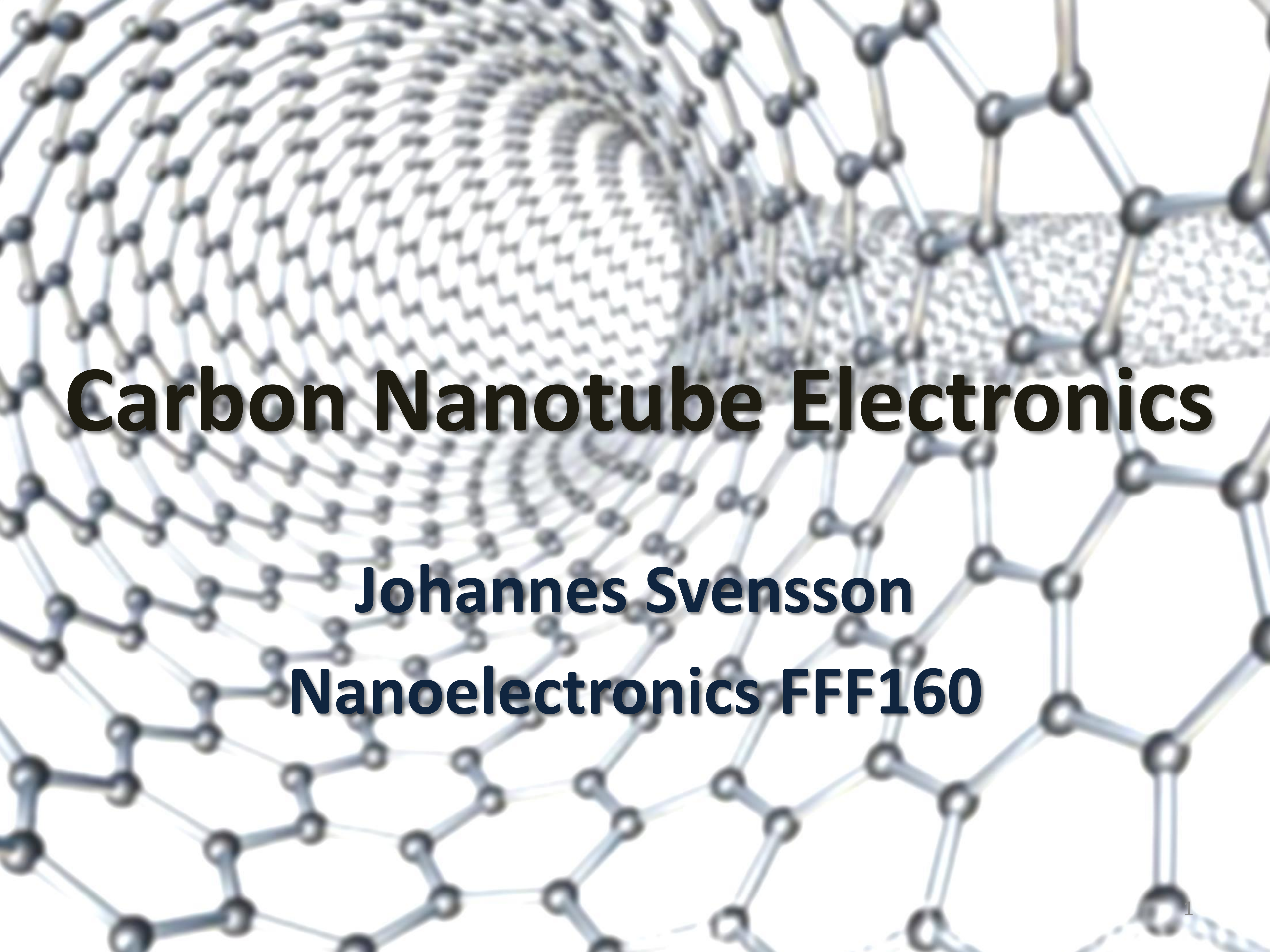

Carbon Nanotube Electronics

Johannes Svensson

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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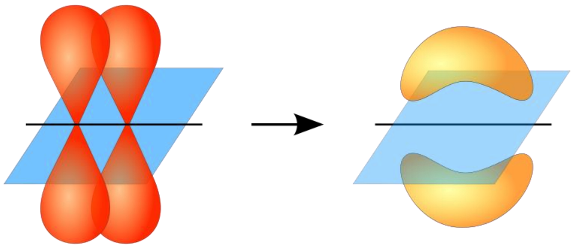
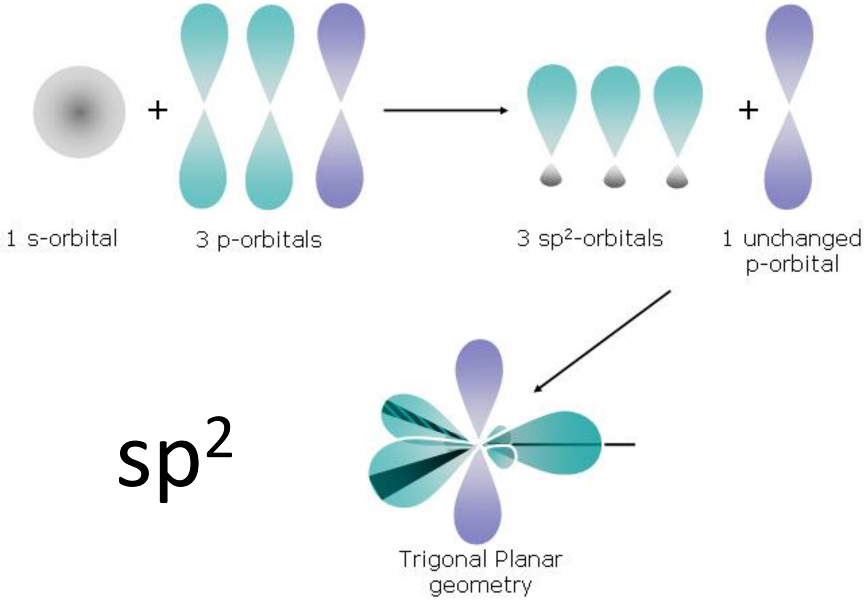
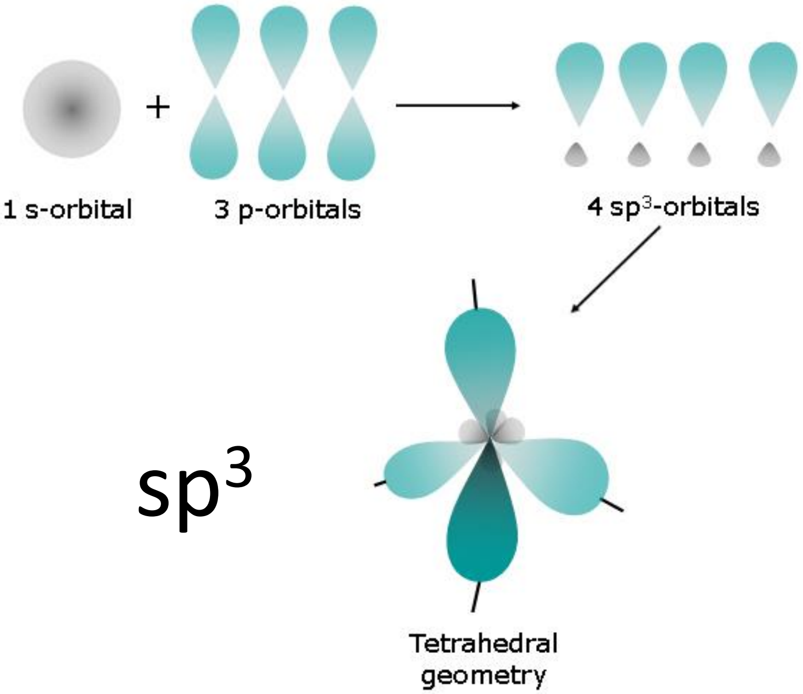
Hybridisation of carbon orbitals

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





sp^2



sp^3

Carbon allotropes

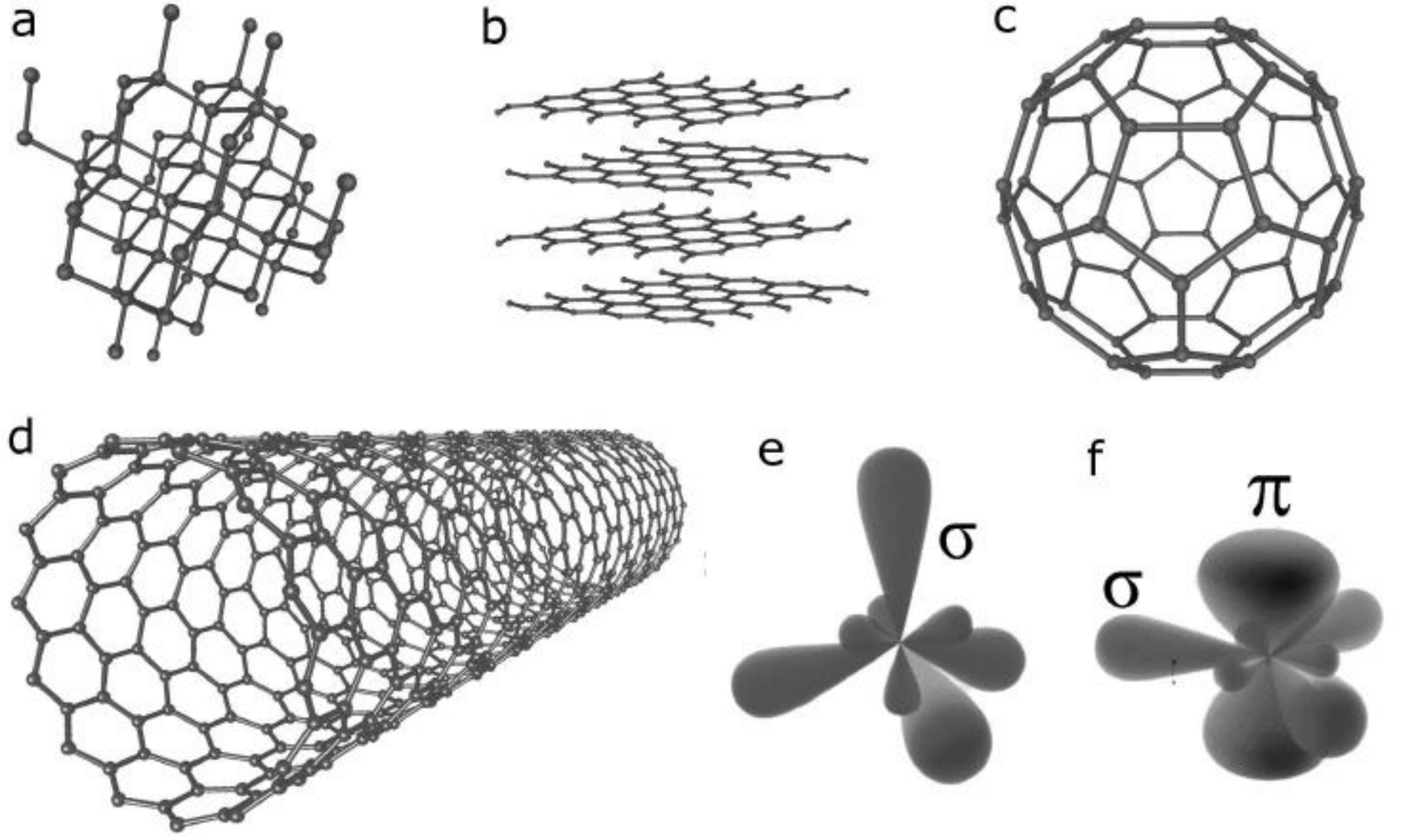
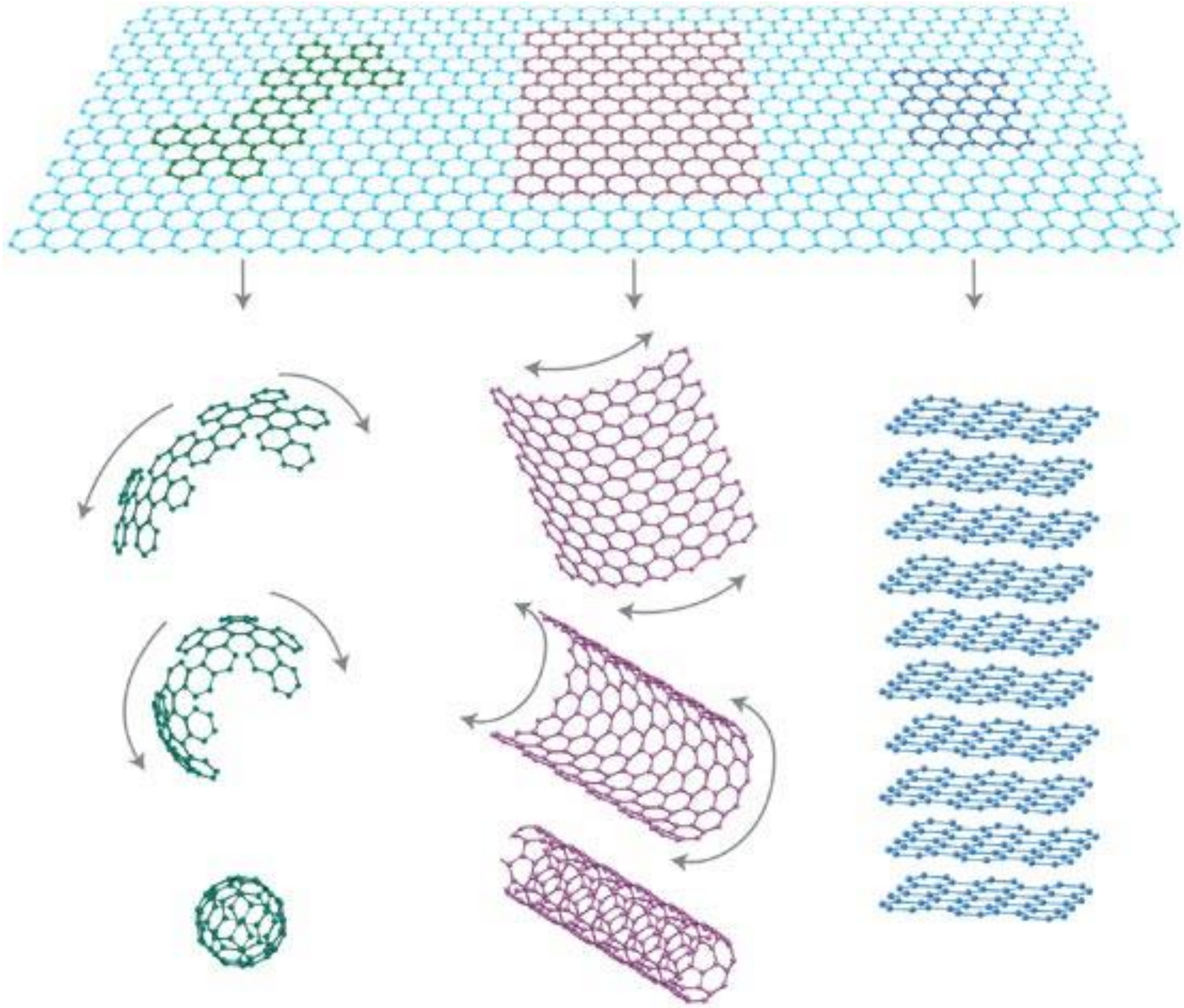


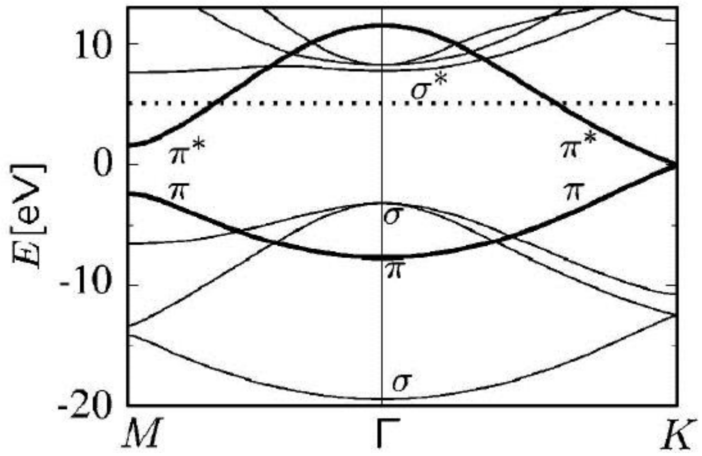
Figure 2.1: *a-d) Crystal structure of a few carbon allotropes a) Diamond b) Graphite c)* C_{60} *d) CNT. e)* sp^3 *hybridised orbitals forming* σ *bonds. f)* sp^2 *hybridised orbitals forming* σ *bonds and the remaining* p_z *orbital giving rise to* π *bonds.*

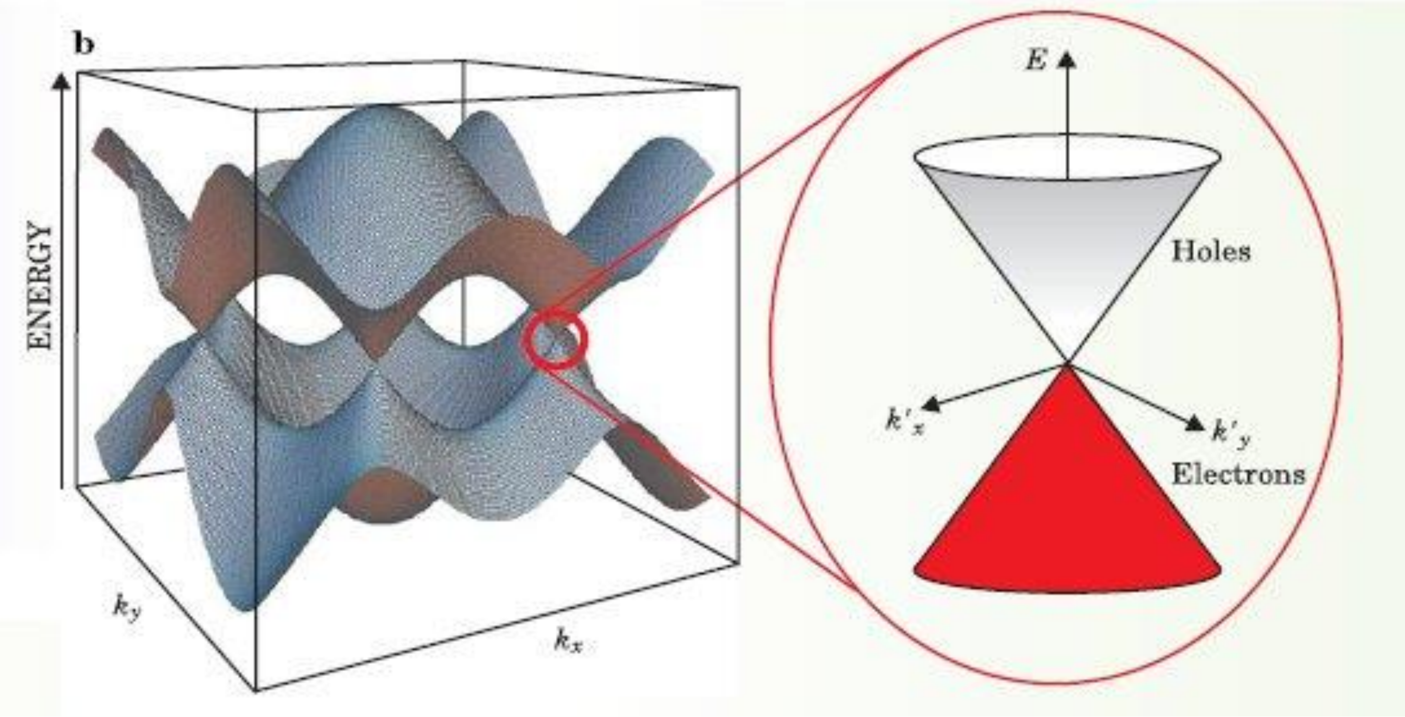
Graphene is mother of all sp^2-carbon



Graphene band structure

- Semimetal: no gap and zero DOS at E_f
- Only π-bands are interesting
- Linear dispersion near E_f
- Conduction and valence bands meet at the K-points



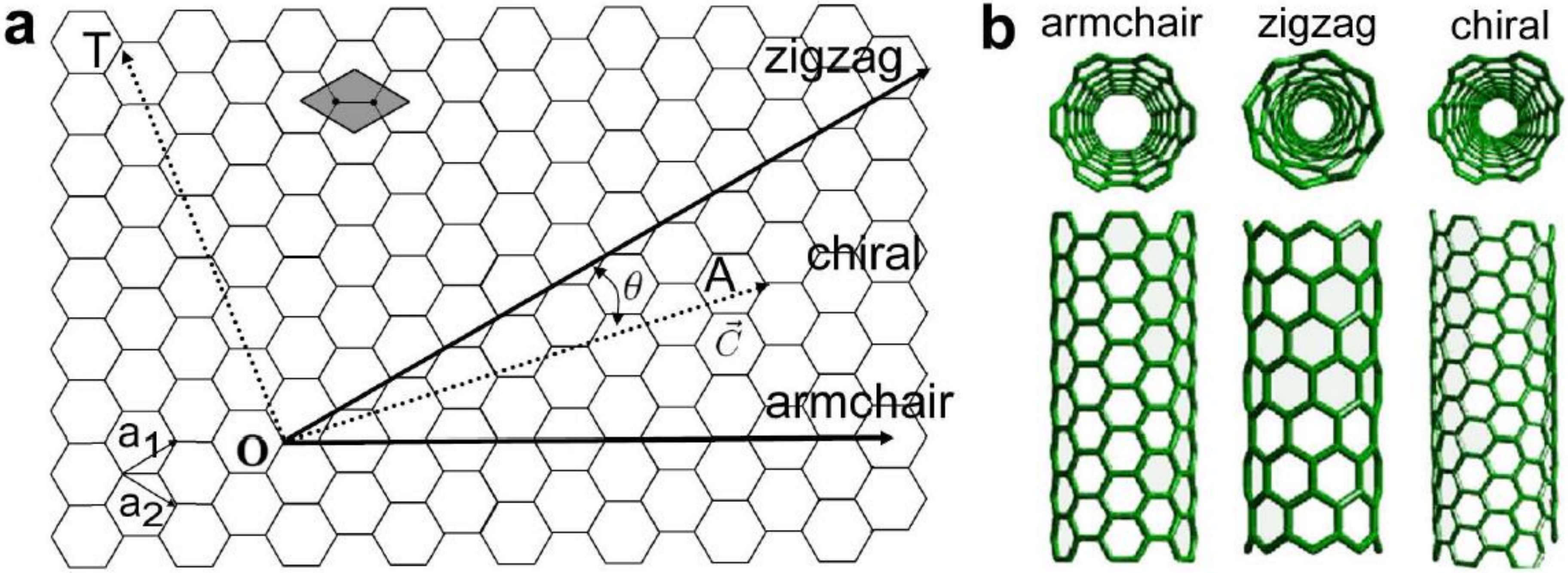


Rolling graphene

- 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)

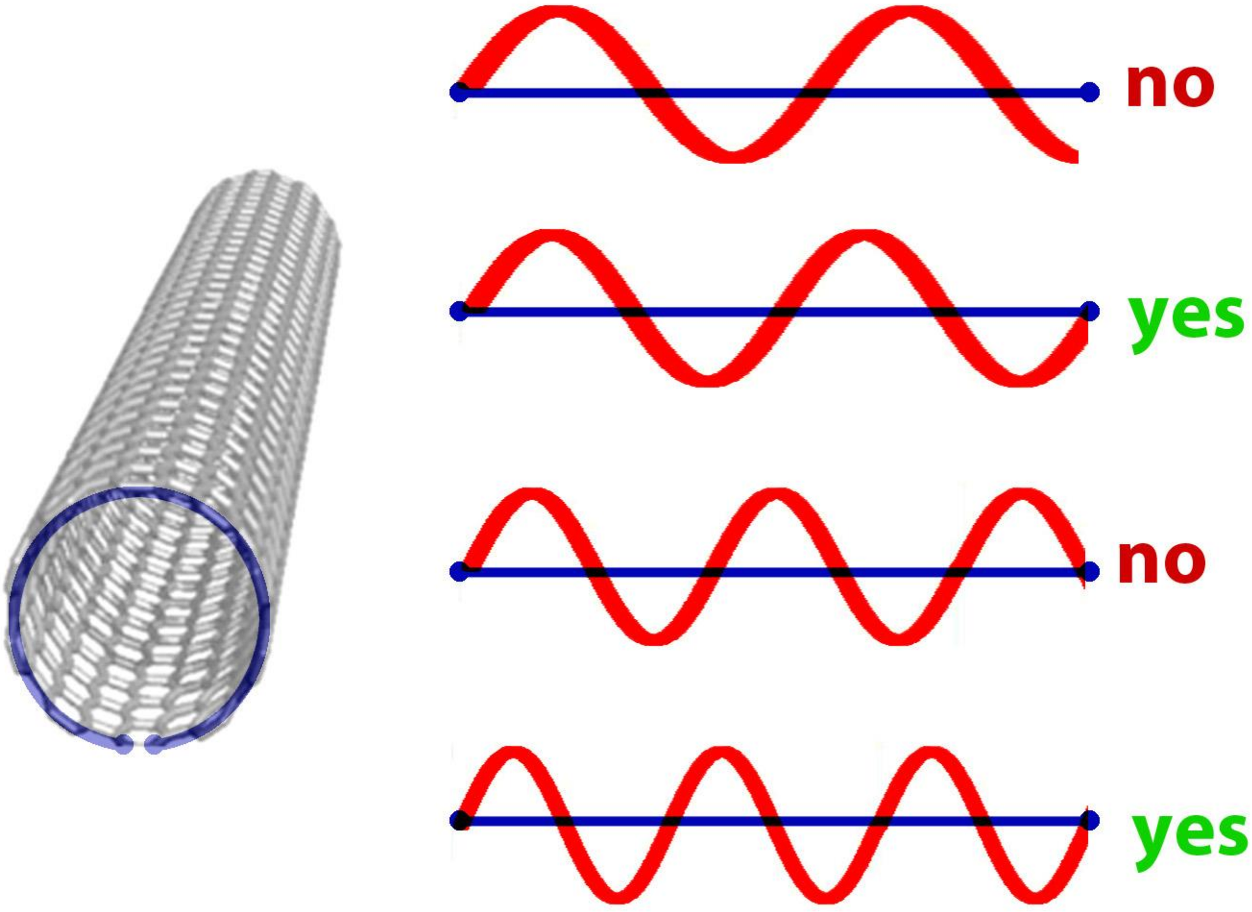
$$\vec{C} = n\vec{a}_1 + m\vec{a}_2$$

$n = m$ $n = 0$



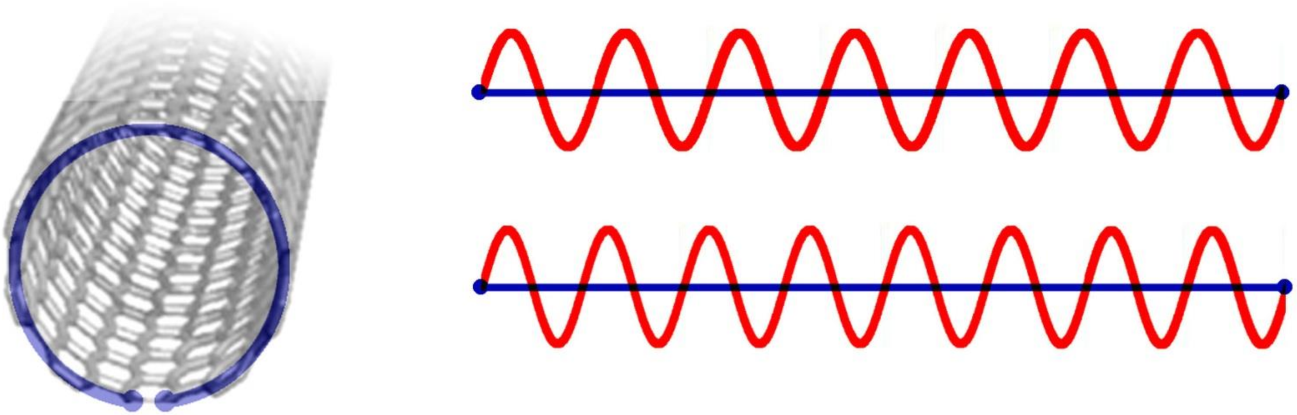
Confinement of electron wavefunctions

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

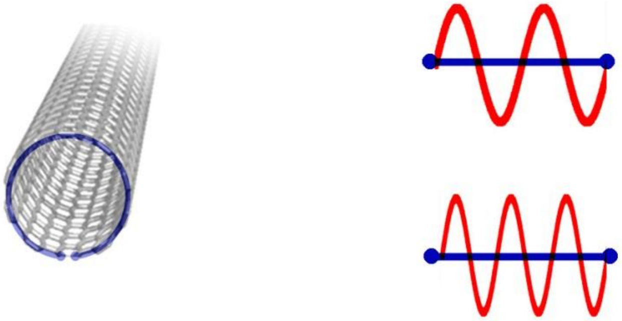


Diameter dependence of confinement

large diameter = small energy difference

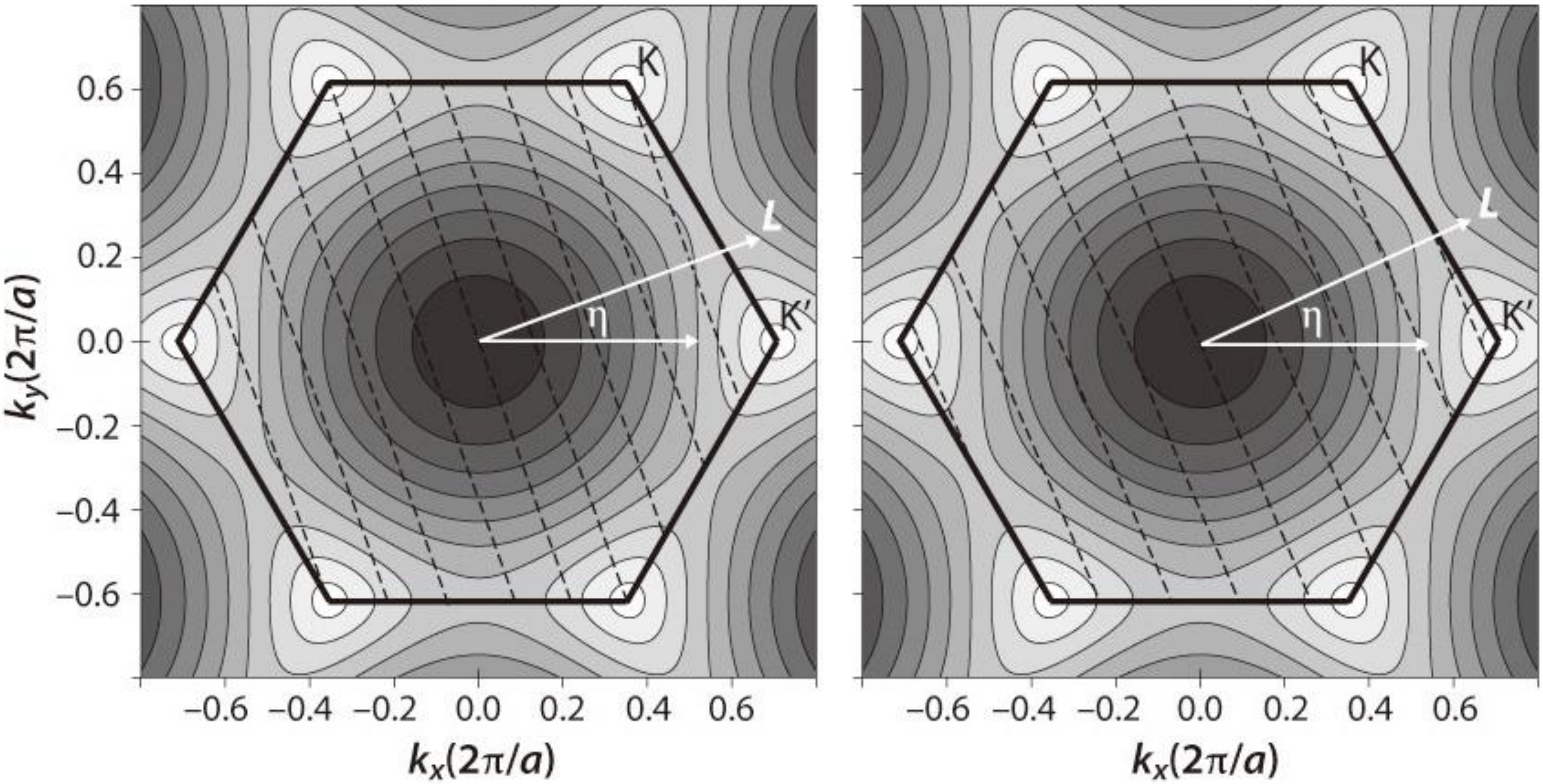


small diameter = large energy difference



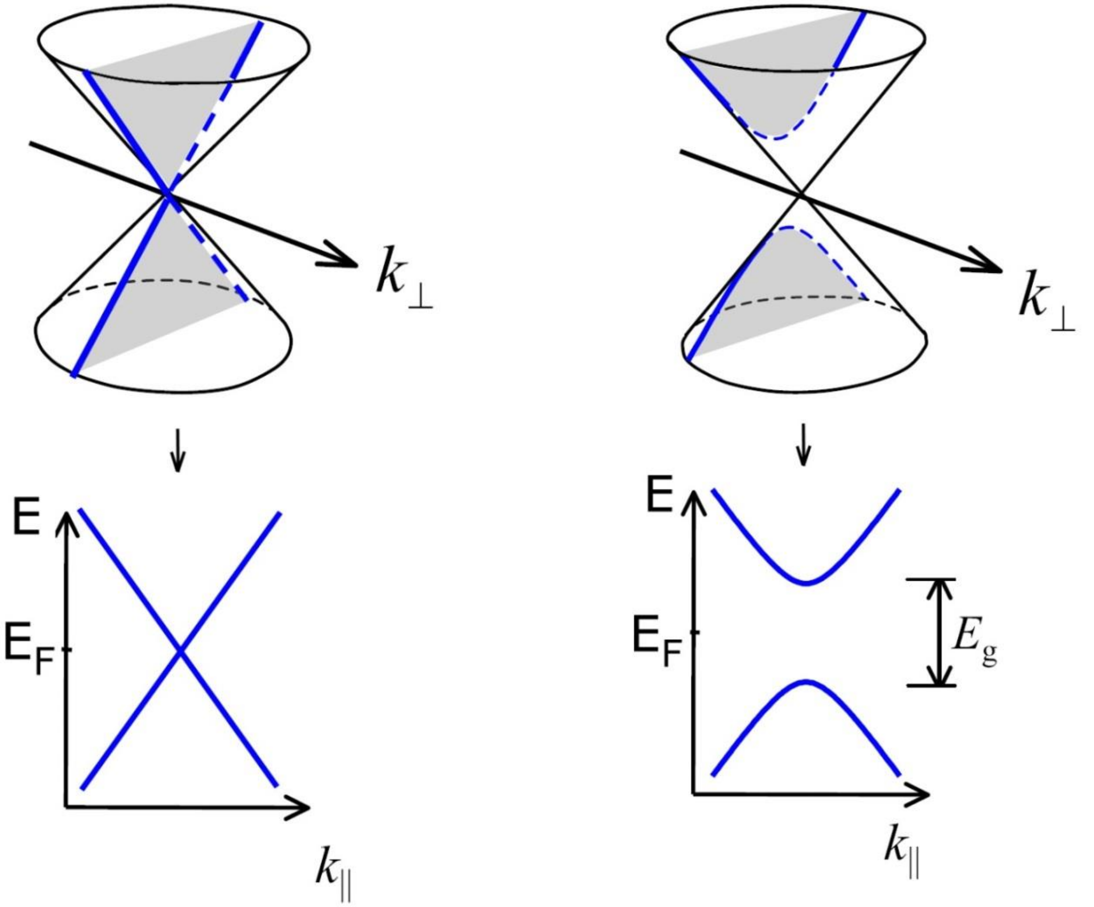
Confinement of electron wavefunctions

- 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

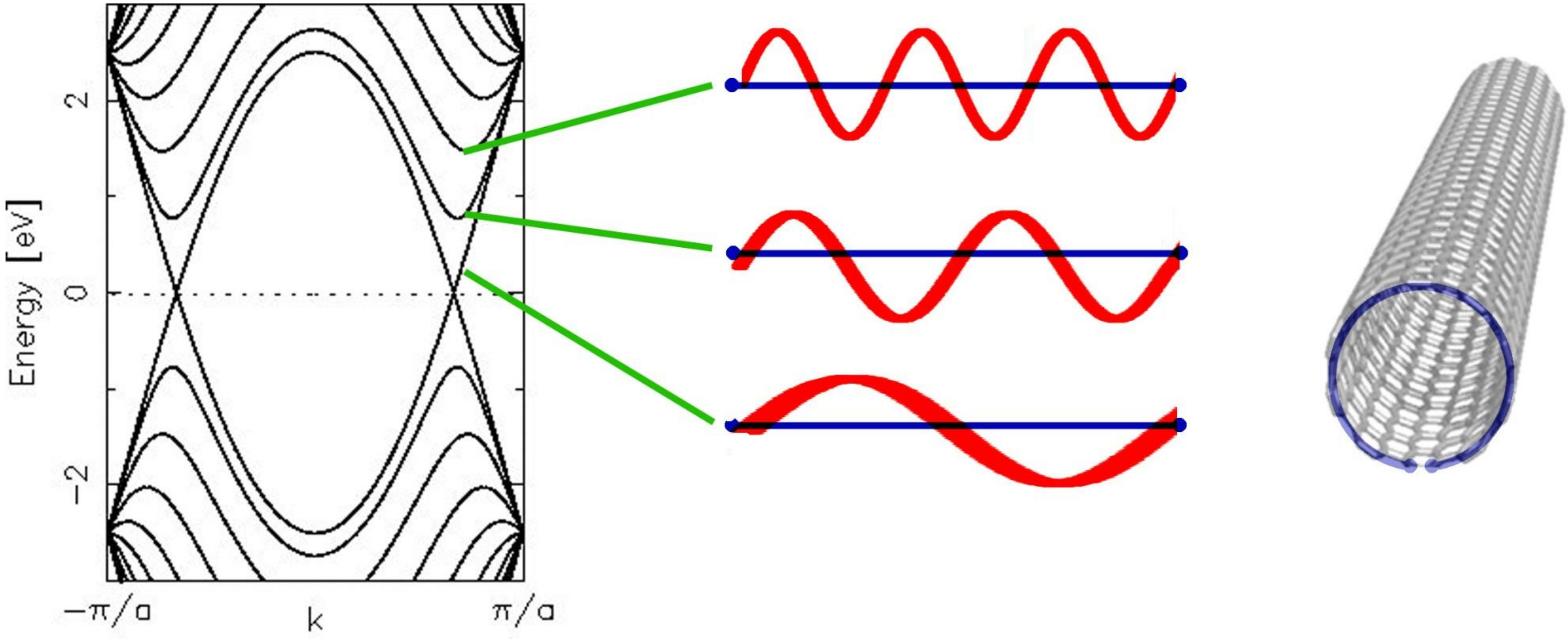
- n-m = 3i with i=1,2,3... -> slice goes through K-point -> metallic CNT
- n-m ≠ 3i -> slice does not go through K-point -> semiconducting CNT with parabolic bands



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

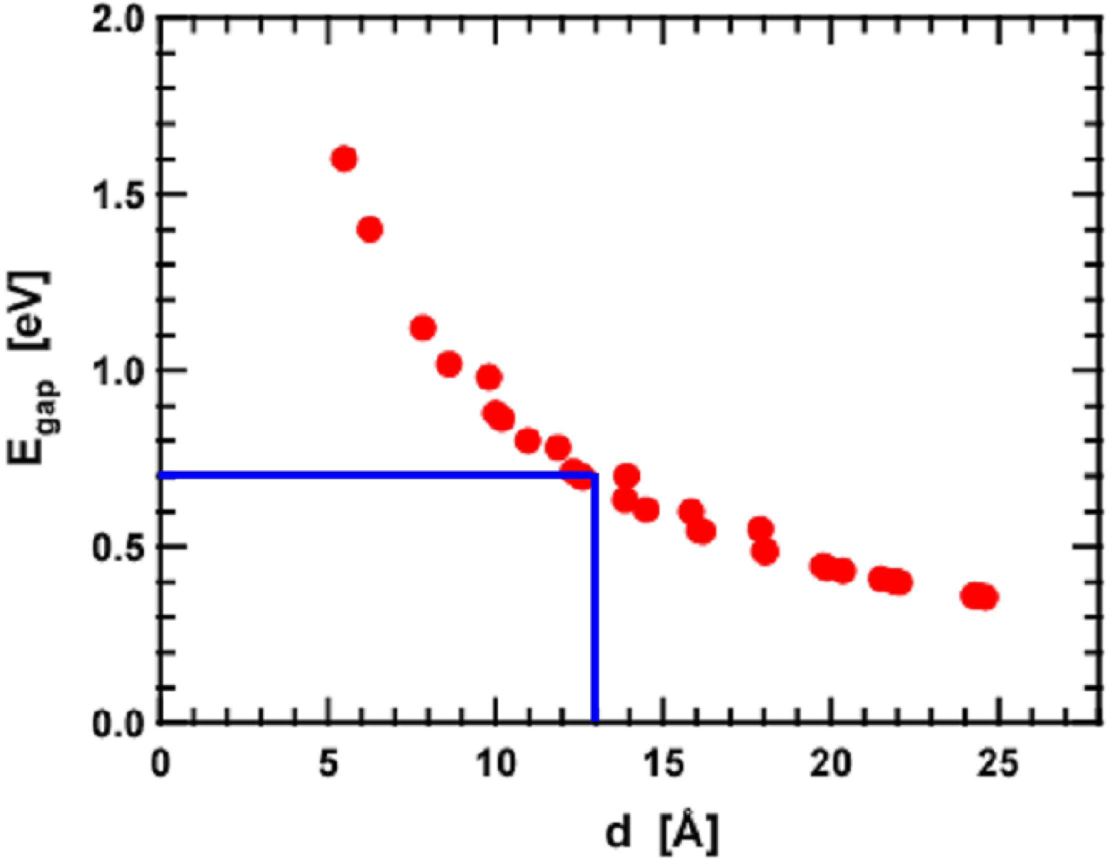
Subbands

- 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



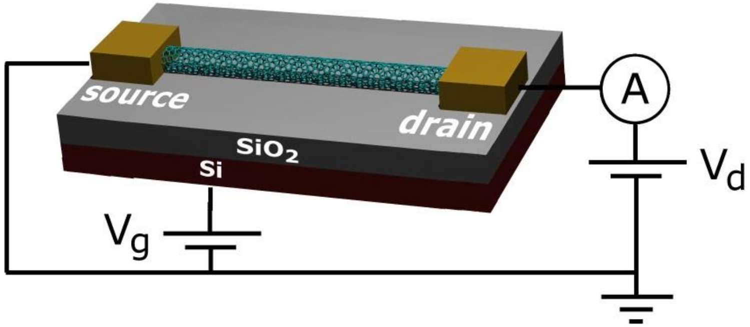
Band gap vs diameter

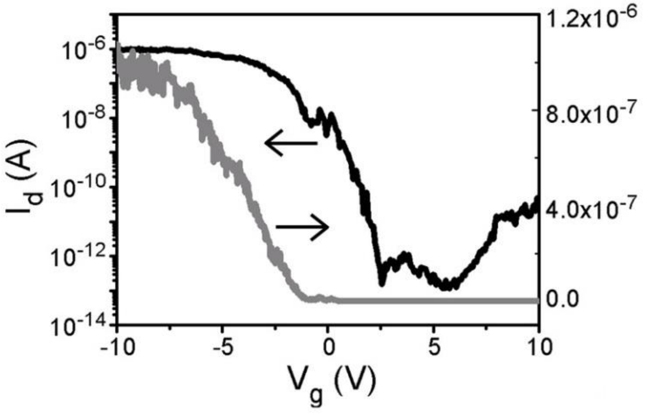
- Linear dispersion of graphene gives E_g=0.8/d [nm]
- Curvature induced gap of 10's of meV in most of the "metallic" CNTs
- Only armchair CNTs truly metallic

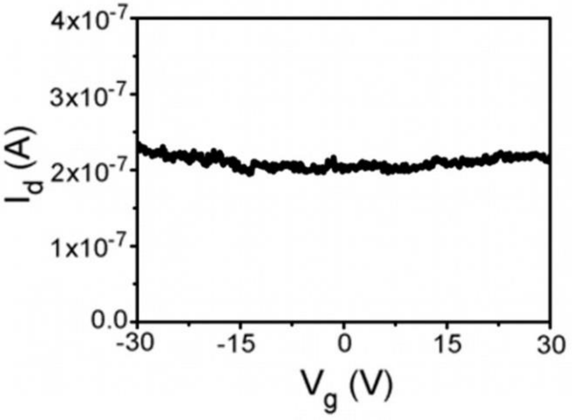


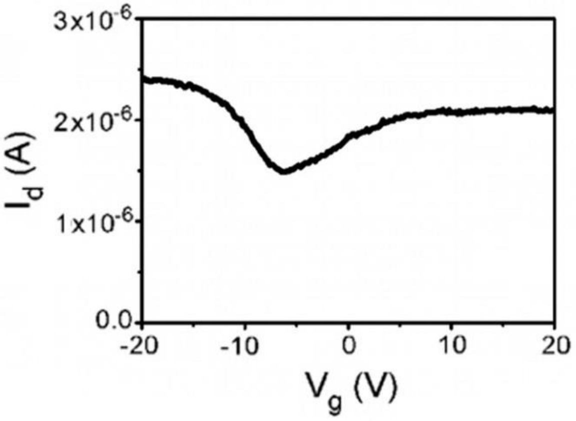
Electrical characteristics

- semiconducting: strong gating effect
- metallic: no gating effect
- small gap semiconducting: some gating effect



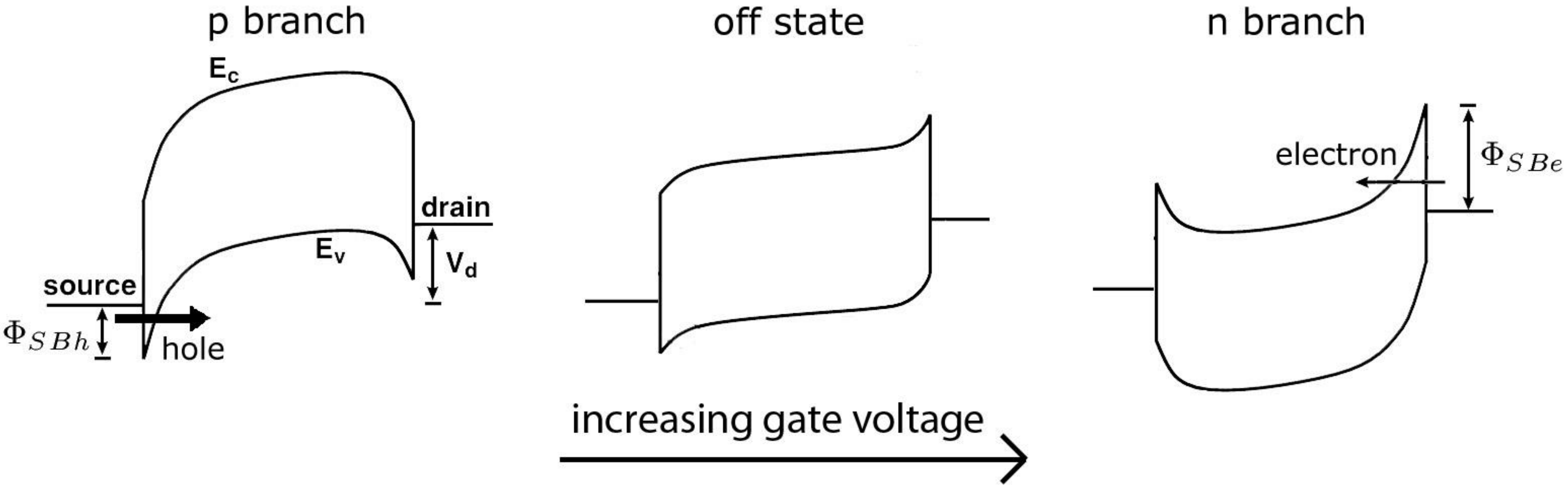

semiconducting


metallic


small band gap

Band diagrams

- 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

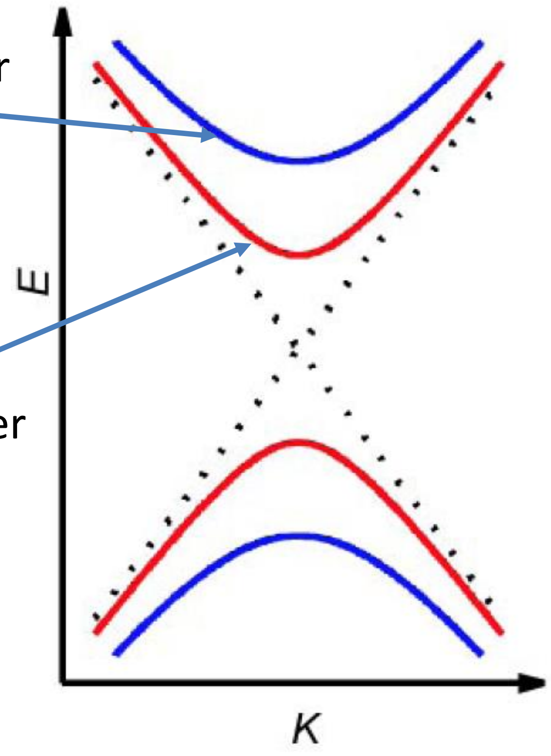


Mobility vs diameter

- Lower curvature of bands for smaller diameter -> mobility proportional to d^2
- μ>100000 cm^2/Vs at 50 K

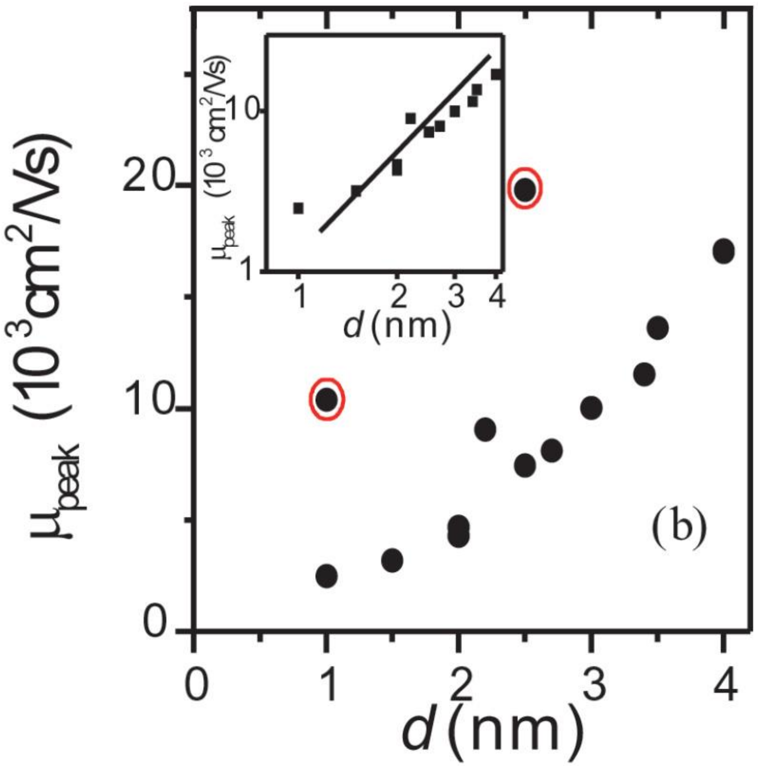
$$m^* = \hbar^2 \cdot \left[\frac{d^2\varepsilon}{dk^2}\right]^{-1} \quad .$$

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



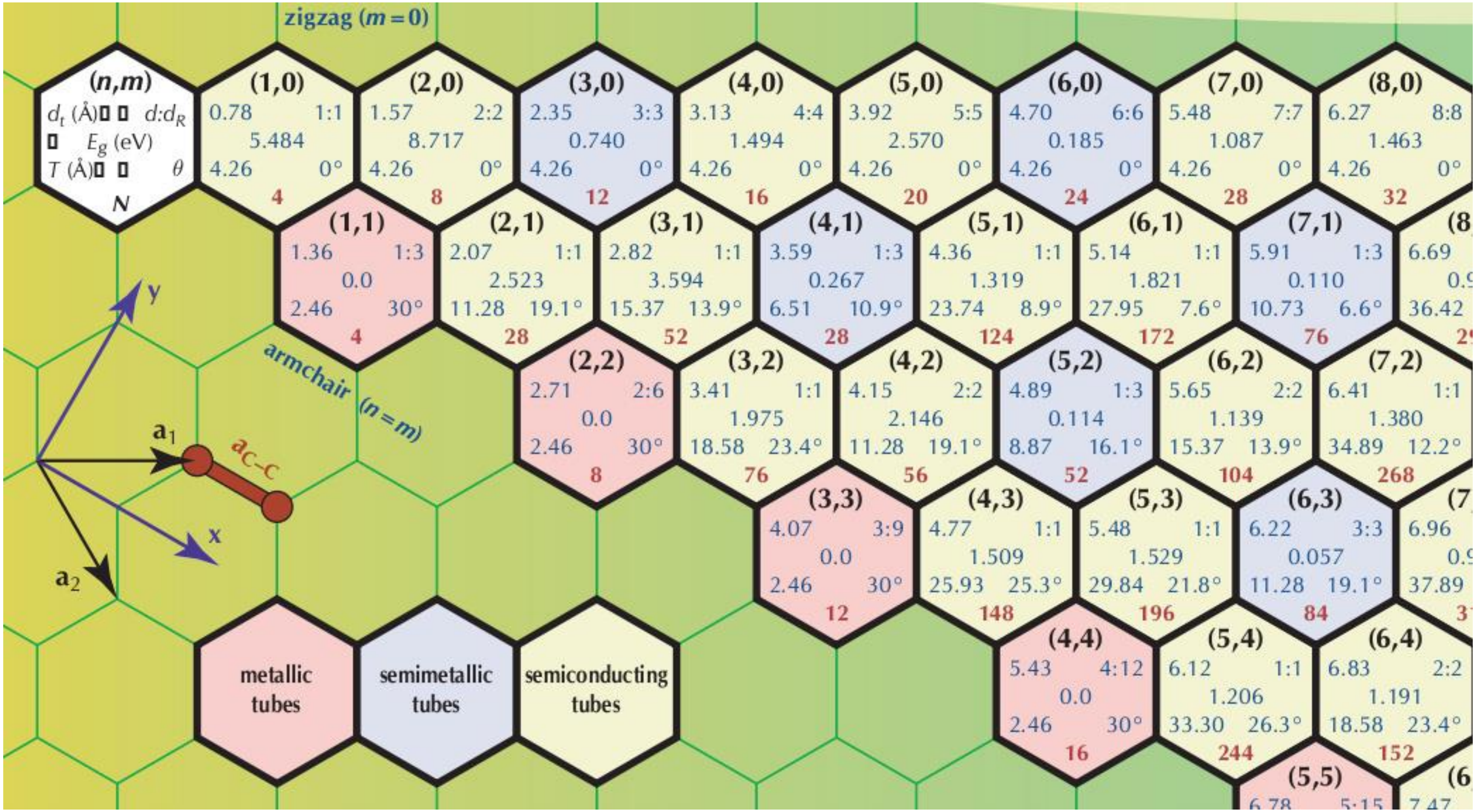
Small diameter

Large diameter



All CNTs are different

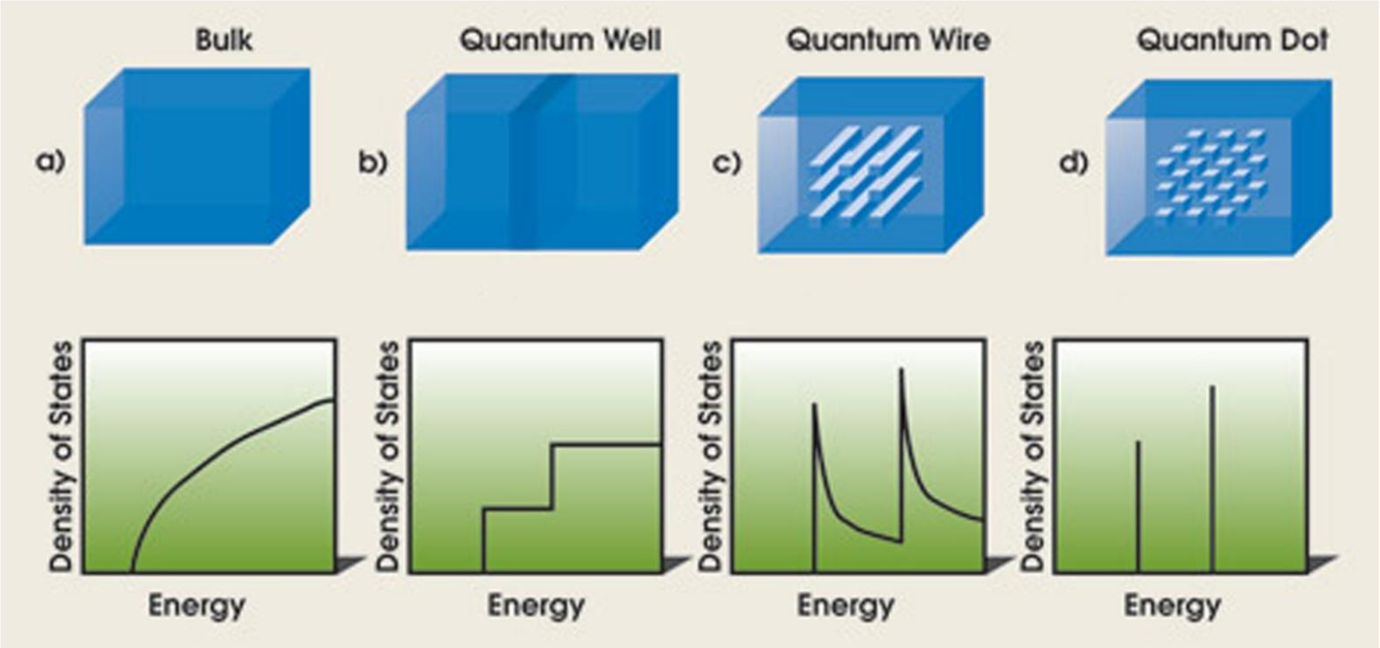
- 1/3 metallic or small gap
- 2/3 semiconducting with different gap

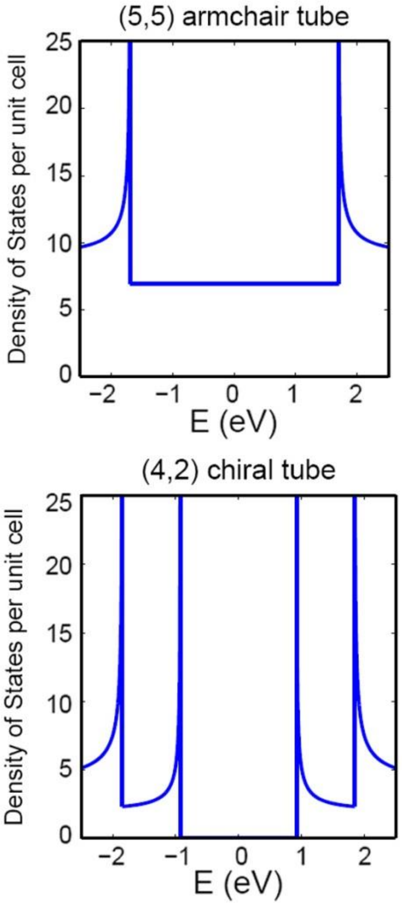


(n,m)	d_t (Å)	$d:d_R$	E_g (eV)	T (Å)	θ	N
(1,0)	0.78	1:1	5.484	4.26	0°	4
(2,0)	1.57	2:2	8.717	4.26	0°	8
(3,0)	2.35	3:3	0.740	4.26	0°	12
(4,0)	3.13	4:4	1.494	4.26	0°	16
(5,0)	3.92	5:5	2.570	4.26	0°	20
(6,0)	4.70	6:6	0.185	4.26	0°	24
(7,0)	5.48	7:7	1.087	4.26	0°	28
(8,0)	6.27	8:8	1.463	4.26	0°	32
(1,1)	1.36	1:3	0.0	2.46	30°	4
(2,1)	2.07	1:1	2.523	11.28	19.1°	28
(3,1)	2.82	1:1	3.594	15.37	13.9°	52
(4,1)	3.59	1:3	0.267	6.51	10.9°	28
(5,1)	4.36	1:1	1.319	23.74	8.9°	124
(6,1)	5.14	1:1	1.821	27.95	7.6°	172
(7,1)	5.91	1:3	0.110	10.73	6.6°	76
(8	6.69		0.	36.42		2
(2,2)	2.71	2:6	0.0	2.46	30°	8
(3,2)	3.41	1:1	1.975	18.58	23.4°	76
(4,2)	4.15	2:2	2.146	11.28	19.1°	56
(5,2)	4.89	1:3	0.114	8.87	16.1°	52
(6,2)	5.65	2:2	1.139	15.37	13.9°	104
(7,2)	6.41	1:1	1.380	34.89	12.2°	268
(3,3)	4.07	3:9	0.0	2.46	30°	12
(4,3)	4.77	1:1	1.509	25.93	25.3°	148
(5,3)	5.48	1:1	1.529	29.84	21.8°	196
(6,3)	6.22	3:3	0.057	11.28	19.1°	84
(7	6.96		0.	37.89		3
(4,4)	5.43	4:12	0.0	2.46	30°	16
(5,4)	6.12	1:1	1.206	33.30	26.3°	244
(6,4)	6.83	2:2	1.191	18.58	23.4°	152
(5,5)	6.78	5:15				
(6	7.47					

Density of states

- Van Hove singularites with high DOS at band edges
- Can be seem in STM or capacitance measurements
- Strong influence on optical properties

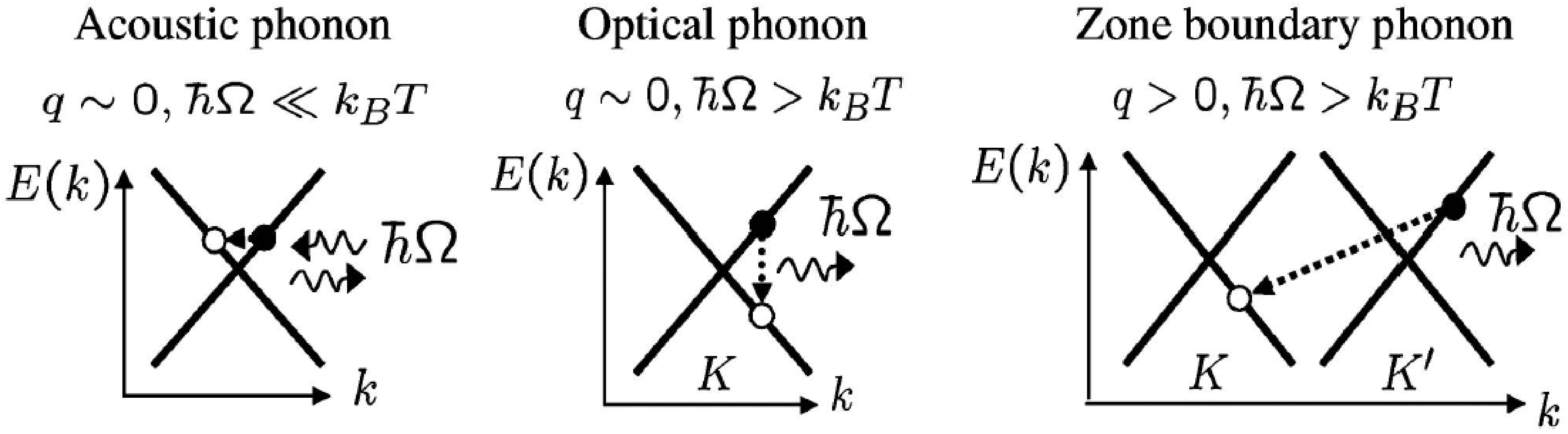




Scattering

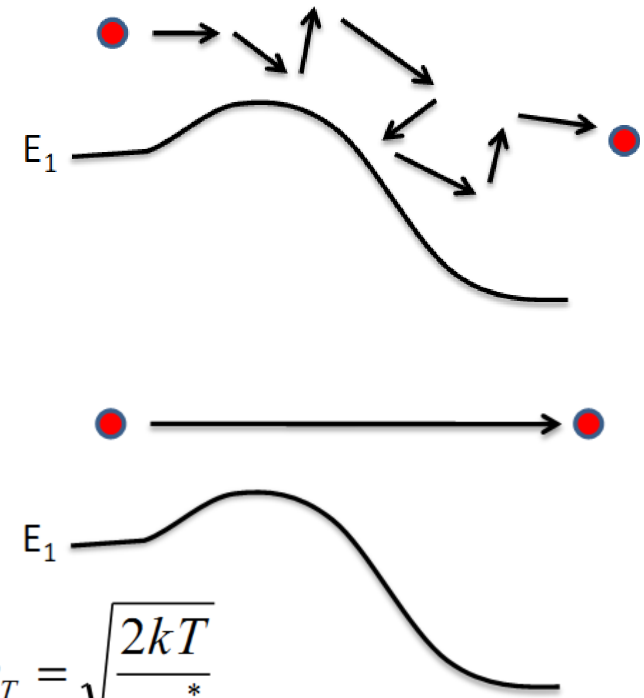
- Elastic scattering have to reverse direction of electron

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

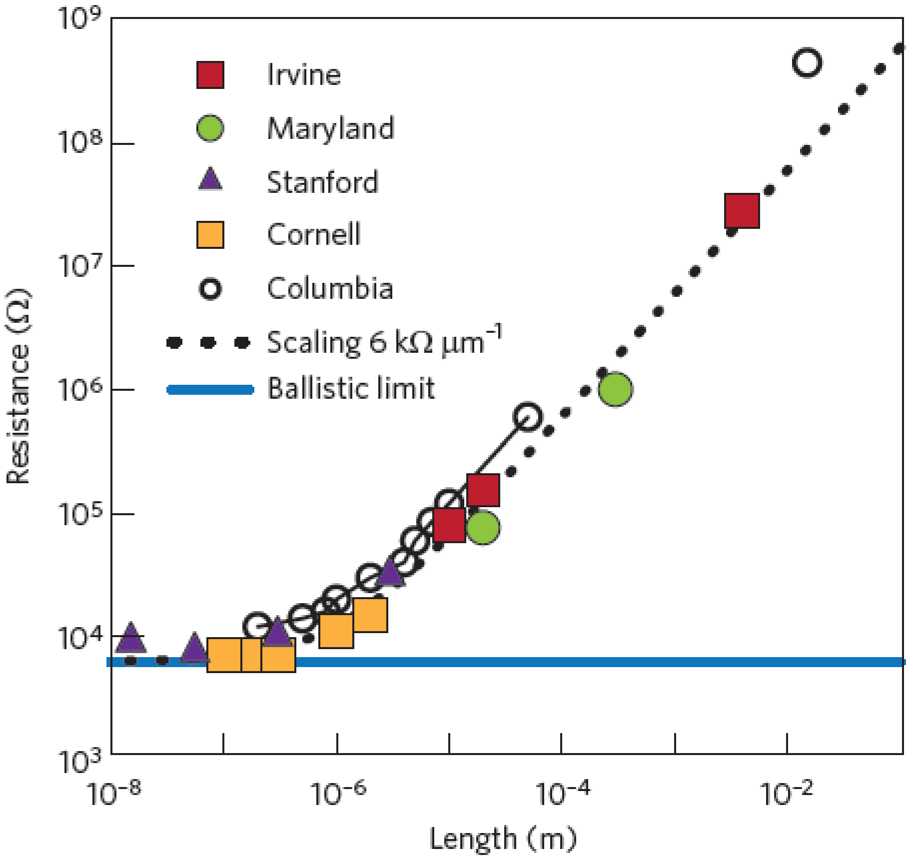


Ballistic transport

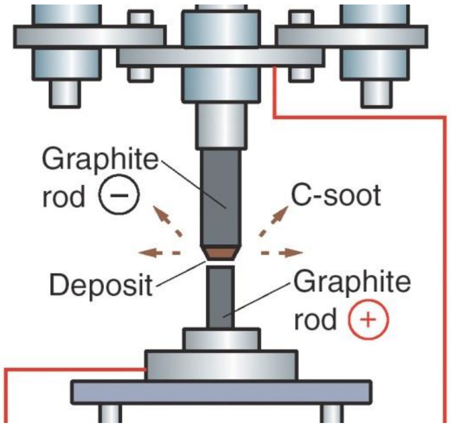
- Channel length << mfp -> no scattering in channel
- Mobility not important but injection velocity is
- R_{min} = 6.5 kOhm in 1D system with 4 modes -> Ballistic transport



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

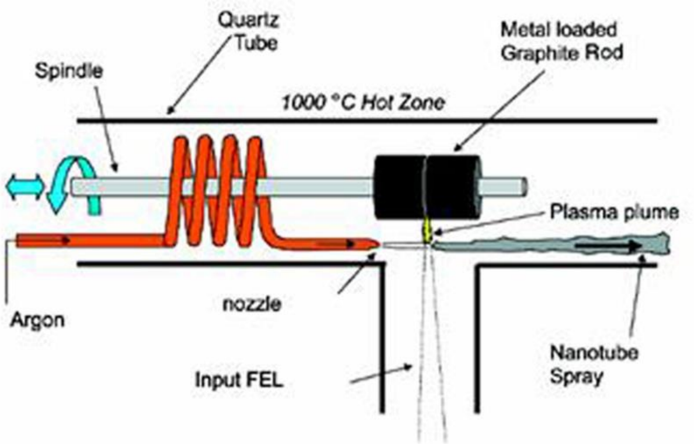


Production of CNTs

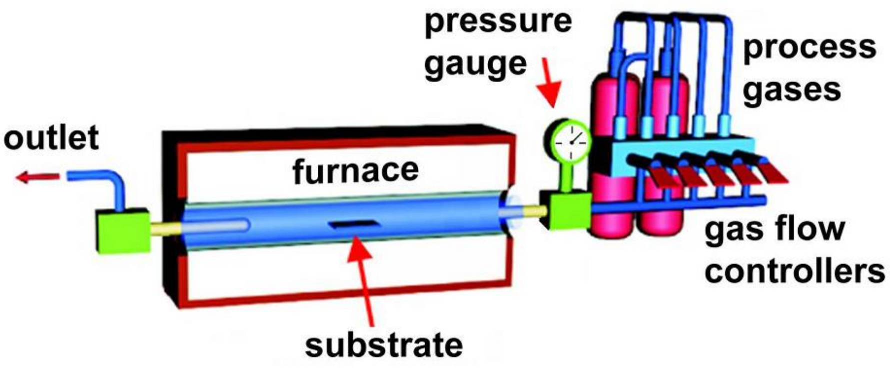


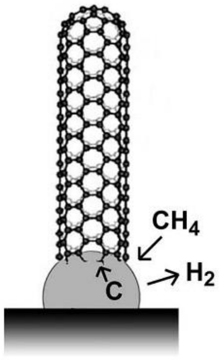
- Arc discharge: high voltage creates spark between graphite rods

- Laser ablation: laser vaporises graphite target



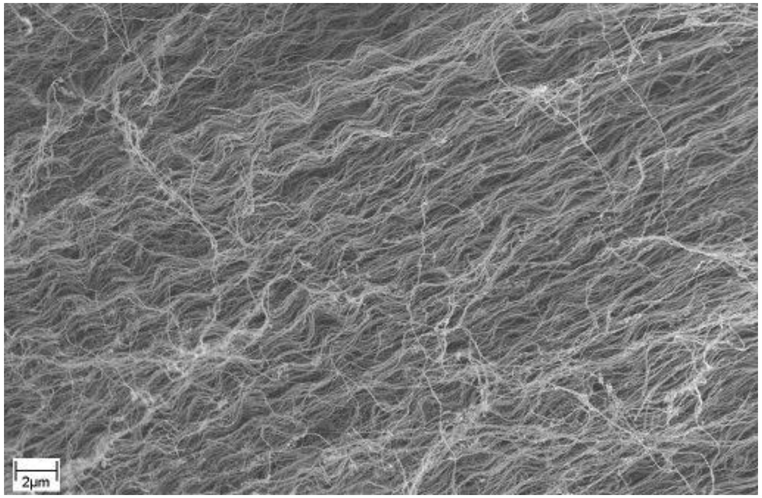
- Chemical vapor deposition: metal catalyst particles decompose hydrocarbon gas

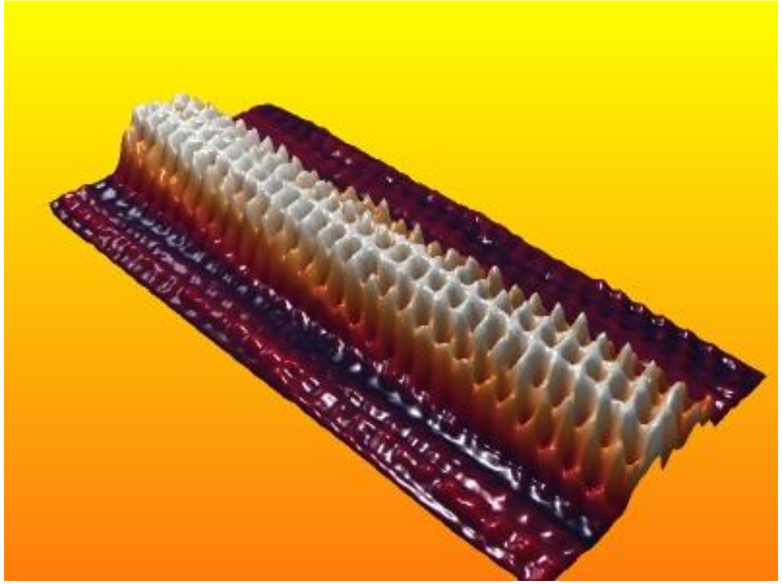


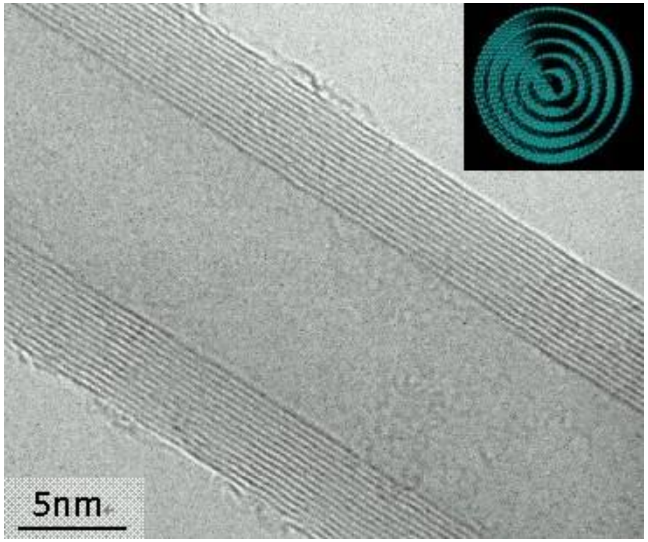


Grown CNTs

- 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 · CV^2)

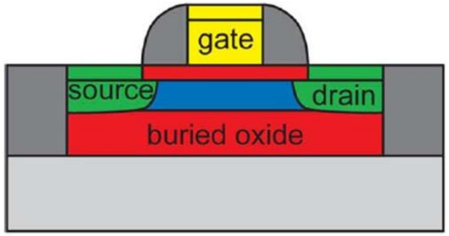
+ Enables higher packing density

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

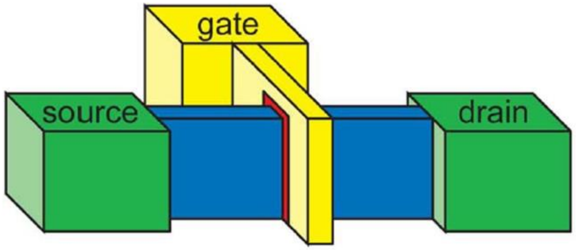
Need to reduce gate dielectric thickness, increase dielectric constant or change design.

Different gating geometries

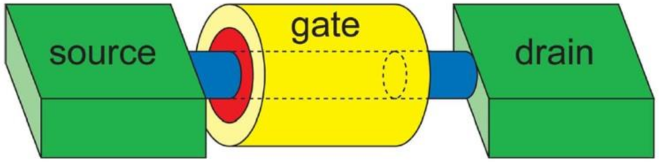
- $L_g > 5\lambda$ to avoid short channel effects
- λ is reduced by higher gate dielectric constant or thinner channel
- More wrapping of the channel gives lower λ
- CNTs and graphene allows for ultimate gate length scaling



$$\lambda_1 \approx \sqrt{\frac{\varepsilon_{ch}}{\varepsilon_{ox}} t_{ox} t_{ch}}$$



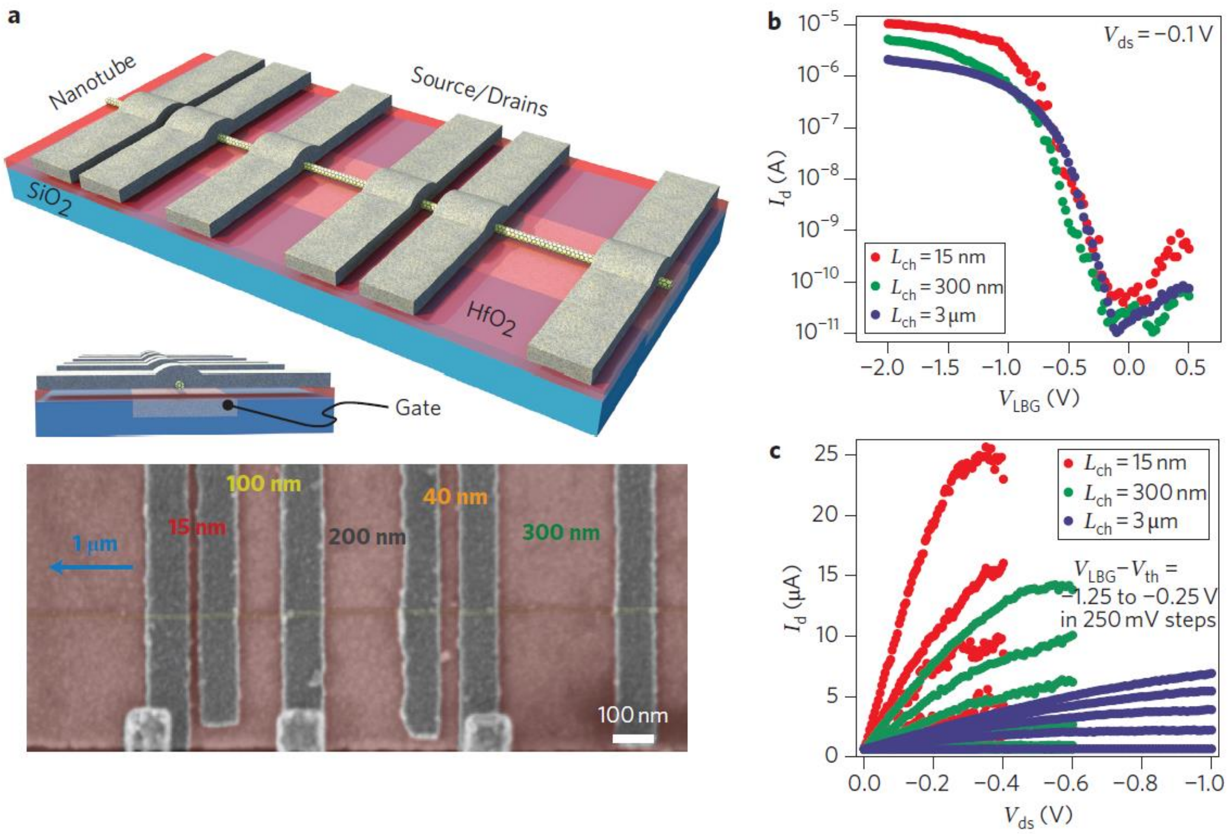
$$\lambda \approx \sqrt{\frac{\varepsilon_{ch}}{2\varepsilon_{ox}} t_{ch} t_{ox} \left(1+\frac{\varepsilon_{ox}}{4\varepsilon_{ch}}\frac{t_{ch}}{t_{ox}}\right)}$$



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

Gate length scaling

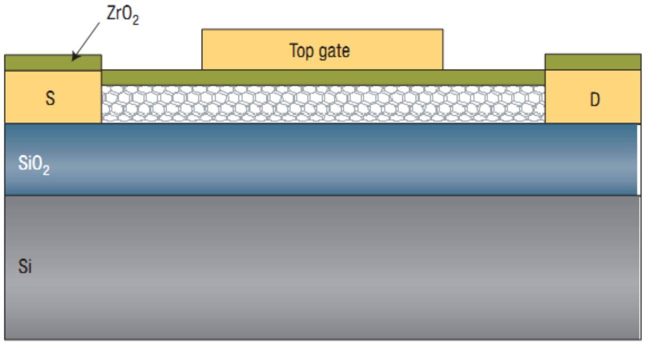
- No short channel effects down to L_g=15 nm
- I_{on}=10 µA
- on/off ratio = 10^5
- S=90 mV/dec also for short devices

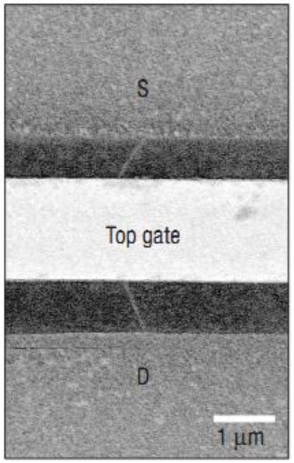


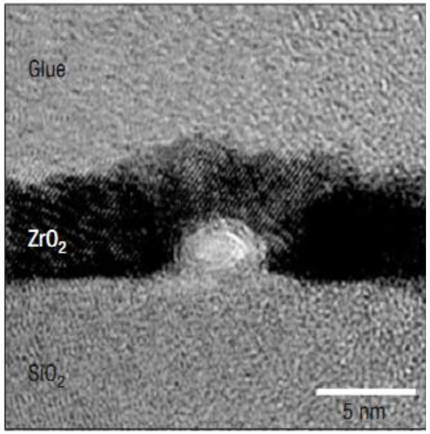
Franklin et al. *Nature Nanotechnol.* **5**, 858–862 (2010)

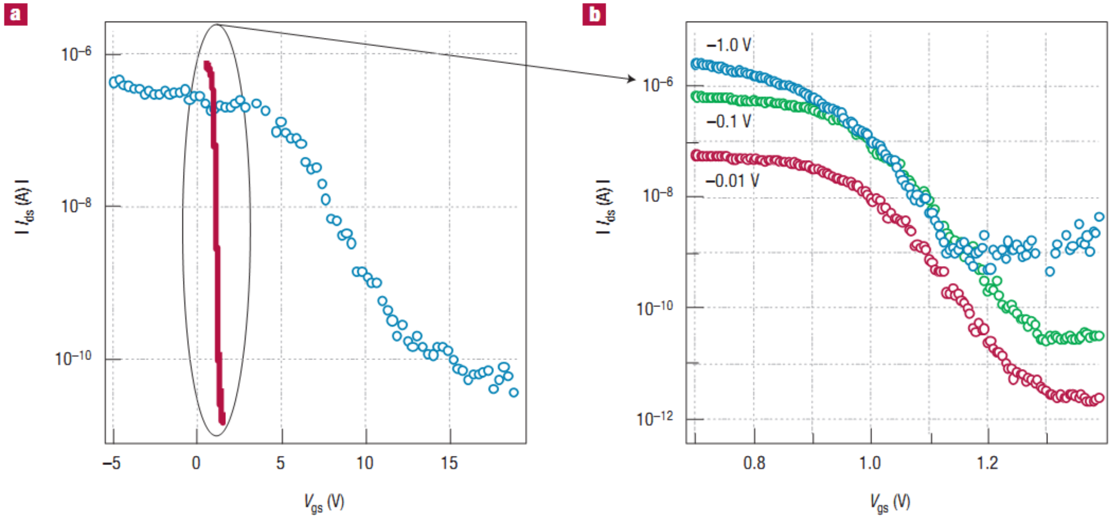
High k gate dielectrics

- No dangling bonds give nice interface
- Difficult to use ALD directly, dielectric grows only on substrate surface





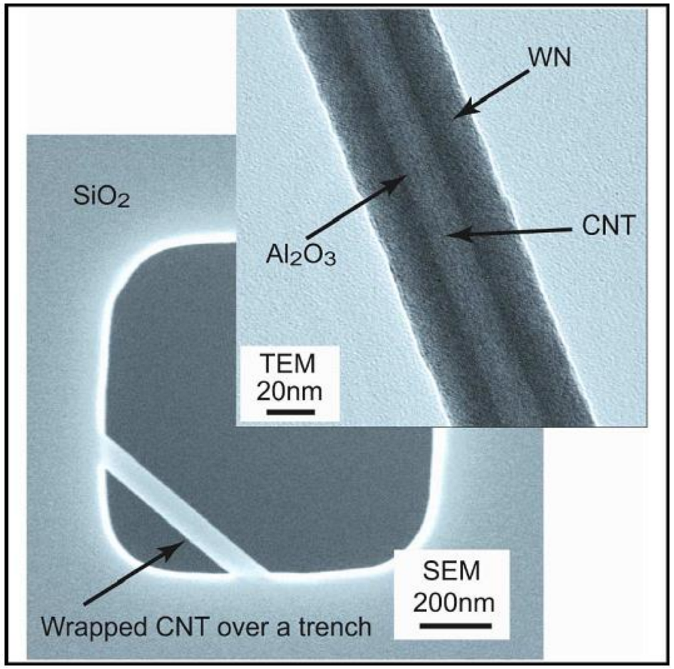


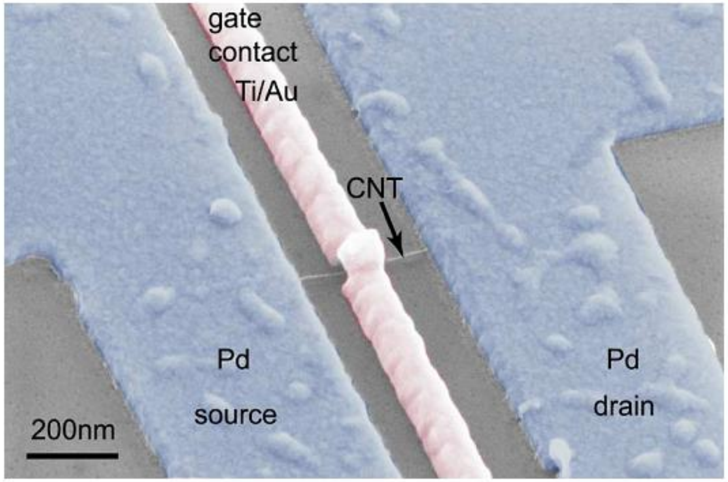


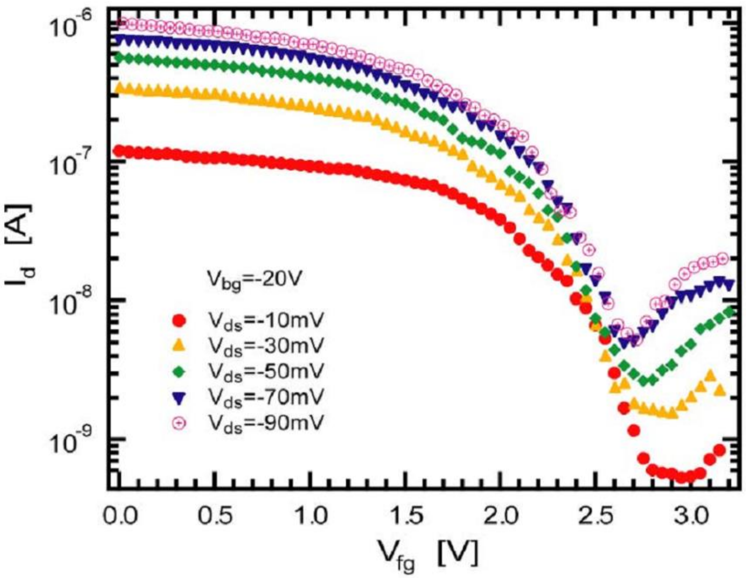
Javey et al. *Nature Materials,* 1 (4), 241-246, 2002

Coaxially gated CNTFET

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



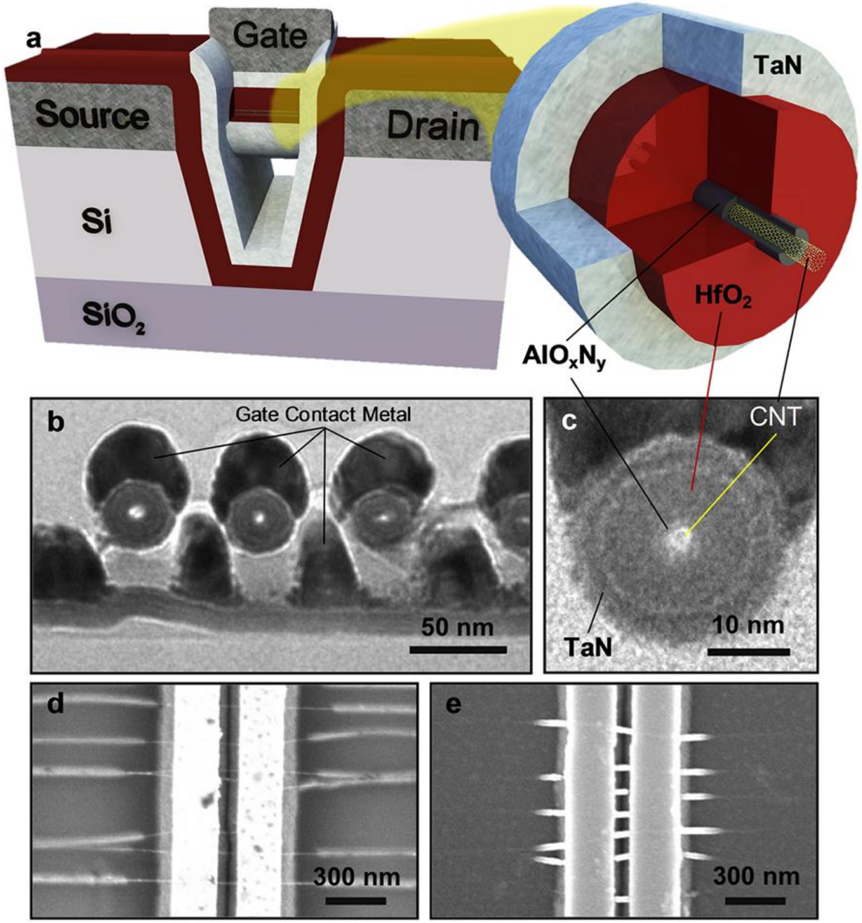


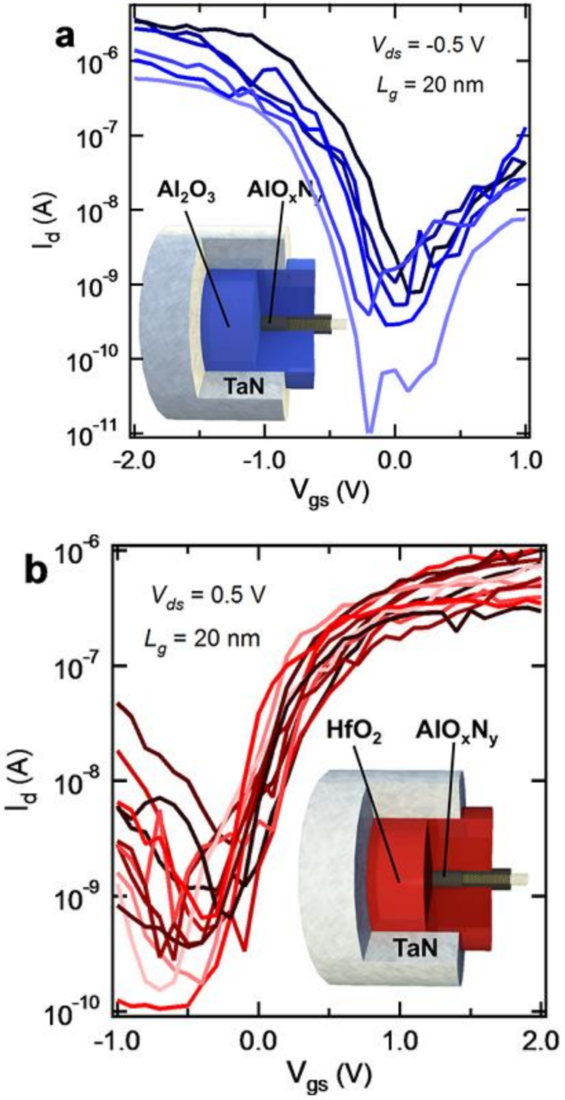


Chen et al. *IEEE Electron. Dev. Lett*. **29**, 2 (2008)

Coaxially gated CNTFET

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

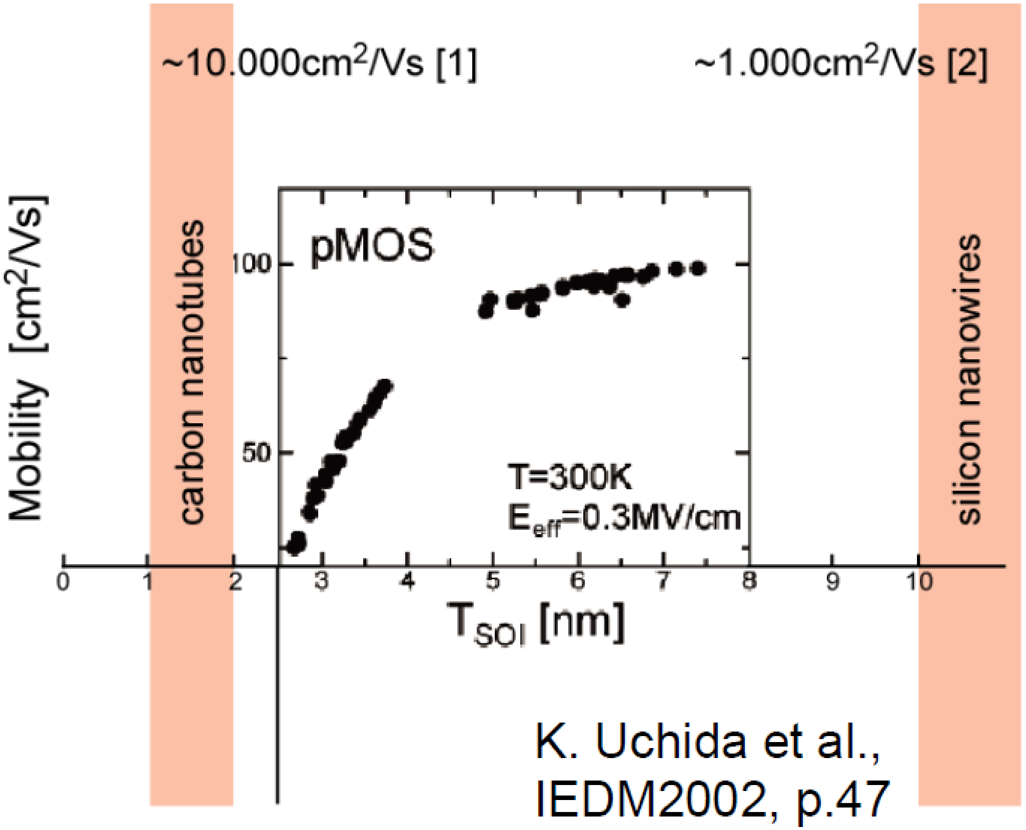




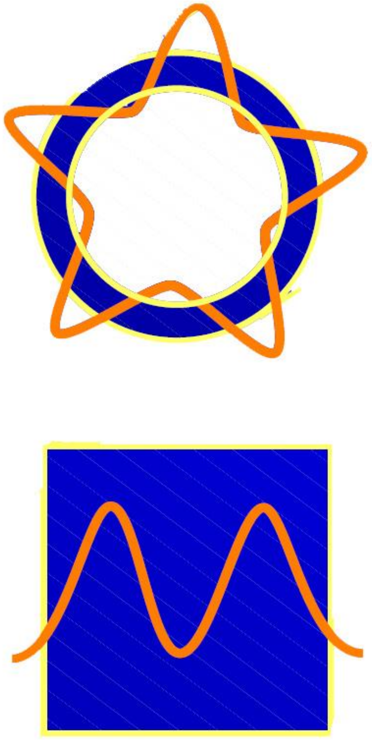
Franklin et al. *Nano Lett.* 13 (6), (2013)

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



K. Uchida et al., IEDM2002, p.47



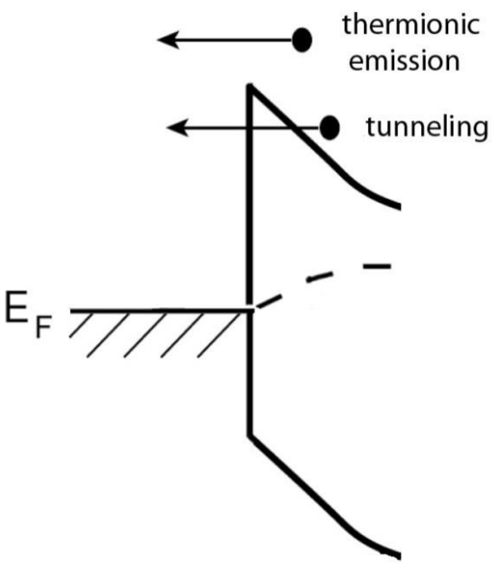
Improving the inverse subthreshold slope

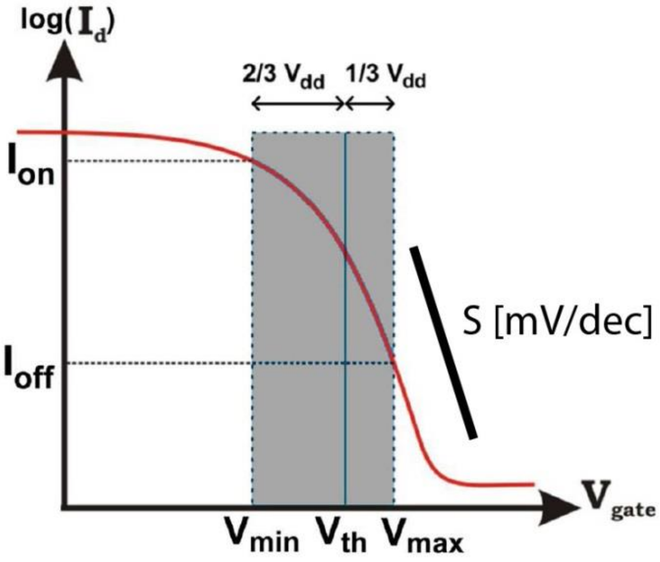
- ”conventional” FETs rely on thermionic emission over a barrier

- $S \geq \ln(10)k_BT$ = 60 mV/dec at RT

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

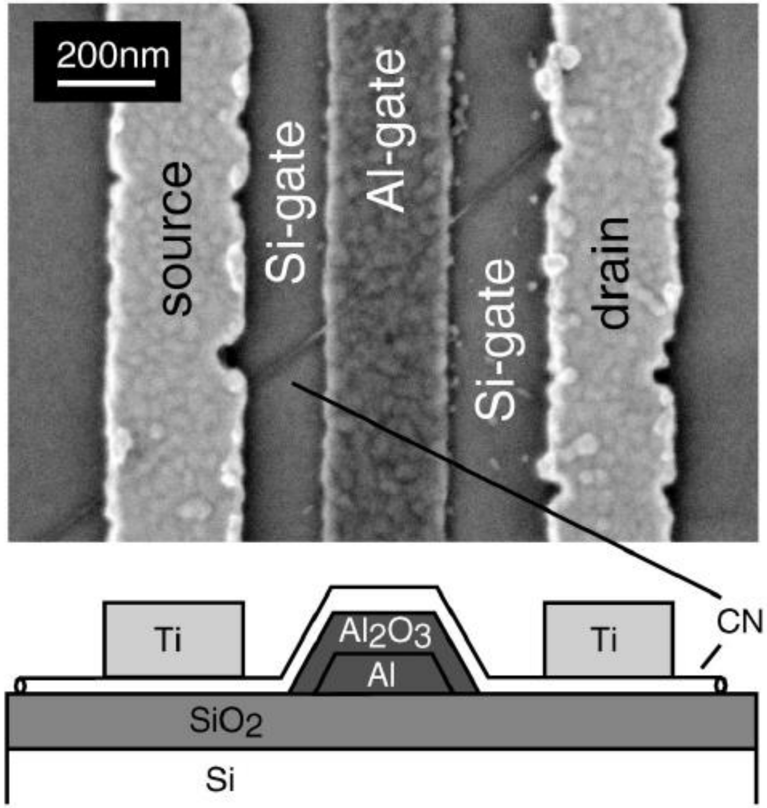
$$S = \left(\frac{d\log_{10}(I_d)}{dV_g}\right)^{-1}$$





Band-to-band tunneling

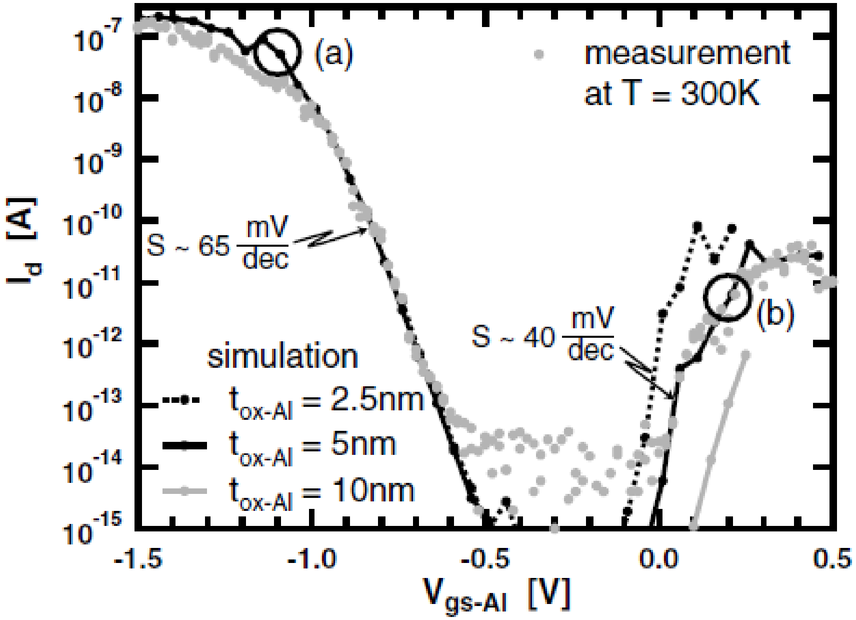
- λ is a few nm in CNT - > sharp band bending
- Low effective mass
- Long mfp
- Same effective mass of electrons and holes
- Direct band gap

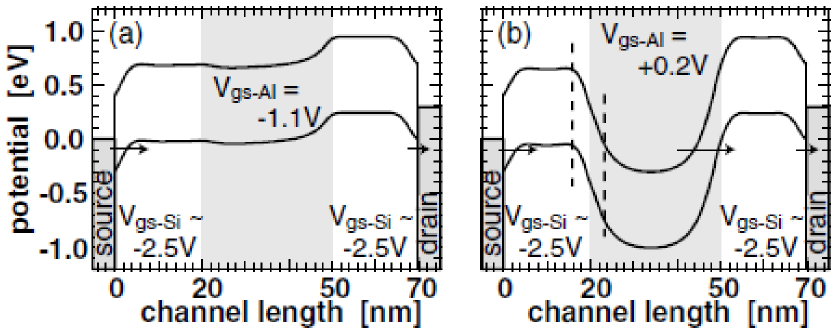


Appenzeller et al. *PRL*. **93**, 196805 (2004)

Electrical characteristics

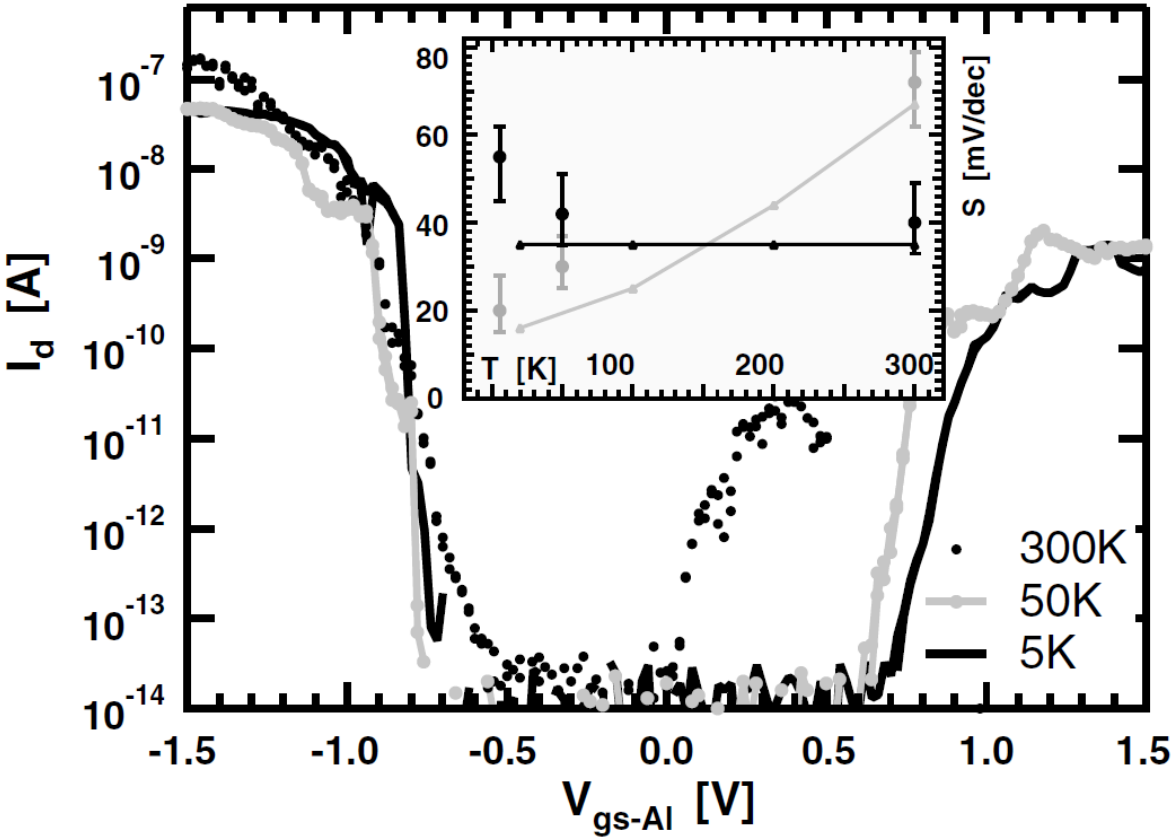
- Back gate to form p-type regions
- Al gate to switch FET
- Ambipolar characteristics
- S=40 mV/dec for the n-branch
- Band-to-band tunneling at the border between the gates





Temperature dependence

- S <u>is not</u> reduced with temperature for the n-branch -> tunneling
- S <u>is</u> reduced with temperature for the p-branch –> thermionic emission

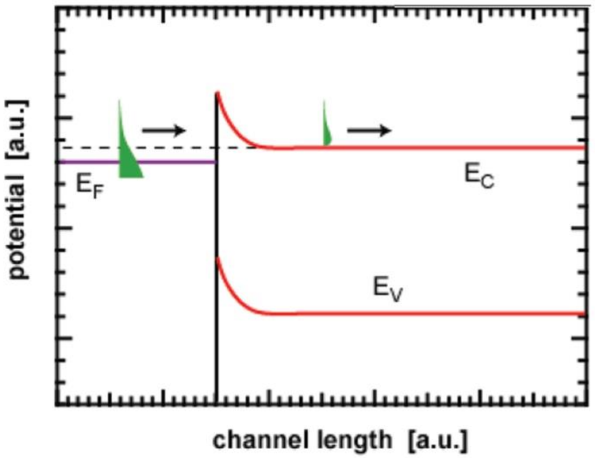


Mechanism of S reduction

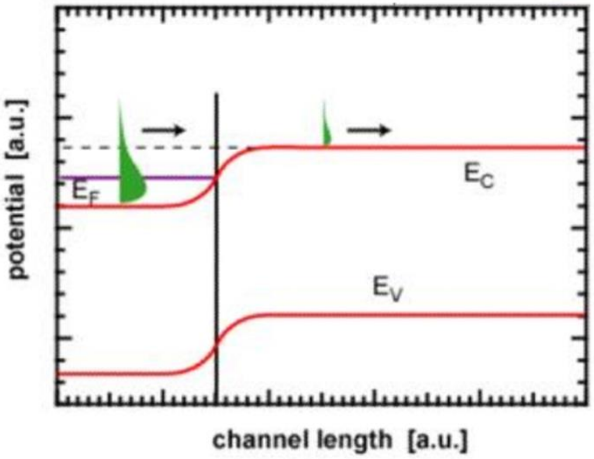
- Only high energy tail of Fermi-Dirac distribution is transferred in thermionic emission or in tunneling through Schottky barrier

- Band-to-band tunneling ”filters” the Fermi-Dirac distribution since the band edges ”cut off” the high energy tail

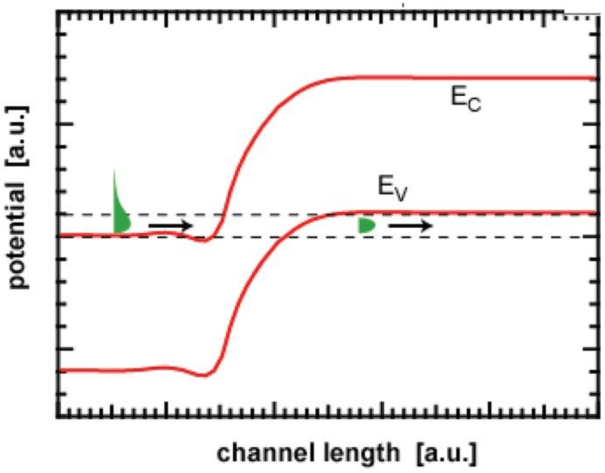
- For BTB tunneling, small movement of bands give large change in current i.e. small S



tunneling at Schottky barrier



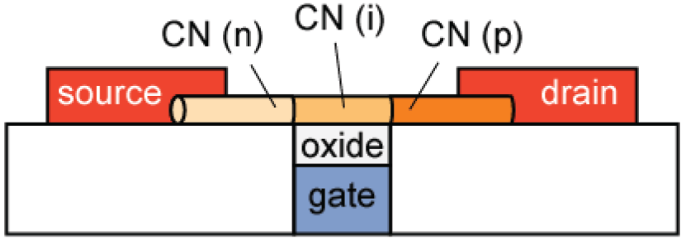
thermionic emission

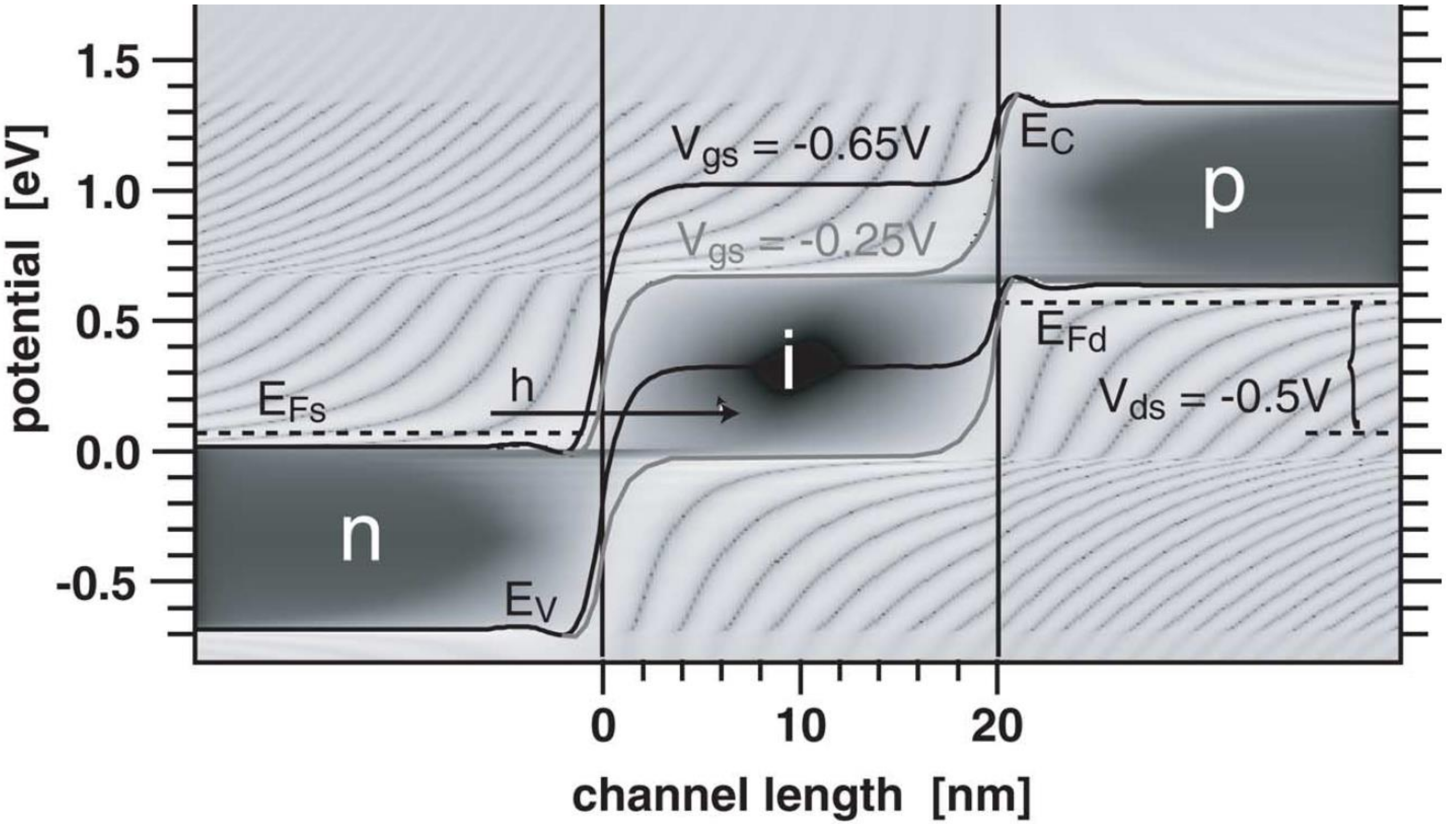


band-to-band tunneling

An improved tunneling CNTFET

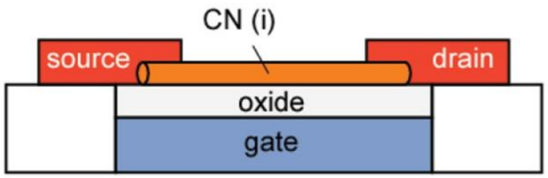
- n-i-p doping
- Only one tunneling event
- Avoids charge pile-up in central region
- Diffcult to make with a CNT

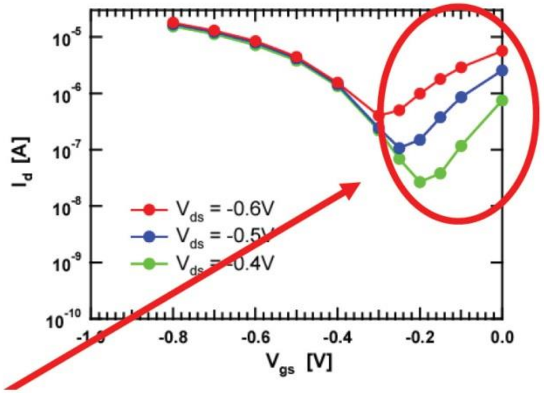




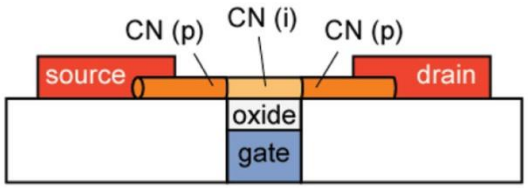
Three types of CNTFETs

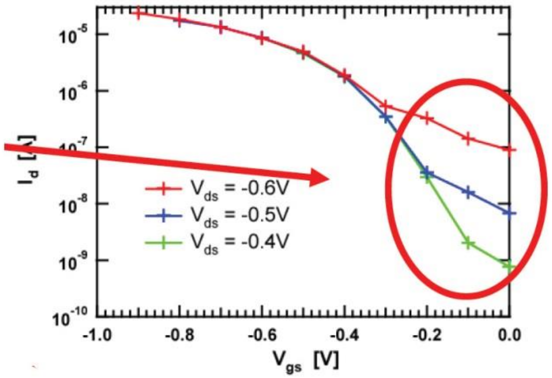
Schottky barrier



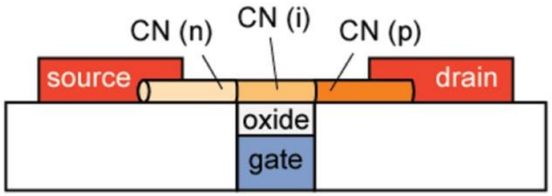


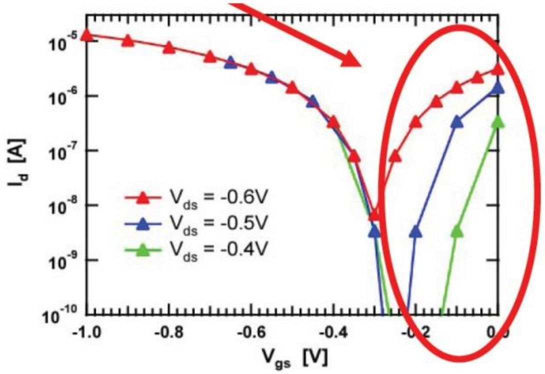
Doped contacts





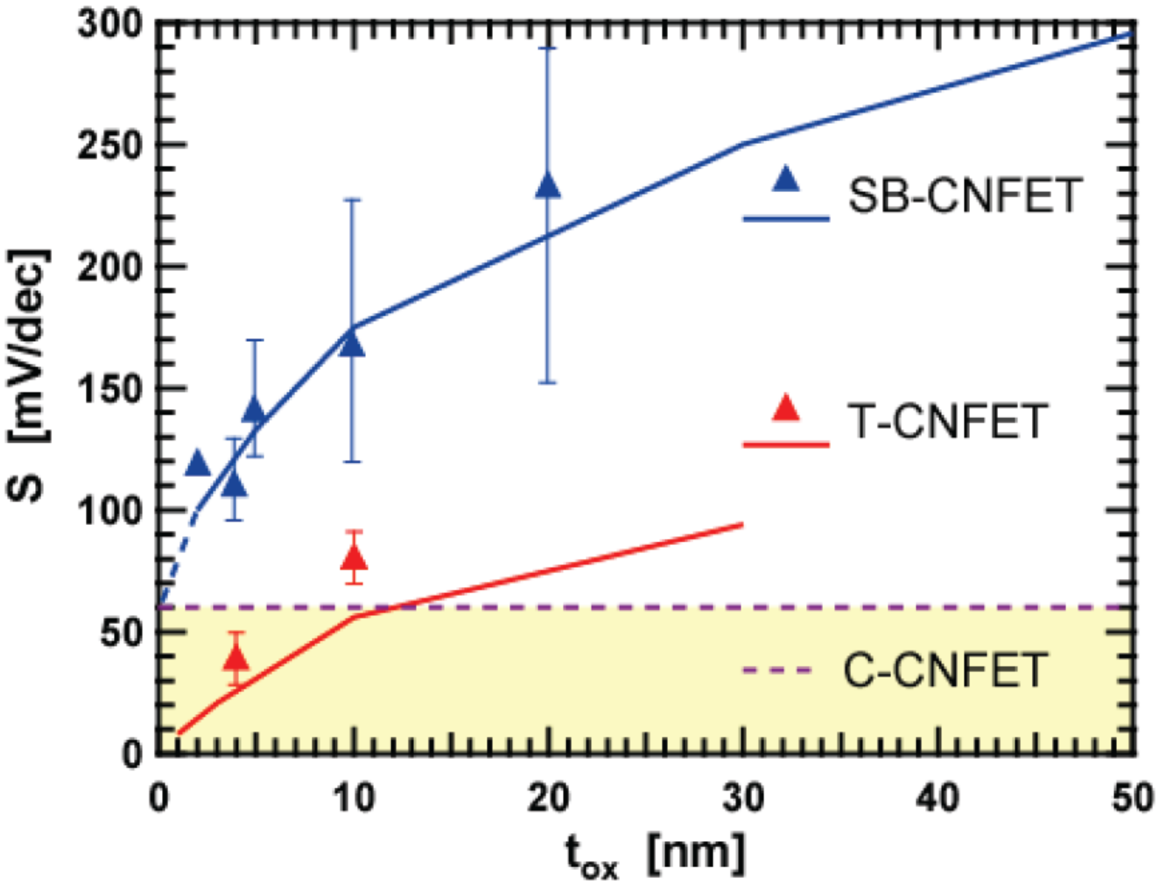
Band-to-band tunneling





Comparing devices

- For thin gate dielectrics the BTB tunneling FET can reach S<60 mV/dec
- Very low I_{on} in n-branch



Outline

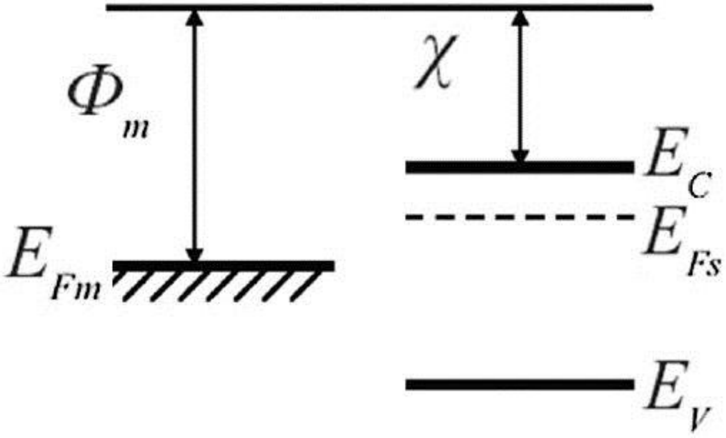
- Basics of graphene and CNTs
  - Structural
  - Electronic
  - Production of CNTs
- Advantages of CNTs for FETs
  - Gate length scaling
  - Coaxial gate
  - High-k compatibility
  - Band-to-band tunneling
- Challenges of CNT integration
  - Contacts
  - Doping
  - Positioning
  - Chirality control
-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

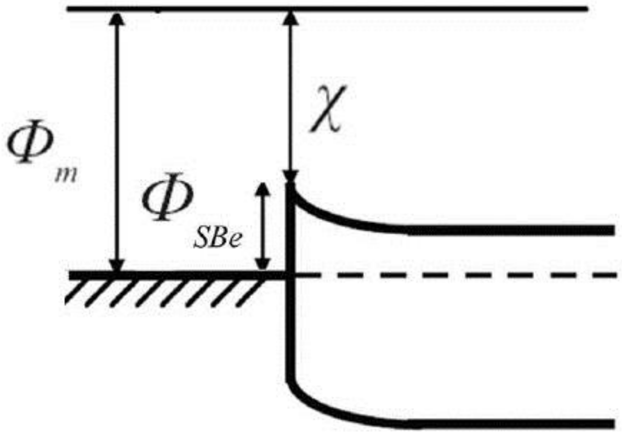
Schottky barrier basics

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

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

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

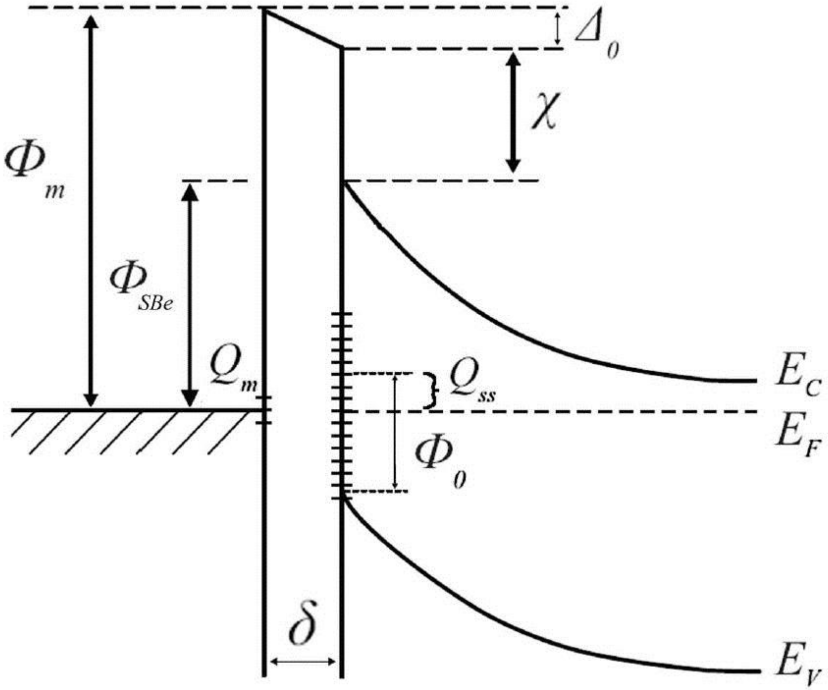


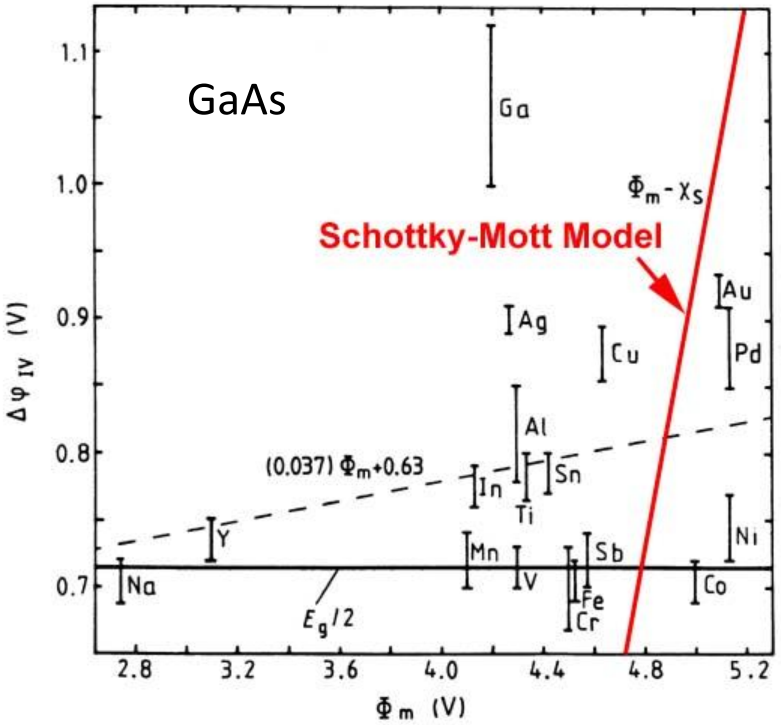


Fermi level pinning

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

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

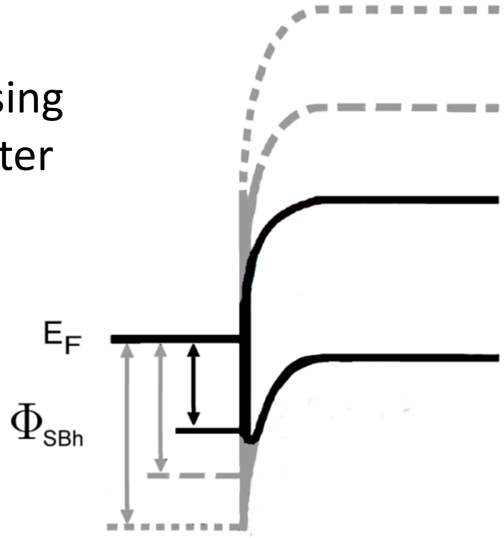




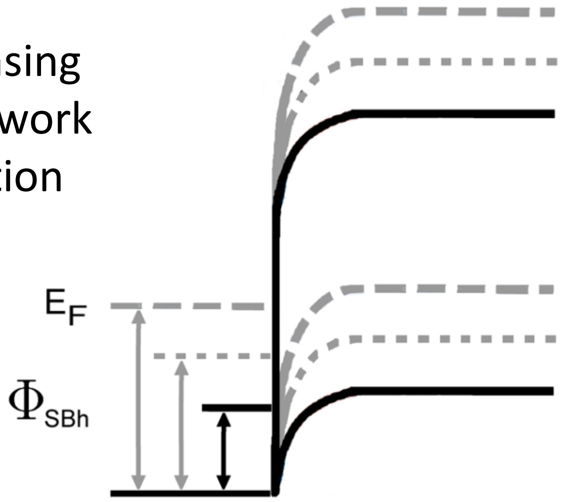
Schottky barrier to CNTs

- 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

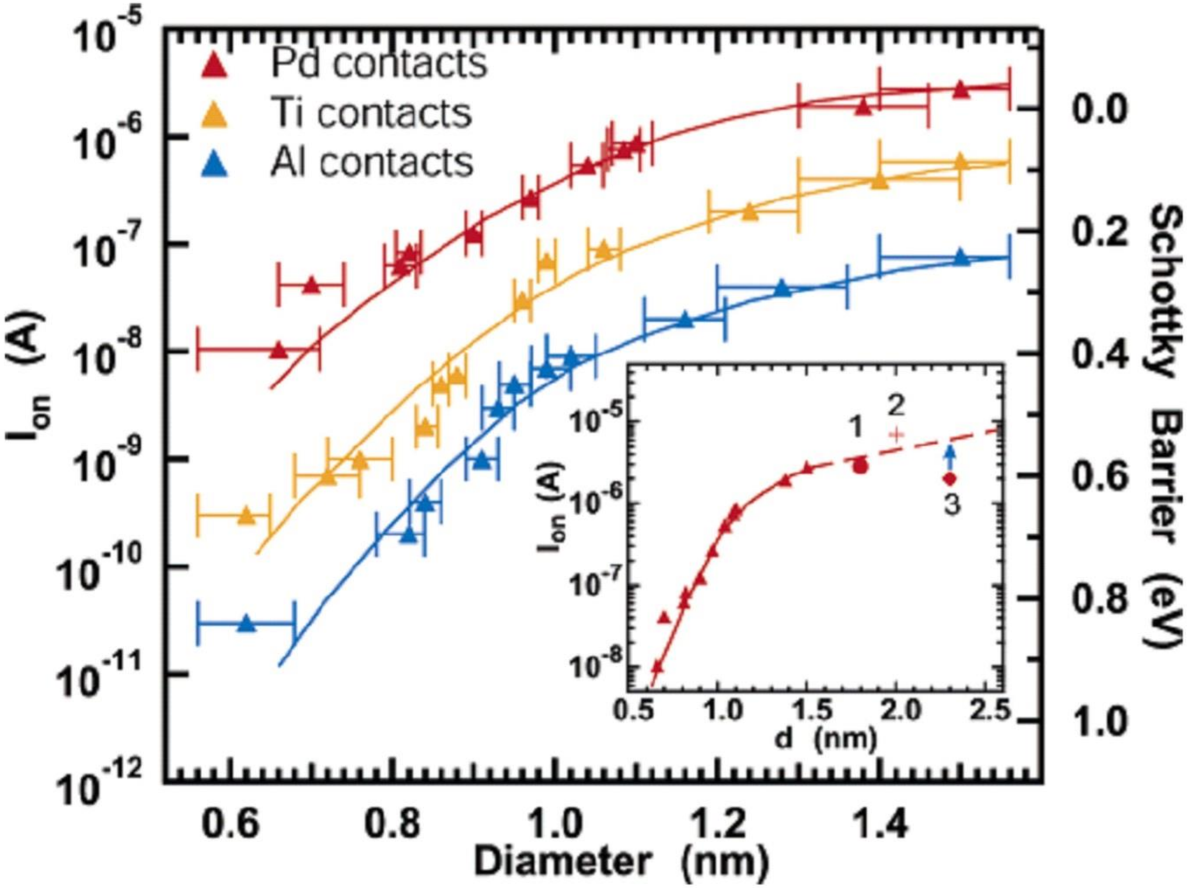


Increasing metal work function



Different contact metals

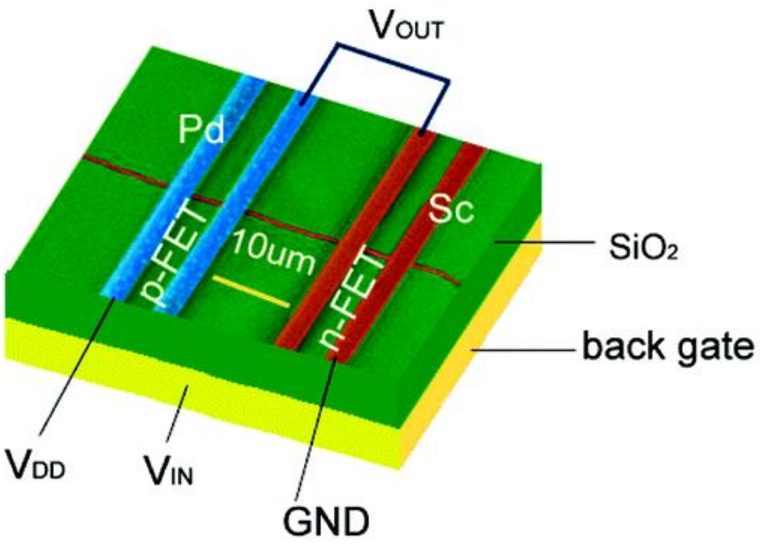
- Increasing I_{on} with larger CNT diameter
- Increasing I_{on} with higher work function
- No or small effect of Fermi level pinning

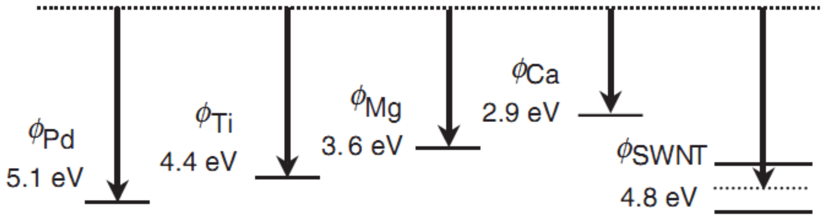


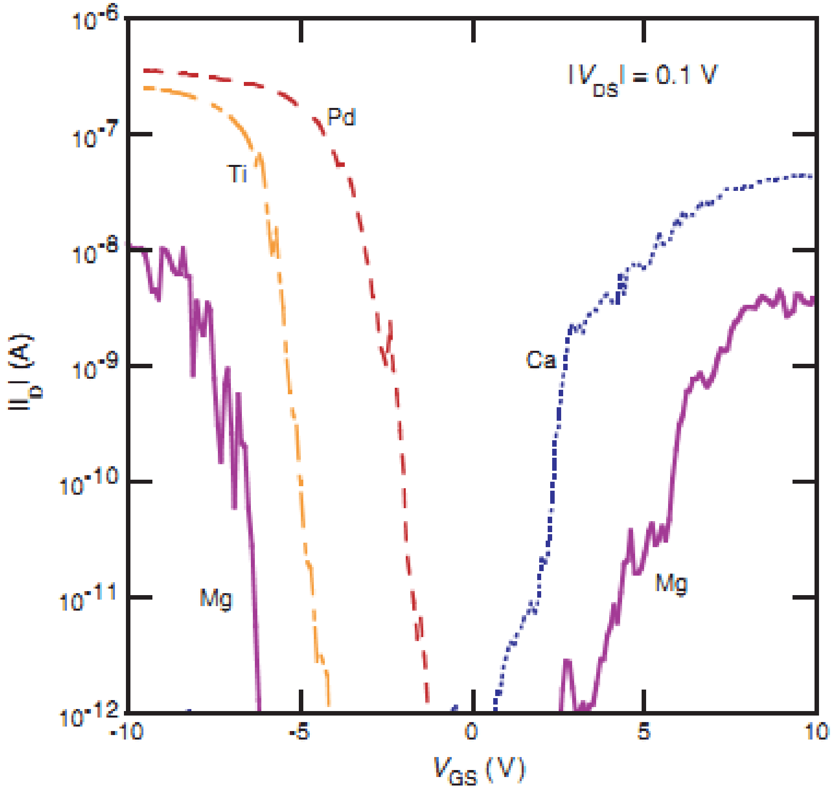
Chen et al. *Nano Lett.* **5,** 1497–1502 (2005)

Metal work function impact

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



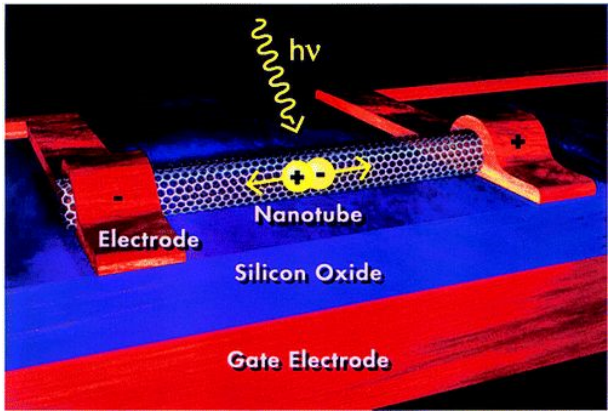


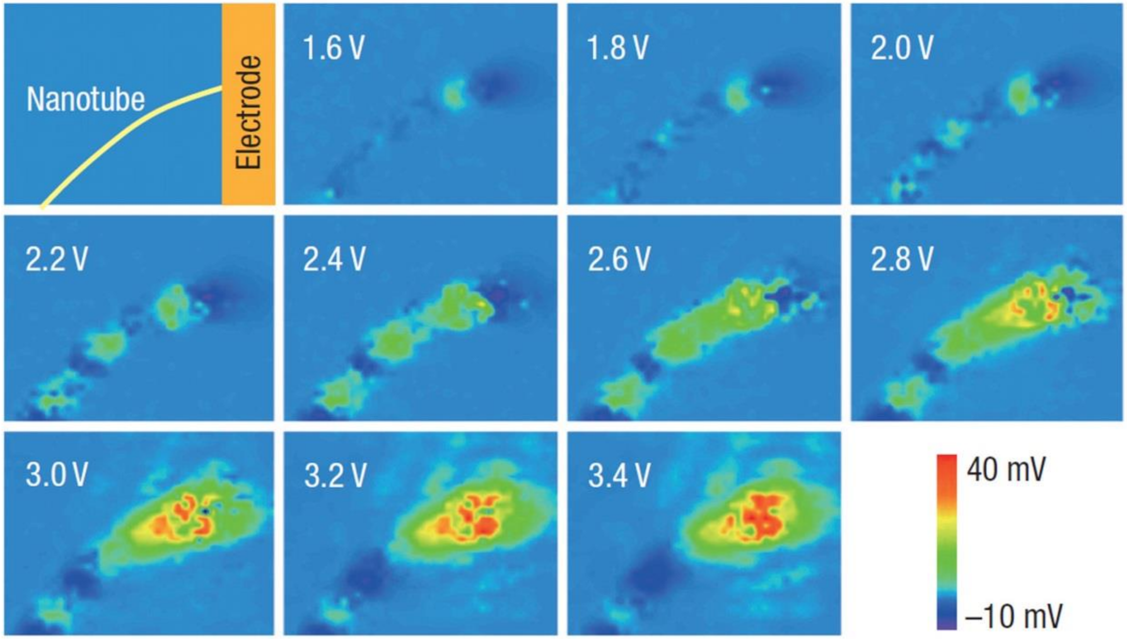


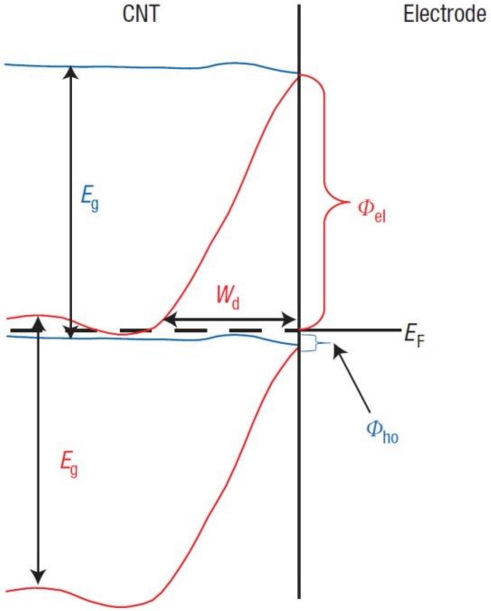
Nosho et al. *Nanotechnology* **17** , 3412 (2006)

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



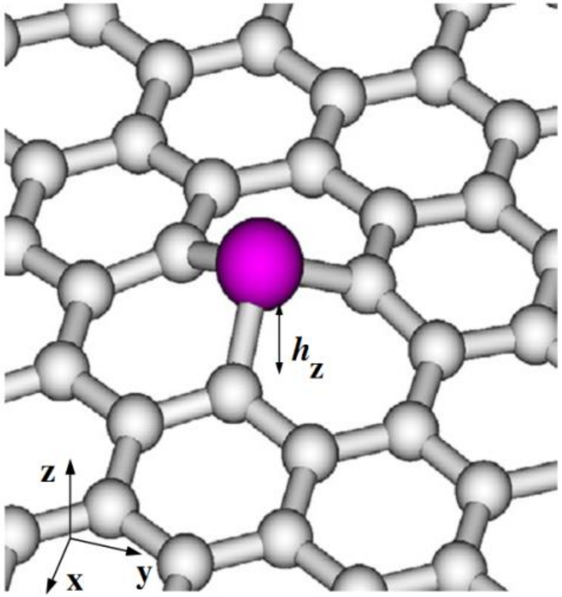


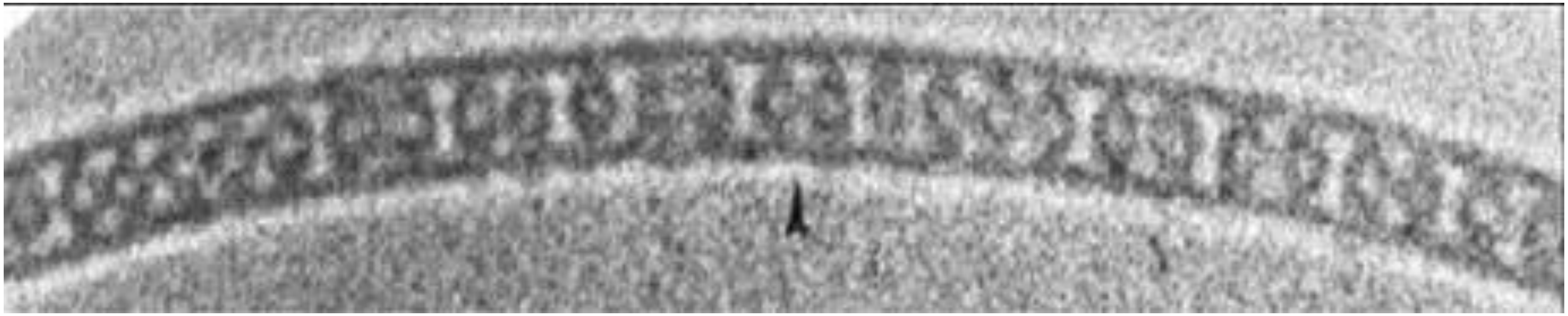


Freitag et al. *Nano Lett.* **7**, 2037–2042 (2007)

Doping

- Important for CMOS and good contacts
- Substitutional doping is difficult
- Use charge transfer doping
- Filling with C_{60} p-dopes
- Filling with Gd@C_{82} n-dopes



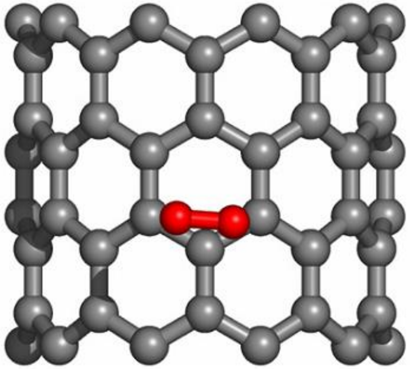


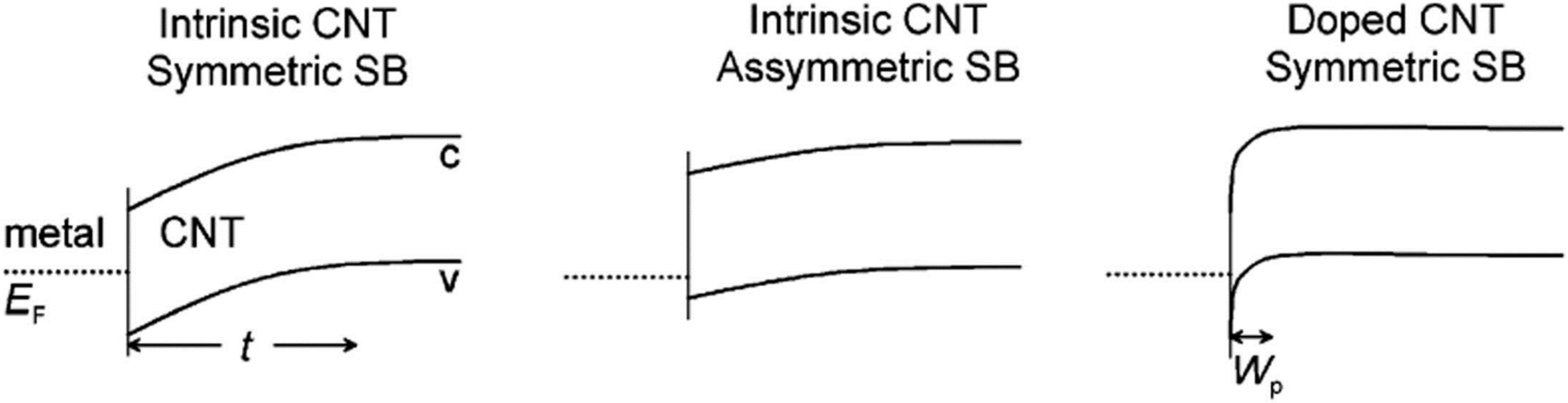
CNTFETs in air

- Physisorbed oxygen p-dopes CNT

OR

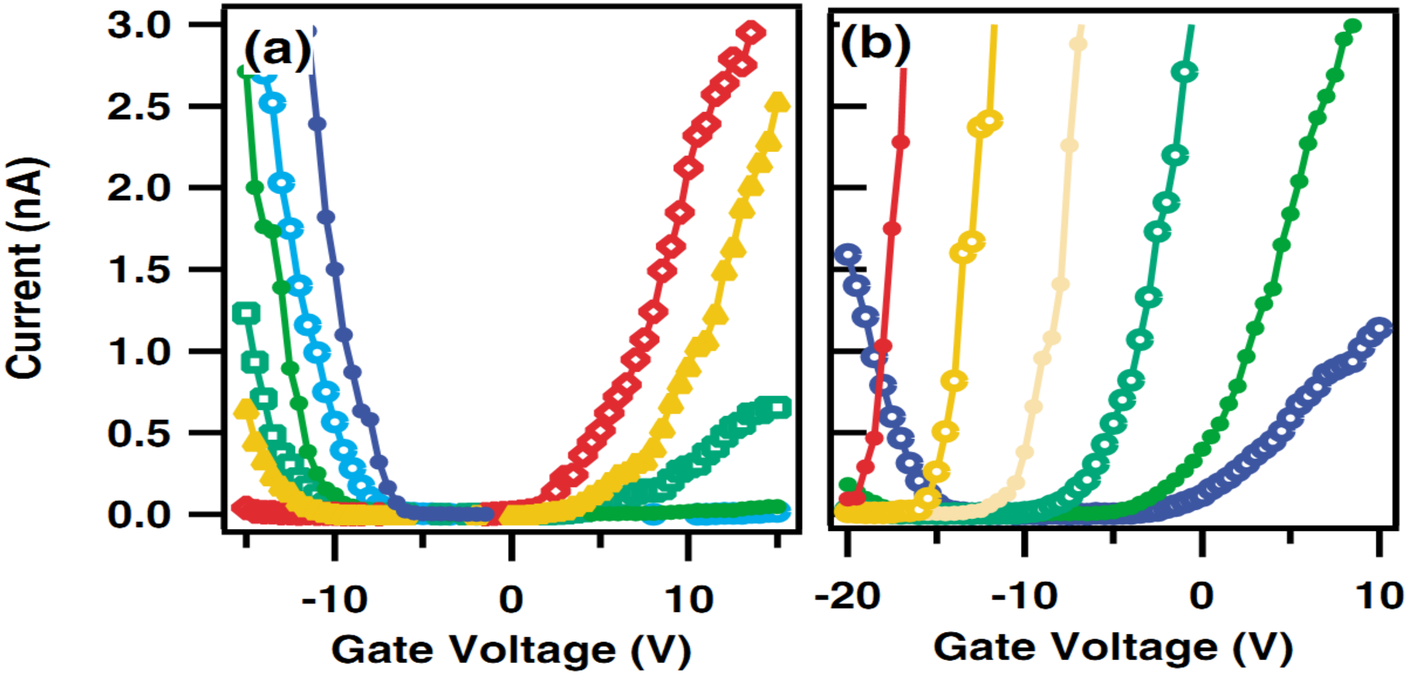
- Increases metal work function of contact





Potassium doping

- K physisorbed on CNT n-dopes by charge transfer
- p-branch is lowered, n-branch is increased, V_{th} shifted
- Not stable in air



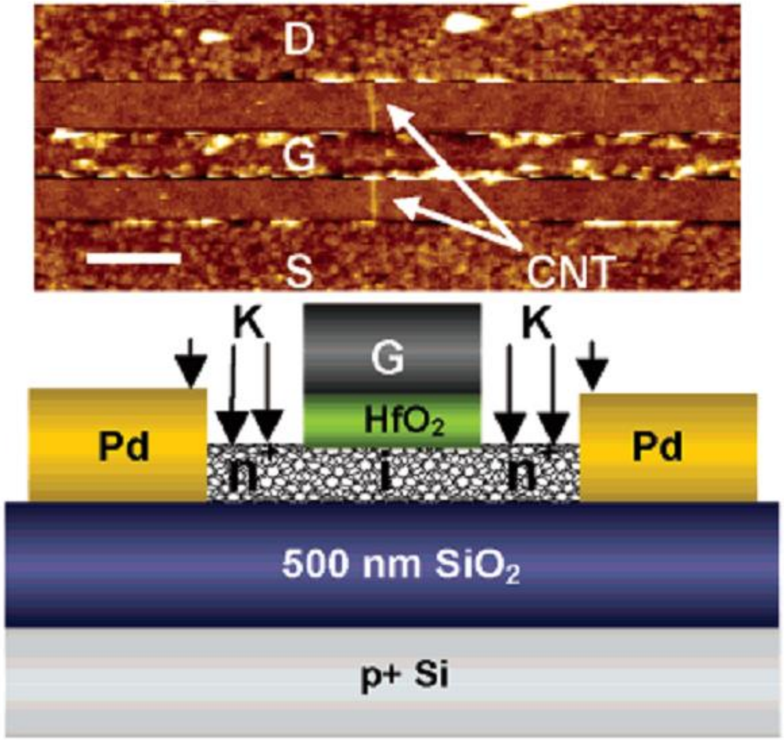
Oxygen exposure (red-> blue)

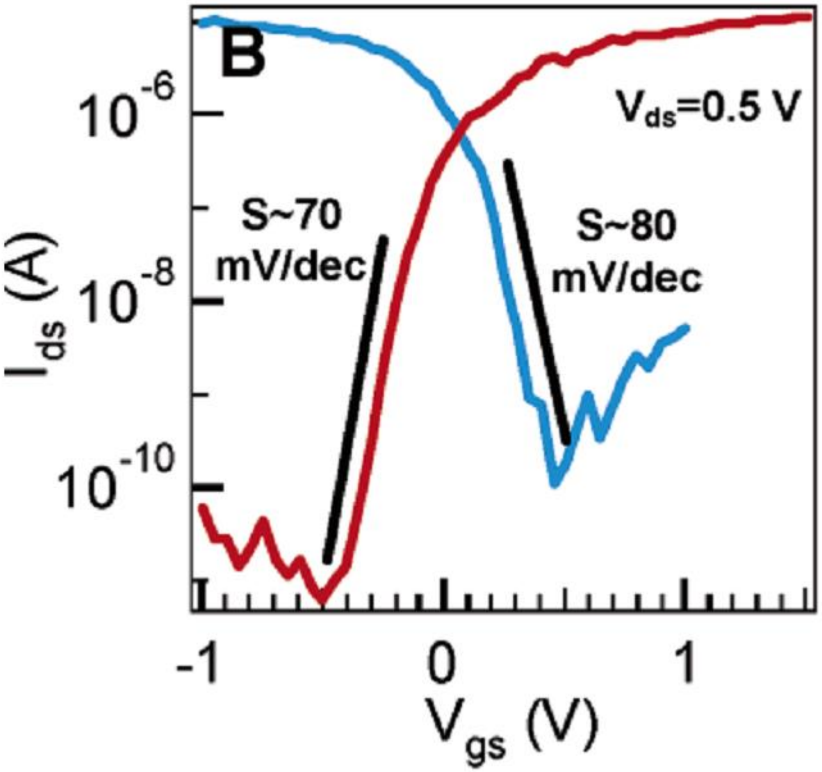
K doping (blue->red)

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

Doped contacts

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

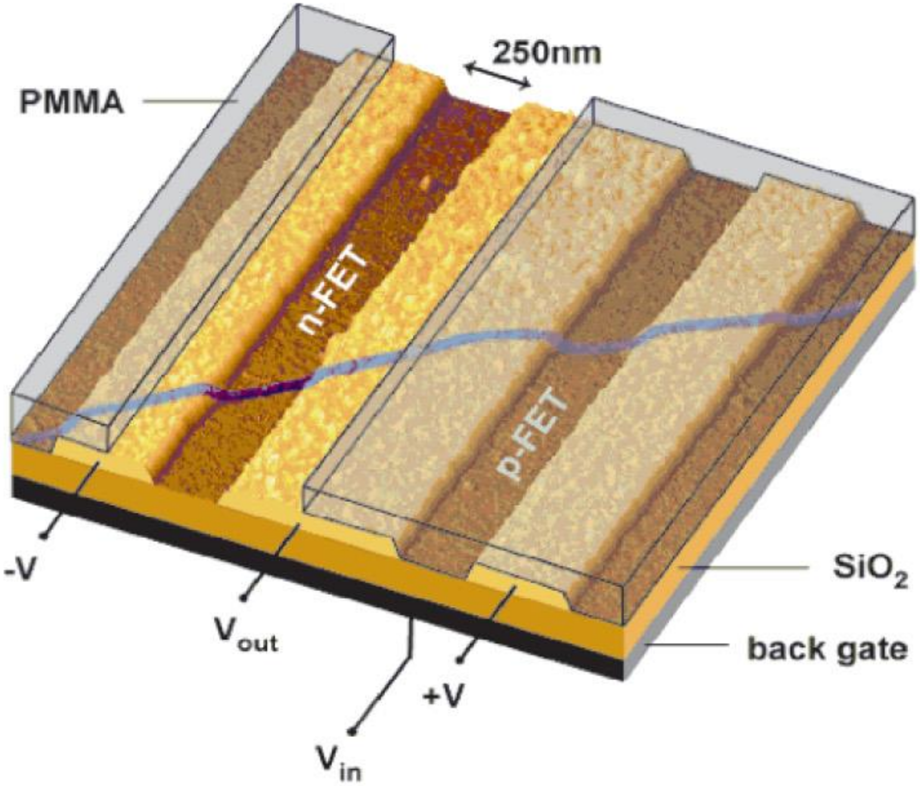


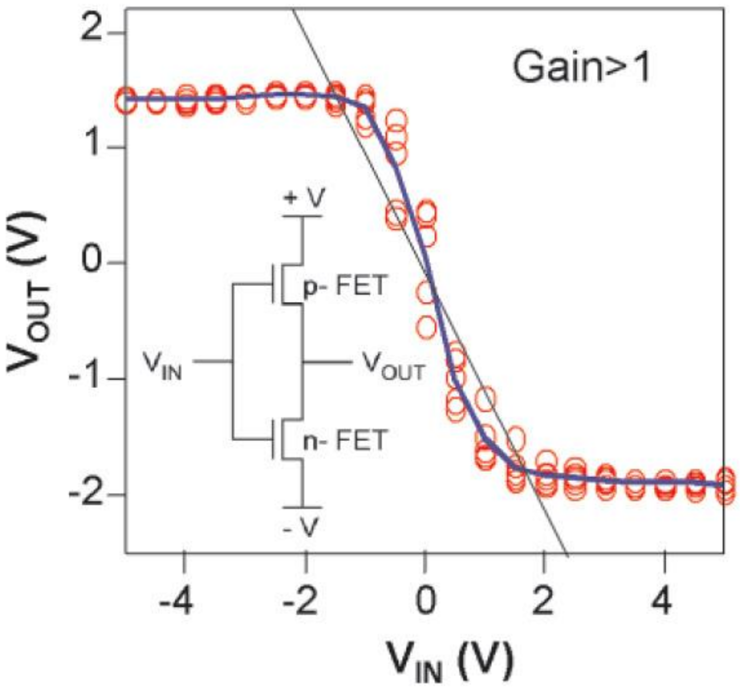


Javey et al. *Nano Lett.*, **5**, 345-348 (2005)

Logic gates

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

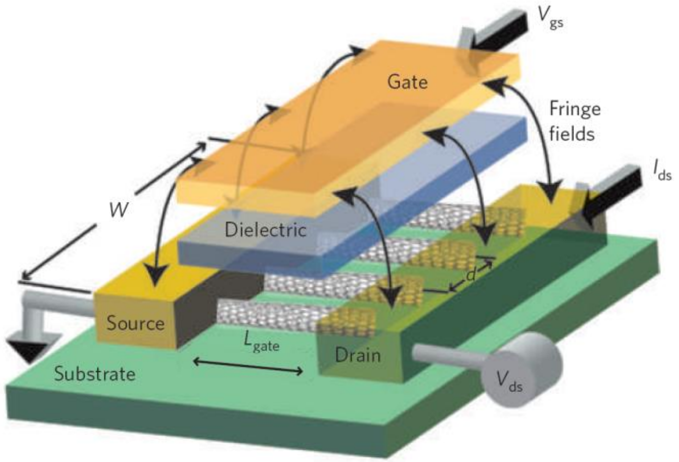


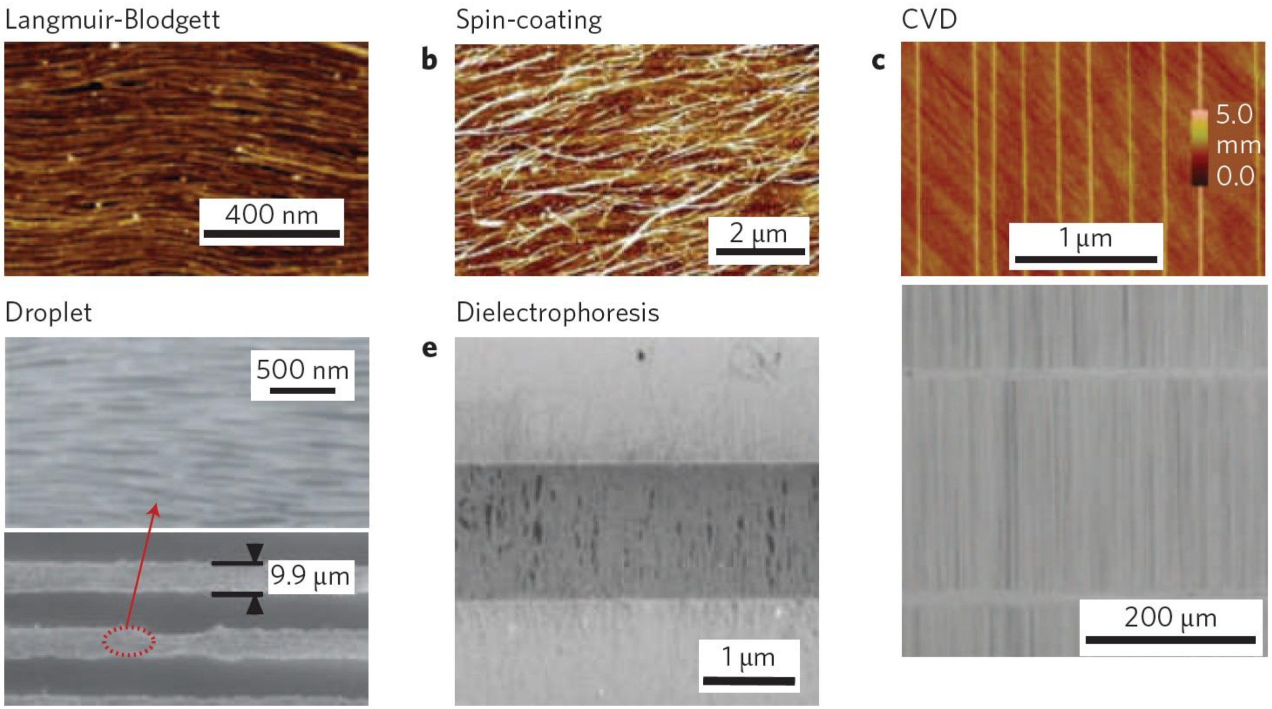


Derycke et al. *Nano Lett.* **1** , 453–456 (2001)

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




Langmuir-Blodgett

Spin-coating

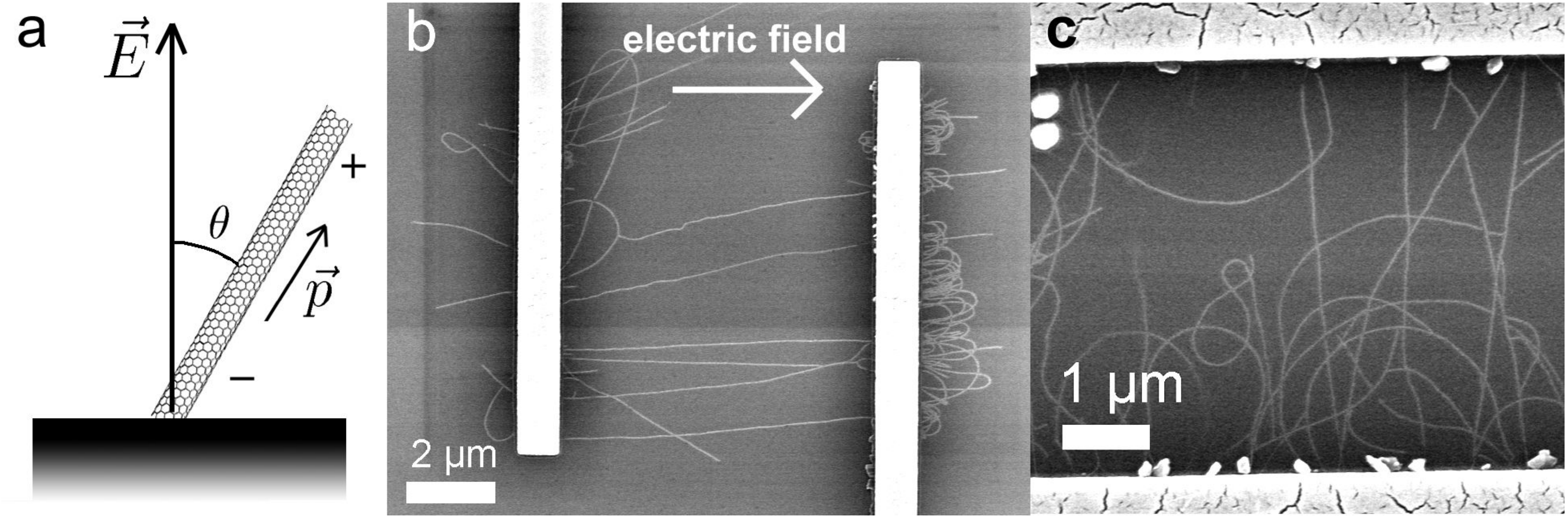
CVD

Droplet

Dielectrophoresis

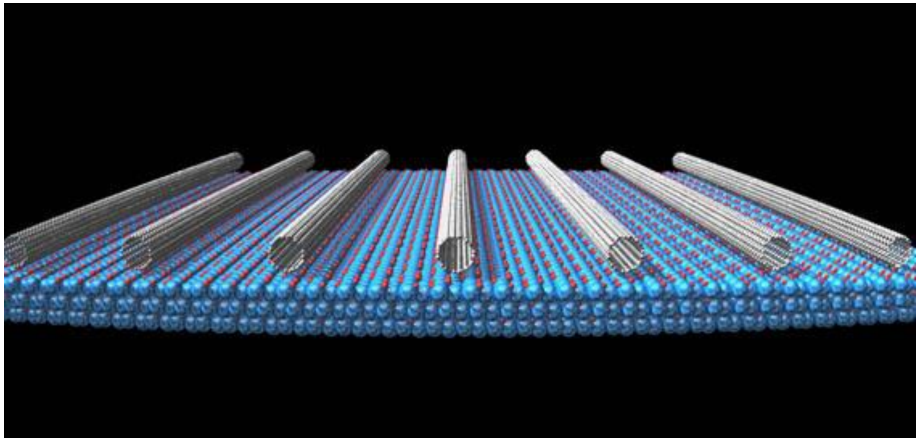
Electric field alignment

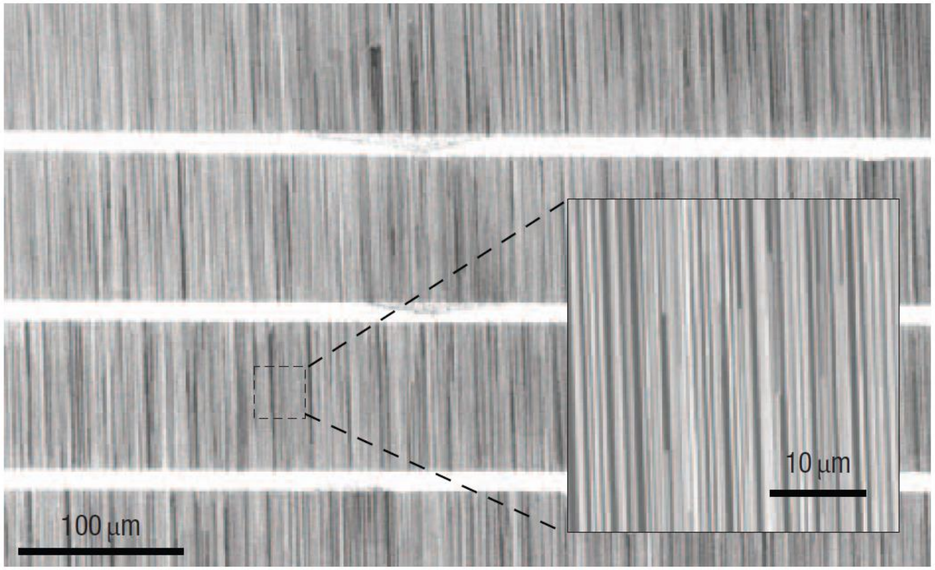
- Apply voltage to electrodes during CVD
- Dipole in CNTs align them with field lines
- Difficult to implement for large scale circuits



”epitaxial” alignment

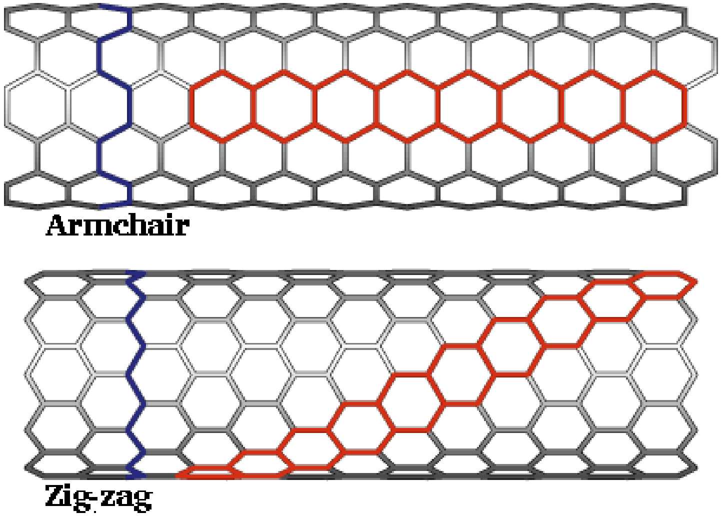
- CNTs align in certain crystal orientations of sapphire or quartz substrates
- CNTs align at atomic steps
- Strong attractive interaction between CNTs and Al atoms
- 99.9% are aligned within 0.01°
- 10 CNTs / µm





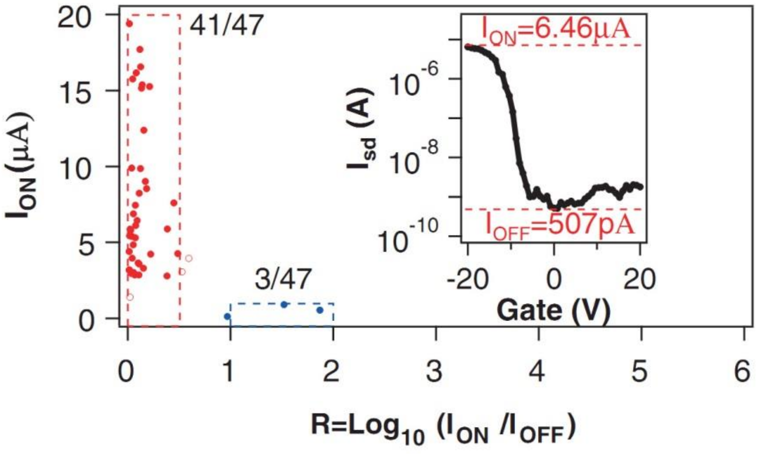
Chirality control

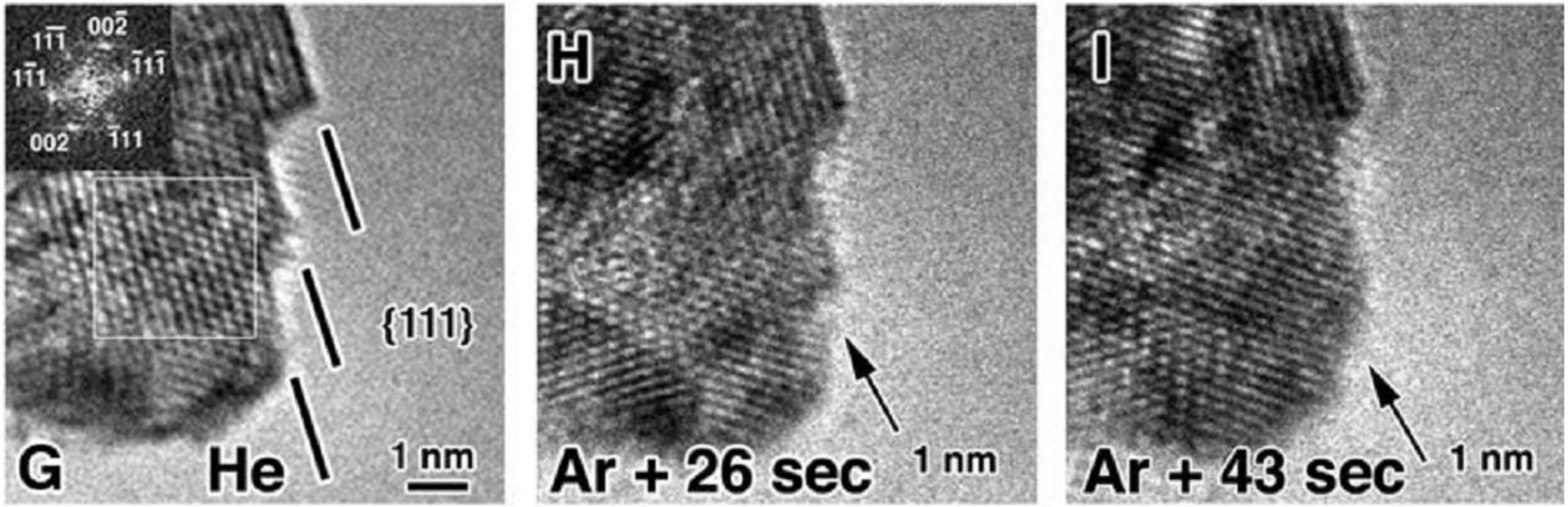
- Metallic CNTs in FETs -> leakage currents - > poor on/off ratio
- Need chirality control or at least control of CNT type
- Need to either:
  - Selectively grow only metallic or semiconducting
  - Separate the two types
  - Selectively destroy one type



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 so good or well understood

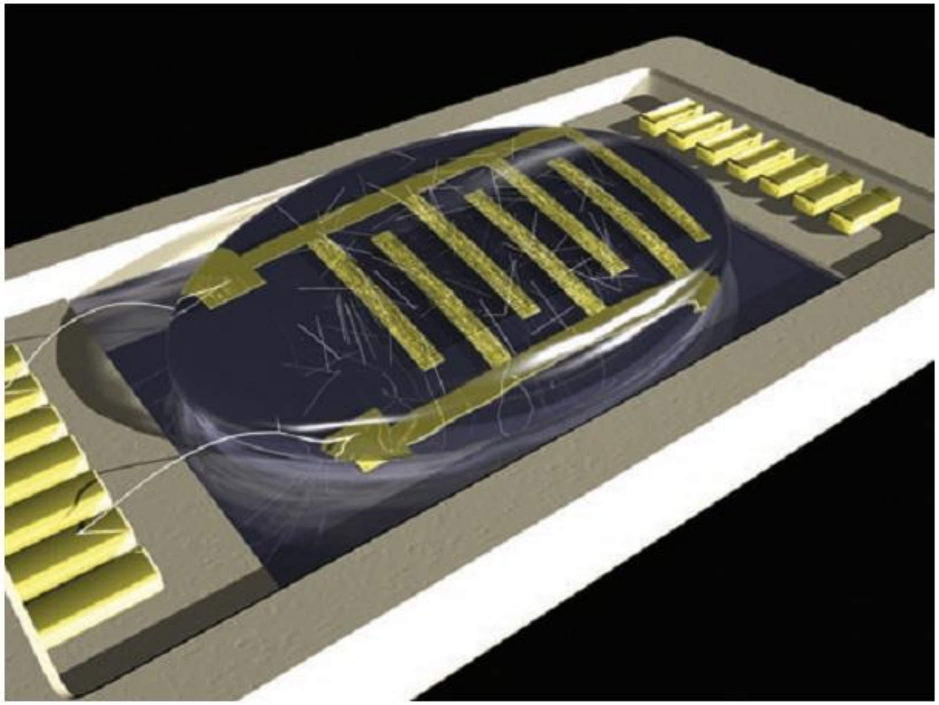


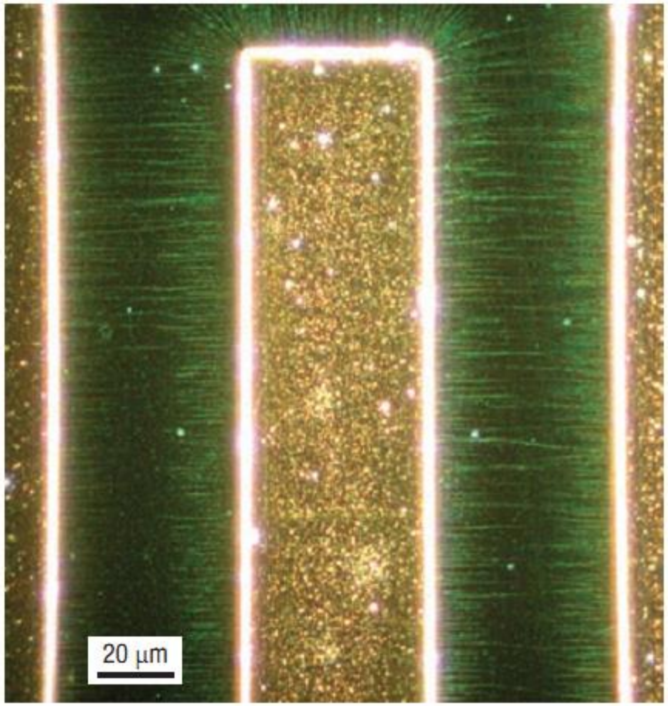


Harutyunyan et al. *Science, **326**, 116-120 (2009)*

Separation by dielectrophoresis

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

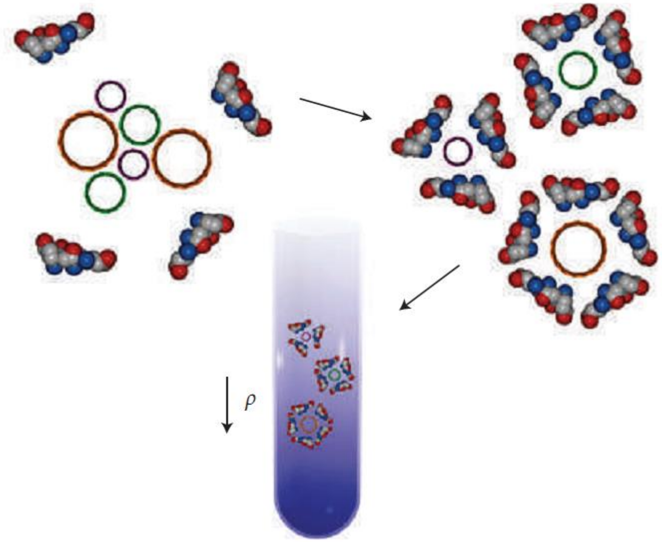


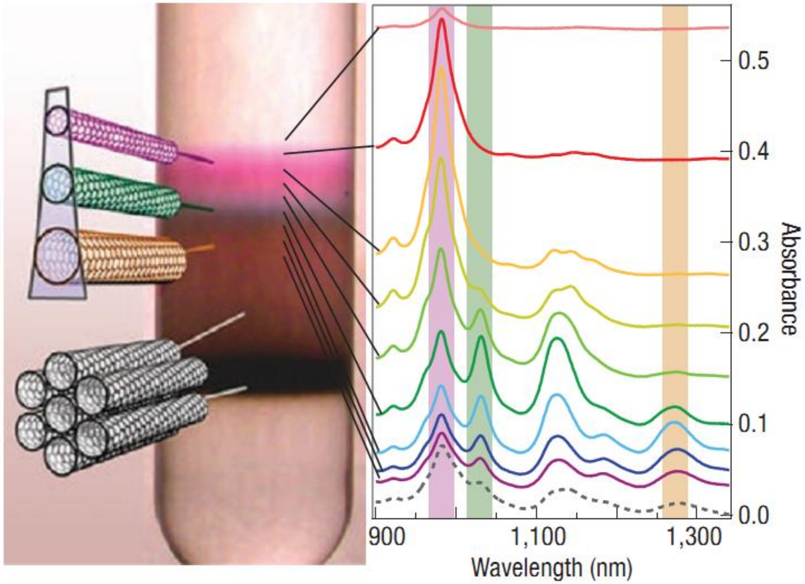


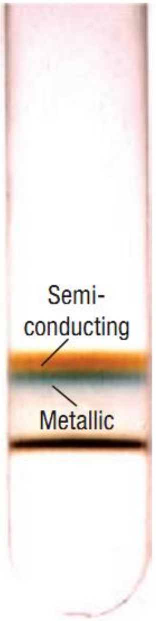
Krupke et al. *Science*, **301**, 344–347 (2003)

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



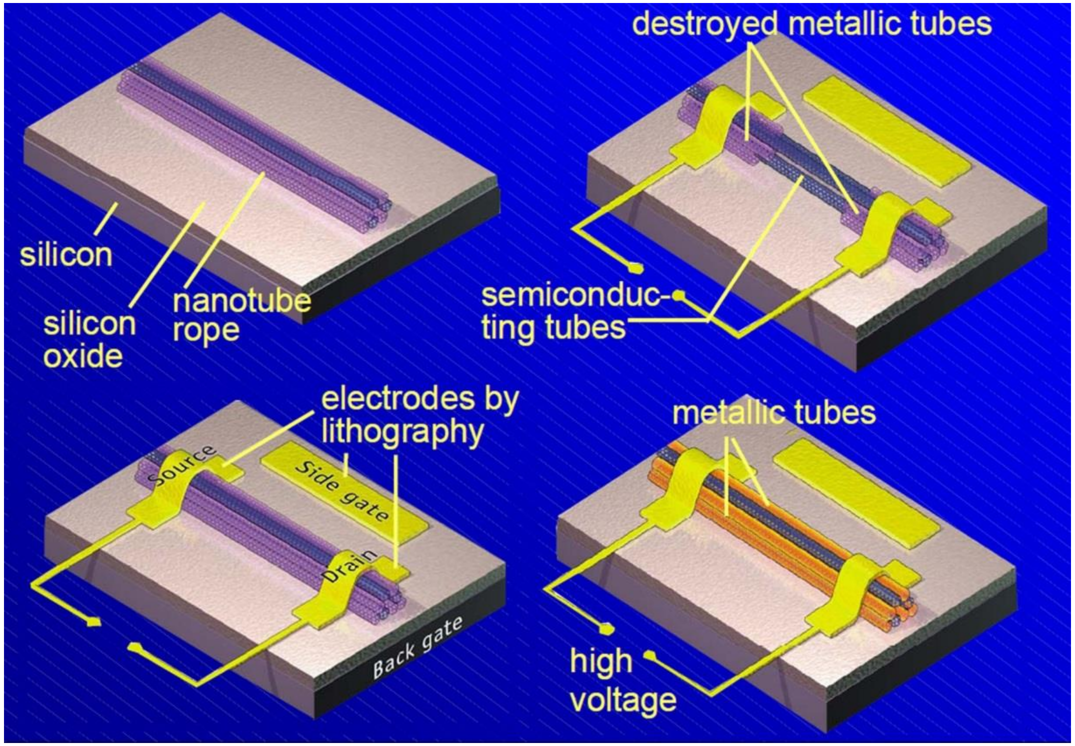


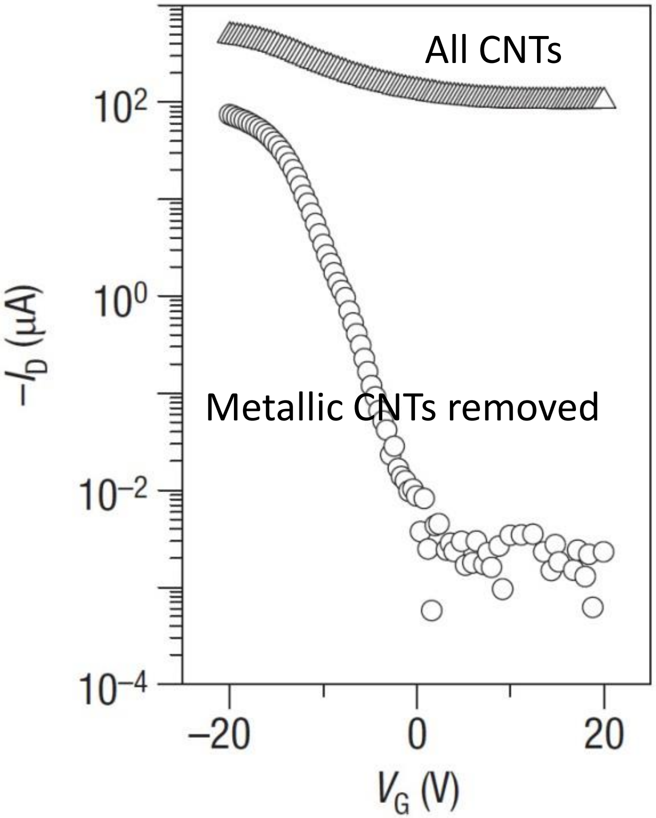


Arnold et al. *Nature Nanotech.* **1**, 60–65 (2006)

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

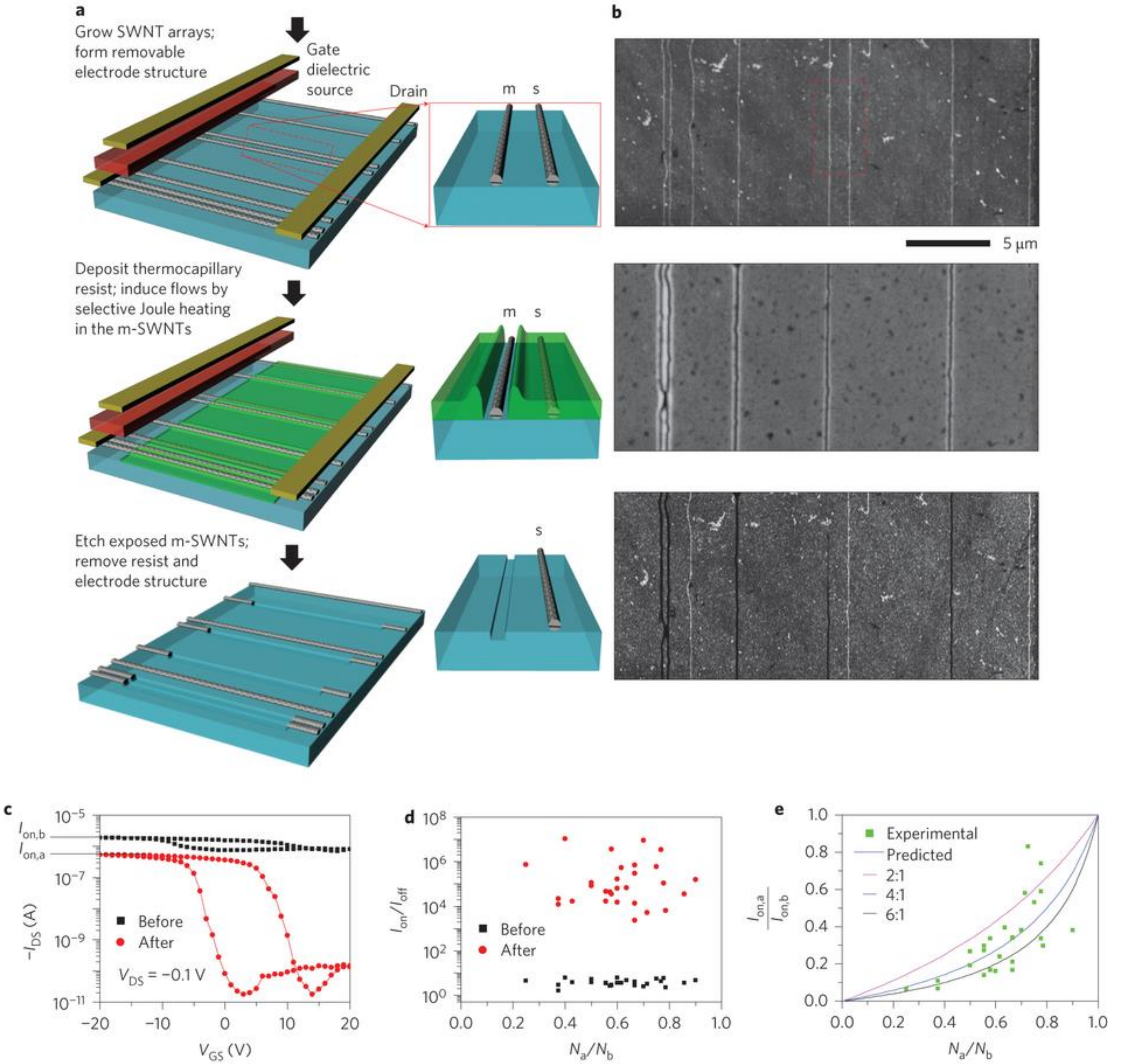




All CNTs

Metallic CNTs removed

Selective destruction

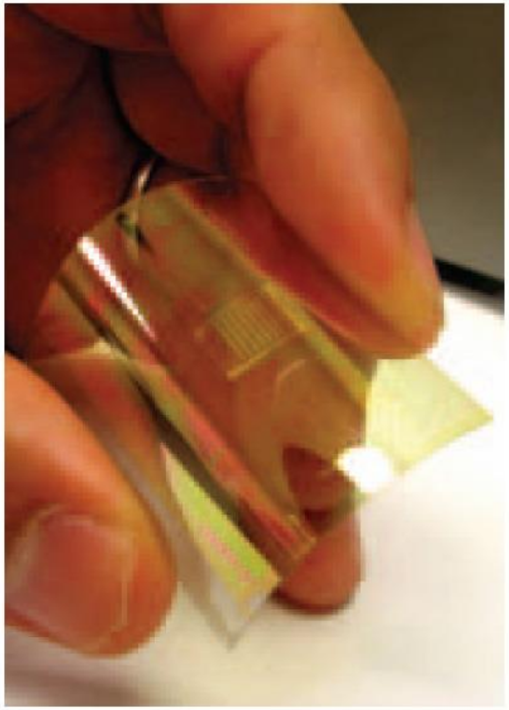


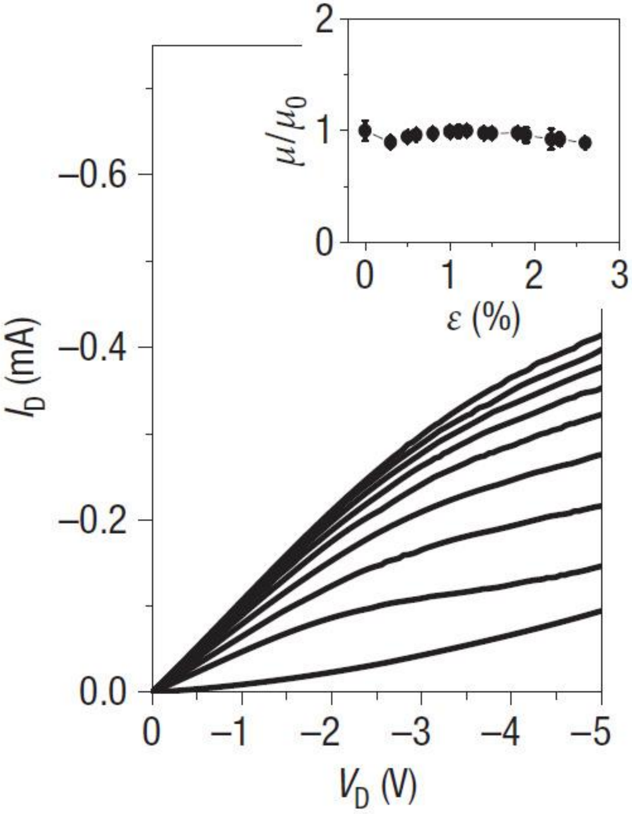
Outline

- 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

Flexible electronics

- Transfer aligned CNTs to plastic substrate
- Highest p-channel mobility (480 cm^2/Vs)
- No degradation when bent

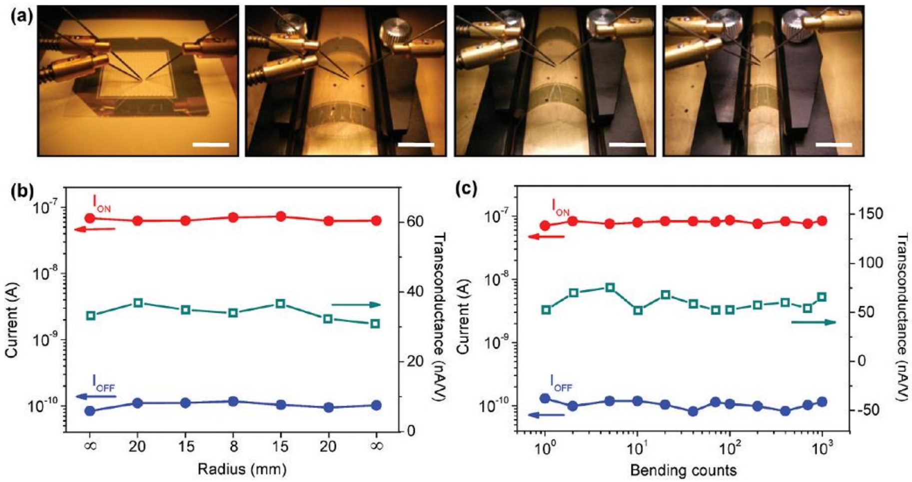


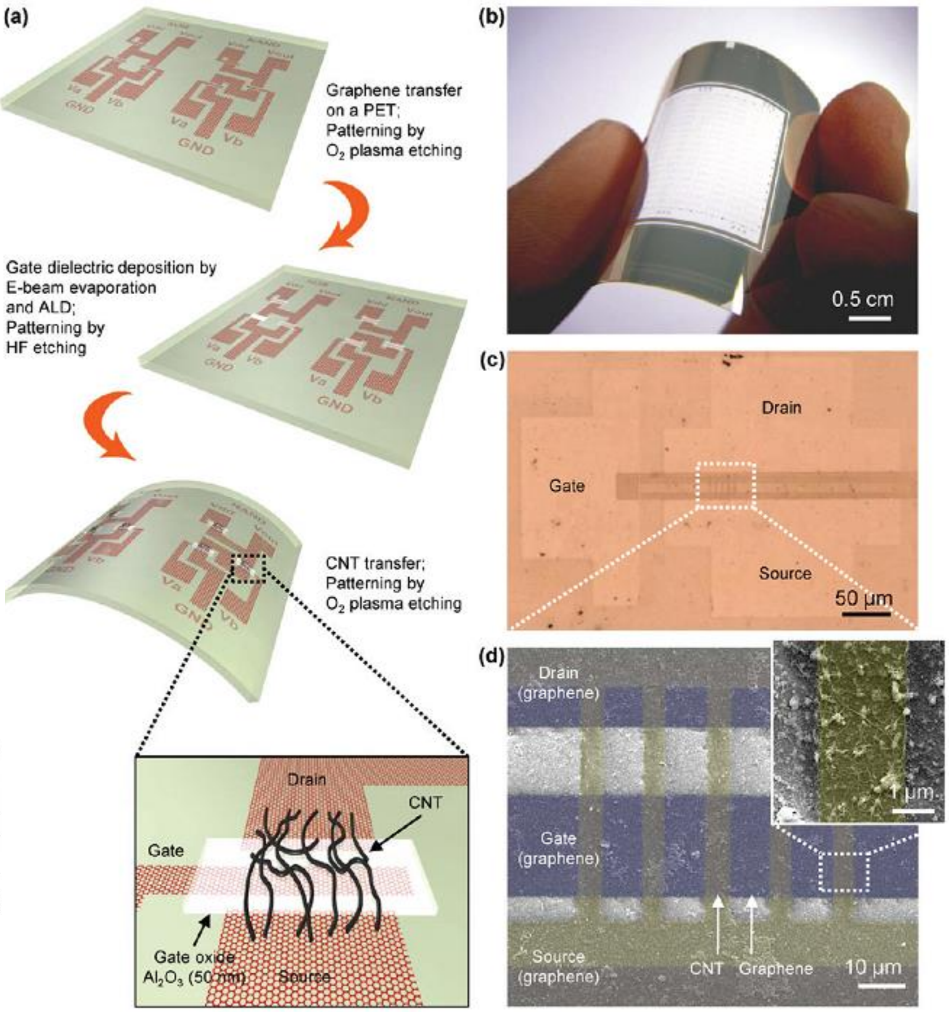


Kang et al. *Nature Nanotechnol*. **2**, 230 - 236 (2007)

Flexible electronics 2

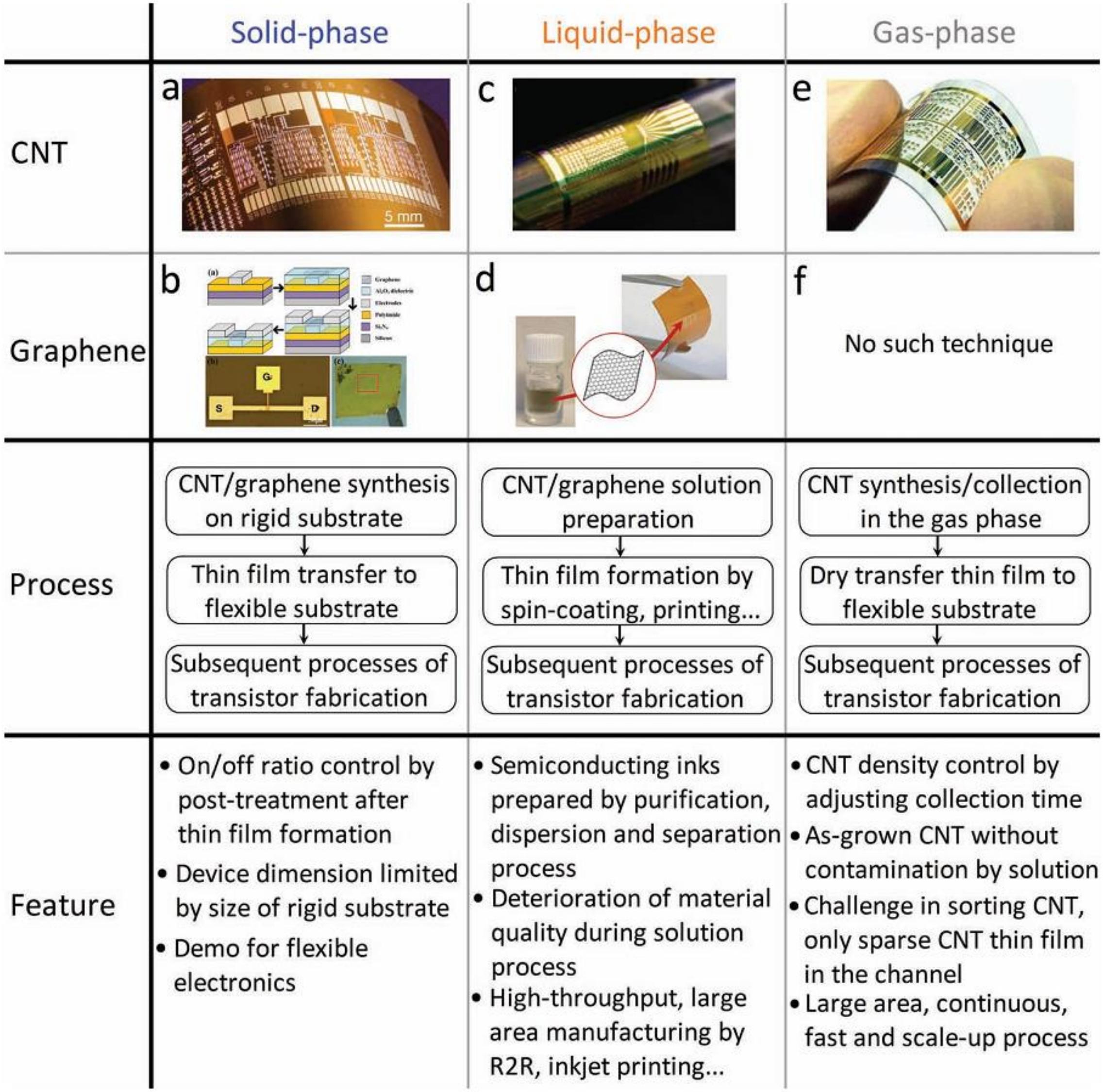
- Graphene for electrodes
- CNTs for channel





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

Transfer techniques

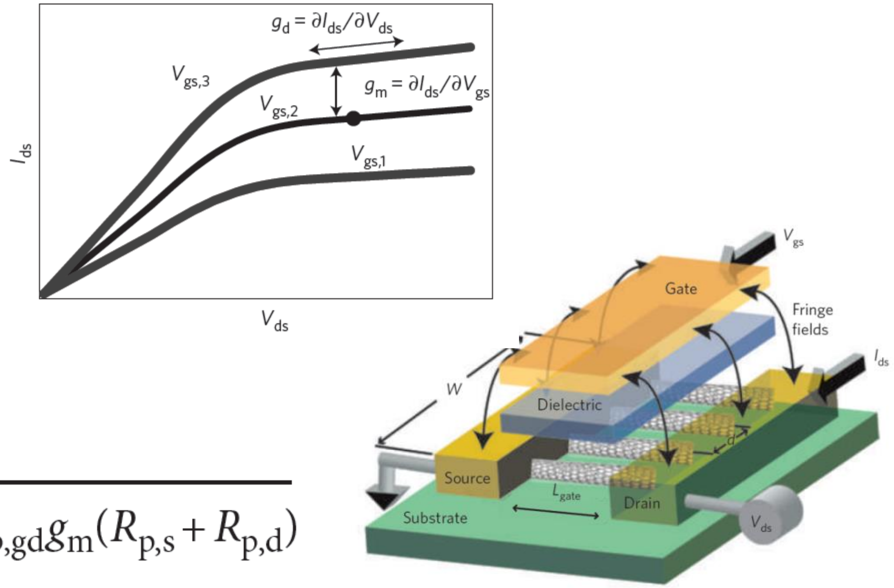


	Solid-phase	Liquid-phase	Gas-phase
CNT	a	c	e
Graphene	b	d	f No such technique
Process	CNT/graphene synthesis on rigid substrate ↓ Thin film transfer to flexible substrate ↓ Subsequent processes of transistor fabrication	CNT/graphene solution preparation ↓ Thin film formation by spin-coating, printing... ↓ Subsequent processes of transistor fabrication	CNT synthesis/collection in the gas phase ↓ Dry transfer thin film to flexible substrate ↓ Subsequent processes of transistor fabrication
Feature	• On/off ratio control by post-treatment after thin film formation • Device dimension limited by size of rigid substrate • Demo for flexible electronics	• Semiconducting inks prepared by purification, dispersion and separation process • Deterioration of material quality during solution process • High-throughput, large area manufacturing by R2R, inkjet printing...	• CNT density control by adjusting collection time • As-grown CNT without contamination by solution • Challenge in sorting CNT, only sparse CNT thin film in the channel • Large area, continuous, fast and scale-up process

Sun et al. *Small,* **9,** 1188–1205 (2013)

Requirements for RF applications

- on/off ratio not so important
- Need high g_m and low g_d -> only semiconducting CNTs
- Minimize paracitic capacitance / CNT -> dense array of CNTs



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

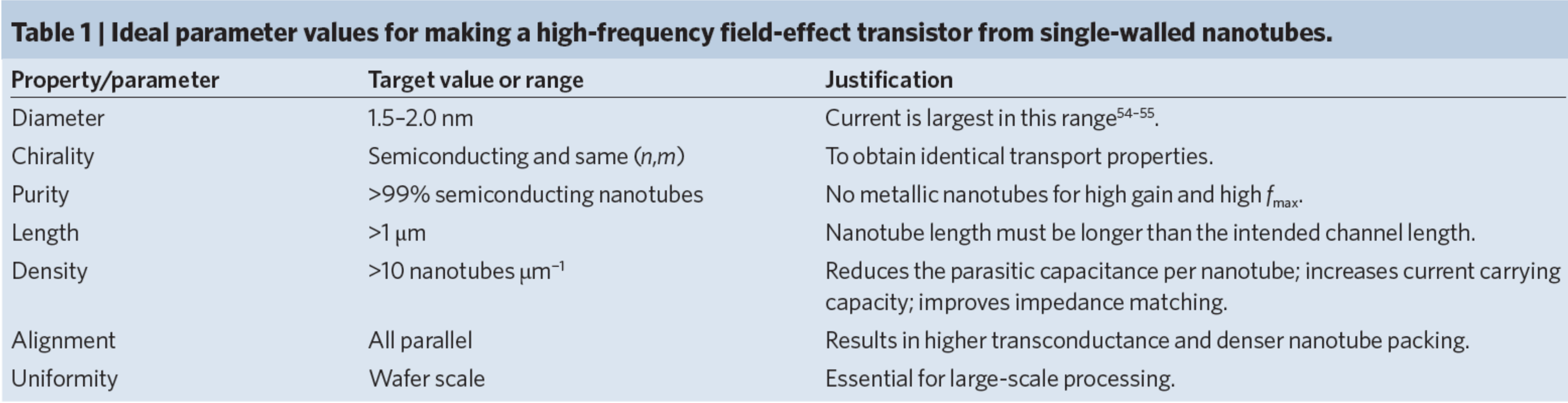


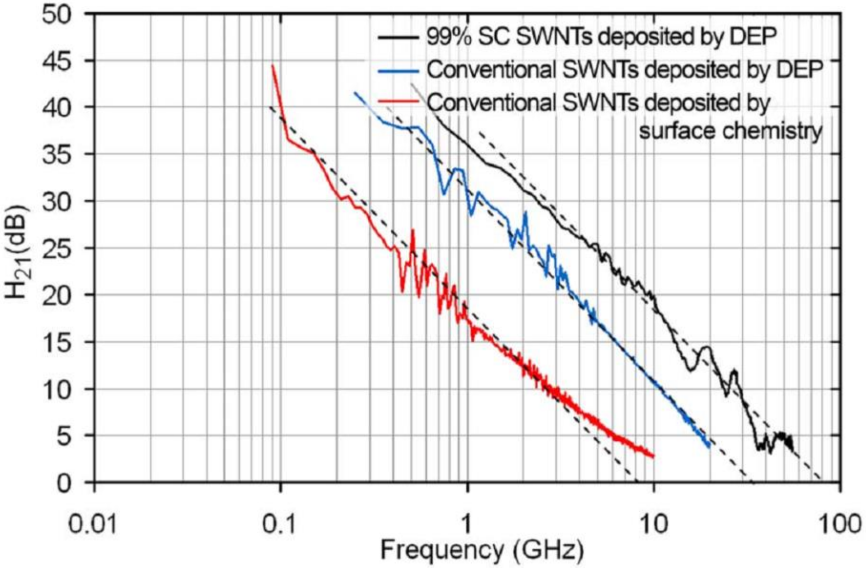
Table 1 | Ideal parameter values for making a high-frequency field-effect transistor from single-walled nanotubes.

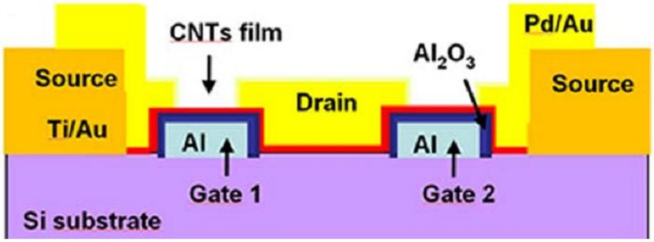
Property/parameter	Target value or range	Justification
Diameter	1.5–2.0 nm	Current is largest in this range[54–55].
Chirality	Semiconducting and same (*n*,*m*)	To obtain identical transport properties.
Purity	>99% semiconducting nanotubes	No metallic nanotubes for high gain and high f_{max}.
Length	>1 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.

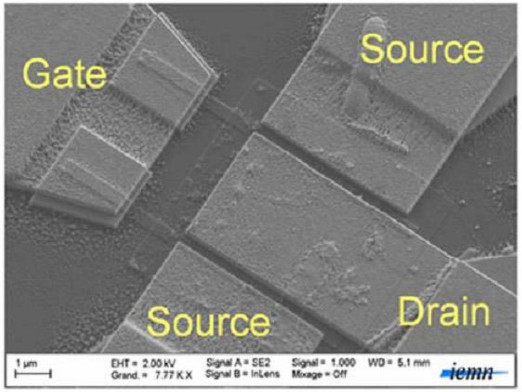
Rutherglen, *Nature nanotechnol*. **4**, 811, 2009

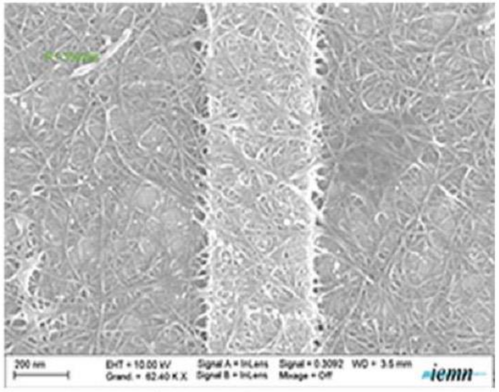
RF performance

- Diffcult to measure on single CNT due to impedance mismatch
- Use dense net of separated semiconducting CNTs
- Extract current gain from S-parameters
- f_T=80 GHz
- Much better than ”original” CNT material





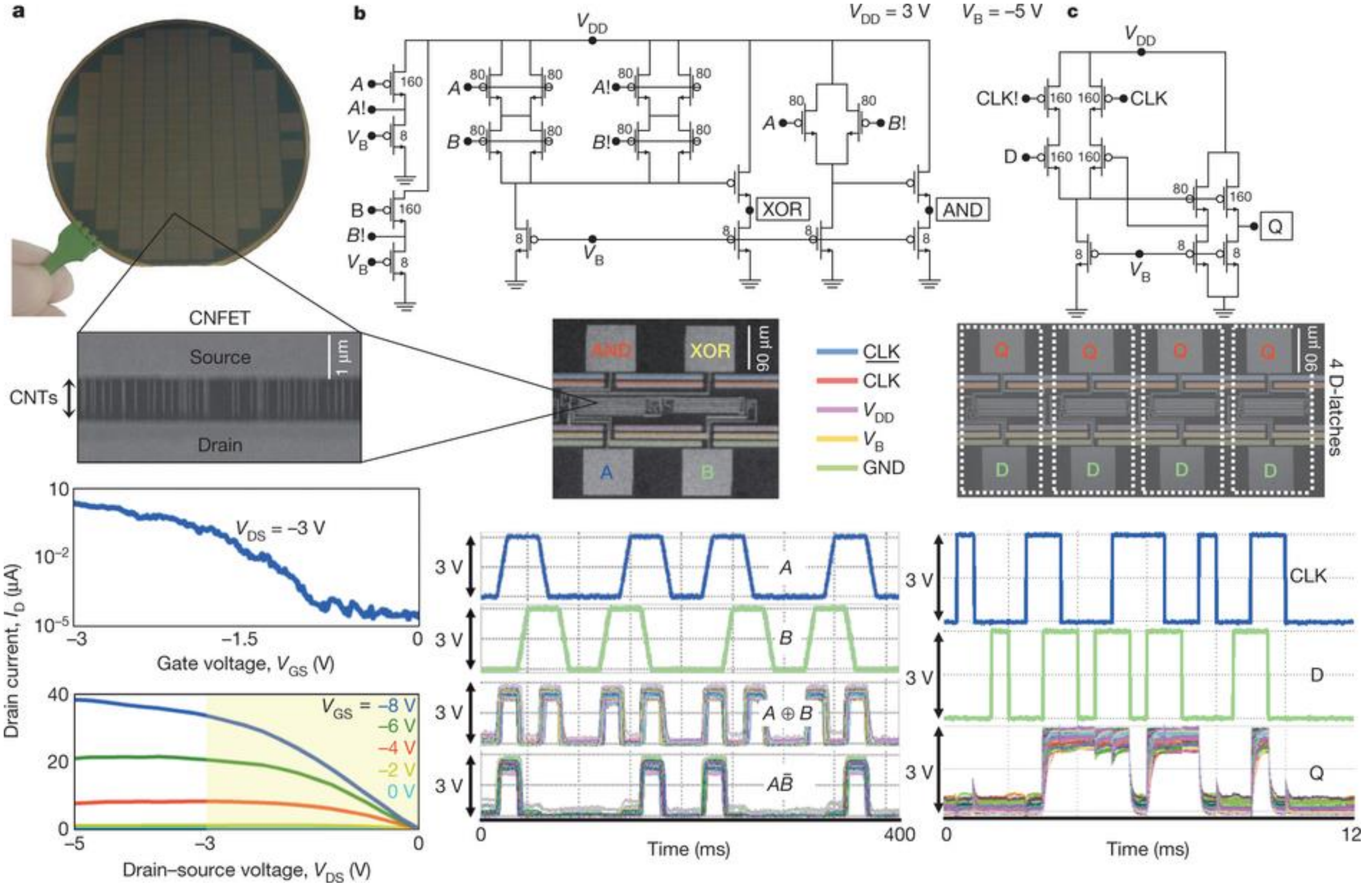




Nougaret et al. *APL*, **94**, 243505 (2009)

CNT computer

- 178 p-type CNTFETs. Aliged growth -> transfer -> burn-off
- Not CMOS
- Multitasking operating system for 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 -> 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