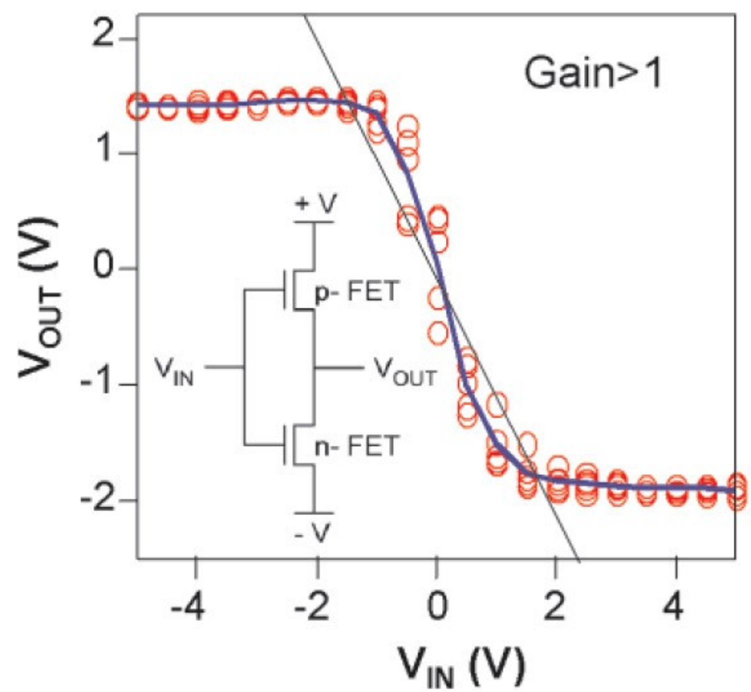


Javey et al. *Nano Lett.*, **5**, 345-348 (2005)

Logic gate on single CNT

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

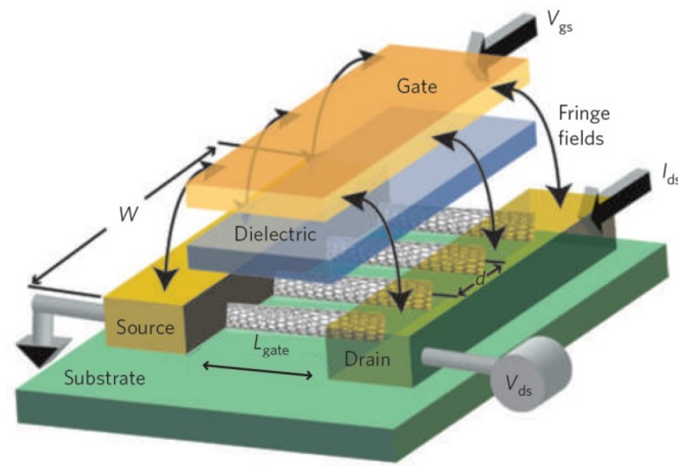


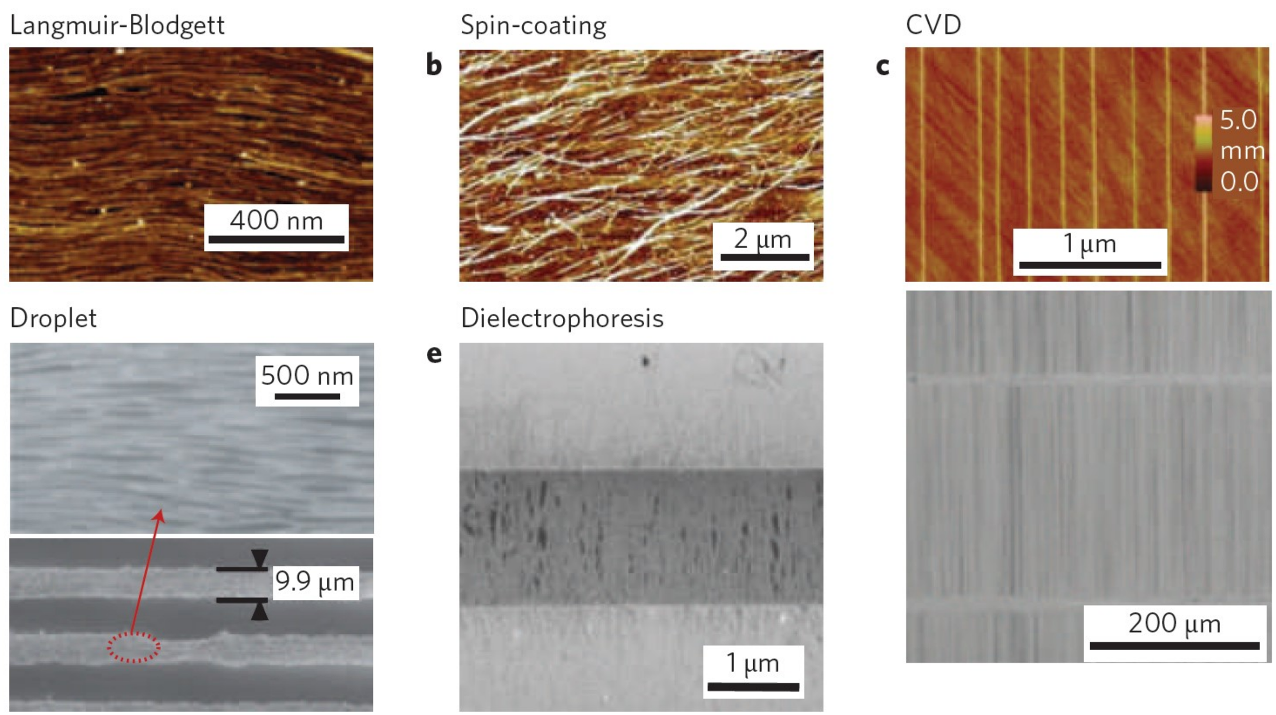


Derycke et al. *Nano Lett.* **1** , 453–456 (2001)

Positioning

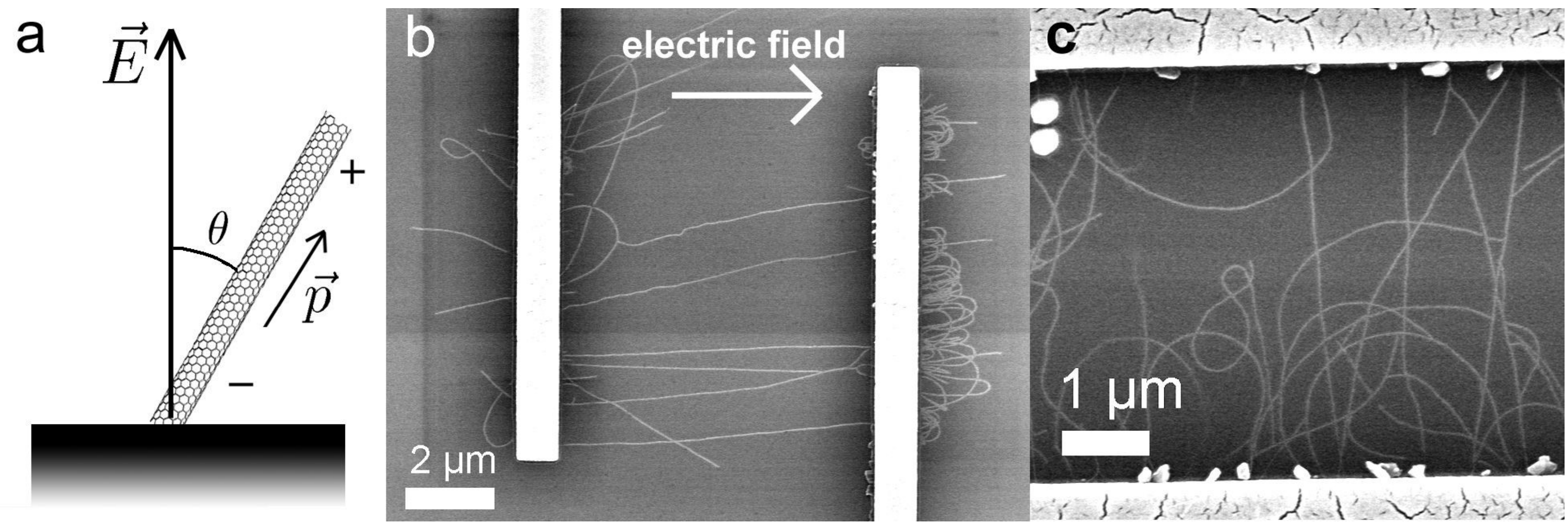
- Multiple parallell CNTs in each FET increases I_{on}, g_m
- Dense packing reduces parasitic capacitances
- Need to control position and orientation of CNTs pre- or postgrowth





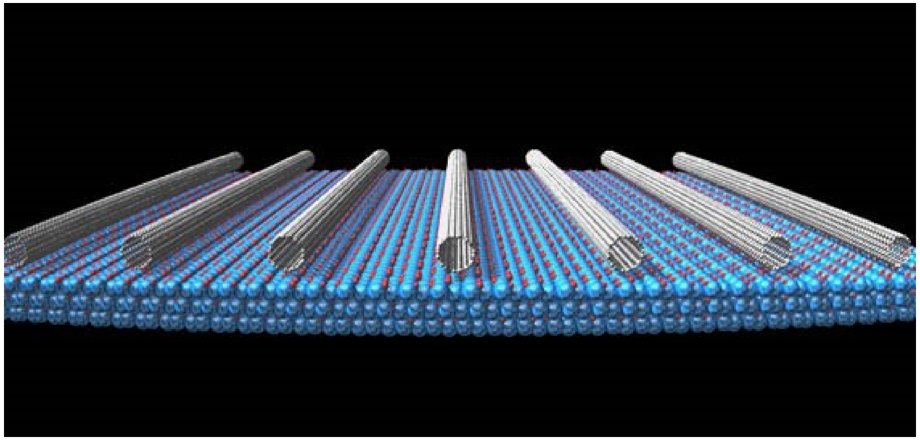
Electric field alignment

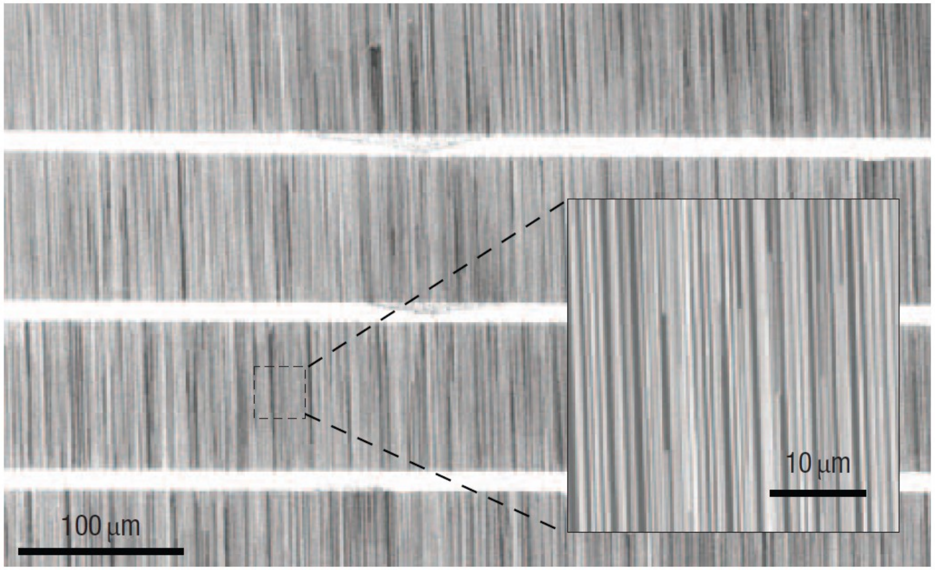
- Apply voltage to electrodes during CVD
- Dipole in CNTs align them with field lines
- Difficult to implement for large scale circuits



”epitaxial” alignment

- CNTs align in certain crystal orientations of sapphire (Al_2O_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



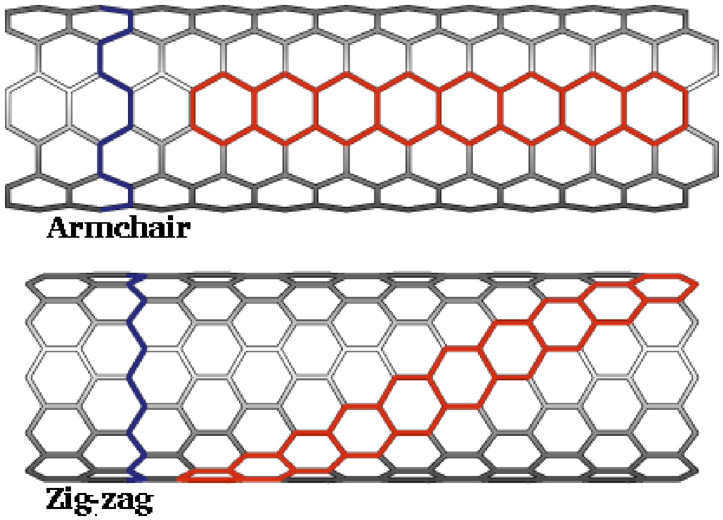


Chirality control

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

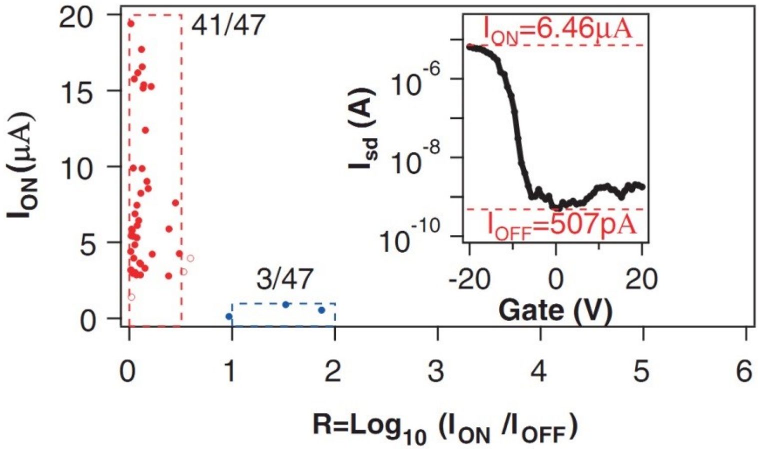
- Need chirality control or at least control of CNT type

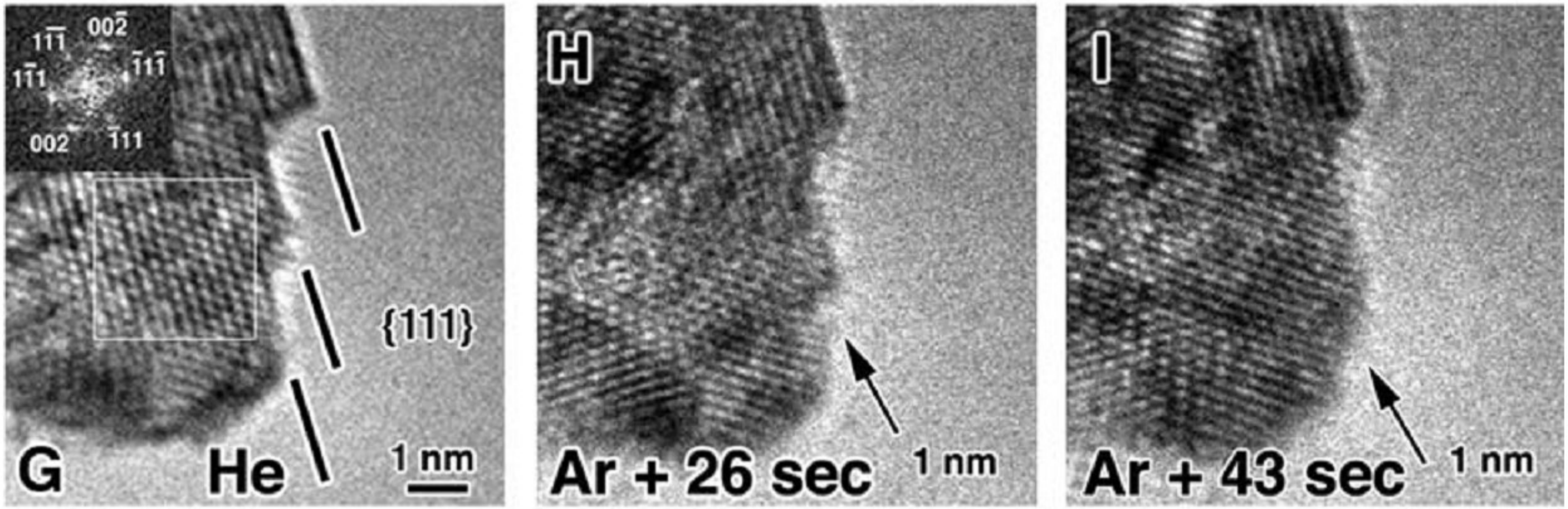
- Need to either:
  - Selectively grow only metallic or semiconducting
  - Separate the two types
  - Selectively destroy one type



Selective growth

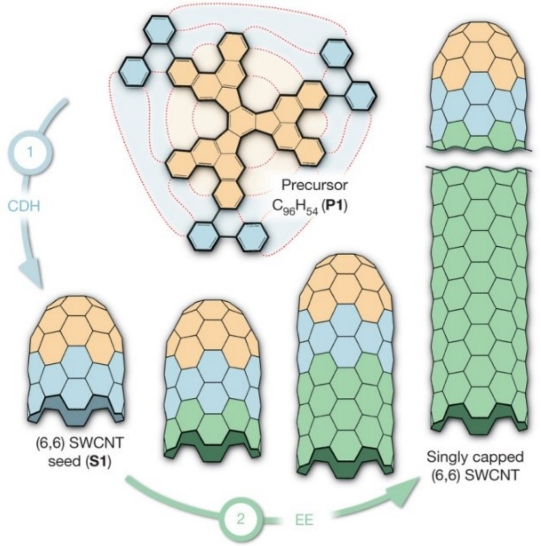
- Anneal metal catalyst in Ar, He or H_2
- Increased metallic CNT part from 33% to 91%
- Strong facets when annealed in He
- Steps in particle important for chirality control?
- Not well understood!



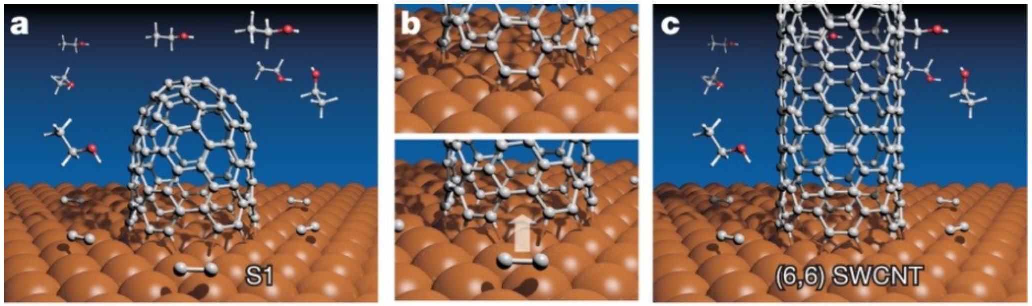


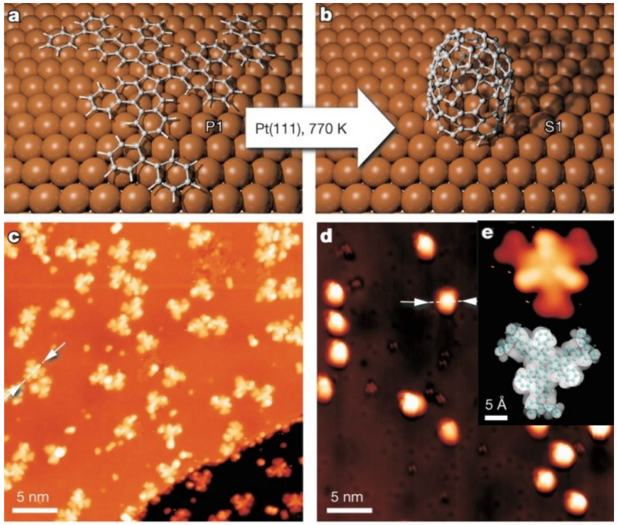
Harutyunyan et al. *Science,* **326**, 116-120 (2009)

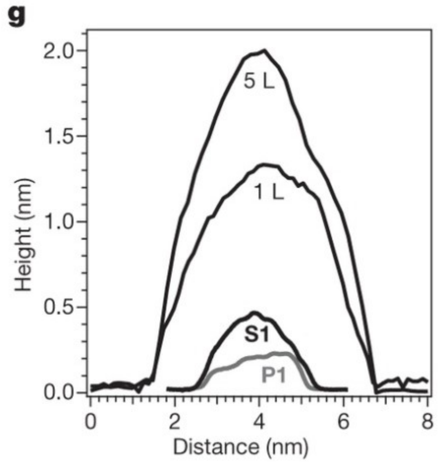
Templated growth

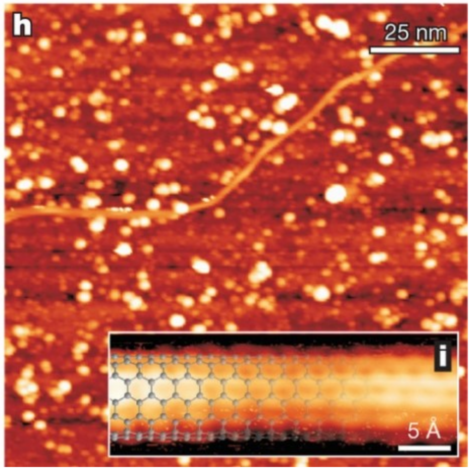


- Molecule defines cap
- Only (6,6) CNTs i.e. ”real” metallic





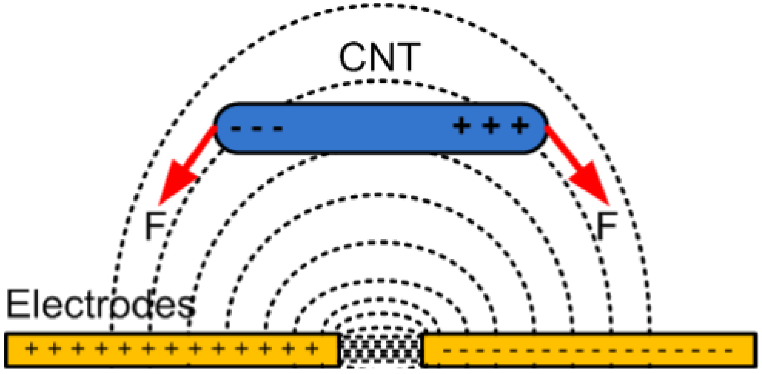


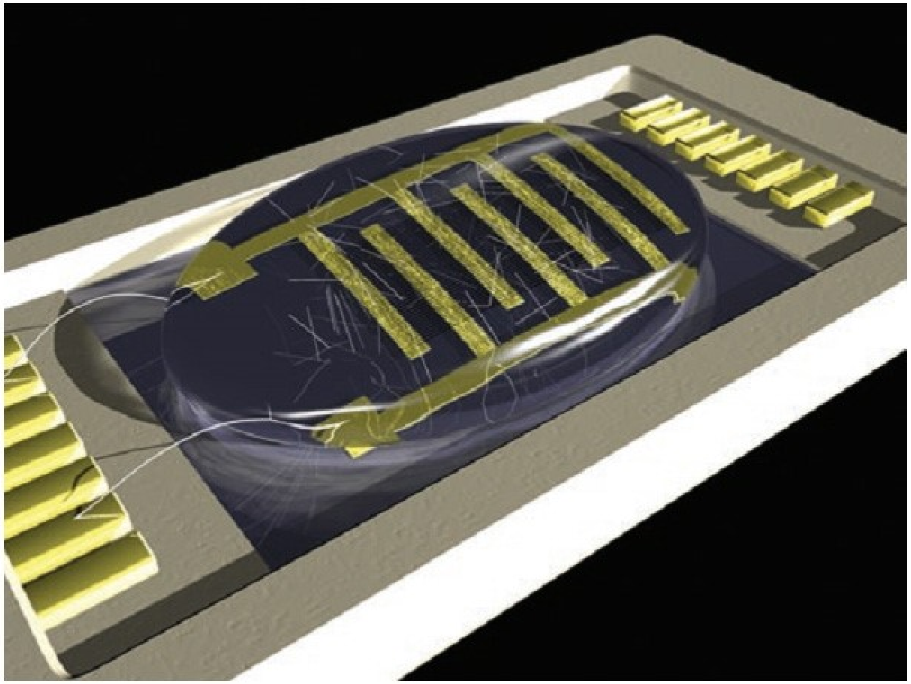


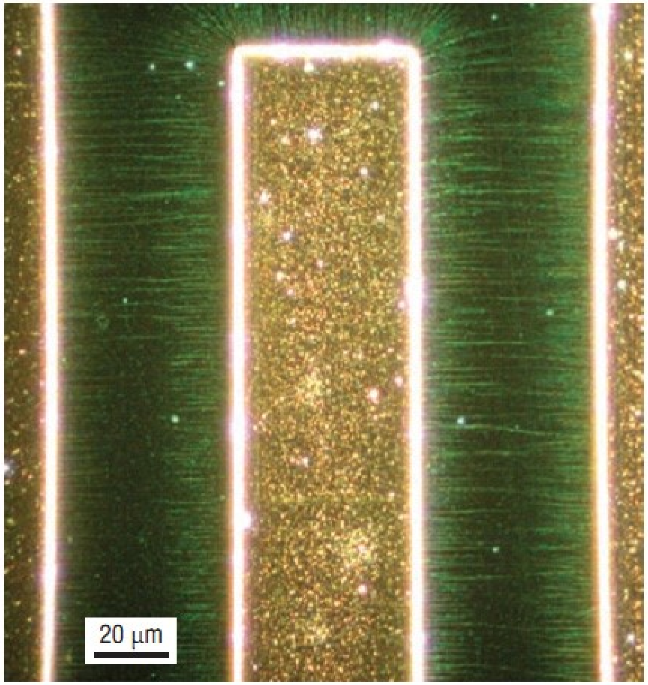
Sanchez-Valencia et al. *Nature 512, 61–64 (2014)*

Separation by dielectrophoresis

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



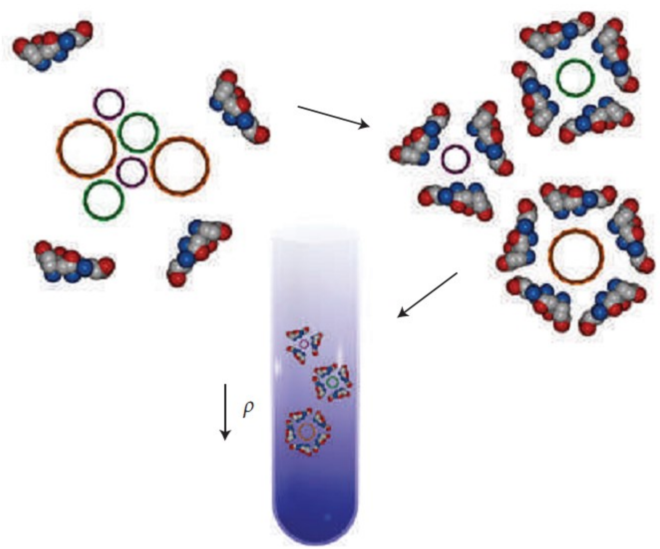


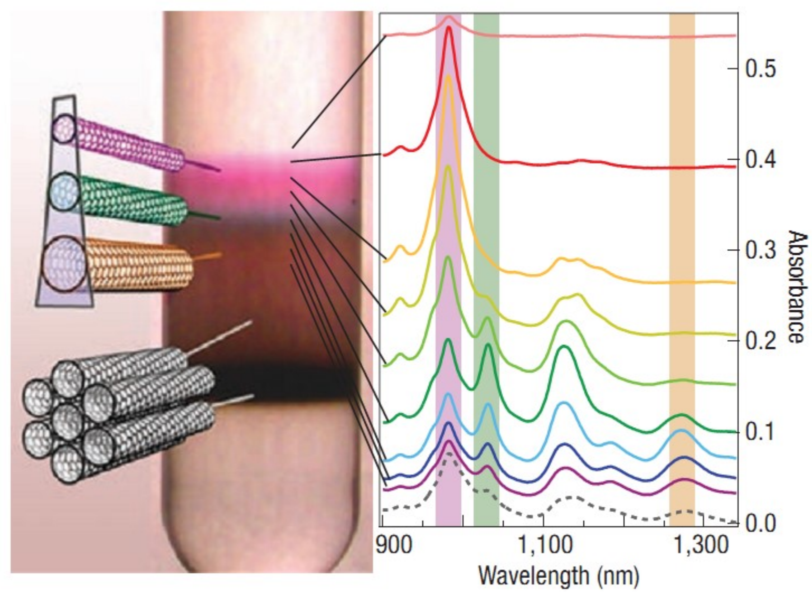


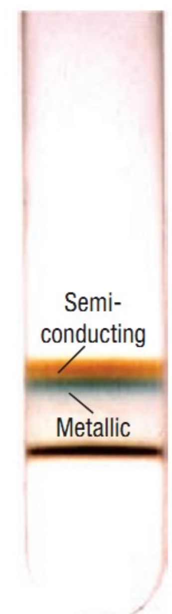
Krupke et al. *Science*, **301**, 344–347 (2003)

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



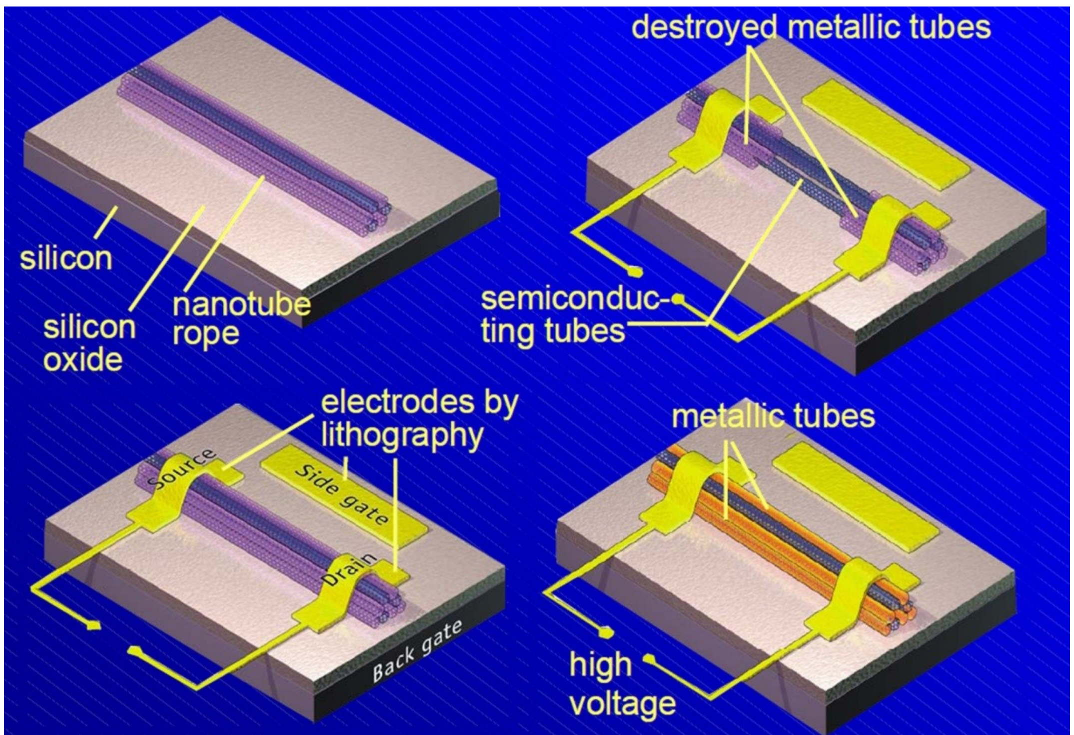


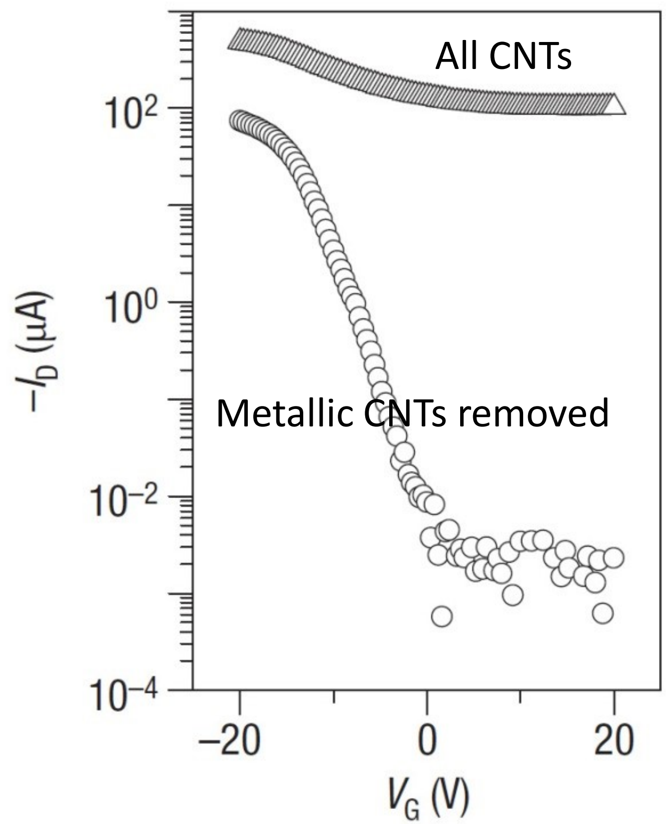


Arnold et al. *Nature Nanotech.* **1**, 60–65 (2006)

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



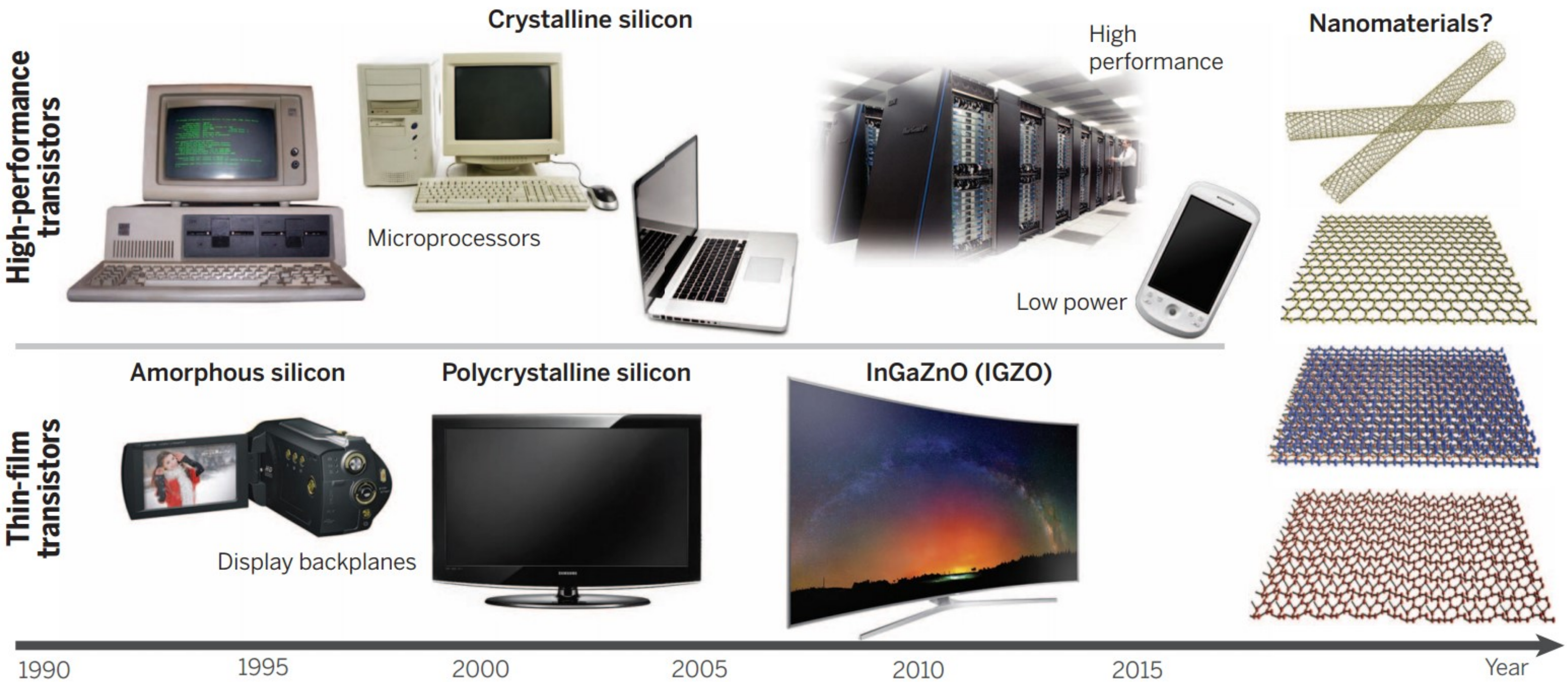


Outline

- Basics of graphene and CNTs
  - Structural
  - Electronic
  - Production of CNTs
- Advantages of CNTs for FETs
  - Electrostatics -> length scaling
  - High-k compatibility
  - Band-to-band tunneling
- Challenges of CNT integration
  - Contacts
  - Doping
  - Positioning
  - Chirality control
- Towards integration
  - Flexible electronics
  - High frequency performance

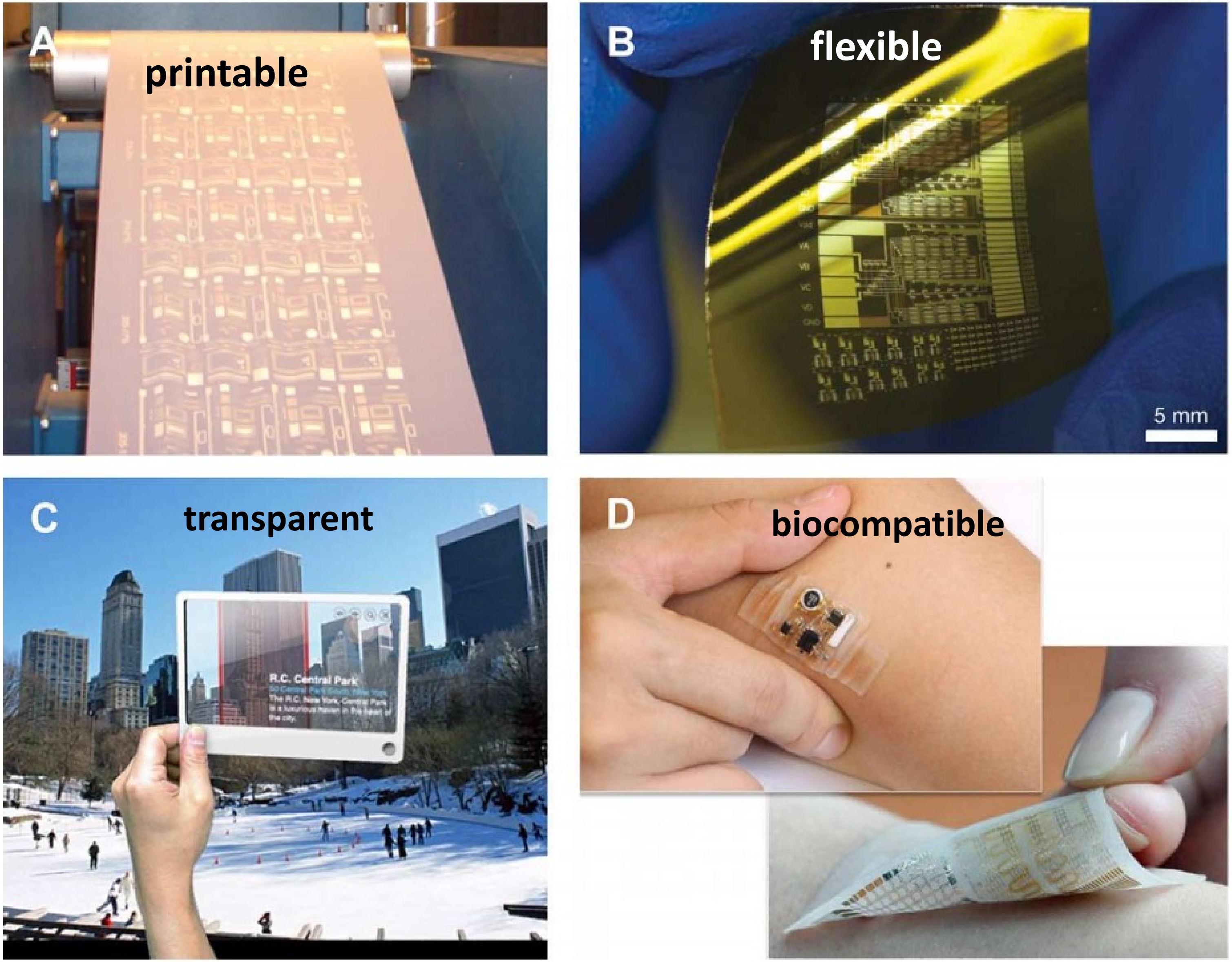
Thin film transistors

- 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



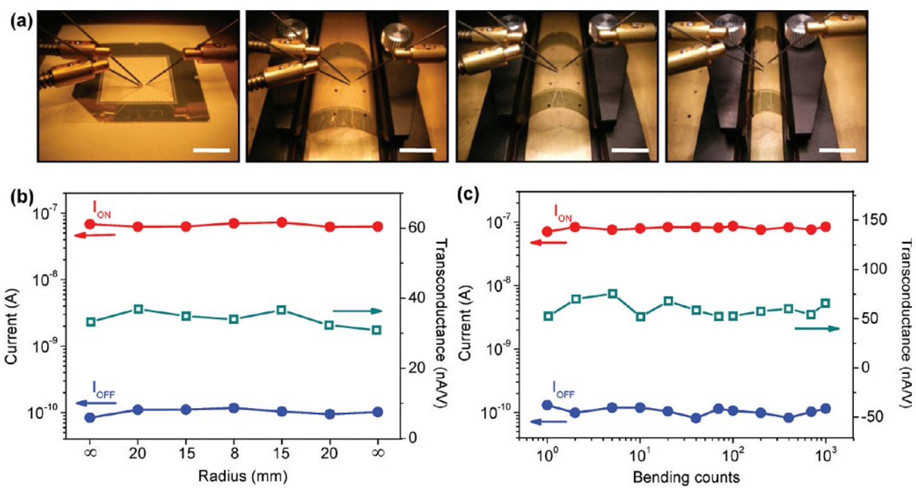
Franklin. *Science*, **349**, 6249 (2015)

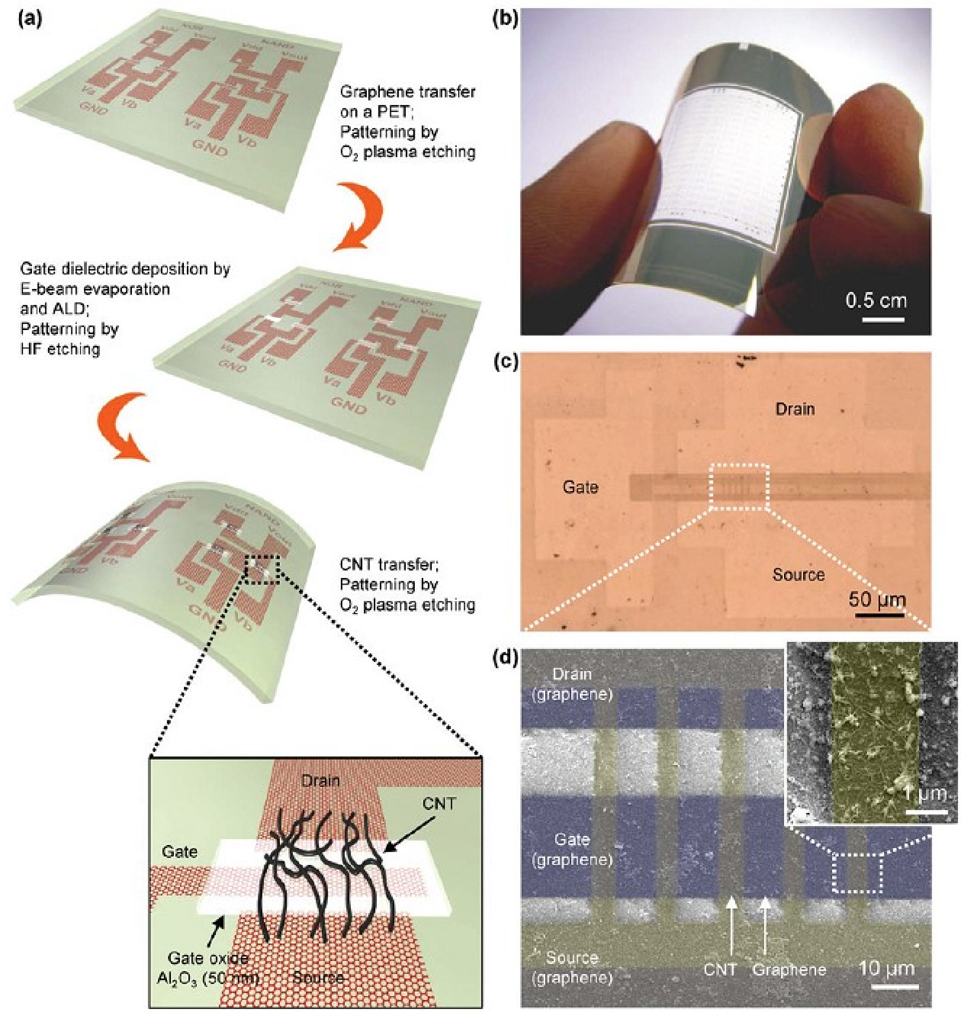
Thin film transistors



Flexible electronics

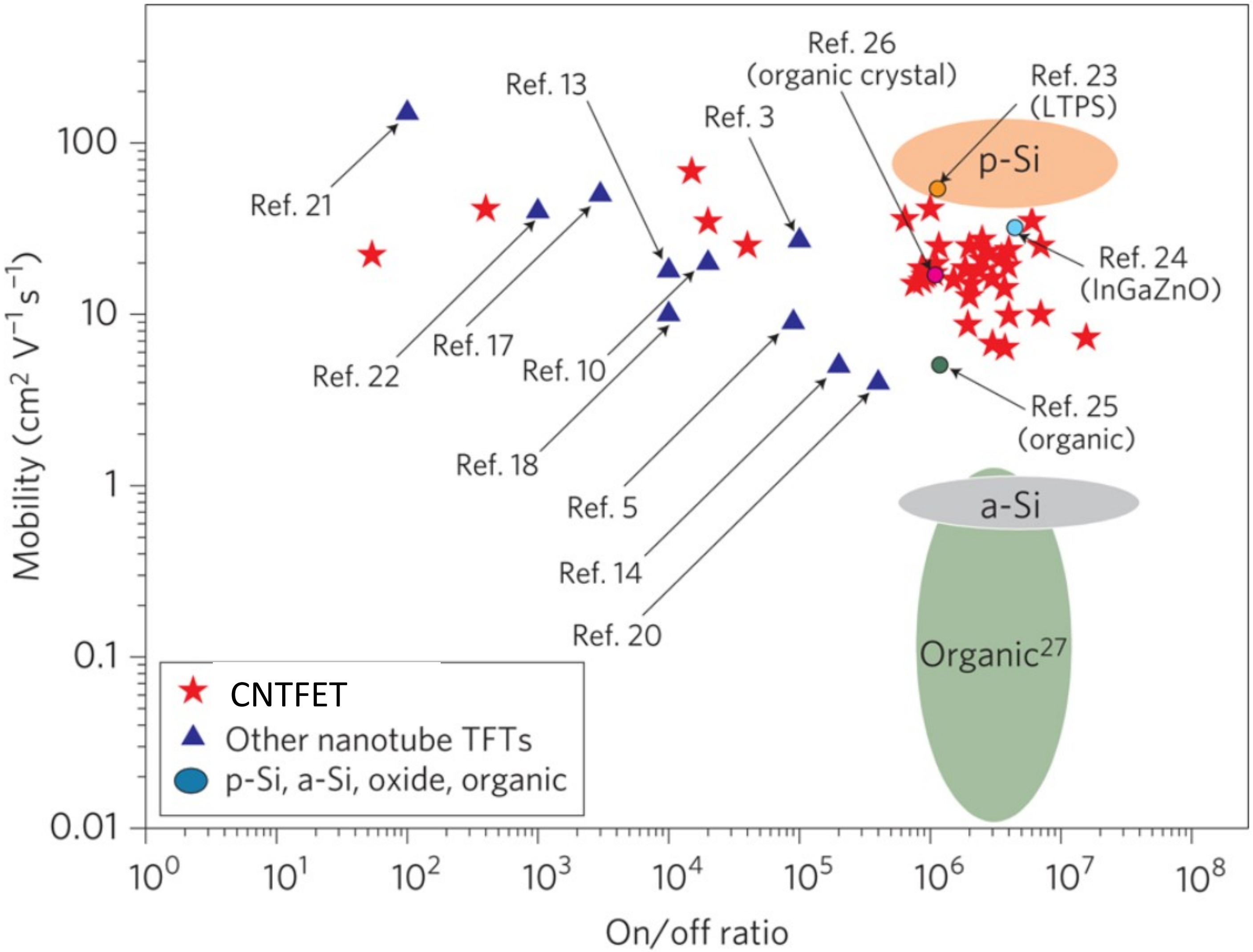
- Graphene for electrodes
- CNTs for channel
- No degradation when bent





Yu et al. *Nano Lett.* **11,** 1344–1350 (2011)

Thin film transistors comparison

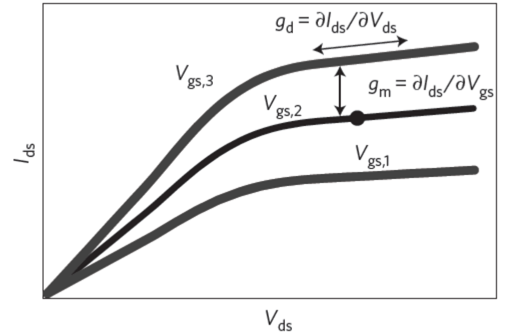


Sun et al. *Nature Nano*. 6, 156–161 (2011)

Requirements for RF applications

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

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



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

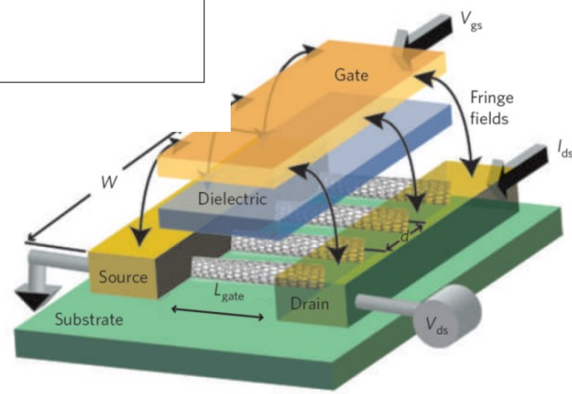


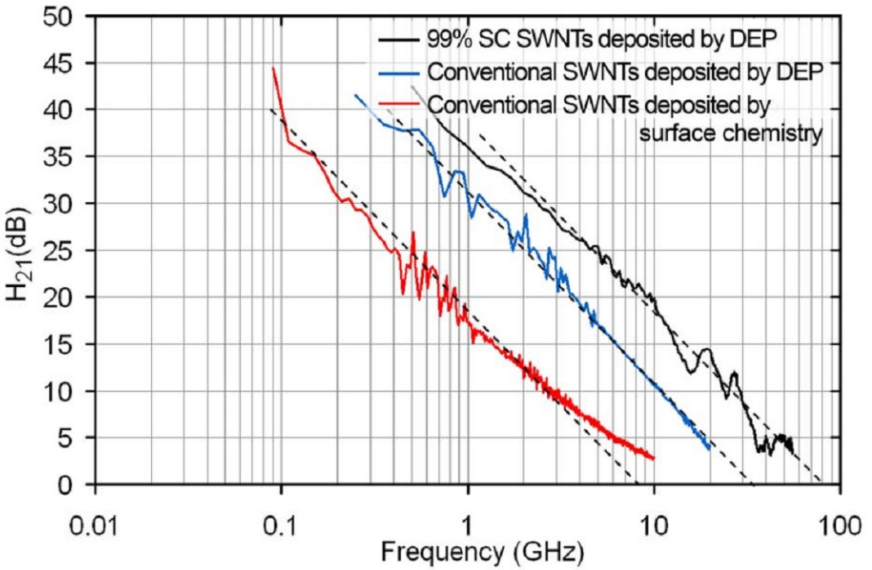
Table 1 | Ideal parameter values for making a high-frequency field-effect transistor from single-walled nanotubes.

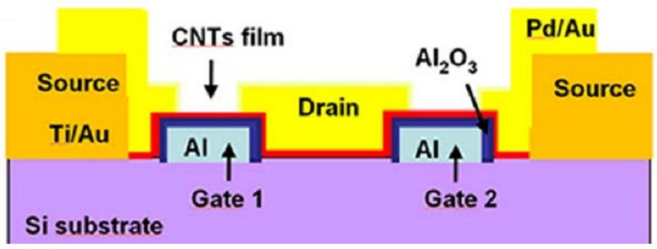
Property/parameter	Target value or range	Justification
Diameter	1.5–2.0 nm	Current is largest in this range[54–55].
Chirality	Semiconducting and same (*n*,*m*)	To obtain identical transport properties.
Purity	>99% semiconducting nanotubes	No metallic nanotubes for high gain and high f_{max}.
Length	>1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

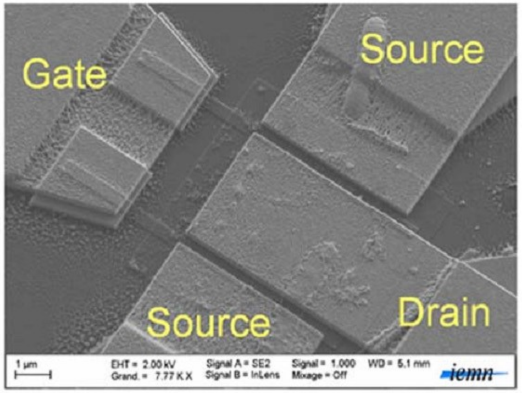
Rutherglen, *Nature nanotechnol*. **4**, 811 (2009)

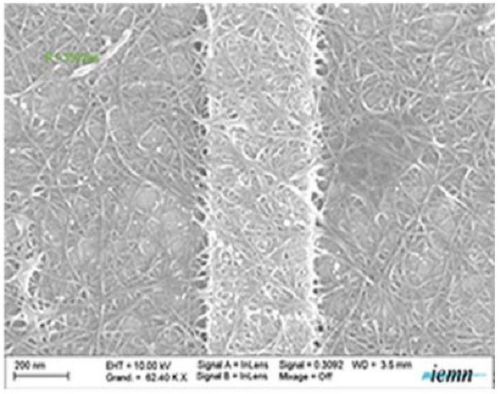
RF performance

- Can not use single CNT due large parasitic capacitance (and impedance mismatch)
- Use semiconducting CNTs separated using centrifugation
- f_T = 80 GHz
- Much better than unseparated CNT material





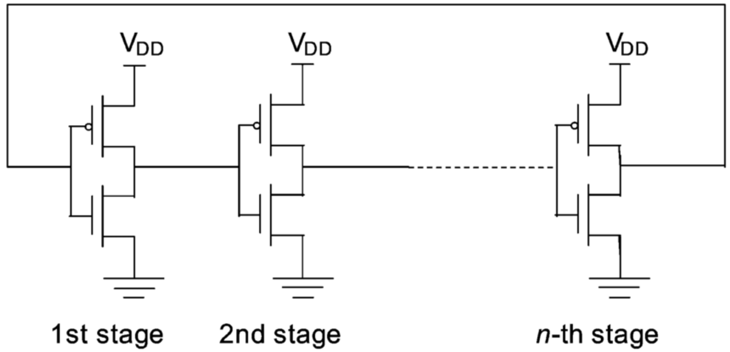


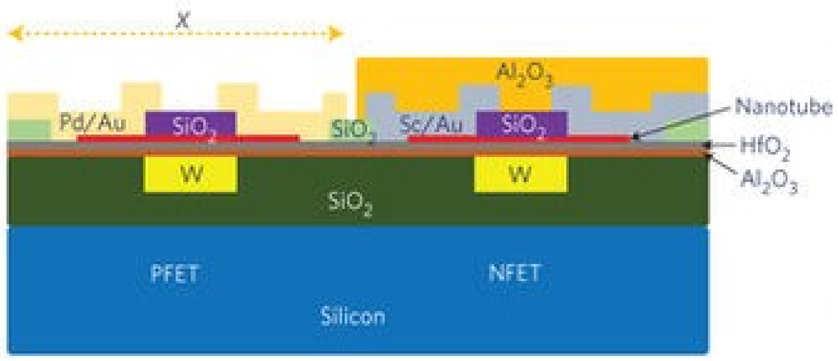


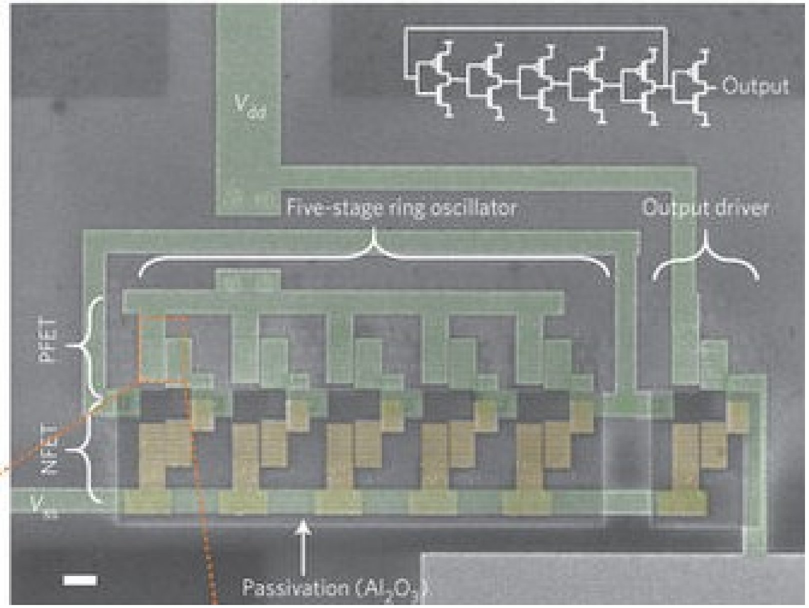
Nougaret et al. *APL*, **94**, 243505 (2009)

Ring Oscillator

- Odd number of inverters in series, output connected to input.
- Used to measure speed of digital technologies.
- Centrifuged NWs = 99.9% semiconducting
- Switching time = 355 ps /stage (2.8 Ghz)



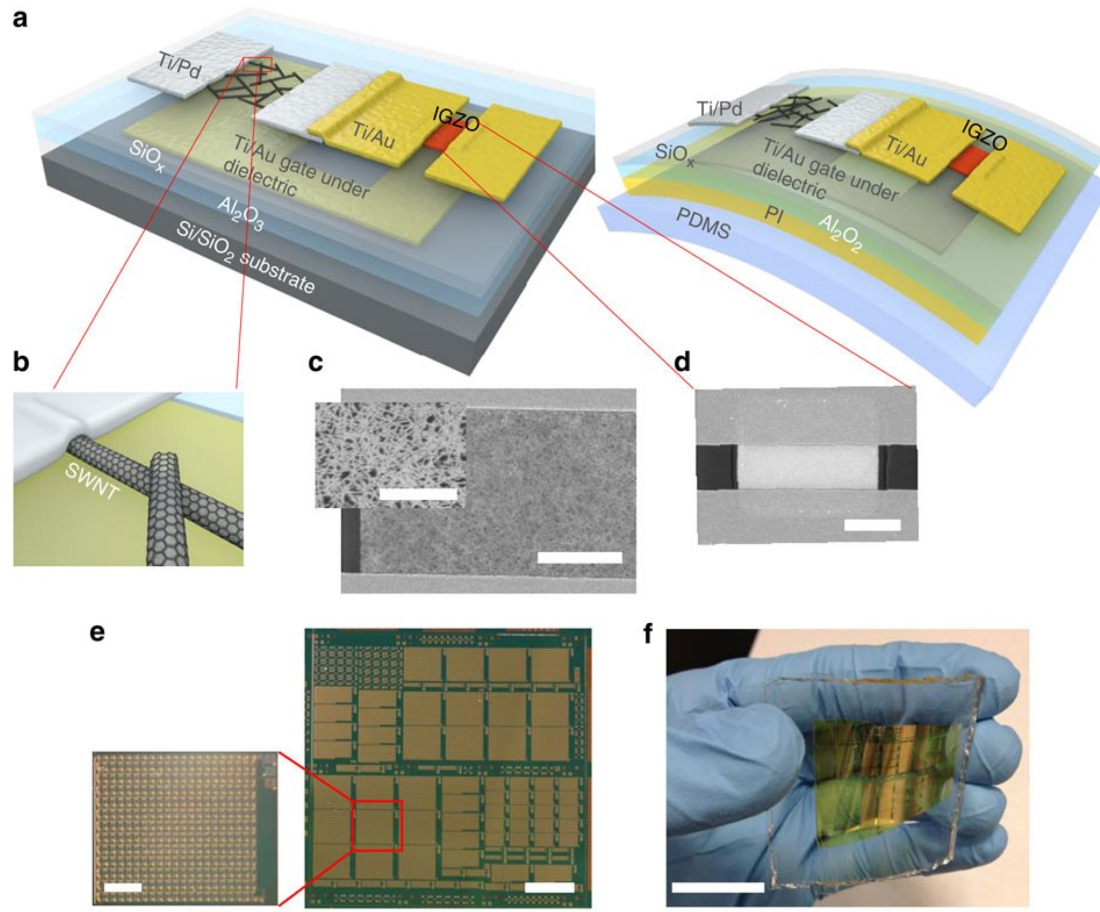


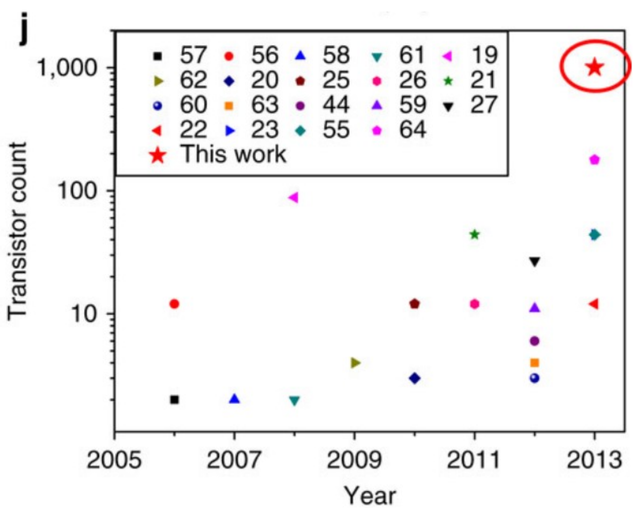


Han, *Nature Nanotechnology* **12**, 861–865 (2017)

Large scale integration

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

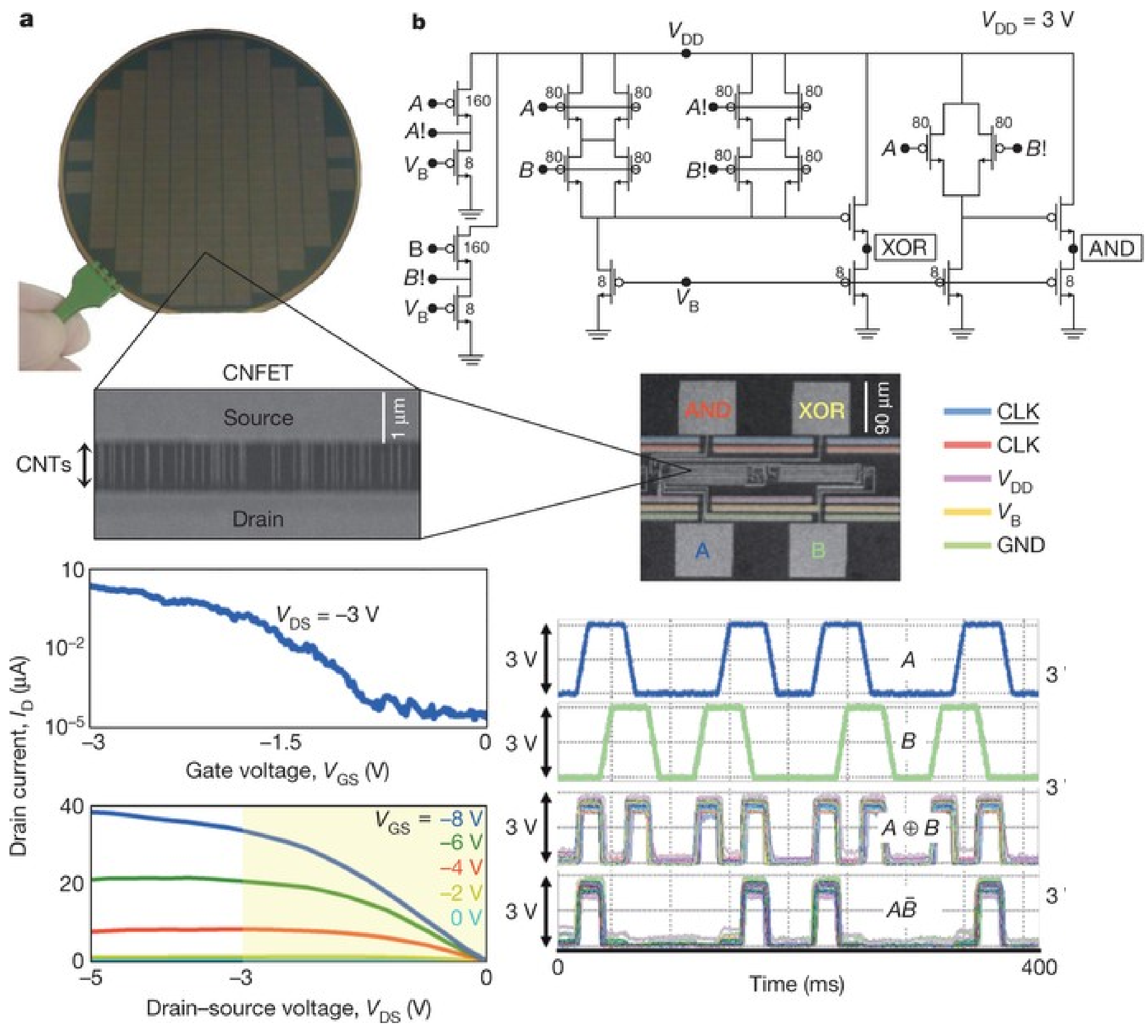




Chen et al. *Nature Comm.* 5, 4097 (2014)

CNT computer

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



Shulaker et al. *Nature*, **501**, 526-530 (2013)

Summary

- **Individual CNTs have great electronic properties**
  - High mobility
  - Coaxial gate + thin gives good electrostatics -> 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