Nanomaterials

CNTs and Applications

2.674

Jeehwan Kim

Nanomaterials

- Growing, Touching and Observing
- For lab #7
  - CNT growth
  - Surface drop test

How small is small?

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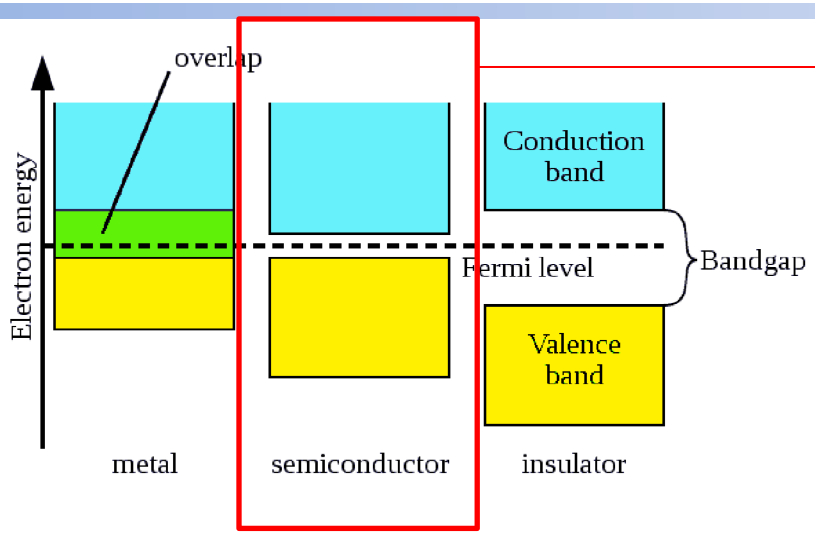
- Atomic radius of silicon = 0.1 nm
- Size of one unit cell of silicon = 0.542 nm

- Atomic radius of carbon = 0.07 nm
- Size of one unit cell of diamond = 0.357 nm

- Thickness of hair/paper = 100 um → 10^5 nm
  → around million atoms

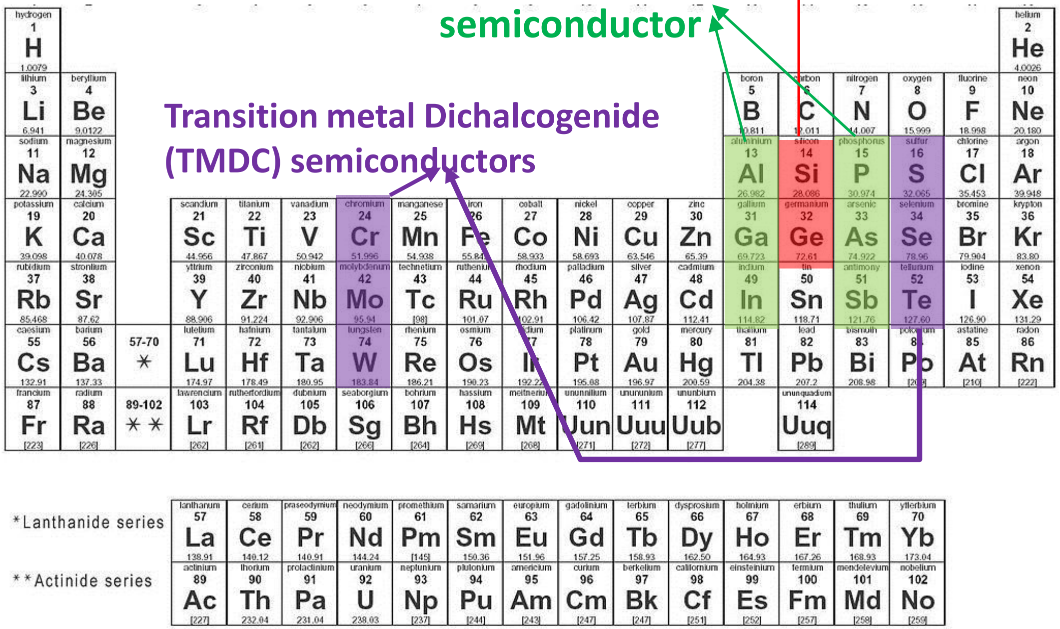
Size of transistors in your computer → 14 nm
→In 14x14 nm^2 channel: 4900 atoms

Semiconductor Materials



Semiconductor
: Materials that can be switched between conductors (1) and insulators (0)

→ Digital electrical signal is composed of 0 (off) and 1 (on) to form logics



IV semiconductor

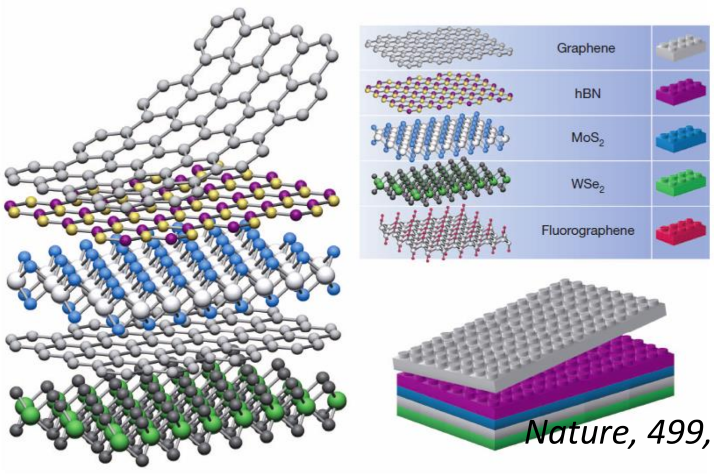
III-V compound semiconductor

Transition metal Dichalcogenide (TMDC) semiconductors

1 H																		2 He
3 Li	4 Be													5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg													13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102 **	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq				

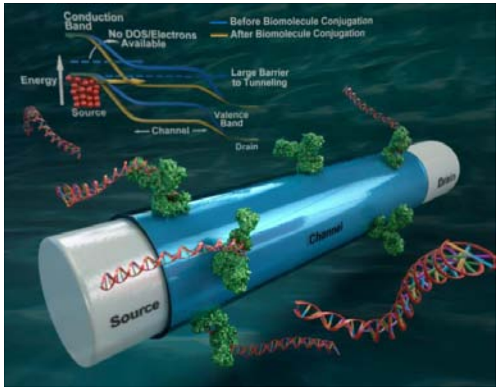
*Lanthanide series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinide series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

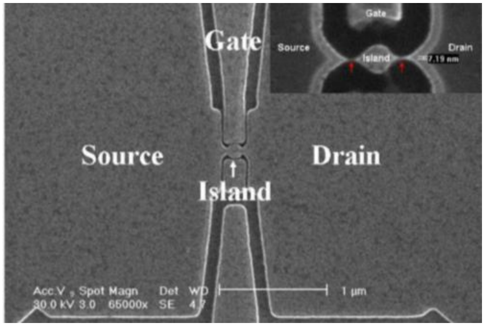
Emerging nanomaterials (Low-dimensional materials)



Nature, 499, 419 (2013)

- 2D: Single-atom thickness films
  - Flexible electronics
  - Sensors
- 1D: Nanowires
  - Quantum electronics
  - Biosensors
  - Solar cell, photodetector
- 0D: Quantum dots
  - Single electron transistor





Intech "Lithography", Michael Wang
ISBN 978-953-307-064-3, p264

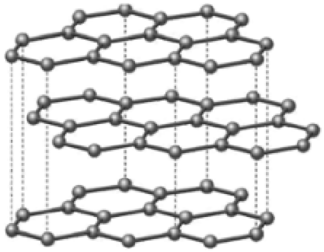
Peter Allen, UCSB
Appl. Phys. Lett. 100, 143108 (2012);

Why small??

Quantum confinement, high surface area, Flexibility

Carbon-based nanomaterials

Basic building block

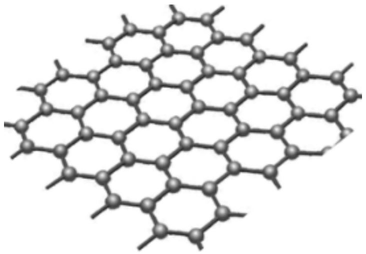


Graphite (3D)

van der Waals stack of graphene

Conductor

Stack



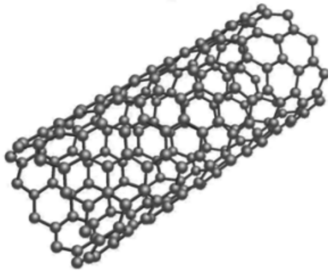
Graphene (2D)

Single-atom-thick carbon layer

sp2 bonding of carbons

Semi-metal

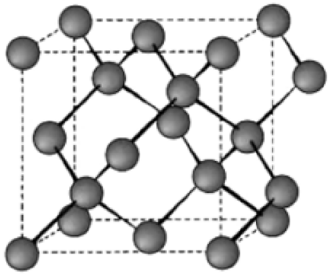
Roll



Carbon nanotube (1D)

Rolled graphene

Semiconductor (2/3) or metal (1/3)

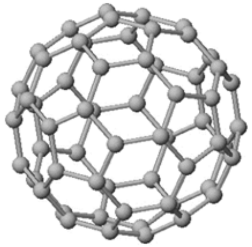


Diamond (3D)

sp3 bonding of carbons

Wide band gap (5.5 eV)

Ball



Fullerene (0D)

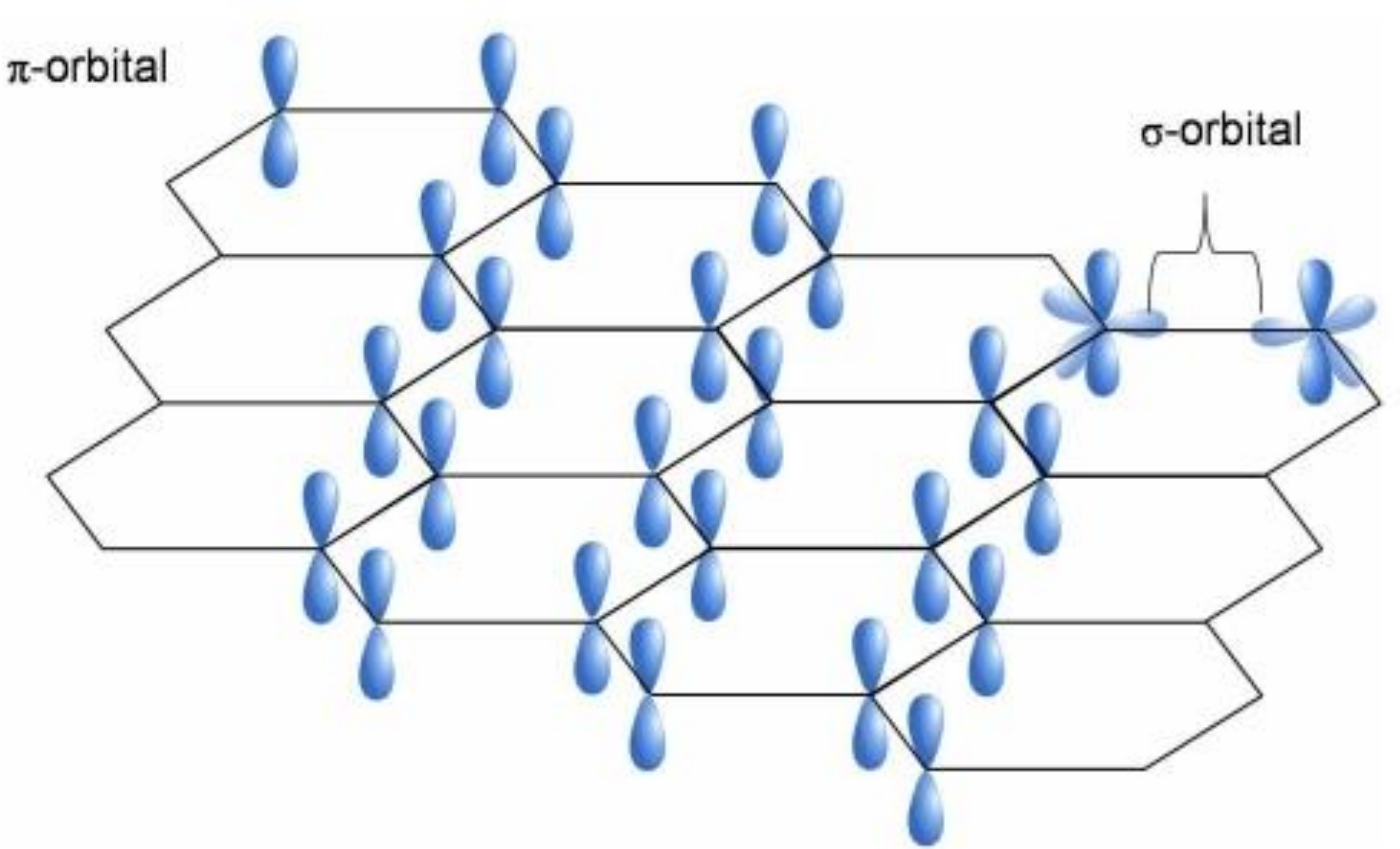
Wide band gap (5.5 eV)

Single element carbon shows different functionality depending on its dimension

History of nanomaterials

- 1959: Richard Feynman’s famed talk.” **There's Plenty of Room at the Bottom** “
- 1981: Binnig and Rohrer created the STM to image individual atoms. (Nobel, Physics 1986)
- 1985: Curl, Kroto, Smalley discovered **fullerene (Nobel, Physics 1996)**
- 1991: Iijima discovered single wall carbon nanotubes.
- 2010 A. Geim and K. Novoselov **(Nobel physics on Graphene)**

Graphene overall orbital structure



Properties of graphene

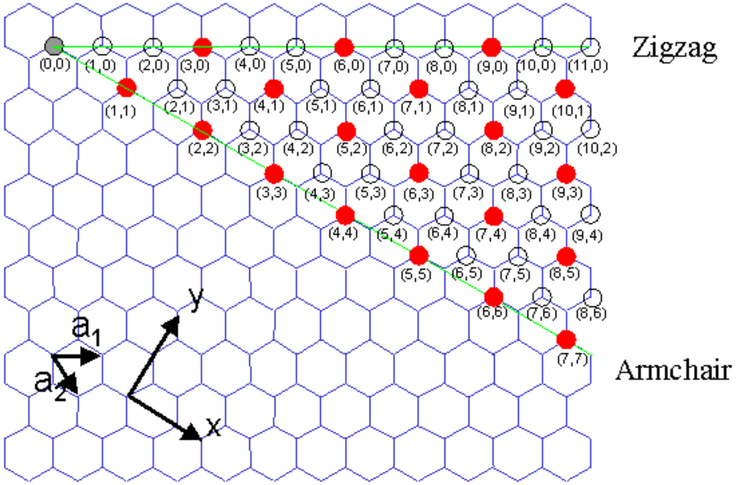
	Graphene	**Si**
Electrical conductivity	~100,000 cm^2/VS	450 cm2/Vs
Thermal conductivity	~5000W/K.m	1.3 W/K.m
Young's modulus	1 TPa	130~170 GPa
Transparency	O	X
Flexibility	O	X

The way of rolling up graphene to form CNT

Diameter determines band gap

Chirality determines semiconductor or metal

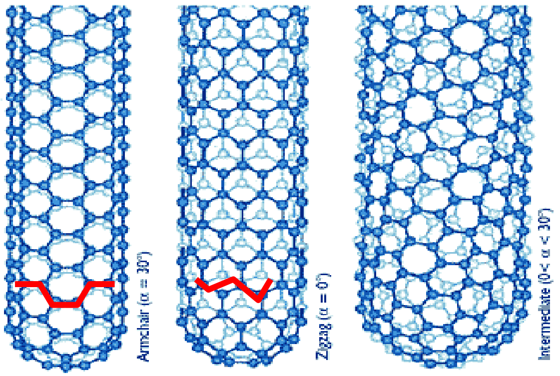
This image has been removed due to copyright restrictions.
Please see http://www.nanotech-now.com/images/SWNT-rollup.jpg.



Armchair

Zigzag

Chiral

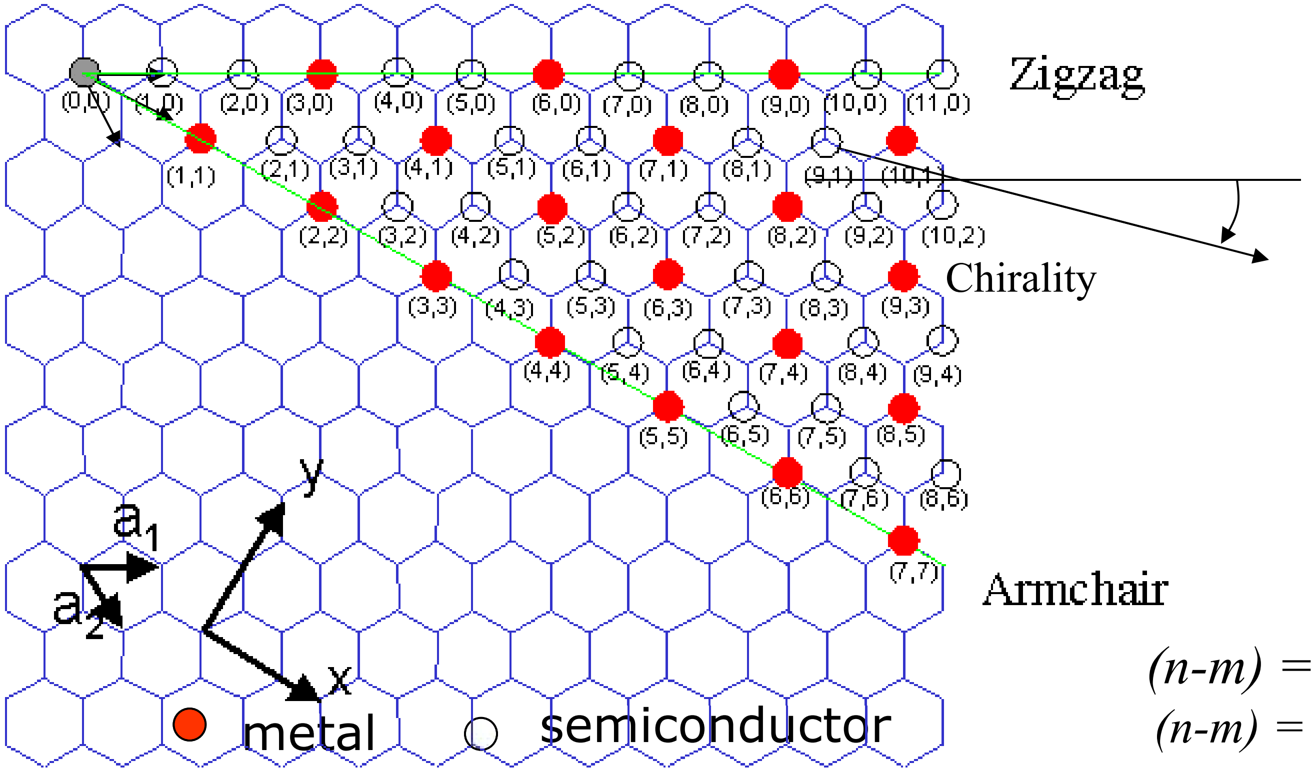


Metallic

Semiconducting

Intermediate

Possible Chiral Vectors



$$Ch = n\bar{a}_1 + m\bar{a}_2$$

$$|Ch| = \sqrt{3}a_{cc}\sqrt{n^2 + nm + m^2}$$

$$d_{tube} = \frac{\sqrt{3}a_{cc}}{\pi}\sqrt{n^2 + nm + m^2}$$

$$\theta = \tan^{-1}\left[\sqrt{3}m/(2n+m)\right]$$

(n-m) = 3q metallic

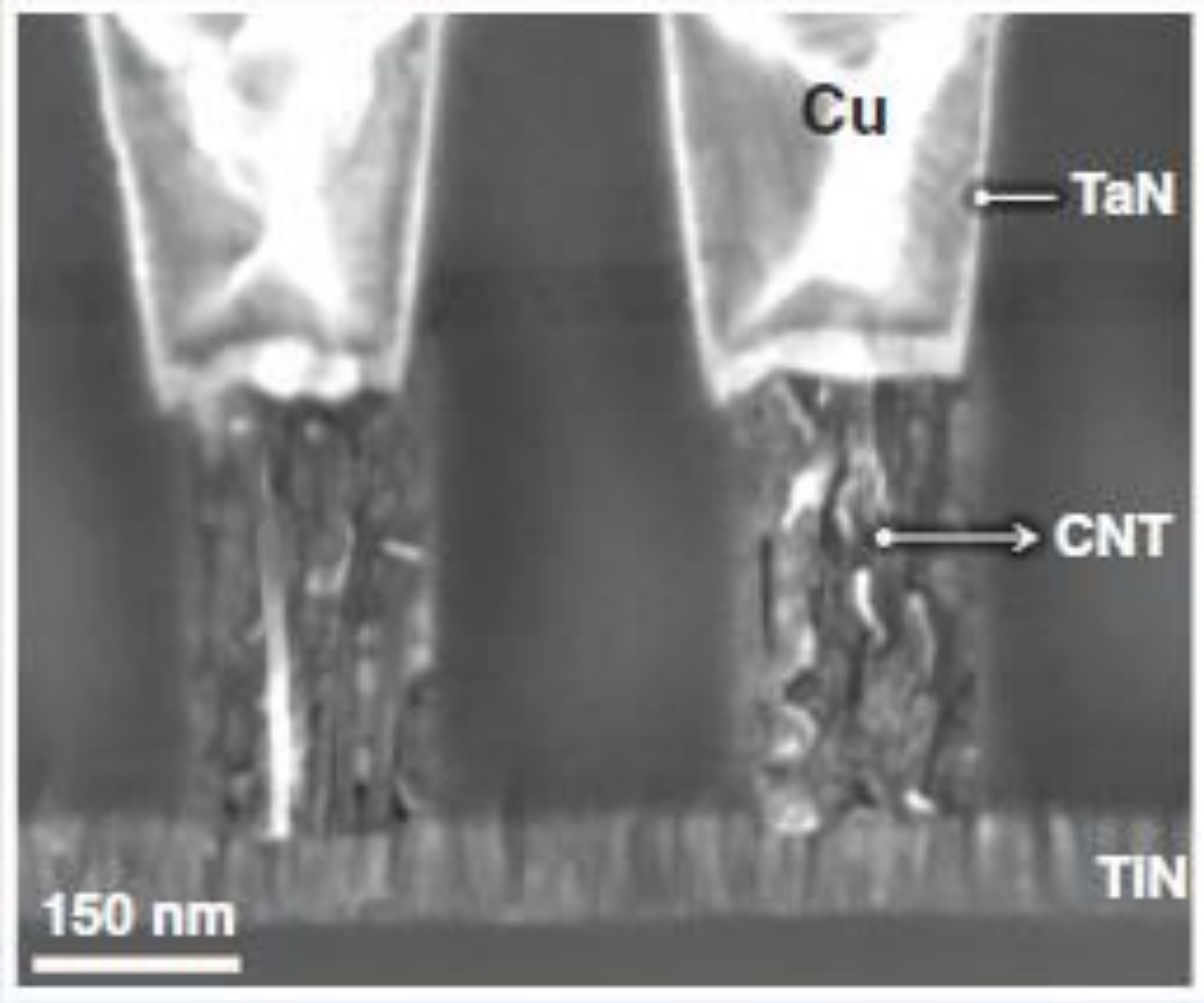
(n-m) = 3q ±1 semiconducting

M. S. Dresselhaus, Electronic Structure of Chiral Graphene Tubules, Appl. Phys. Lett. 60 (18), 1992

Properties of Carbon Nanotubes

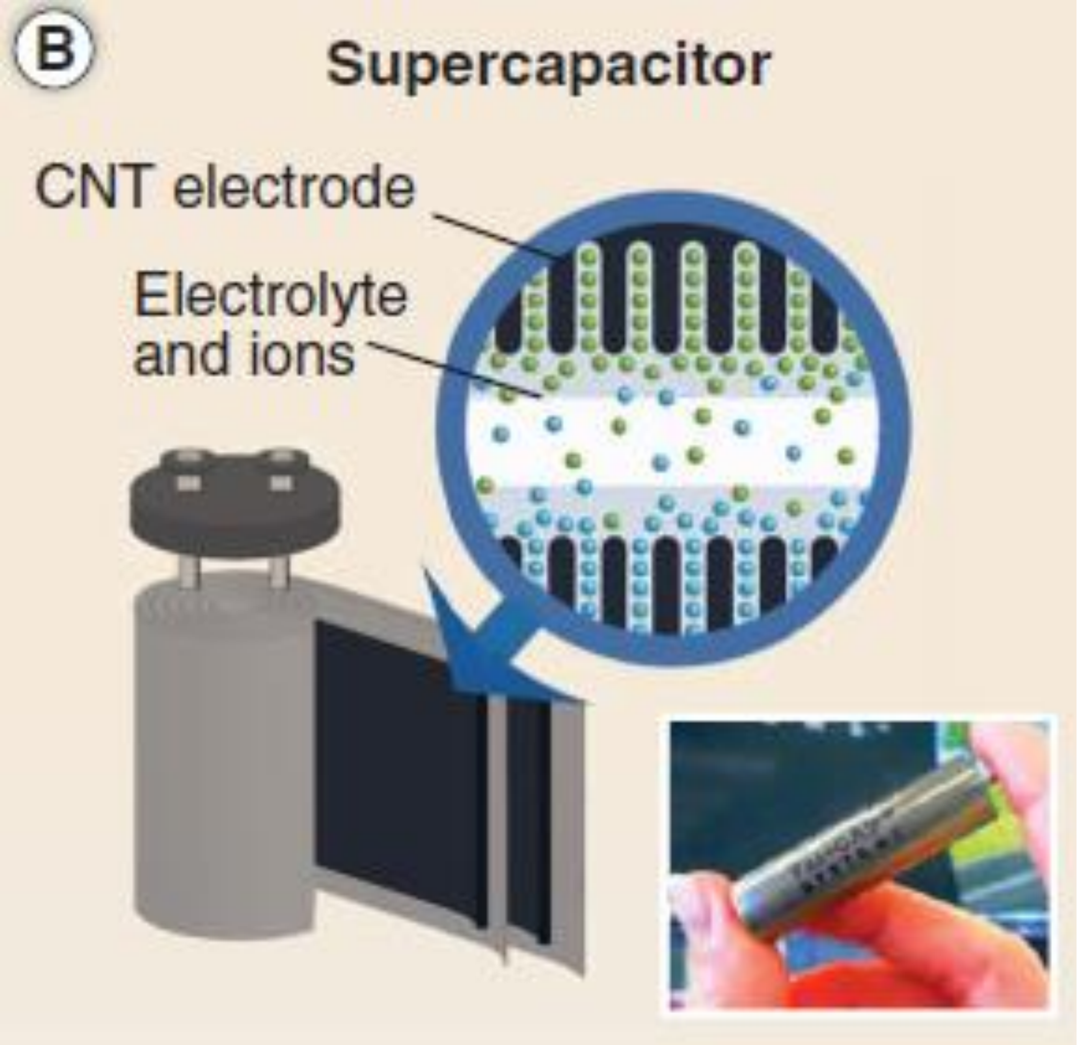
	CNT	**Graphene**	**Si**
Electrical conductivity	~100,000 cm^2/VS	>100,000 cm^2/VS	450 cm2/Vs
Thermal conductivity	~5000W/K.m	~5000W/K.m	1.3 W/K.m
Young's modulus	0.9 ~1.1TPa	1 TPa	130~170 GPa
Transparency	O	O	X
Flexibility	O	O	X
Band gap	**Semiconductor & Metal**	**Semi-metal**	**Semiconductor**

Application of CNT: Electronics (CNT forest)



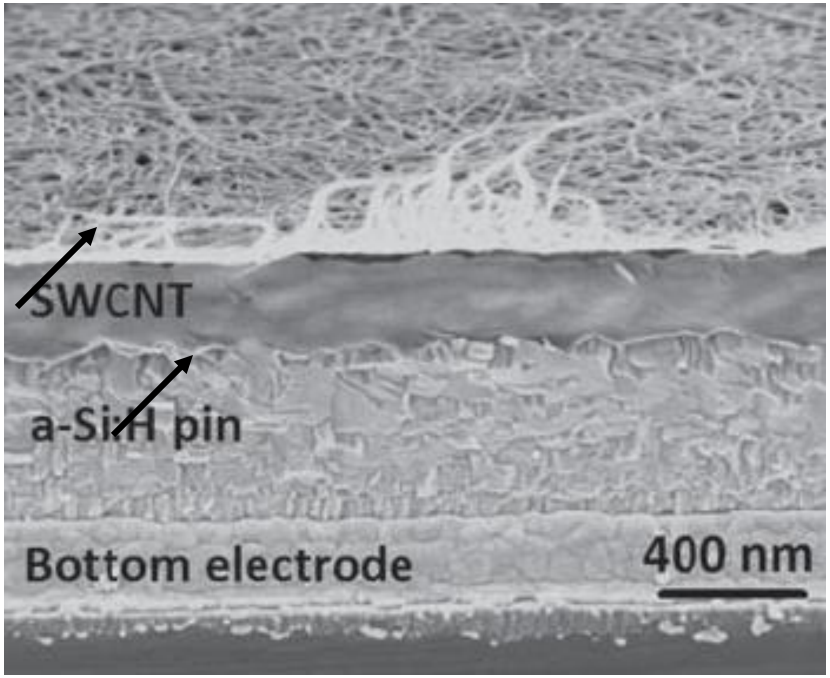
Volder et al. Science, 339, 535 (2013)

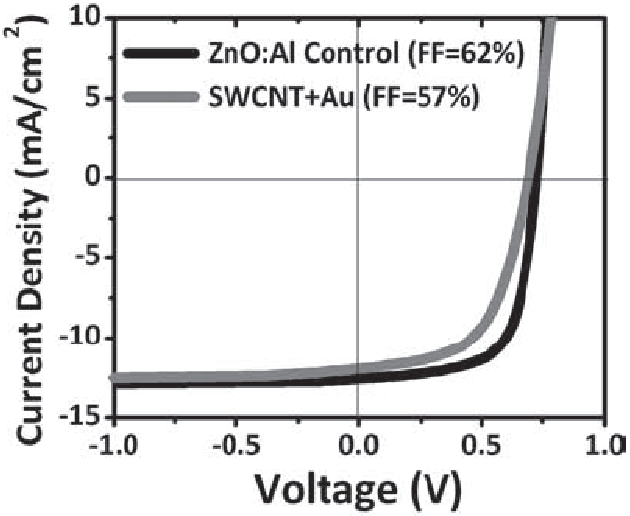
Application of CNT: Energy storage (CNT forest)

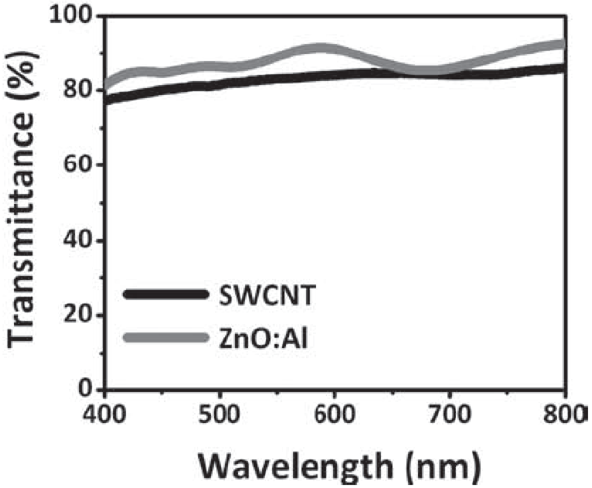


Volder et al. Science, 339, 535 (2013)

Application of CNT: Solar cell electrode (CNT network)



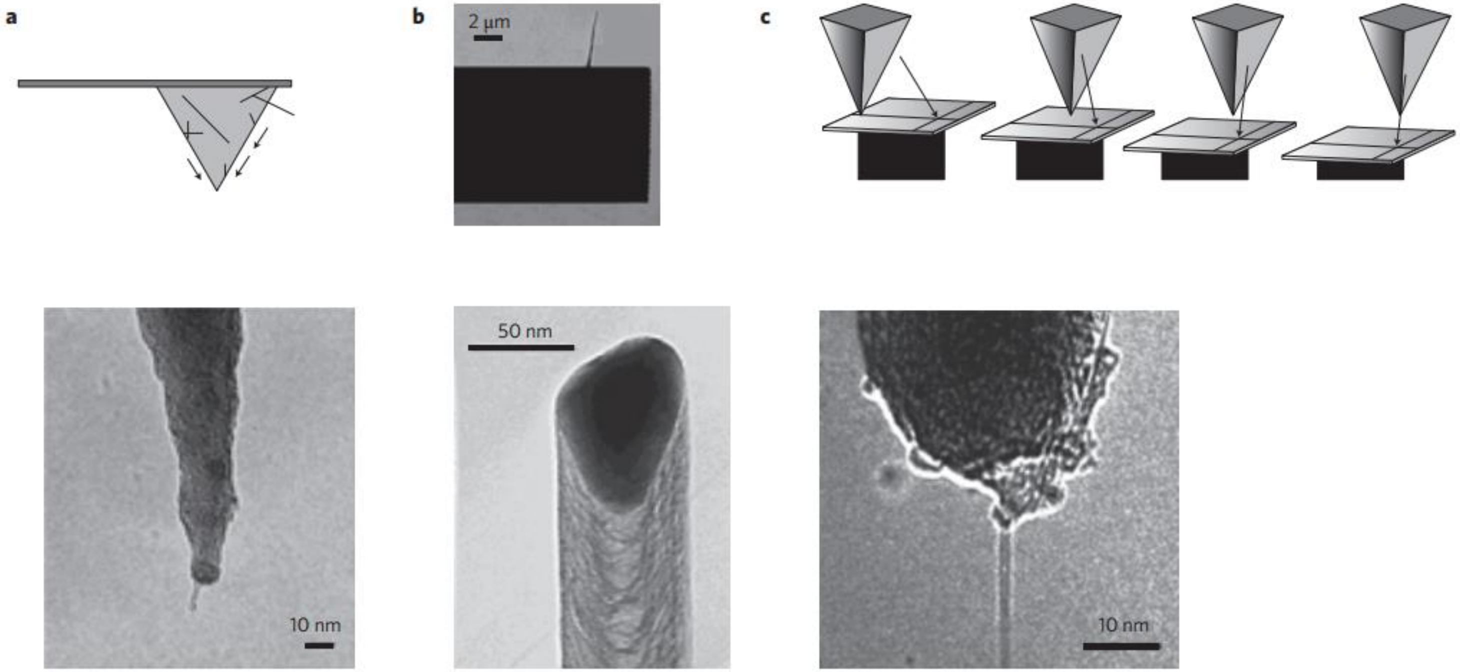




J. Kim et al. Advanced Materials, Vol. 24, 1899 (2012)

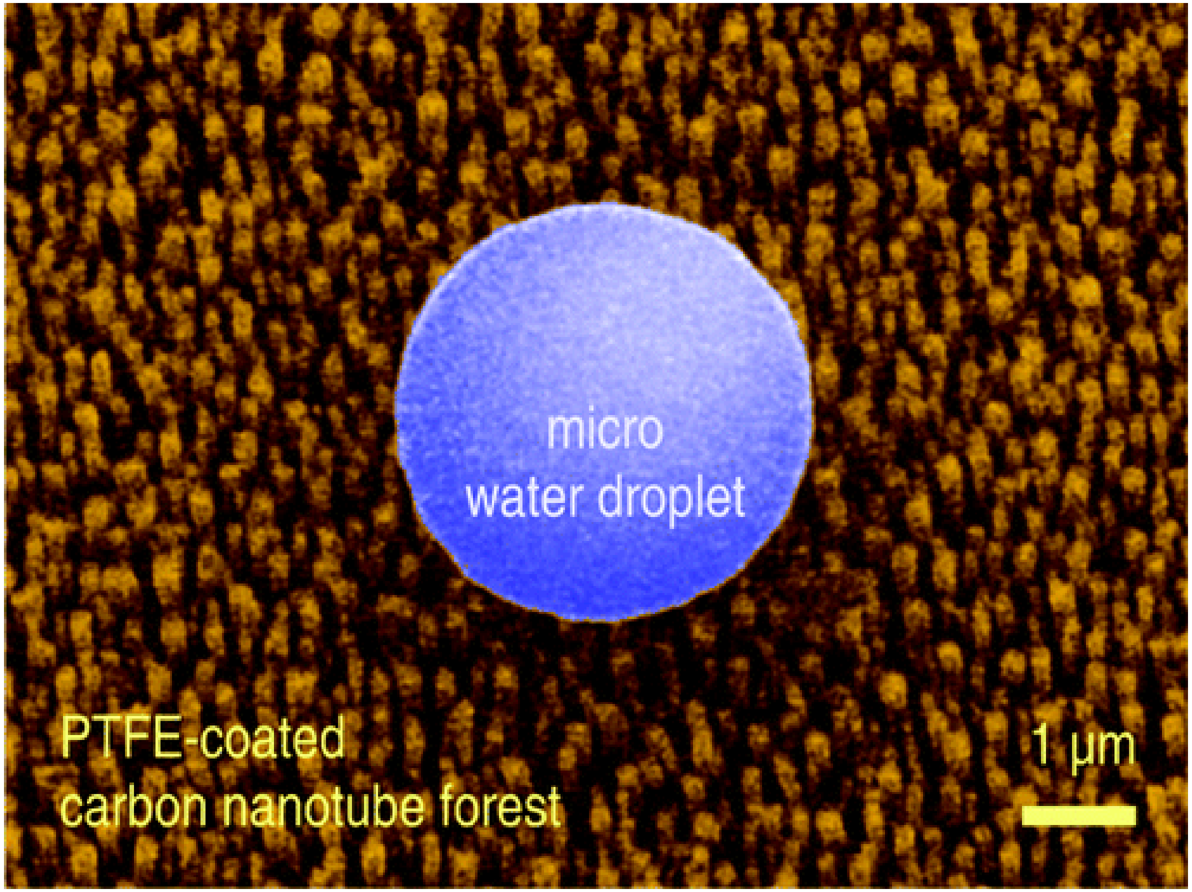
Application of CNTs: Atomic Force Microscope tips

Reduced diameter – maximum atomic imaging resolution (Lab 10)



Nature Nanotechnology, 4, 483 (2009)

Application of CNT: Superhydrophobic surface (CNT forest)

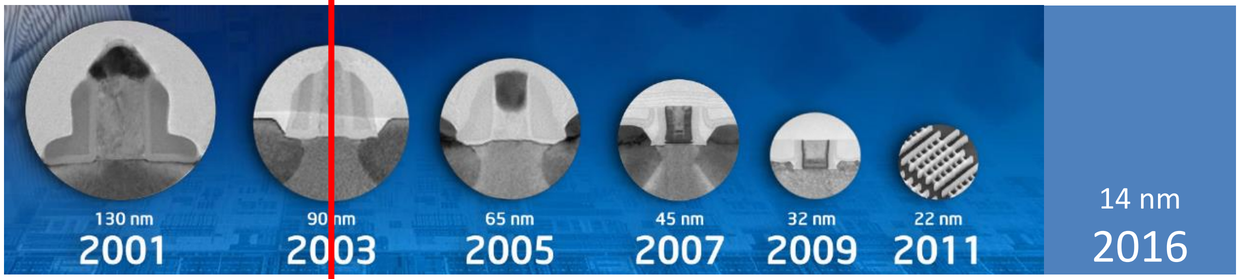


Nano Letters, **2003**, *3* (12), pp 1701–1705

Application of CNTs: Electronics (Single CNT)

- Transistor technology

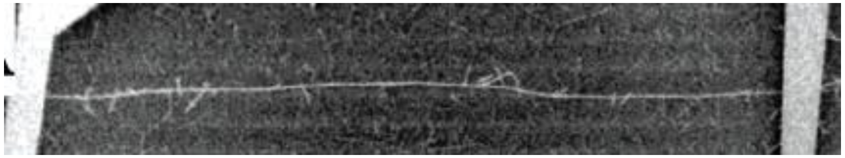
Past: Silicon **Past: Strained Silicon** **Current: FIN Silicon** **Future???**



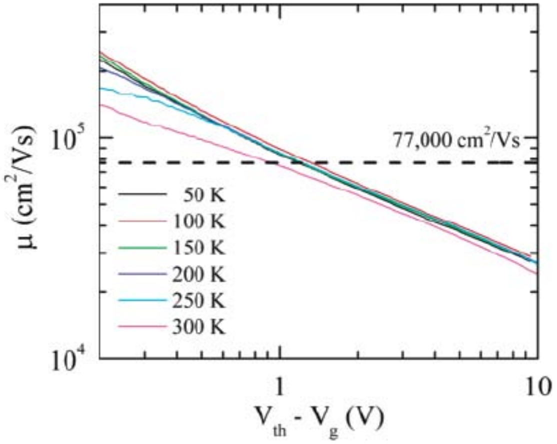
Ge pFETs/
III-V nFETs
CNT FETs
Nanowire FETs

Introduction of strained silicon technology

Single CNT transistor

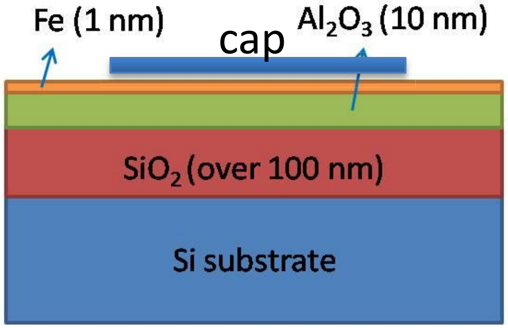


Electron mobility of CNT is 2 orders of magnitude higher than that of silicon



Nano Lett., Vol. 4, No. 1, 2004

Chemical vapour deposition (CVD)



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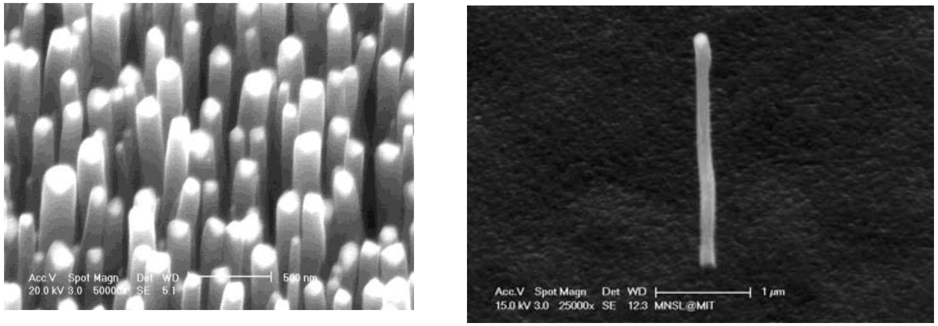
Please see the images on Page 25 in http://nt13.aalto.fi/docs/NT13_TutorialB.pdf.

http://nt13.aalto.fi/docs/NT13_TutorialB.pdf, Christophe Bichara

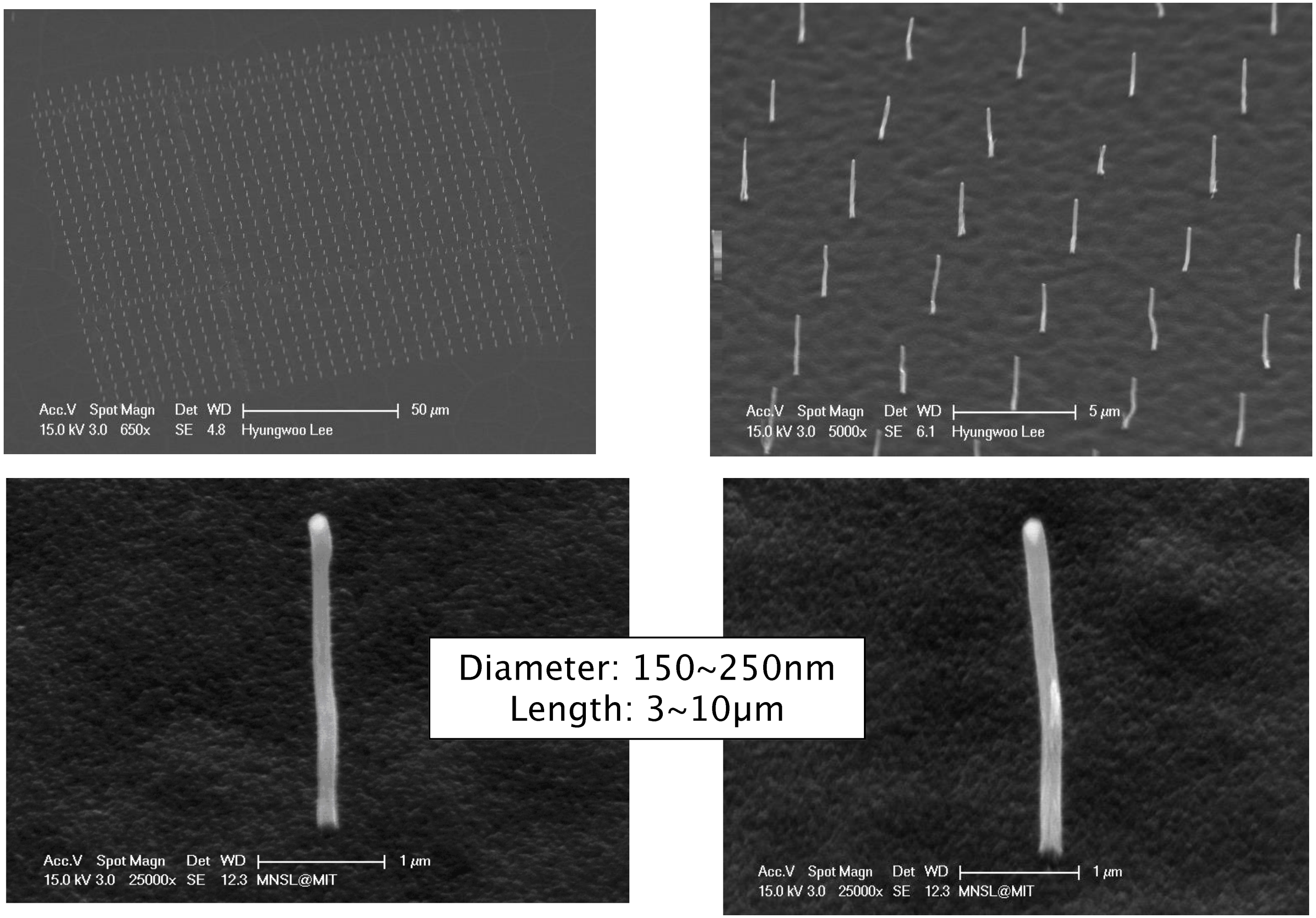
CNT Forest formed by metal nanosphere catalyst



Longest CNTs grown?

Class award

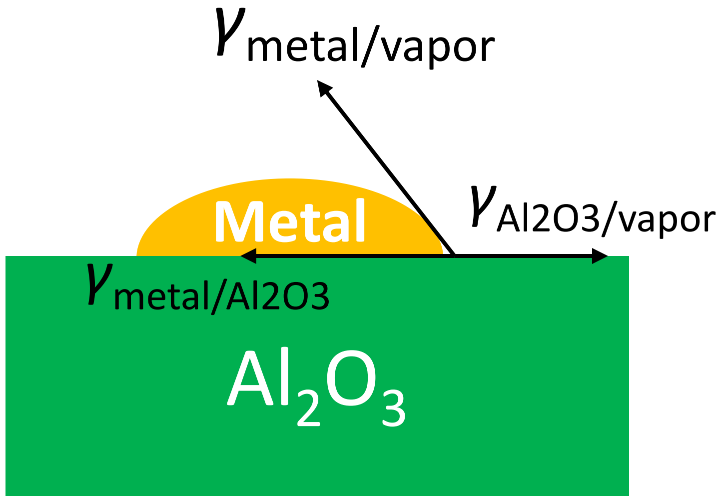
H.W. Lee, S. Kim, and S.G. Kim, App. Phys., 2009

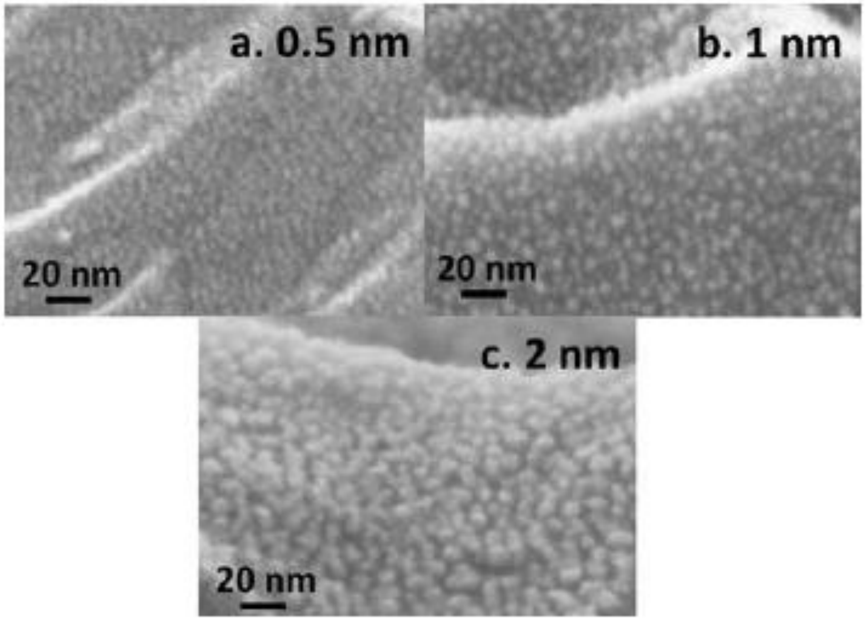


Diameter: 150~250nm
Length: 3~10µm

(H.W. Lee, S. Kim, and S.G. Kim, MIT)

Understanding CNT growth
: Formation of metal nanoparticles





J. Kim et al, ACS Nano, 2010

$$\gamma_{metal/Al2O3} + \cos\theta\,\gamma_{metal/vapor} > \gamma_{Al2O3/vapor}$$

Metal cannot completely wet Al_2O_3
→ Discontinuous metal islands are automatically formed at ultrathin thickness

Understanding CNT growth
: Catalytic reaction with metal particles

Catalytic metals: Fe, Ni, Co

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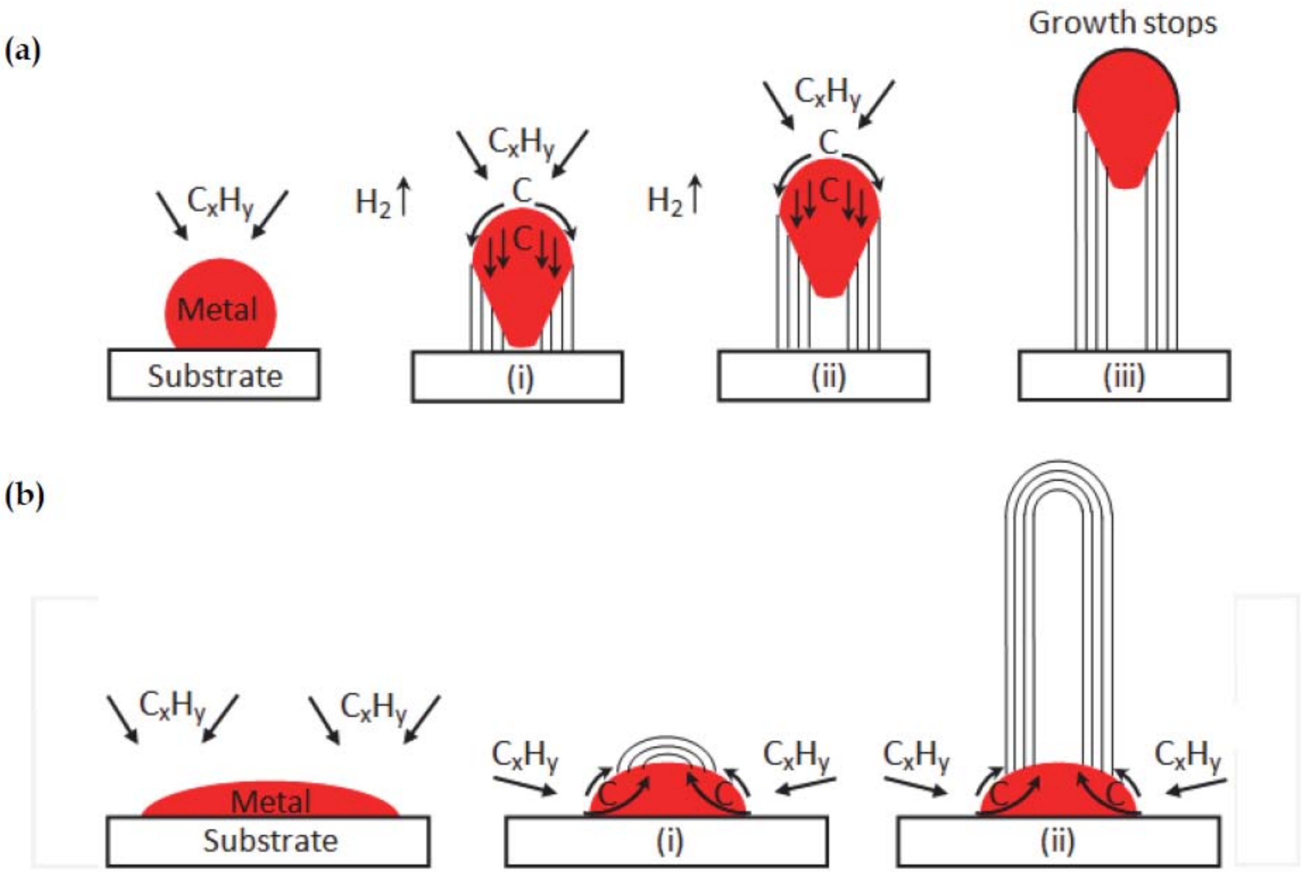
Please see http://www.nanobliss.com/departments/techniques/techniqueimages/basegrowth_nanobliss_350wide.jpg.

http://nt13.aalto.fi/docs/NT13_TutorialB.pdf
Christophe Bichara

Growth modes

Tip-growth mode (weak interaction at substrate/metal)

Base-growth mode (strong interaction at substrate/metal)



- SWNT, single-walled nanotube (0.3 < d < 3 nm)
- MWNT, multi-walled nanotube (d > 10 nm)

Carbon Nanotube Synthesis and Growth Mechanism
By Mukul Kumar (intechopen.com)

Understanding CNT growth
: Role of catalytic metals & Al_2O_3

Role of catalytic metals

http://nt13.aalto.fi/docs/NT13_TutorialB.pdf,

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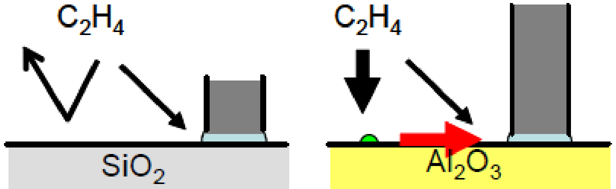
CNT growth sequence

C dissolution into the catalyst
→ C supersaturation
→ C precipitation on catalytic nanoparticles
→ CNT growth from the periphery of nanoparticles

Role of Al_2O_3

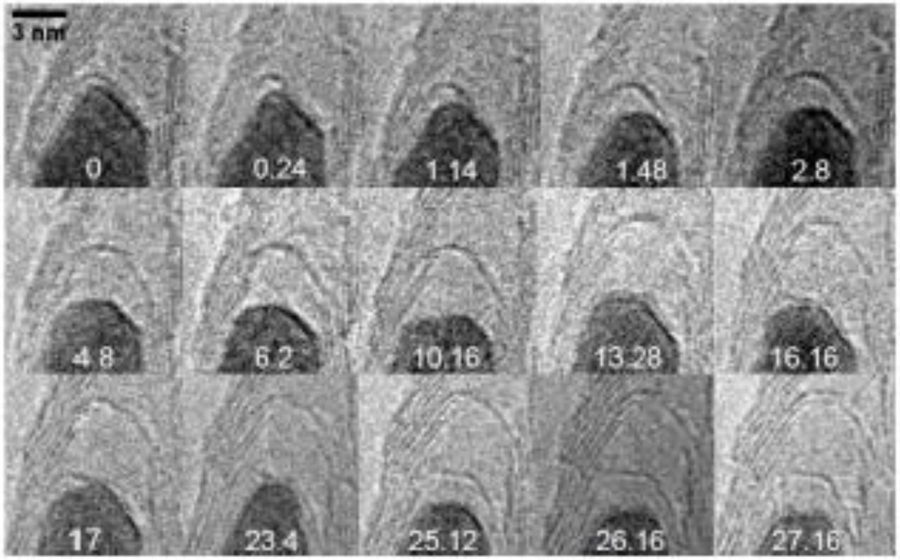


Al2O3 enhances CNT growth

Journal of Nanoscience and Nanotechnology, 8, (2008) 6123

In-situ observation of CNT growth

- In-situ TEM



Pigos *et al.* *ACS Nano*, 5, 12, 10096–10101 (2011)

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https://www.youtube.com/watch?v=TaNCWcumeyg

Challenges for Carbon Nanotube Applications

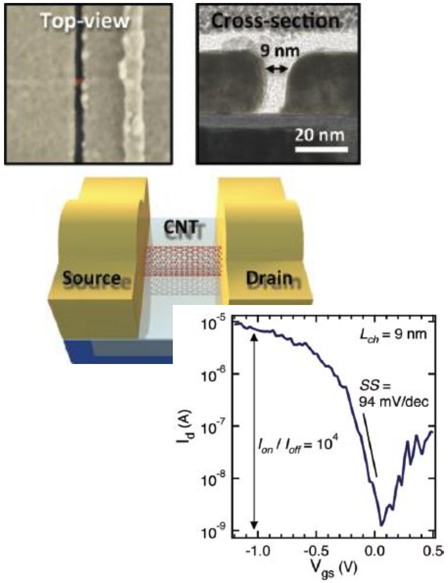
- Process control to produce nanotubes with same diameter and chirality.
  - **Purification**/sorting methods required for uniform CNT
  - **Placement**/alignment methods required for long-range order

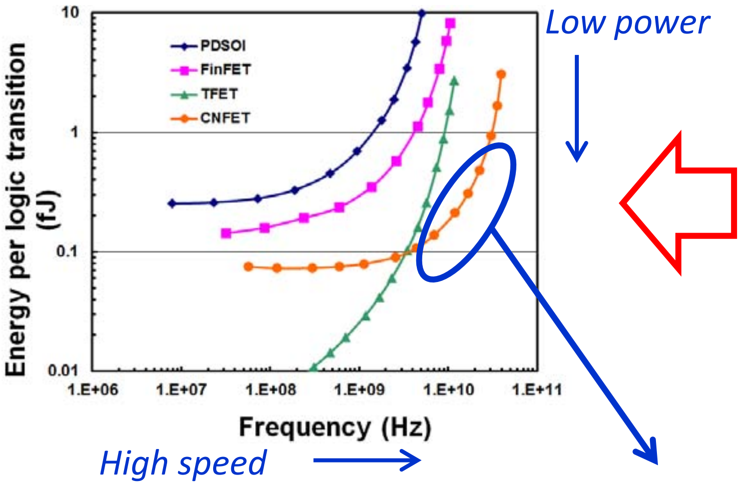
- Develop large-scale, high productivity synthesis methods.

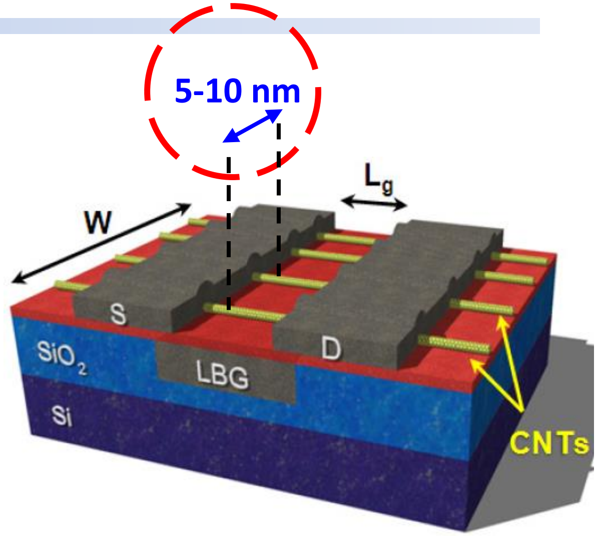
- Develop large-scale, long range order assembly processes deterministically.

- ASSEMBLY, ASSEMBLY, ASSEMBLY!!!
- Graphene → Lab 11

Placement: Key issue to realized benefit of CNT







By David Frank, IBM, 2013

CNT-FETs (high speed with low power)

Sub-10 nm CNTFET, IBM, 2012

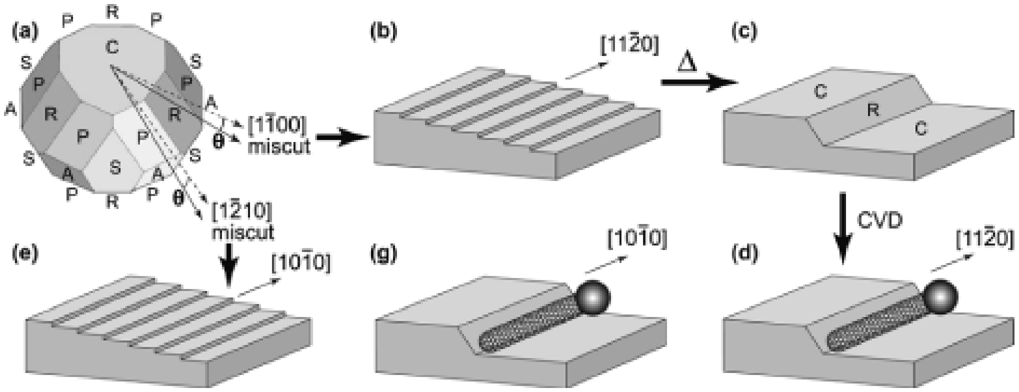
(Franklin et. al., Nano Lett. 12, 758)

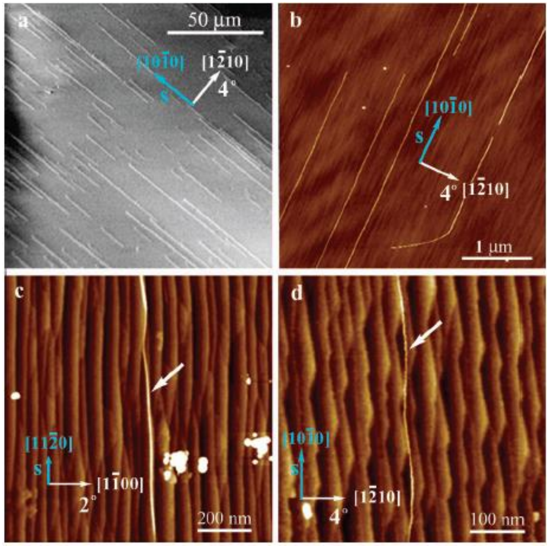
Requirement:

- High density of individual CNTs (transistor density x CNTs/transistor ~ $10^{10}/cm^2$)
- Alignment with a constant pitch (< 10 nm)
- Compatibility with wafer-scale CMOS process
- Compatibility with a process for high purity of semiconducting CNTs

Aligned growth of CNTs

Lateral growth of CNT at the step edges of sapphire wafers

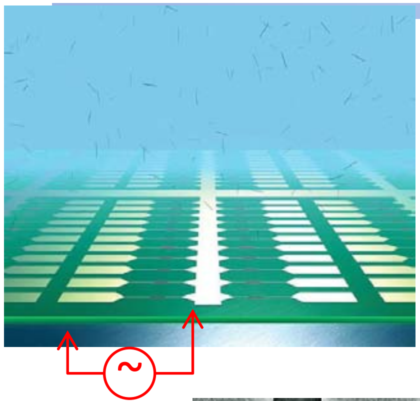




J. AM. CHEM. SOC. 2005, 127, 11554

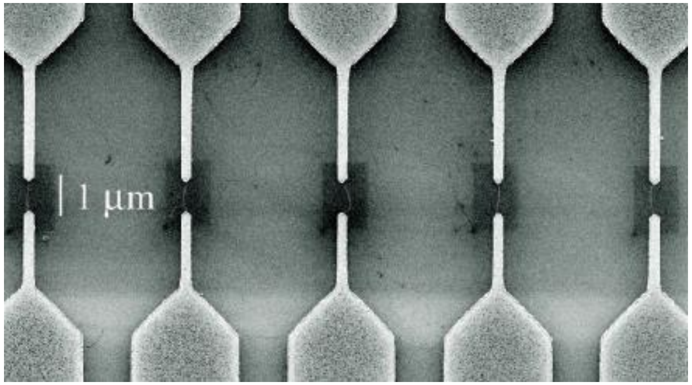
Conventional placement options

Dielectrophoresis



AC bias
(~ MHz)

4×10^6 sites/cm^2



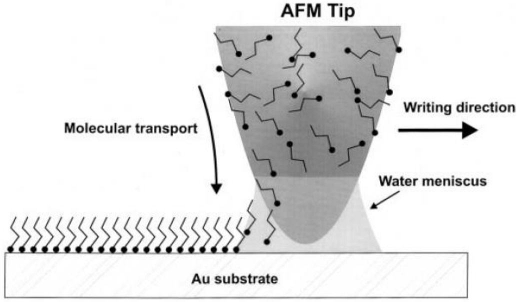
Nano Lett. 7, 1556 (2007)

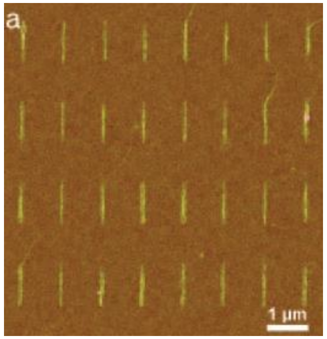
Challenges:

- Biasing to billions of transistors
- Scaling: limitation of minimum pad size
- Density: interference between electrodes

Dip-pen Nanolithography

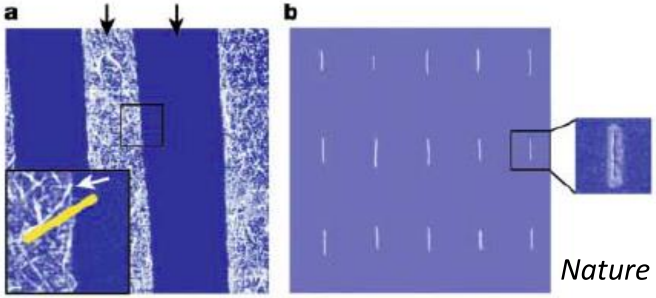
10^7 sites/cm^2





PNAS 103, 2026 (2006)

10^6 sites/cm^2

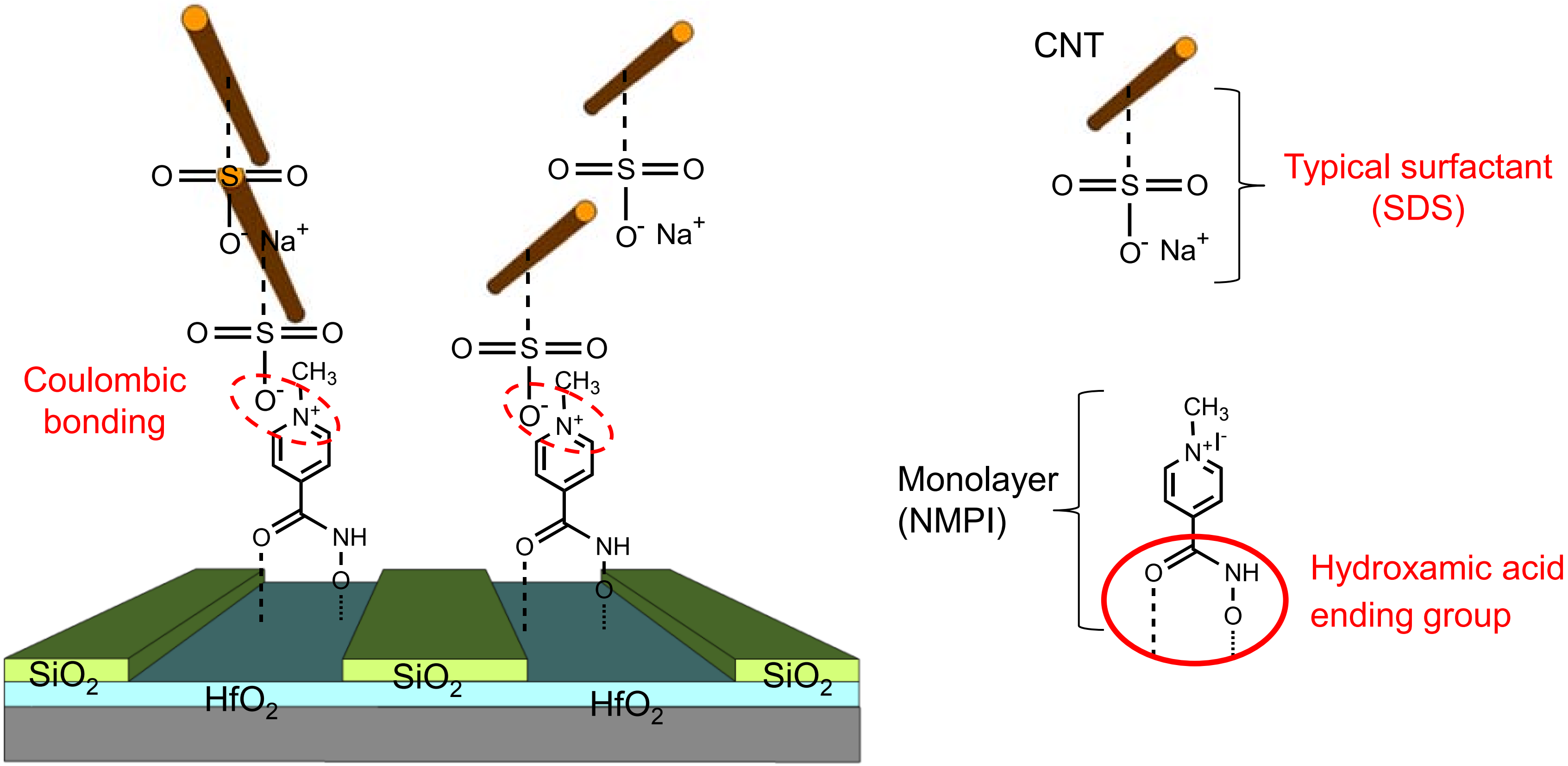


Nature 425, 36 (2003)

Challenges:

- Throughput of scanning probe techniques
- Demonstrated on Au substrates

Specific Surface Functionalization



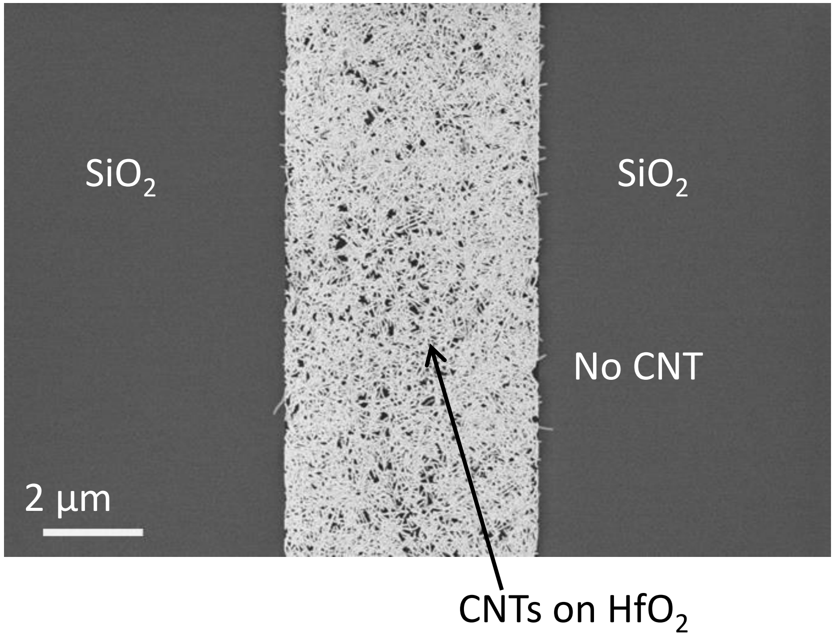
Strong electrostatic interaction between CNTs and surface monolayer

- Surface monolayer (NMPI): self-assembled on HfO_2 → Positively charged
- CNTs: dispersed in a normal surfactant solution (1% SDS) → Negatively charged

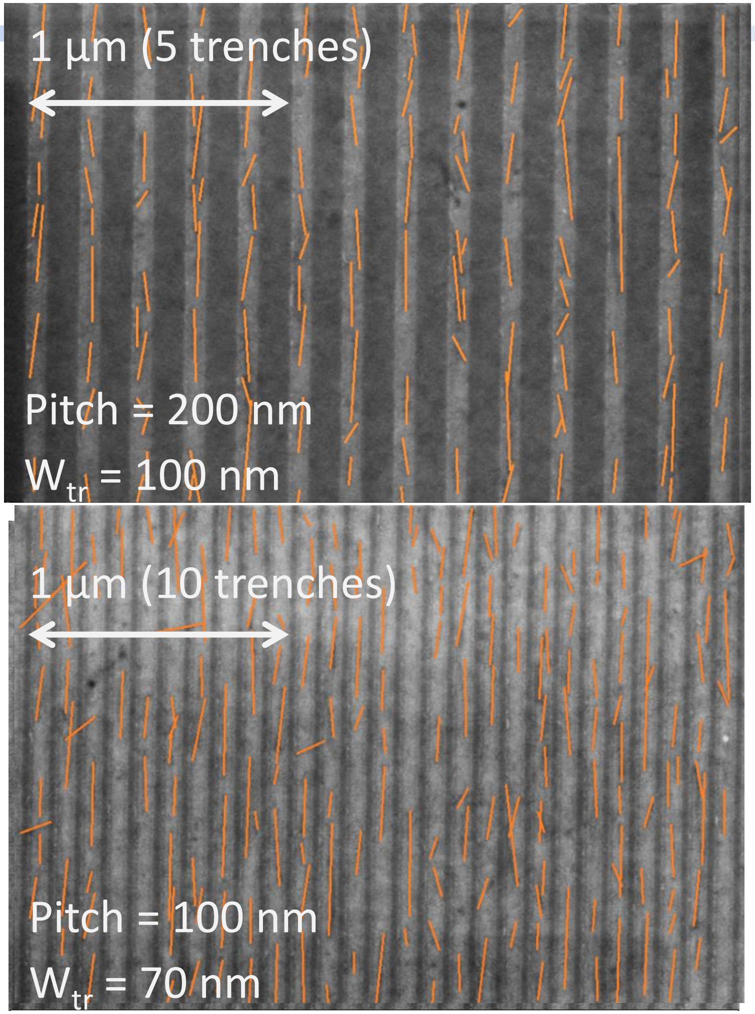
H. Park *et al.*, *Nature Nanotechnology* 7, 787(2012)

NMPI: 4-(N-hydroxycarboxamido)-1-methylpyridinium iodide

Position control: excellent selectivity and high density



Nearly perfect selectivity

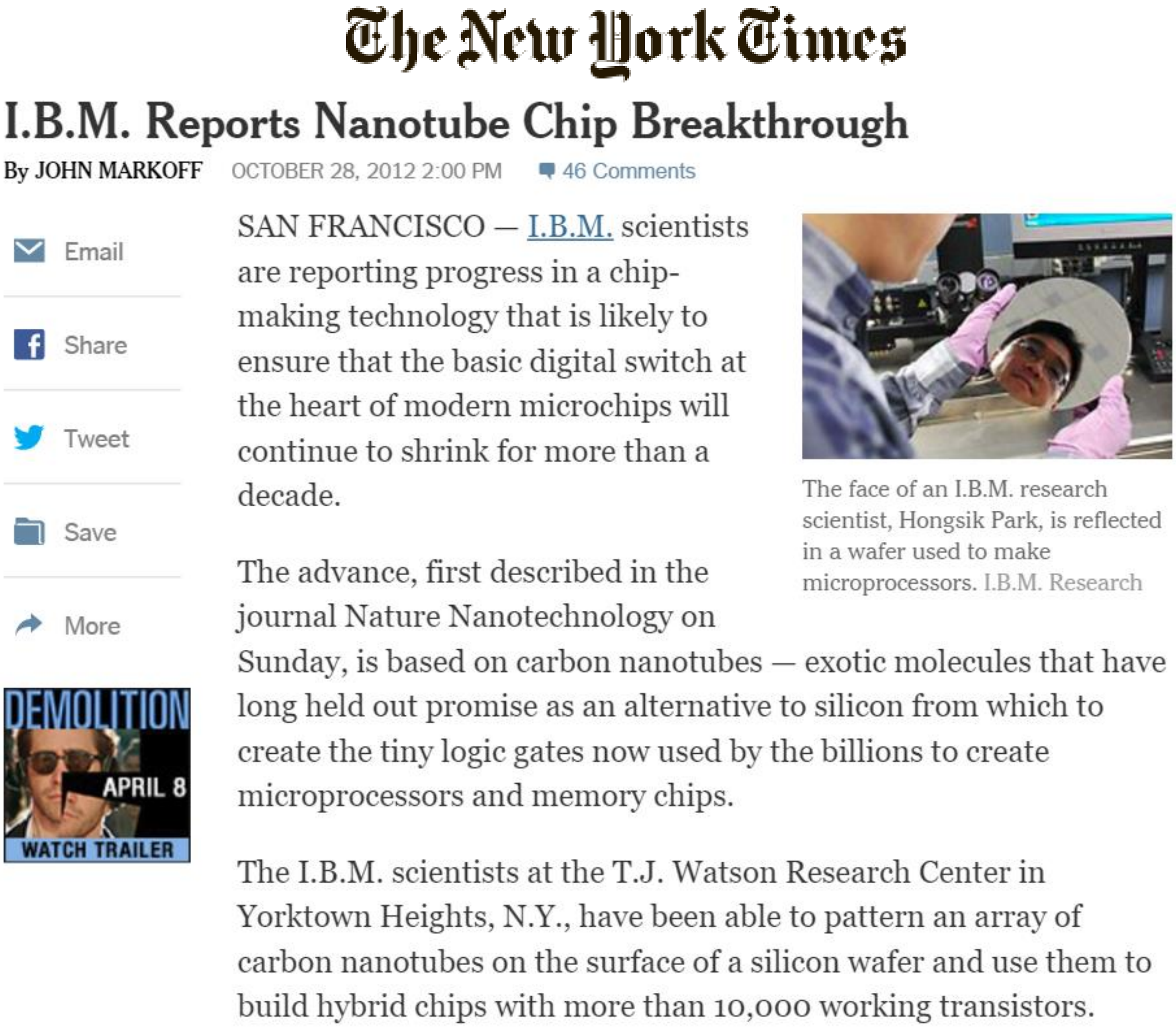


Ion-exchange chemistry enables high density and potential for scaling

- Coulombic bonding → high density in small dimensions

H. Park *et al.*, *Nature Nanotechnology* 7, 787(2012)

Record density: 10^9/cm^2



The New York Times

I.B.M. Reports Nanotube Chip Breakthrough

By JOHN MARKOFF OCTOBER 28, 2012 2:00 PM 46 Comments

SAN FRANCISCO — I.B.M. scientists are reporting progress in a chip-making technology that is likely to ensure that the basic digital switch at the heart of modern microchips will continue to shrink for more than a decade.

The face of an I.B.M. research scientist, Hongsik Park, is reflected in a wafer used to make microprocessors. I.B.M. Research

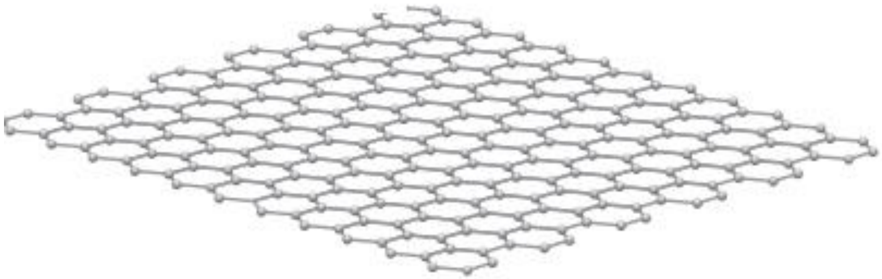
The advance, first described in the journal Nature Nanotechnology on Sunday, is based on carbon nanotubes — exotic molecules that have long held out promise as an alternative to silicon from which to create the tiny logic gates now used by the billions to create microprocessors and memory chips.

The I.B.M. scientists at the T.J. Watson Research Center in Yorktown Heights, N.Y., have been able to pattern an array of carbon nanotubes on the surface of a silicon wafer and use them to build hybrid chips with more than 10,000 working transistors.

CNT vs Graphene

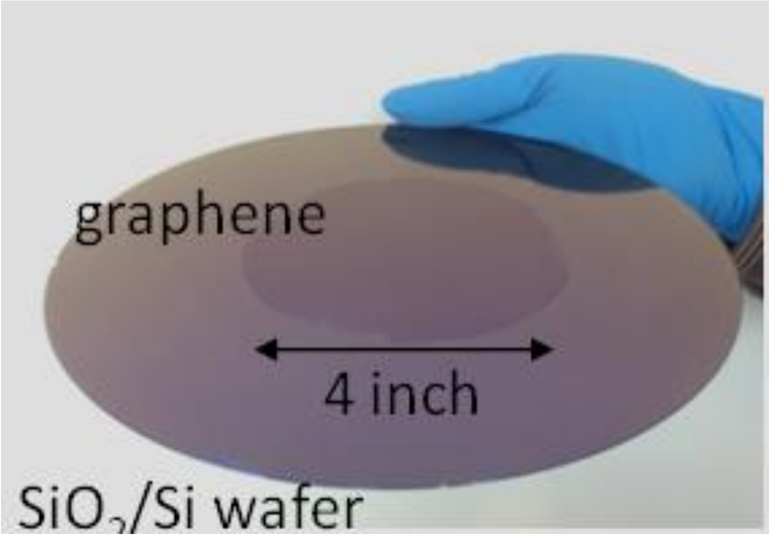
	CNT	Graphene	Si
Electrical conductivity	~100,000 cm^2/VS	~100,000 cm^2/VS	450 cm2/Vs
Thermal conductivity	~5000W/K.m	~5000W/K.m	1.3 W/K.m
Young's modulus	0.9 ~1.1TPa	1 TPa	130~170 GPa
Transparency	O	O	X
Flexibility	O	O	X
Band gap	Semiconductor	Semi-metal	Semiconductor
Scalability	**X**	**O**	

Why graphene?



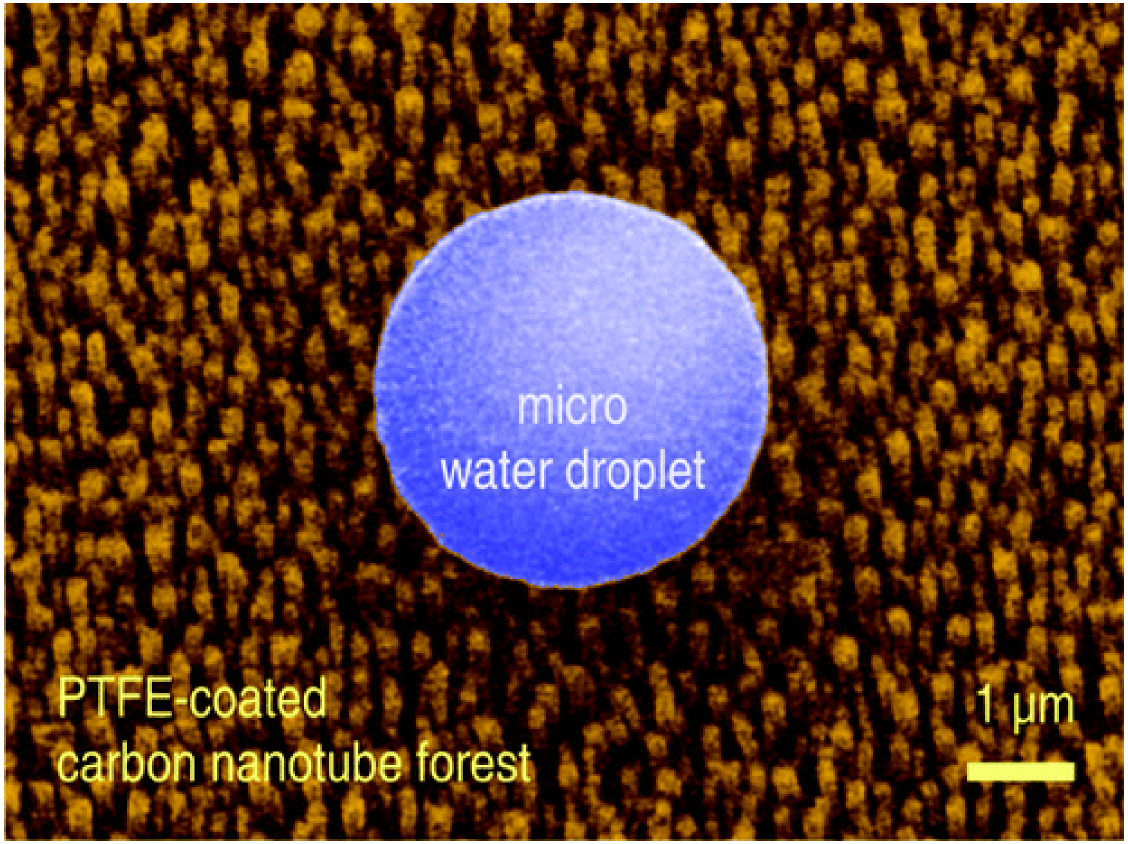
Flat/Monolayer/Single-crystalline
Uniform in a LARGE SCALE

First single-crystalline wafer-scale graphene



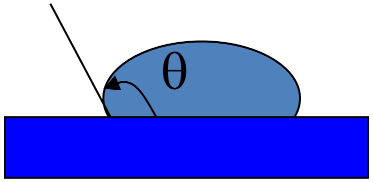
Jeehwan Kim *et al. Science,* 342, 833 (2013)

Application of CNT: Superhydrophobic surface (CNT forest)

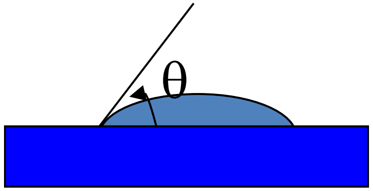


Nano Letters, **2003**, *3* (12), pp 1701–1705

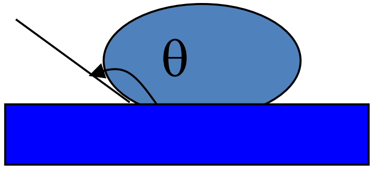
Super hydrophobicity (Lab 7)



Hydrophobic, $\theta > 90^0$

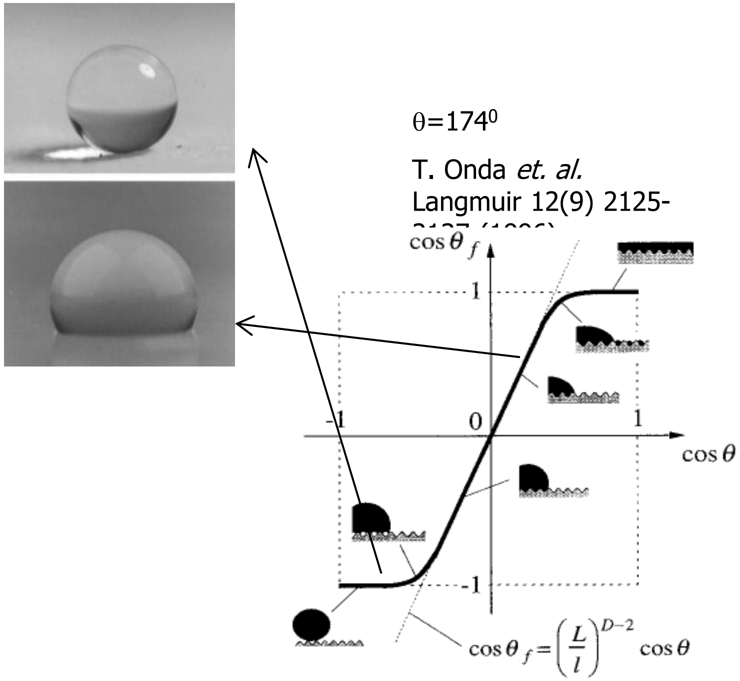


Hydropilic, $\theta < 90^0$



Super hydrophobic, $\theta > 150^0$

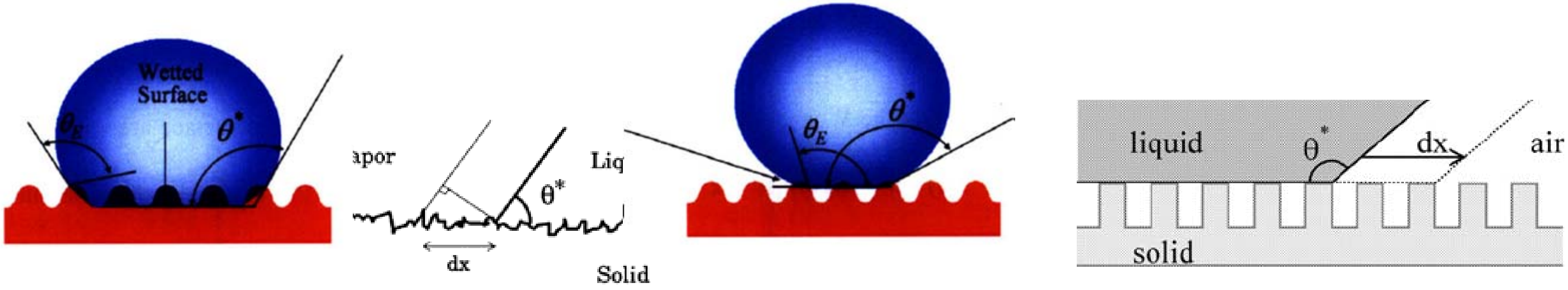
- Chemical modification, coating
- Nanostructured surface



$\theta = 174^0$

T. Onda *et. al.* Langmuir 12(9) 2125-2127 (1996).

Super hydrophobicity (Lab 7)



Wenzel' s model

- If the surface has a high free energy, roughness promotes wetting.
- If it has low free energy, roughness promotes hydrophobicity.

$$\cos\theta^* = r\cos\theta$$

$$r = \frac{actual\_area}{projected\_area}$$

$$\theta^* = apparent\_contact\_angle$$

Cassie' s model

- Wettability of heterogeneous (solid+air) surfaces
- Contact angle on air fraction is 180^0.

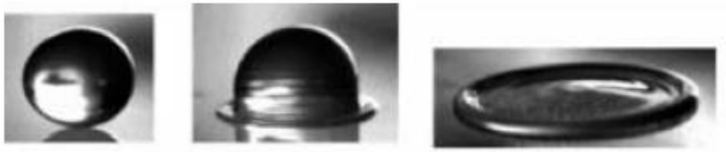
$$\cos\theta^* = -1 + \phi_s(\cos\theta + 1)$$

$$\phi_s = solid\_fraction\_surface$$

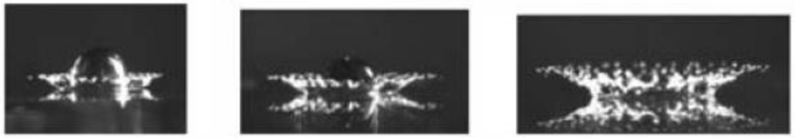
Super hydrophobicity (Lab 7)

Bouncing a water drop

Deposition



Splash

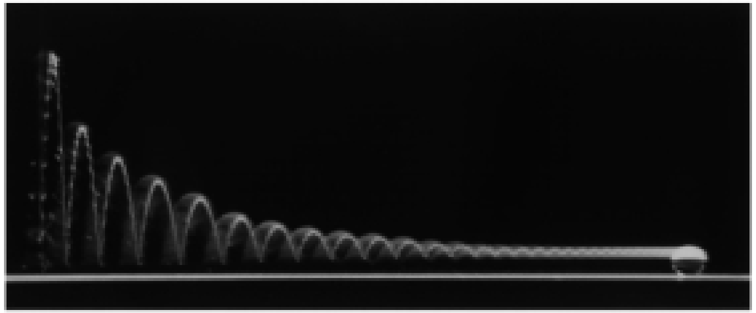


Breakup

rebounding

Super hydrophobicity (Lab 7)

When kinetic energy is very high



Restitution ratio=|v' /v|

= Relative speed after collision/

Relative speed before collision/

$We = \rho V^2 R/\gamma$= kinetic energy/surface energy

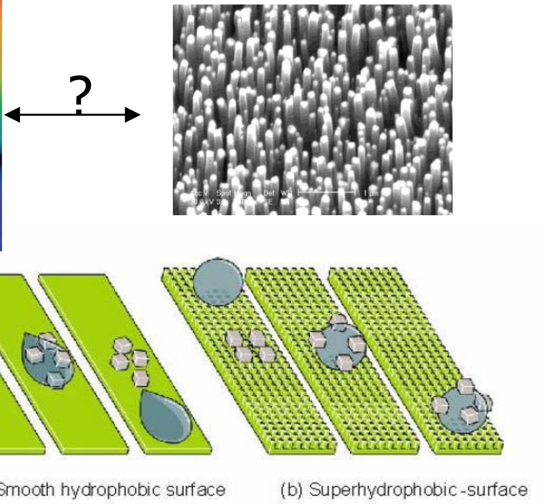
→ Bouncing patterns determined by Weber number

Low We: No deformation/Mid We: Deformation/High We: Break off

Lotus Effect

- Some plant leaves have near 170^0 contact angle, and show no accumulation of dirt. (Lotus Effect)
- Superhydrophobicity by nano patterned surface
- Self-cleaning surface (no car wash?)

W. Barthlott and C. Neinhuis, Planta 202, 1 (1997)

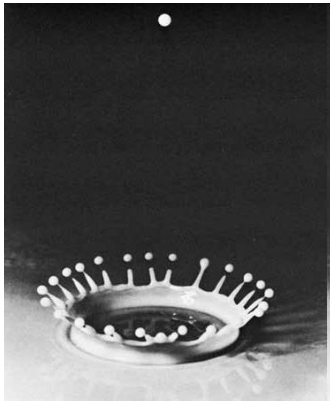


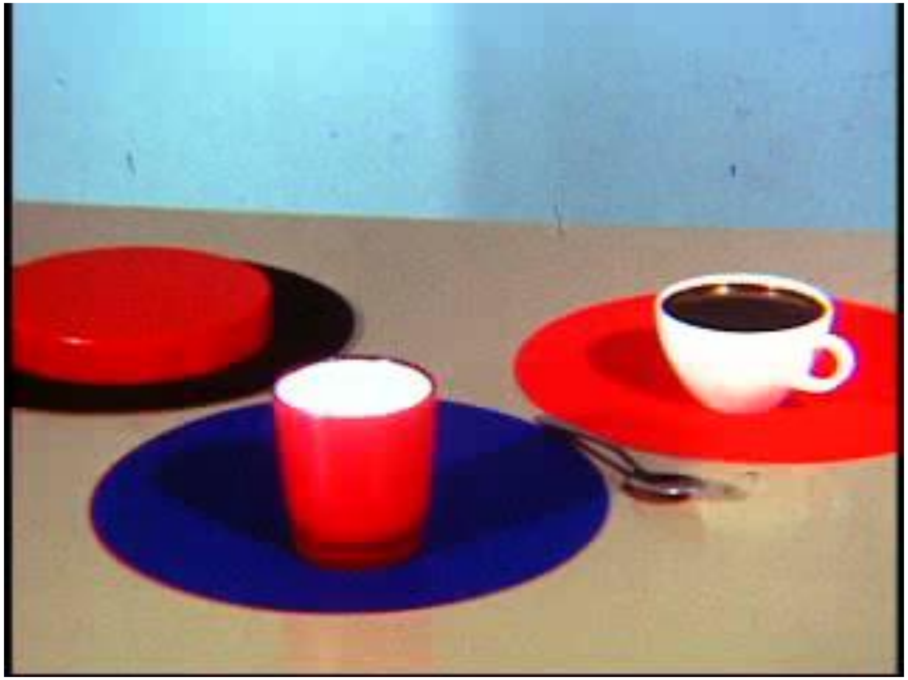
Nanotech Lecture: ‘Self-Cleaning Surfaces’ by Dr. Vesselin Paunov

Super hydrophobicity (Lab 7)

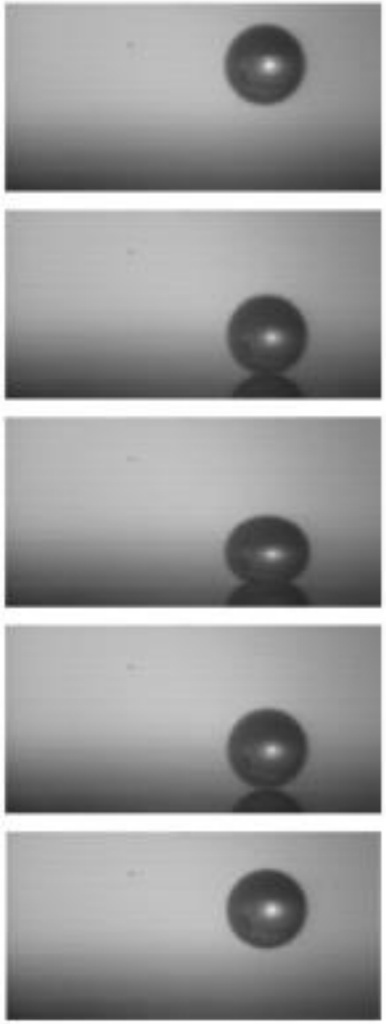
Bouncing a milk drop

H. Doc Edgerton, MIT





MIT TechTV



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