2016 fall 〈Freshman Seminar〉

“New materials to open the future”

10.24.2016

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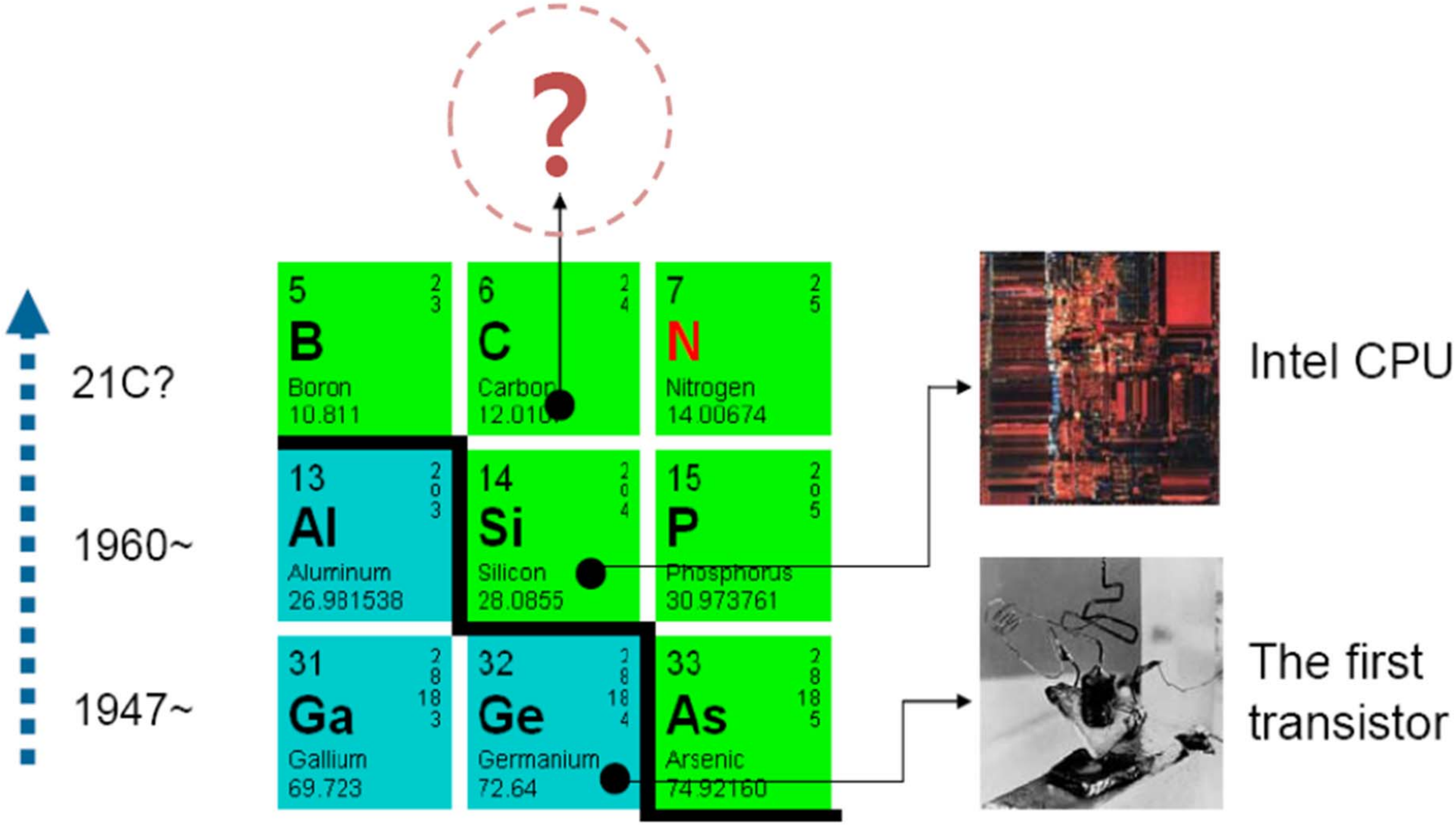
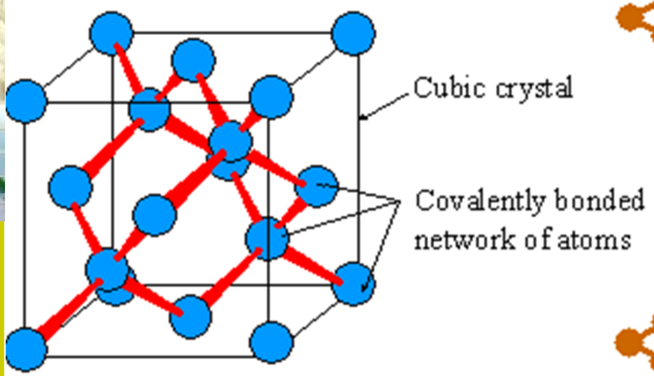
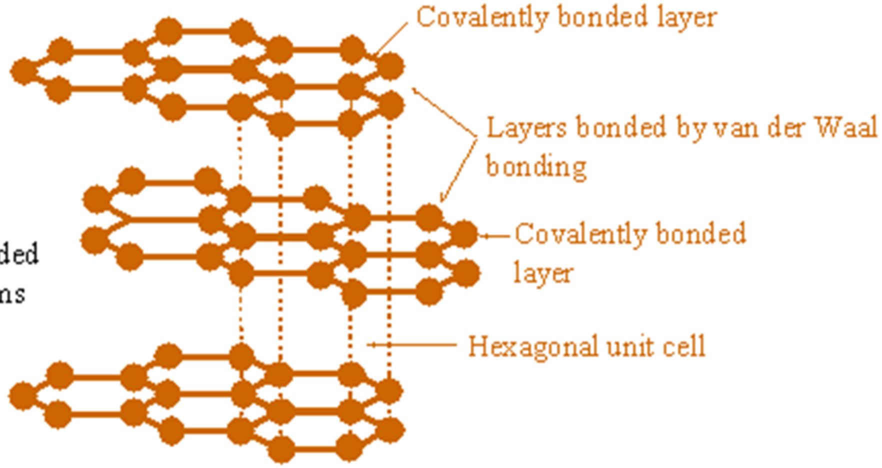
Carbon materials



Carbon Family

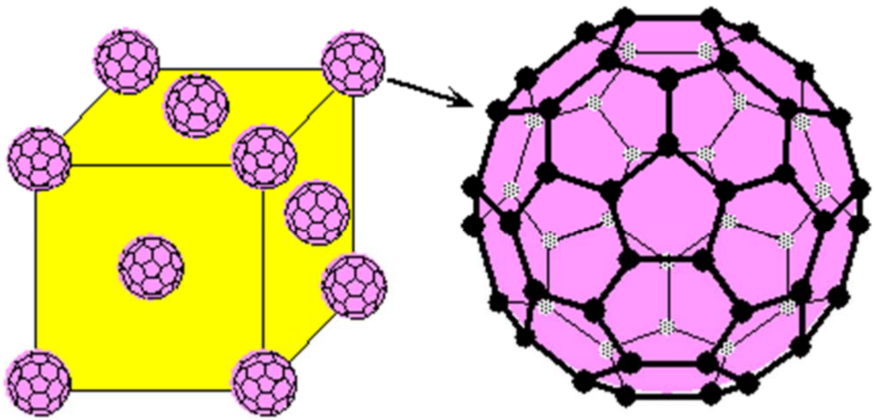


(a) Diamond unit cell



(b) Graphite

Three Allotropes of Carbon



The FCC unit cell of the Buckminsterfullerene crystal. Each lattice point has a C_{60} molecule

Buckminsterfullerene (C_{60}) molecule (the "buckyball" molecule)

(c) Buckminsterfullerene

Richard E. Smalley (1985)

Bonding in Carbon Materials

sp^2

sp^3

Mixture of sp^2 and sp^3

Graphite

Diamond

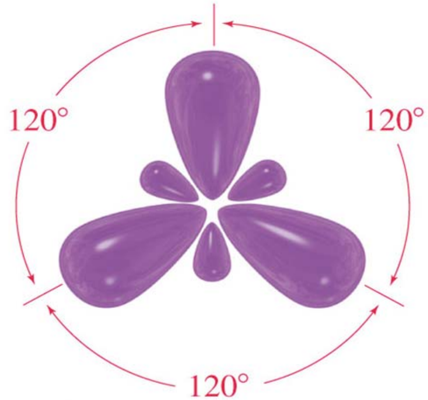
C_{60}

Carbon Nanotube

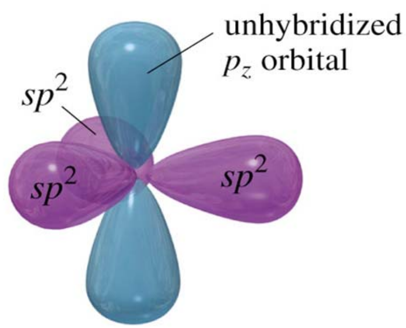
Graphene

Bonding in Graphite

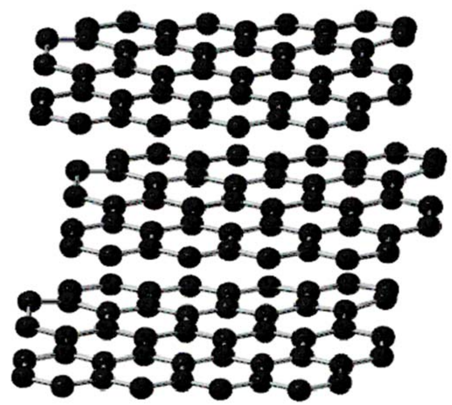
- One of the 2s electrons hybridizes with two of the 2p electrons to give sp^2 orbitals to each other in a plane, with the remaining orbital having a p_z configuration, at 90º to this plane.
- The sp^2 orbitals form the strong bonds between carbon atoms in the graphite planes.
- The p_z orbitals (p orbitals) provide the weak van der Waals bonds between the planes.
- The overlap of orbitals on adjacent atoms in a given plane provides the electron bond network which gives graphite its relatively high electrical conductivity.



three sp^2 hybrid orbitals superimposed

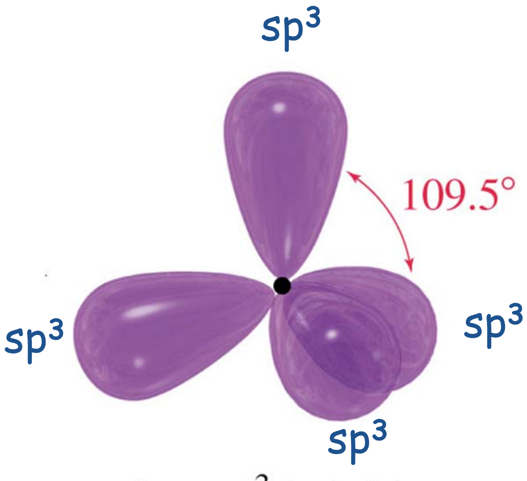


sp^2 hybrid carbon atom (viewed from the side)

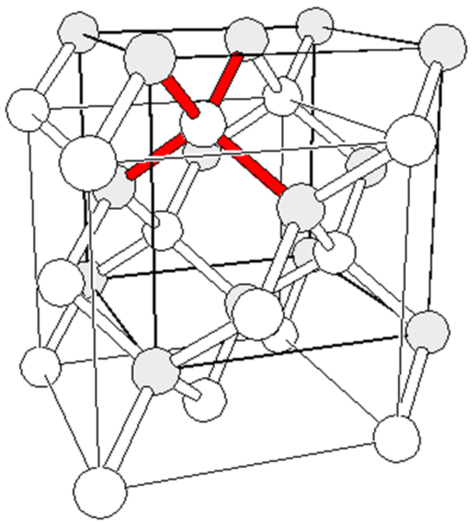


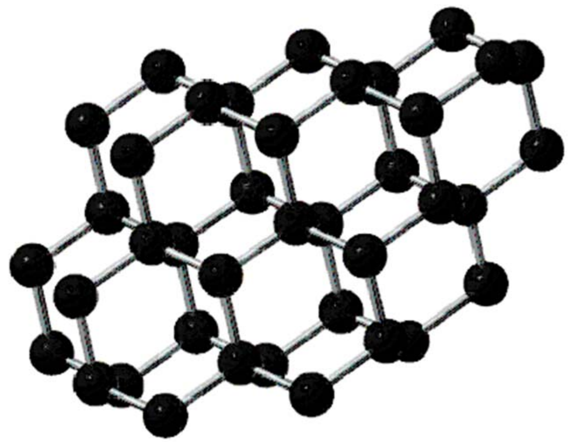
Bonding in Diamond

- Each carbon atom is joined to 4 neighbors in a tetrahedral structure.
- The bonding in this structure is sp^3 and results from the mixing of one 2s and three 2p orbitals.
- Diamond is less stable than graphite, and is converted to graphite at a temperature of 1700ºC at normal pressures.



four sp^3 hybrids



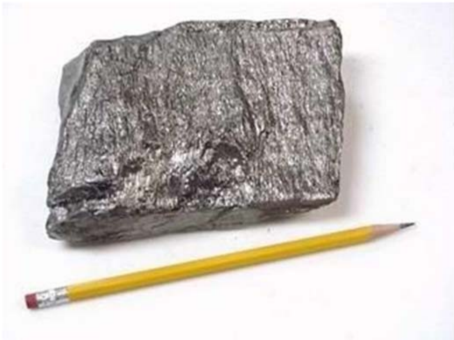


How does thermodynamics different from kinetics?

Thermodynamics ➡ There is no time variable.

says which process is possible or not and never says how long it will take.

The existence of a thermodynamic driving force does not mean that the reaction will necessarily occur!!!



Allotrope (同質異像): any of two or more physical forms in which an element can exist

화학성분 같고 결정구조 다름

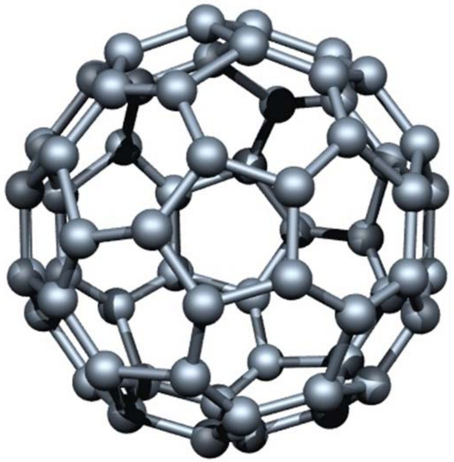
There is a driving force for diamond to convert to graphite but there is (huge) nucleation barrier.

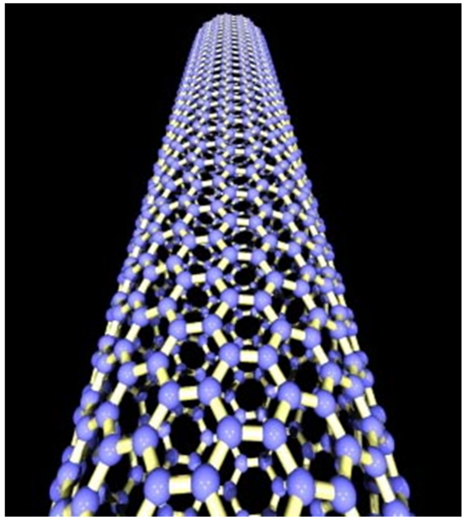
How long it will take is the problem of kinetics.

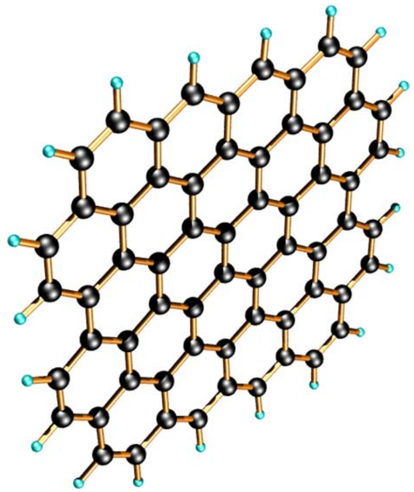
The time variable is a key parameter.

Bonding in C_{60}, CNT and Graphene

- In the C_{60} molecules, the carbon atoms are bonded in an icosahedral structure made up of 20 hexagons and 12 pentagons (20 x 6 x 1/3 + 12 x 5 x 1/3 = 60).
- Each of the carbon atoms in C_{60} molecules is joined to three neighbors, so the bonding is essentially sp^2, although there may be a small amount of sp^3 character due to the curvature.
- The bonding in carbon nanotube is also primarily sp^2, although once there may be some sp^3 character in regions of high curvature
- In the graphene, the bonding is sp^2.







Nano Milestones

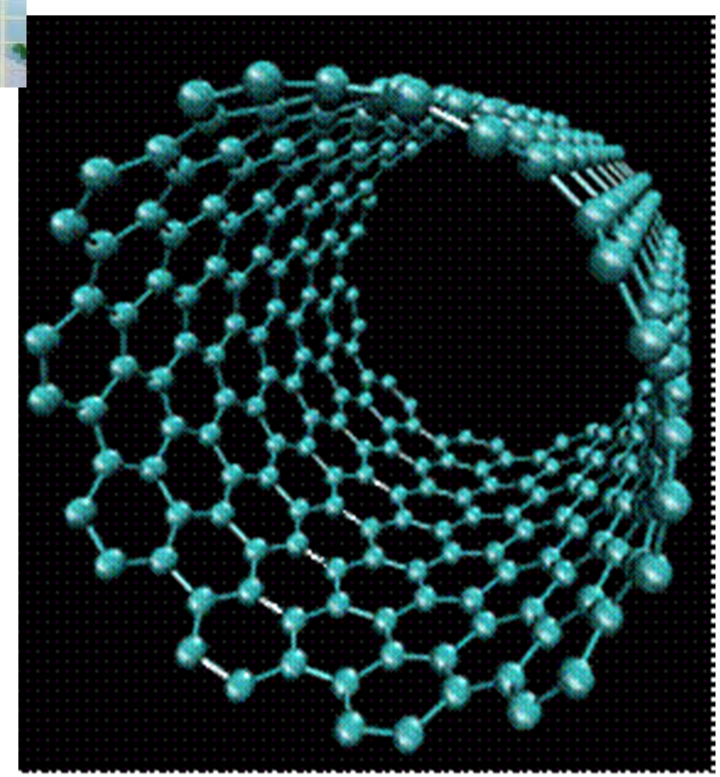
1985: Robert F. Curl, Jr., Harold W. Kroto and Richard E. Smalley discover buckminsterfullerenes (buckyballs), which measure 0.7 nanometer in diameter.

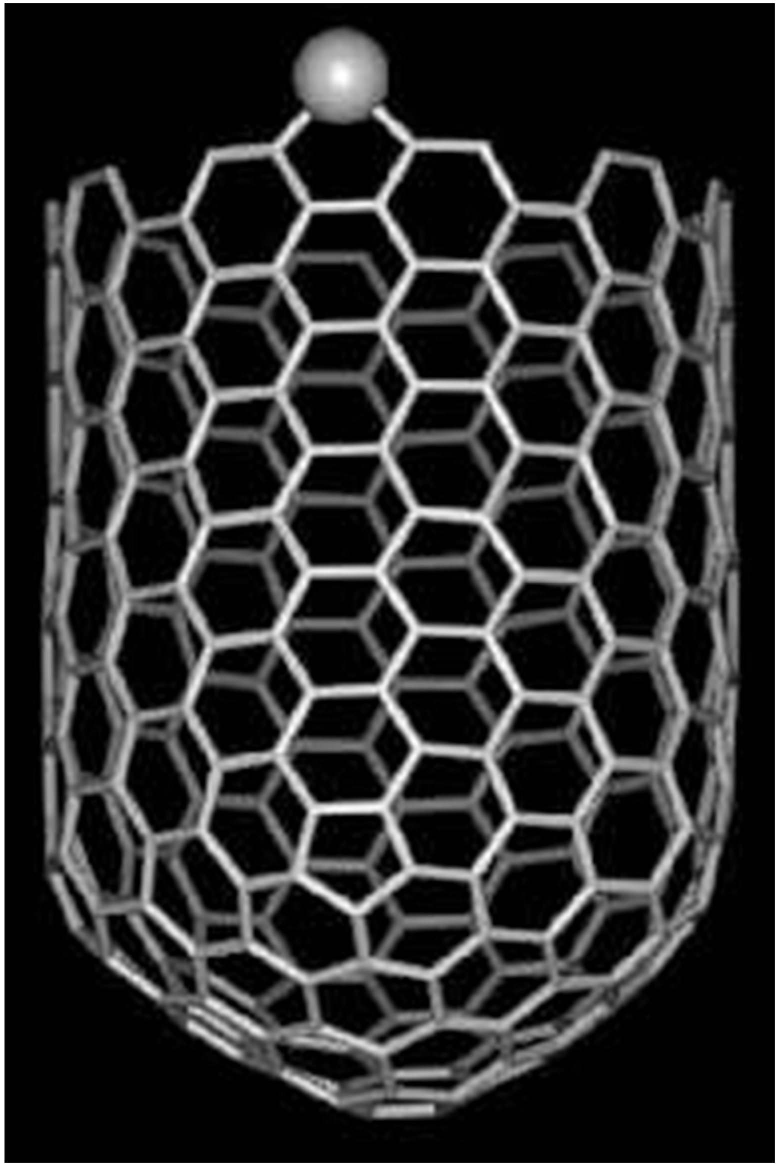
1991: Sumio Iijima of NEC discovers carbon nanotubes.

1998: Cees Dekker's research group at the Delft University of Technology creates a transistor from a single molecule (carbon nanotube).

2004: Geim and Novoselov discover graphene.

Carbon Nanotube

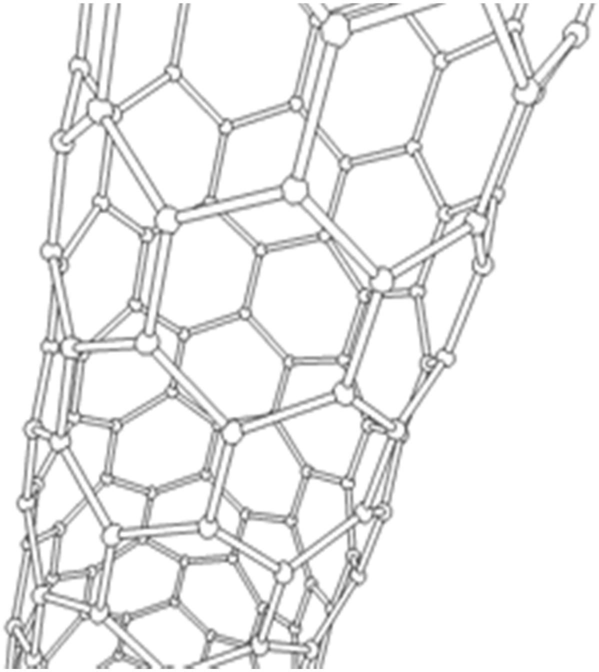




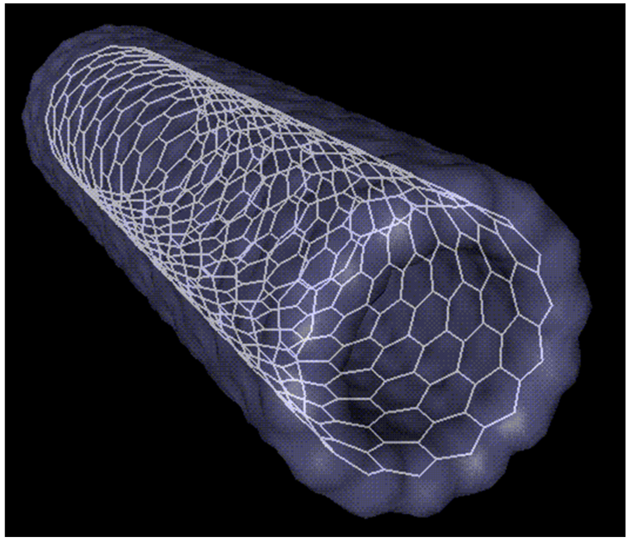
Sumio Iijima (1991)

What is the CNT?

- 탄소 나노튜브 (Carbon nanotube, CNT)



← SP^2 bonding
← Honeycomb structure
← Radius: less than 10 nm



Introduction

➢ Development stage

- 1985 Kroto와 Smalley – Fullerene (C60) 발견
- 1991 Iijima박사 – 탄소나노튜브 발견
- 1992 Ebbesen Ajayan – 전기방전법으로 탄소나노튜브 합성
- 1993 IBM의 Bethune와 Iijima 박사

  – 1nm 수준의 단중벽 나노튜브 합성
- 1996 Smalley

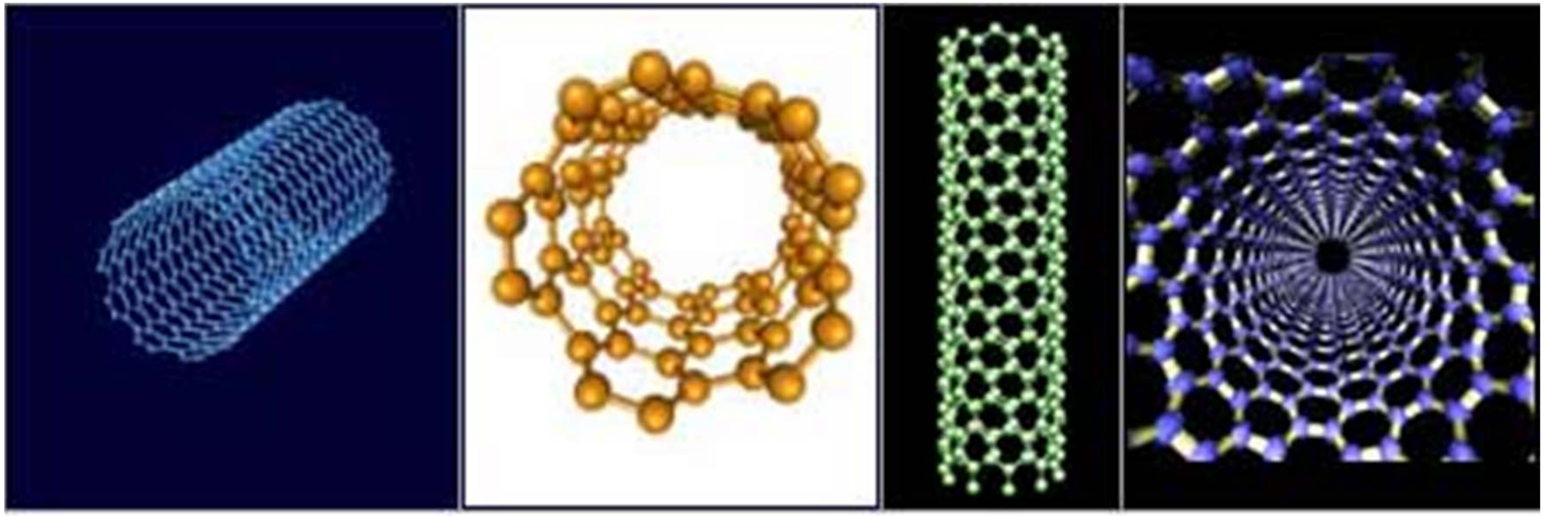
  – 레이저 증착법: SWNT를 고수율로 성장
- 1998 Ren

  – 플라즈마 화학기상증착법

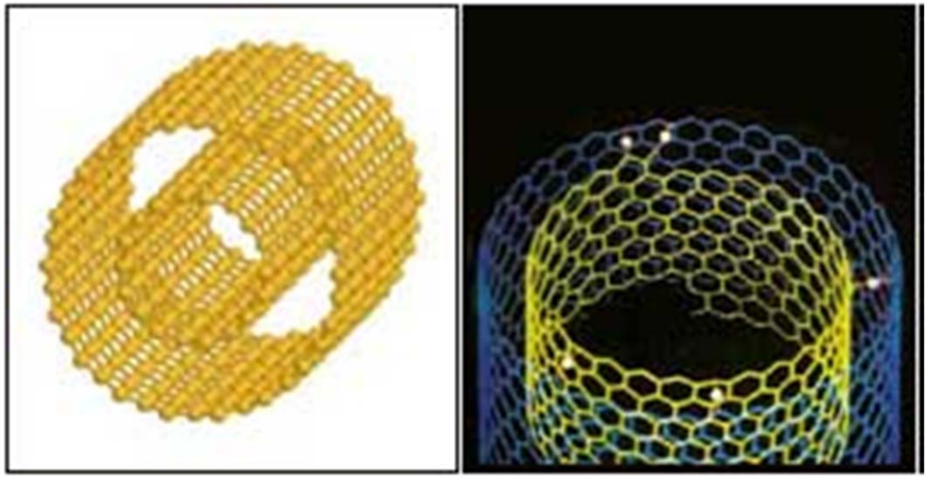
  – Glass위에 고순도의 탄소나노튜브 합성

Various forms – by depending on number

(1) Single-walled Carbon Nanotube(SWCNT)

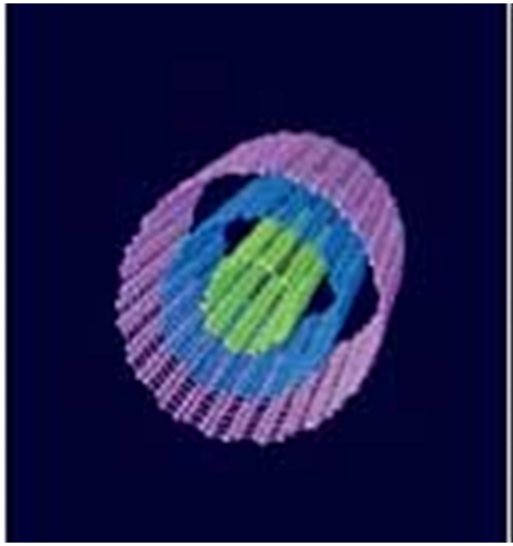


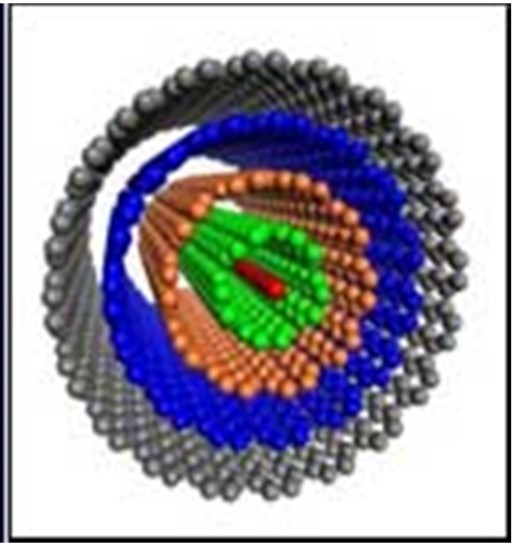
(2) Double-walled Carbon Nanotube(DWCNT)



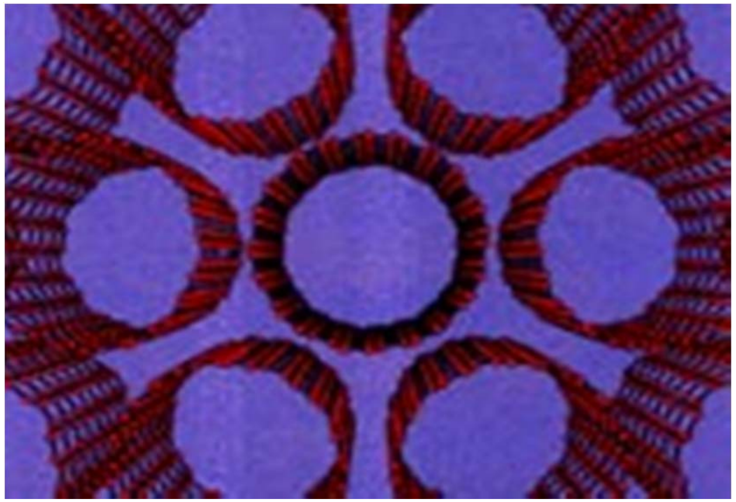
Various forms – by depending on number

(3) Multi-walled Nanotube(MWCNT)





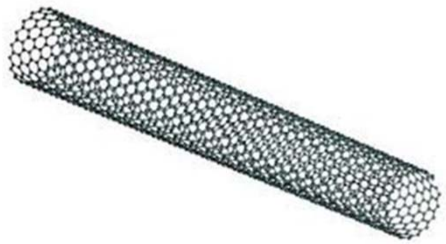
(4) Rope carbon Nanotube



Basic Properties of CNT

➢ Physical Property

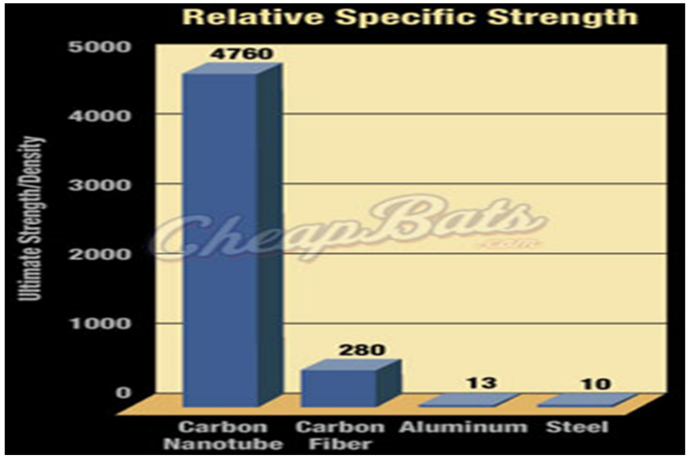
Tensile strength = 30 ~ 180 GPa



VS

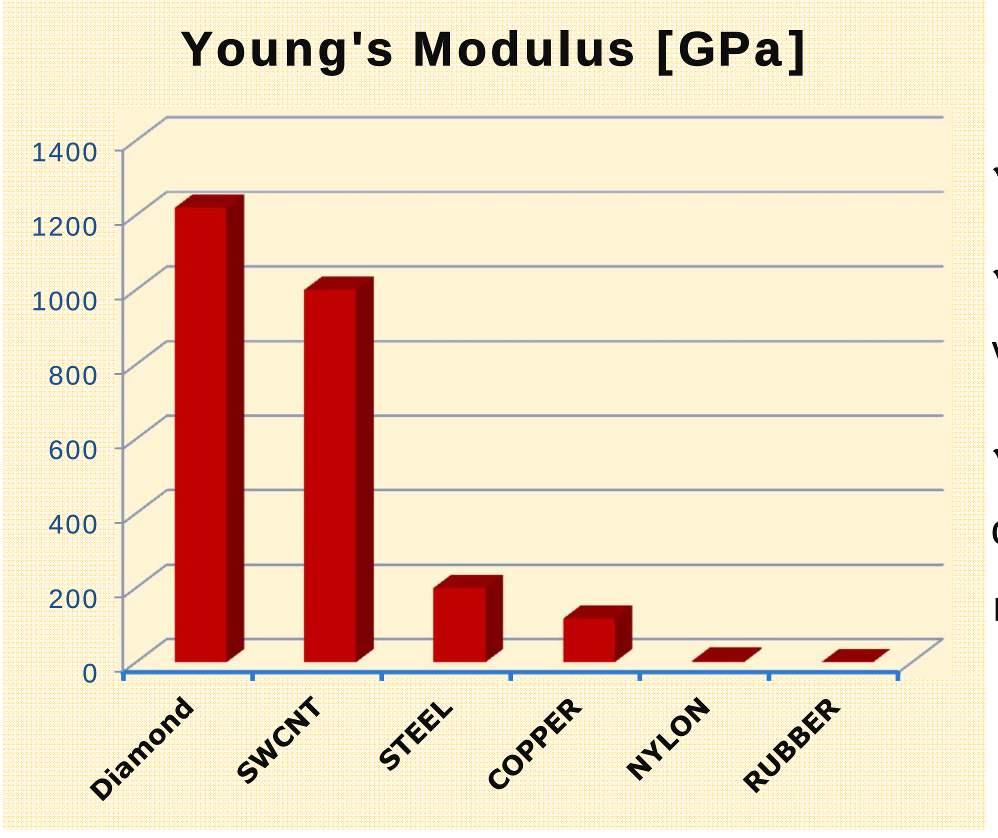
1.5 GPa

Strong Covalent bonding between Carbon atoms



Basic Properties of CNT

➢ Physical Property

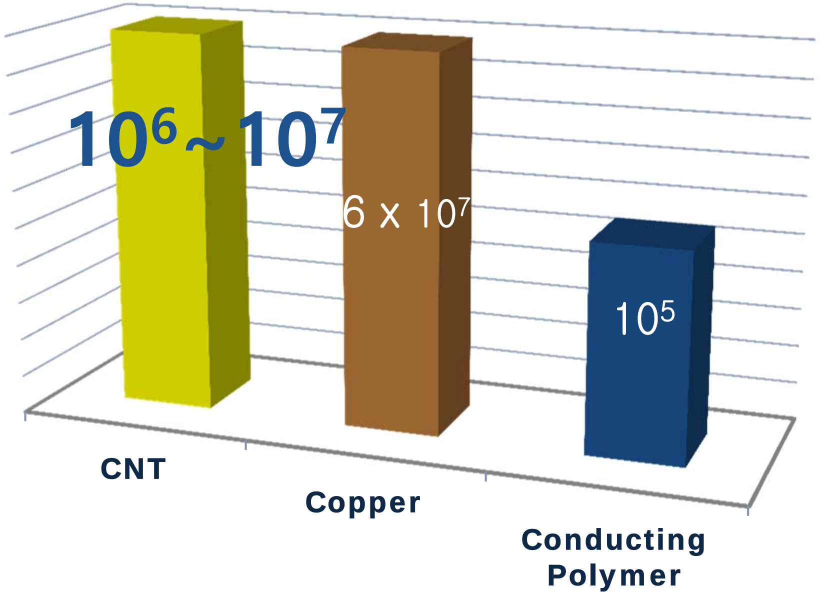


- ✓ Extremely High Young`s modulus
- ✓ Thermal stability in 2800°C in vacuum.
- ✓ Similar value of Tensile strength of Diamond (60GPa) but, light material

Basic Properties of CNT

➢ Electrical Property

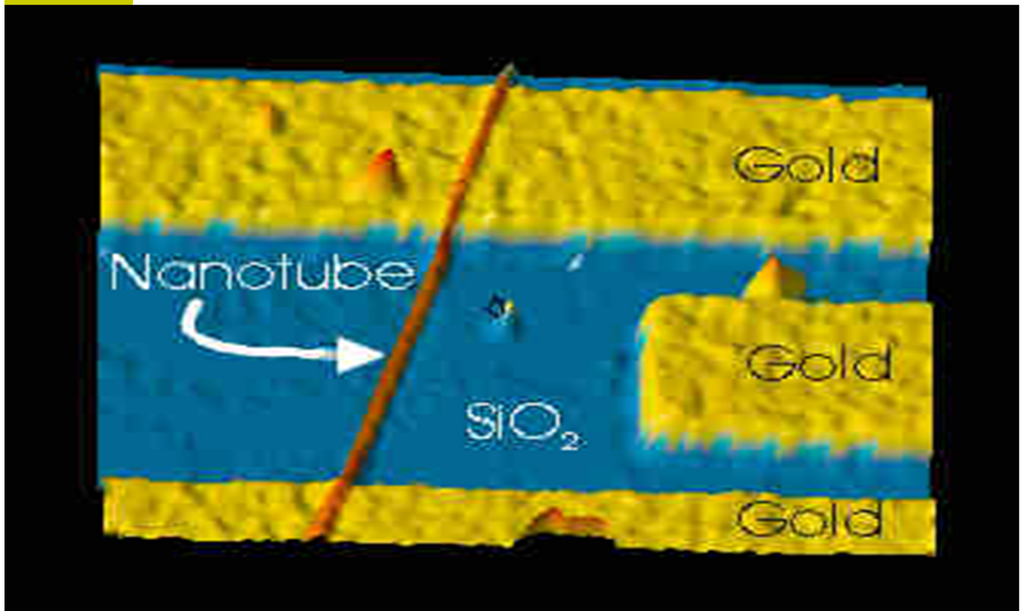
Electrical conductivity

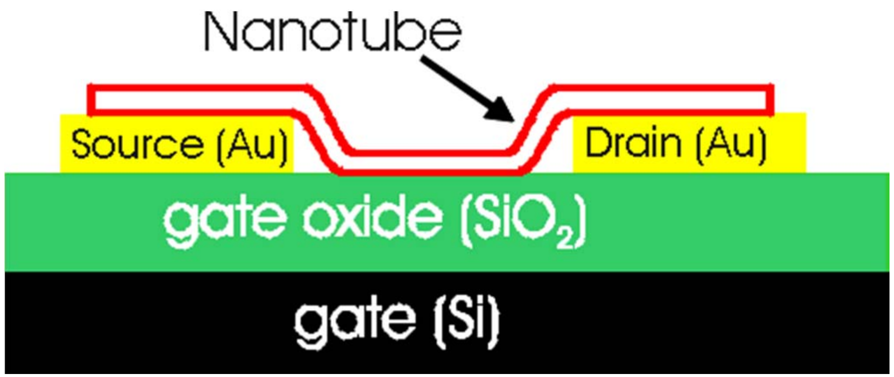


- ✓ High electrical/thermal conductivity
- ✓ High Sensitivity of external change of electric Field

Carbon Nanotube Transistor

1998: Cees Dekker's research group at the Delft University of Technology creates a transistor from a single molecule (carbon nanotube).

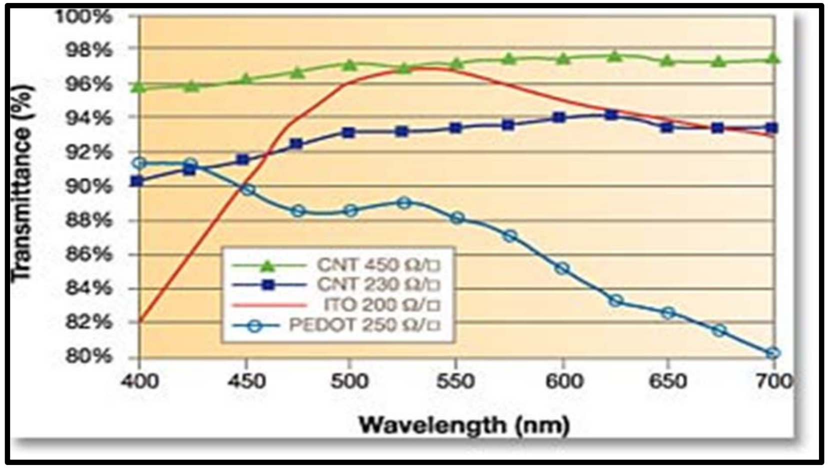




나노 트렌지스터: 나노물질을 이용해서 처음으로 트랜지스터를 만든게 바로 나노튜브를 이용해서 임.
mobility 가 굉장히 높아서 고속 동작이 가능함.

Basic Properties of CNT

➢ Optical Property



〈표 2〉 SWCNT을 이용한 투명전도성 박막의 물성

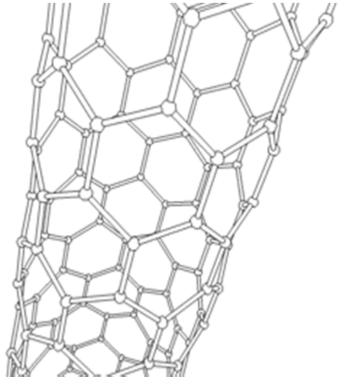
Transparent conductive films		Surface resistivity (Ω/□)	Conductivity (S/cm)	Average visible light transmittance
SWCNT films fabricated from the surfactant-assisted wet-coating approach	Using acid-treated CVD-SWCNT	6 k	16.6	88%
	Using as-received CVD-SWCNT	18 k	5.5	85%
	Using laser-SWCNT	1 k	50	85%
Filtrated pure SWCNT thin films	HiPCo SWCNT	1~1.5 k	N/A	85%
	Laser-SWCNT	30	6,600	70%

- ✓ 파장이 변해도 일정한 투과율
- ✓ 낮은 면저항, 높은 투과도

  → 투명전극으로 기준을 만족
- ✓ 코팅면적에 제한이 없음
- ✓ 계면 접착력 우수
- ✓ 각도에 따라 면저항 유지

Carbon NanoTube ……

So what?



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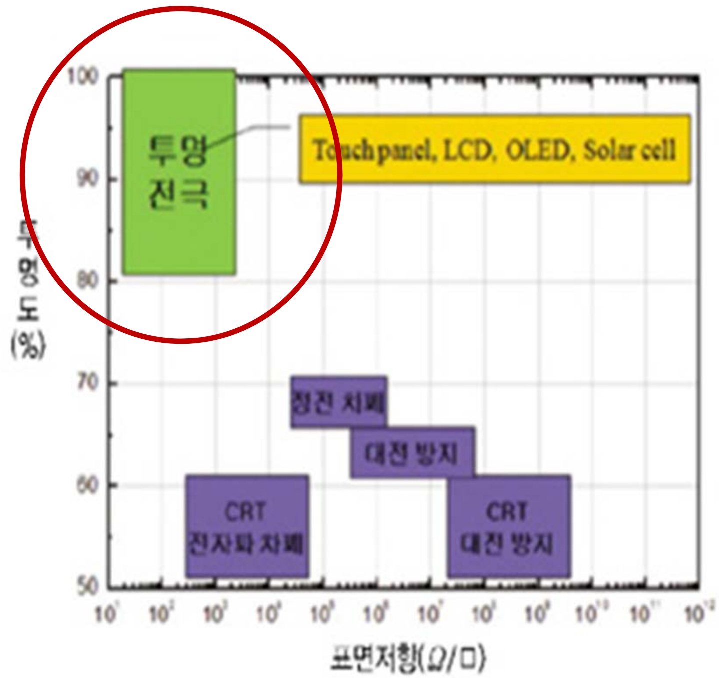
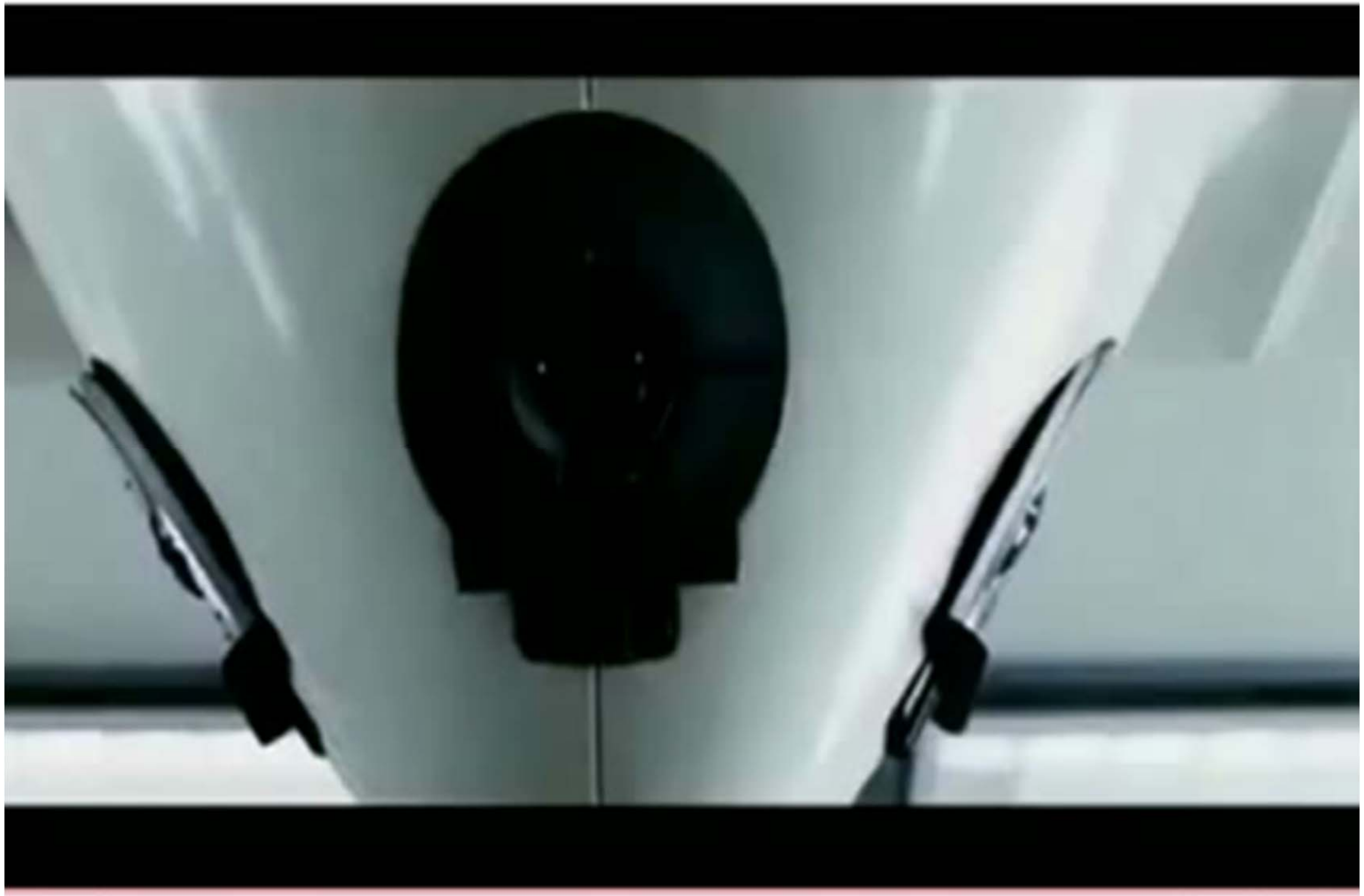
Application – Transparent Electrode

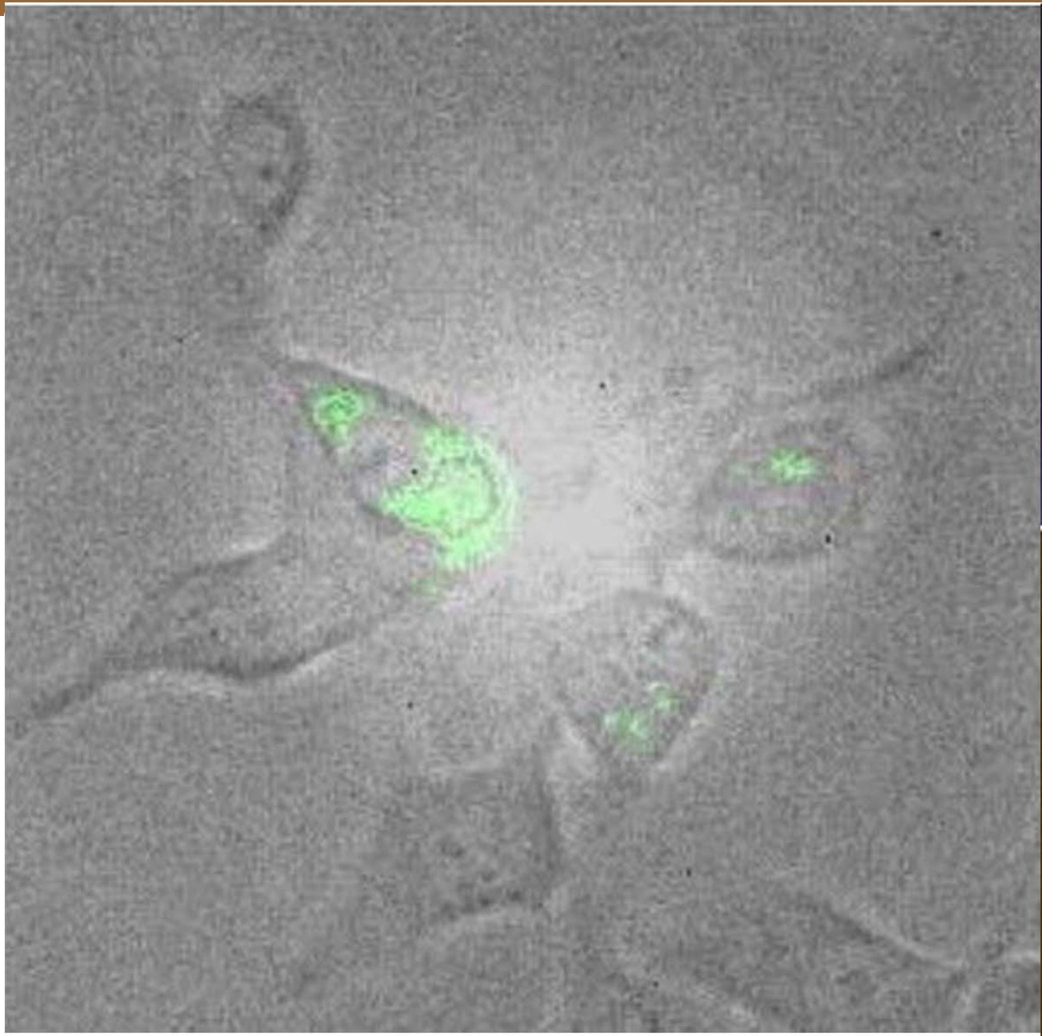
➢ Optical & Electrical Property



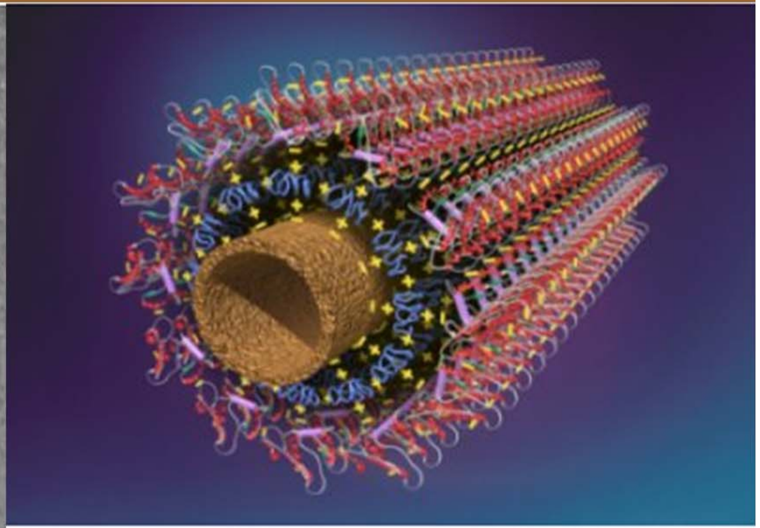
Application – Electronic Paper

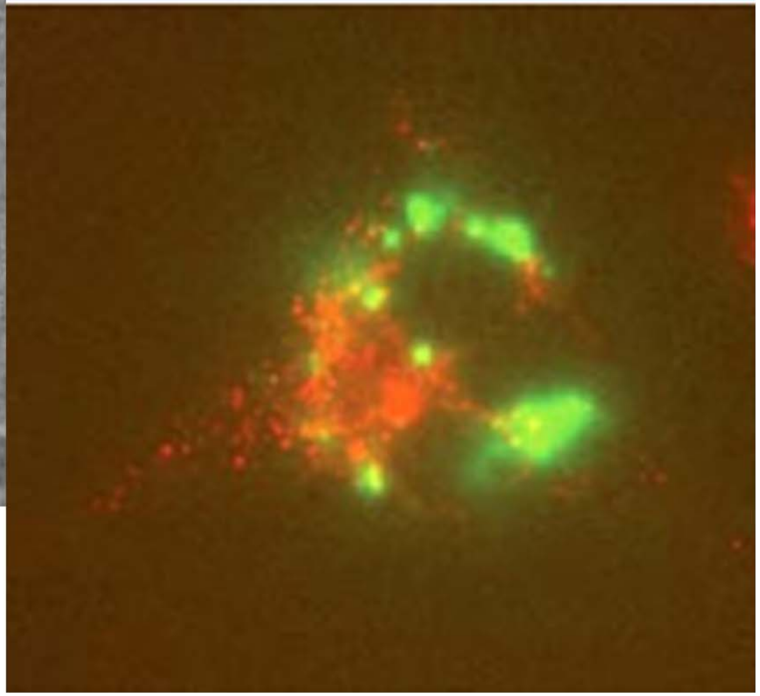


Application - CNT BIO SENSOR



Heller, Daniel A, multimodal optical sensing and analyte specificity using single walled carbon nanotubes, Nature techonology, 2008





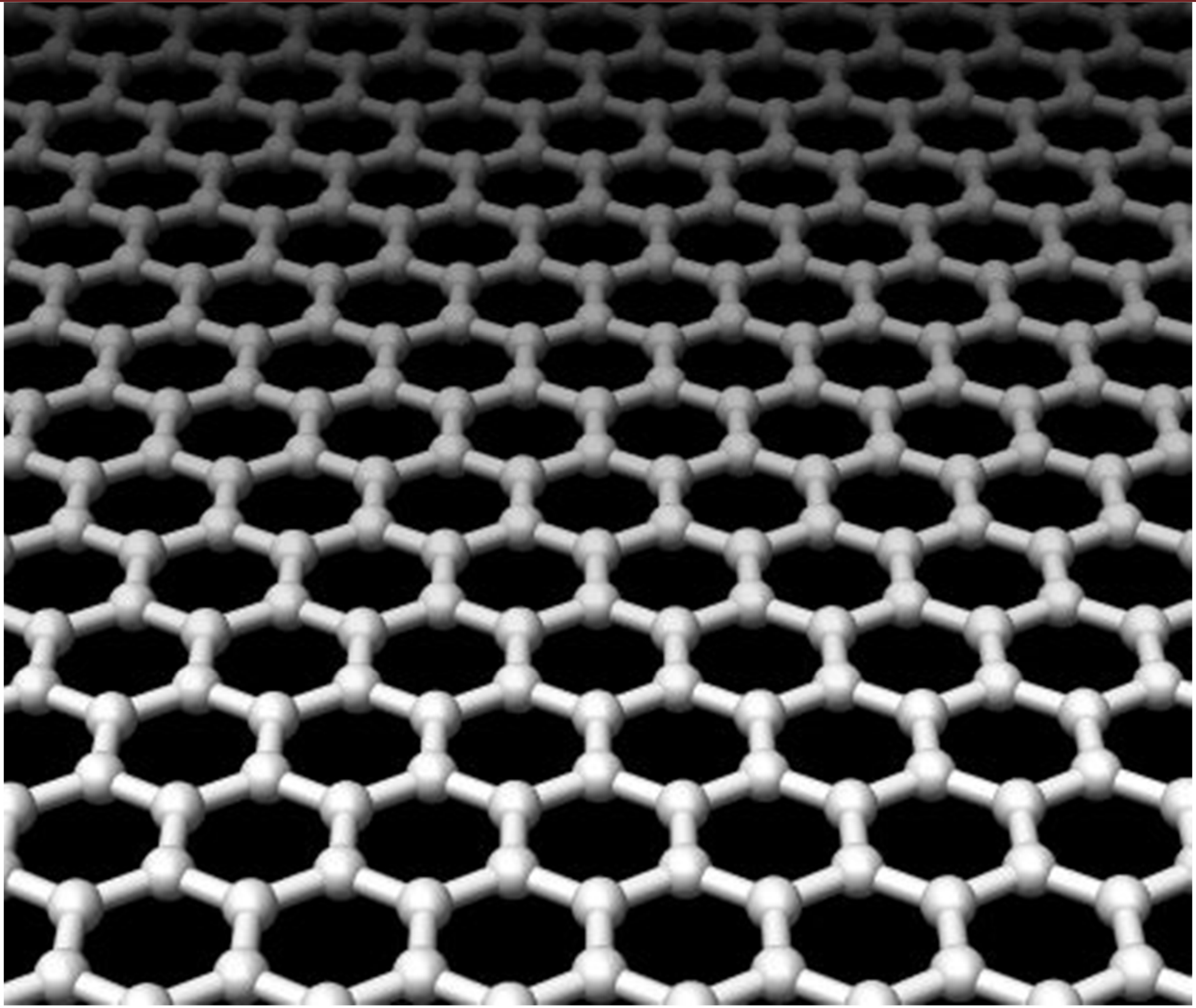
Science Fiction or Not??????

Application - Space Elevator

진짜???

헉!!!!!!!!!

Graphene



Discovery of graphene

' What is the thinnest substance in the world? '

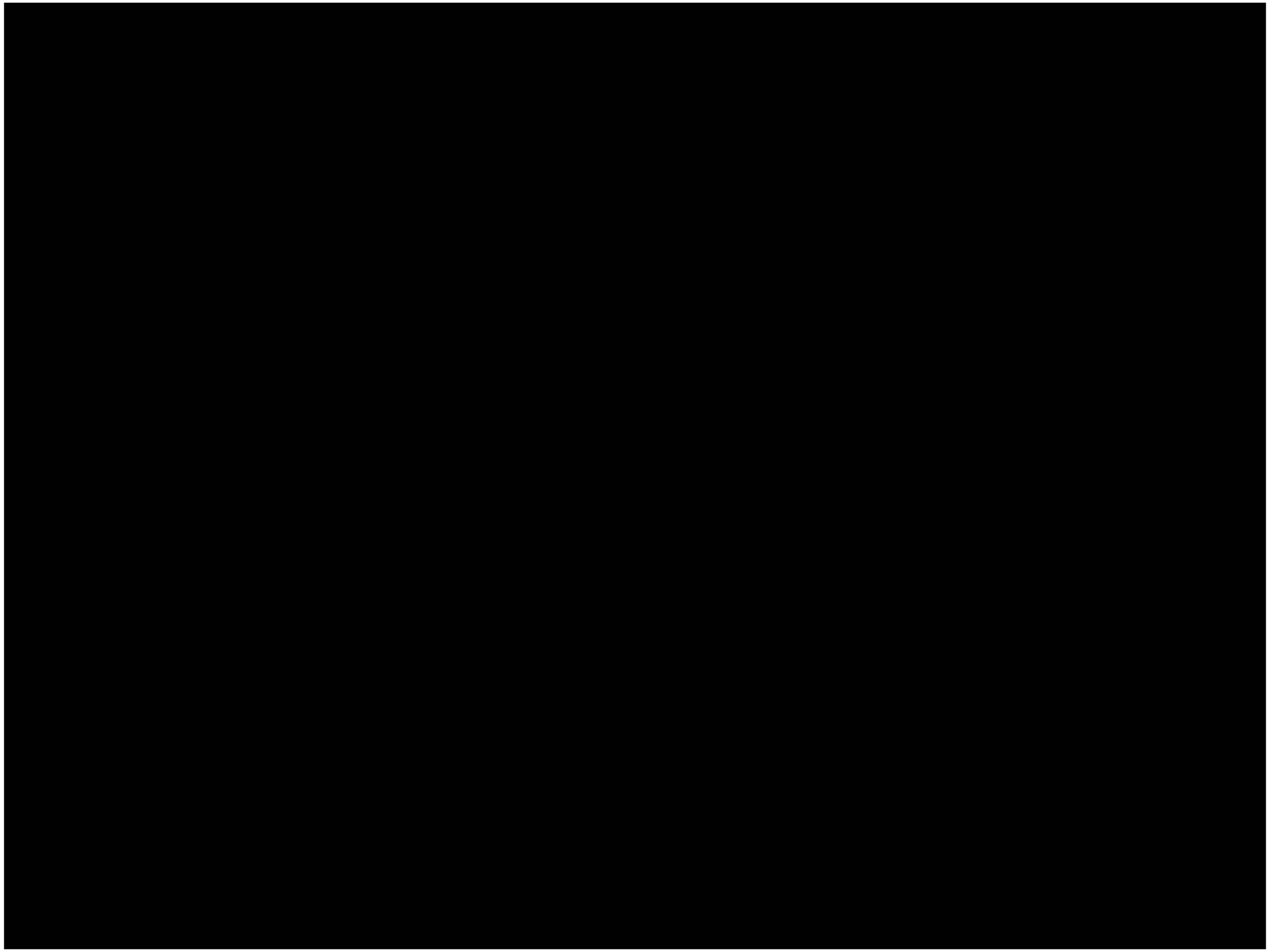
< Dr. Constantin Novoselov >

'Friday night's quirky experiment'

In 2004, Professor Andrew Gam of Manchester found a way to separate the graphene layer from graphite and published it in "Science".

http://www.youtube.com/watch?v=rphiCdR68TE

Discovery of graphene



Discovery of graphene

In 2005, “Nature”

Demonstration of a semi-quantum Hall effect

Because of the spin effect of the electron, it should show the same half-life (n + 1/2) as if the electron split.

The effective mass of electrons and holes approaches zero and the charge carrier moves closer to the speed of light

Graphene has the potential to be used as a new concept device that overcomes limitations of conventional semiconductors.

- 2-D mater. is thermodynamically unstable
- Can not exist in a natural form
- It has a low melting point.

Before 2004

- Single layer graphene is very stable.
- Superior crystallinity
- It matches the theoretical predictions.

2004

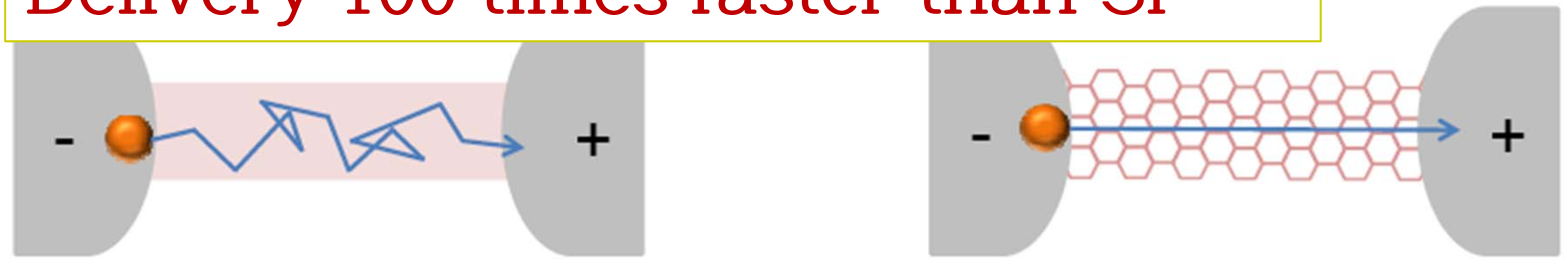
- amazing properties of graphene
- Increased interest in graphene research

After 2004

Characteristics of graphene

High electron Mobility

At room temp.
100 times more current than Cu
Delivery 100 times faster than Si



Characteristics of graphene

High thermal conductivity

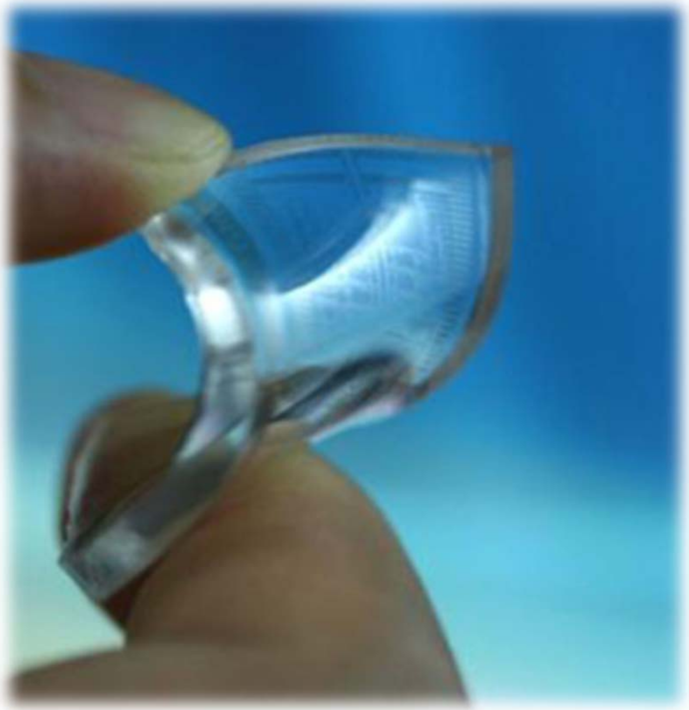
- More than double the diamonds

Mechanical Strength

- More than 200 times of steel

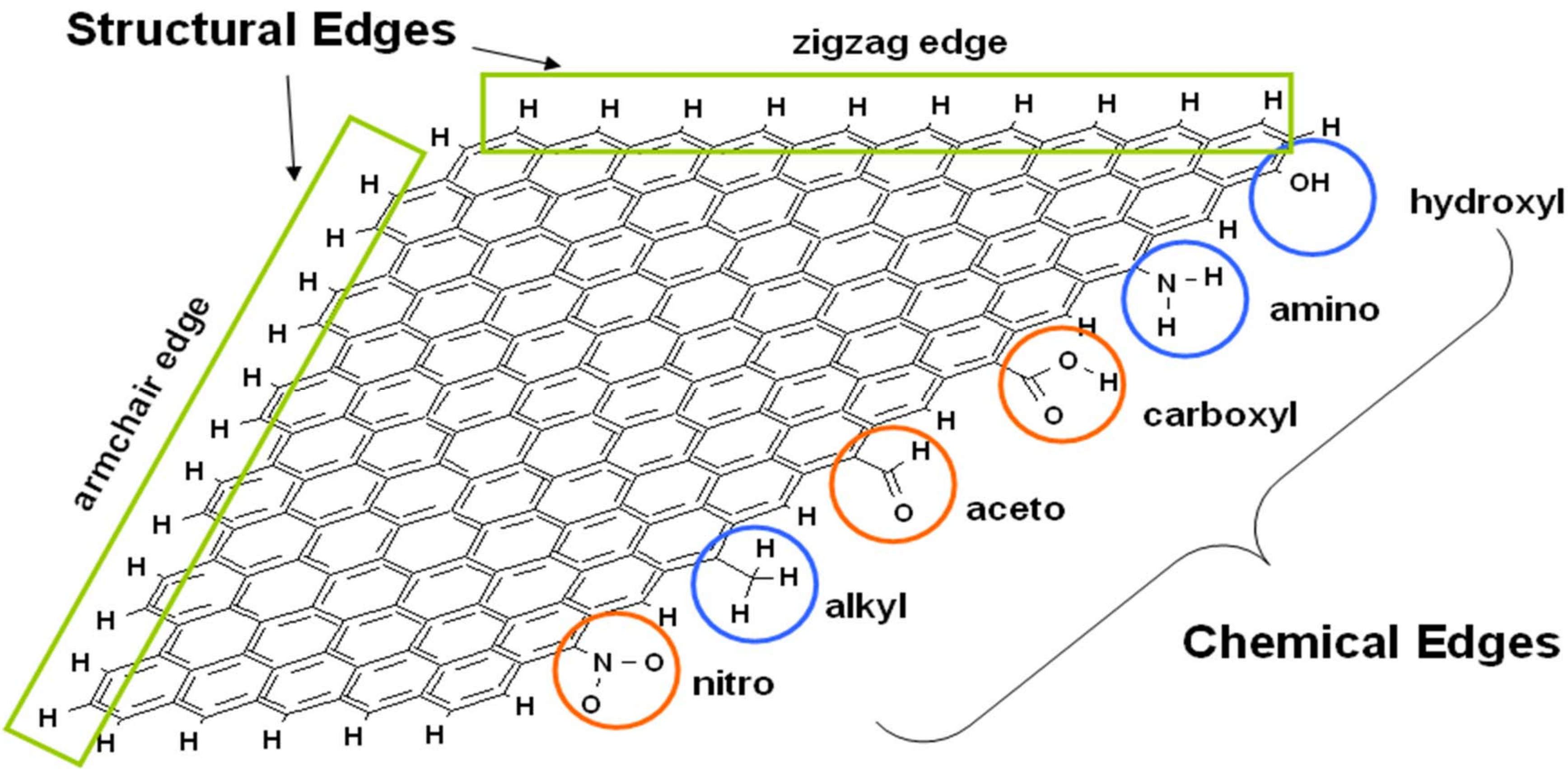
High Flexibility

- Honeycomb structure connected like a net / Spacious space improves elasticity



< A 10x10cm graphene made by Prof. Hong Byung-hee's group >

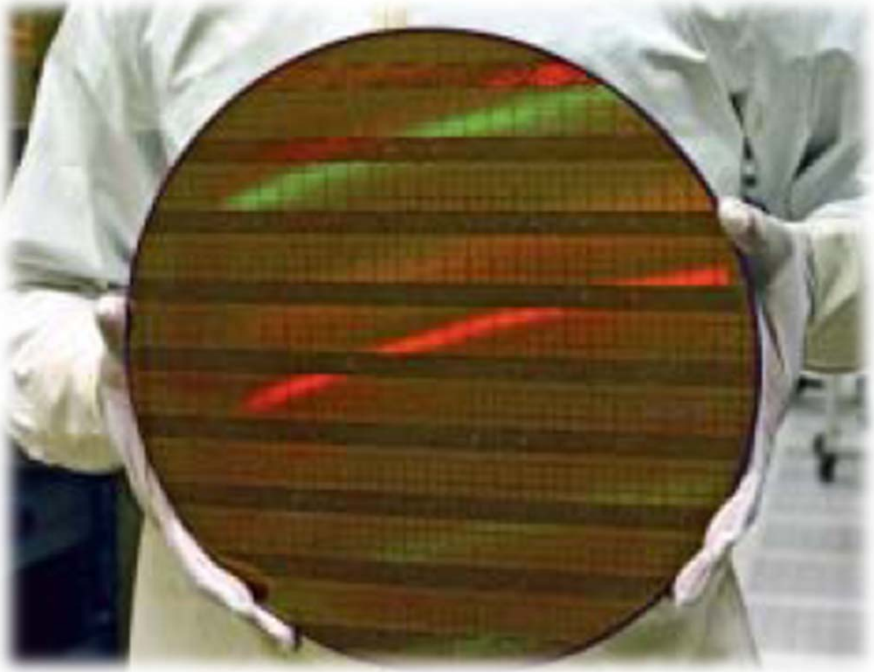
Characteristics of graphene



Zigzag shape → metallic **- electron withdrawing**

Armrest chair shape → semiconductor **- electron donating**

Characteristics of graphene



How do we use graphene for what we want?

Need graphene mass production technology & multi-layer graphene control technology!

Graphene Synthesis

- Chemical exfoliation of graphite through oxidation and then dispersion in water down to single graphene sheets

- Thermal exfoliation of graphite.

  - thermal decomposition method : semiconducting SiC substrate heated to over 1200°C until the silicon begins to evaporate, at which point the remaining carbon on top of the substrate nucleates into graphitic film

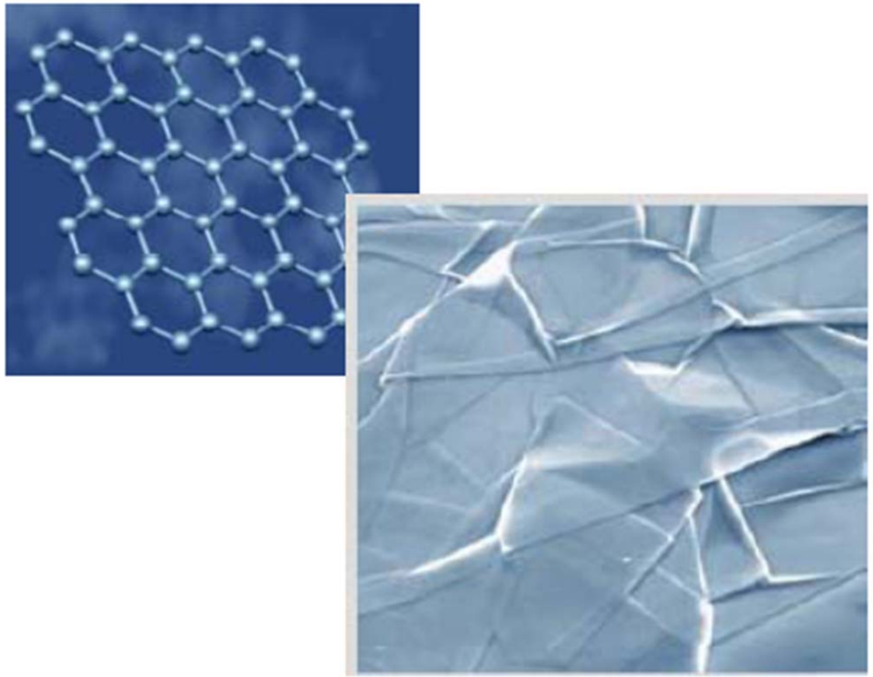
  - chemical vapor deposition (CVD) of hydrocarbons deposited on a metal substrate

- Liquid-phase exfoliation of graphite

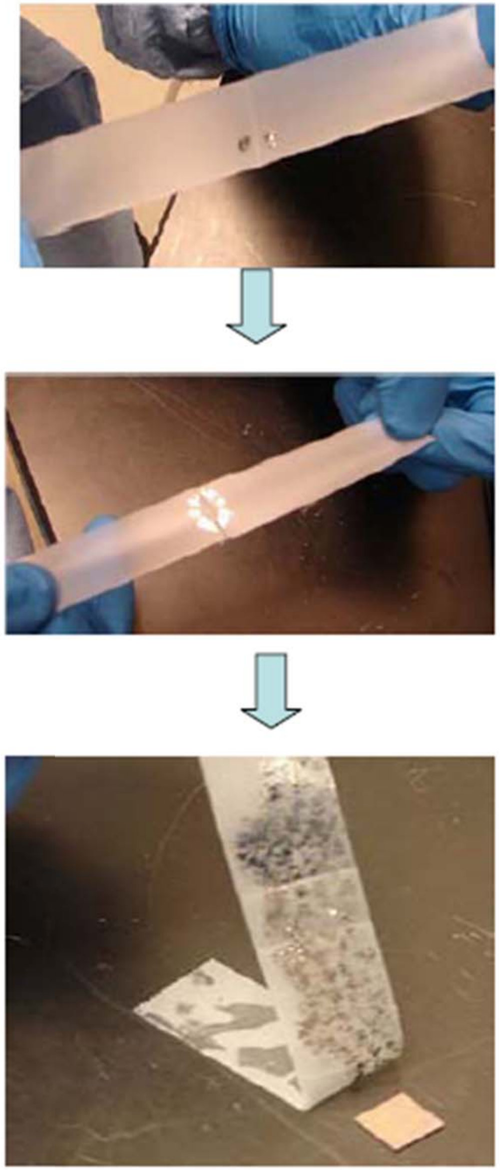
- Expandable graphite powders

Graphene Synthesis: Mechanical Cleavage

- **Mechanical cleavage is a research grade procedure**
- **Can extract single-atom-thick graphene from bulk graphite by using adhesive tape to repeatedly split graphite crystals into increasingly thinner pieces**



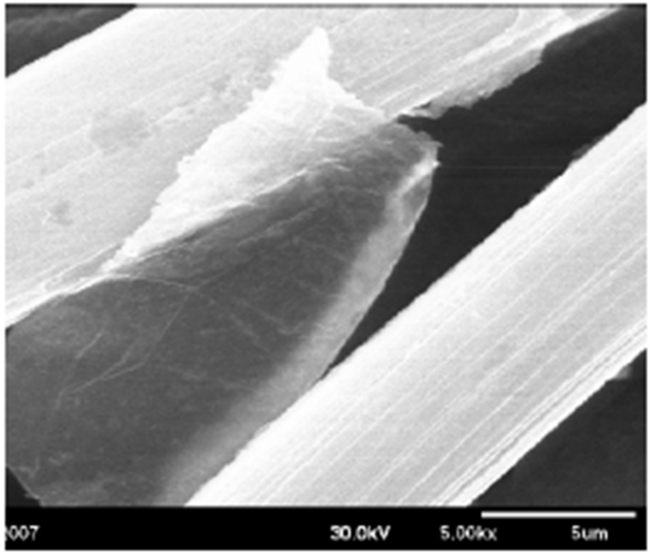
(d) Optical image

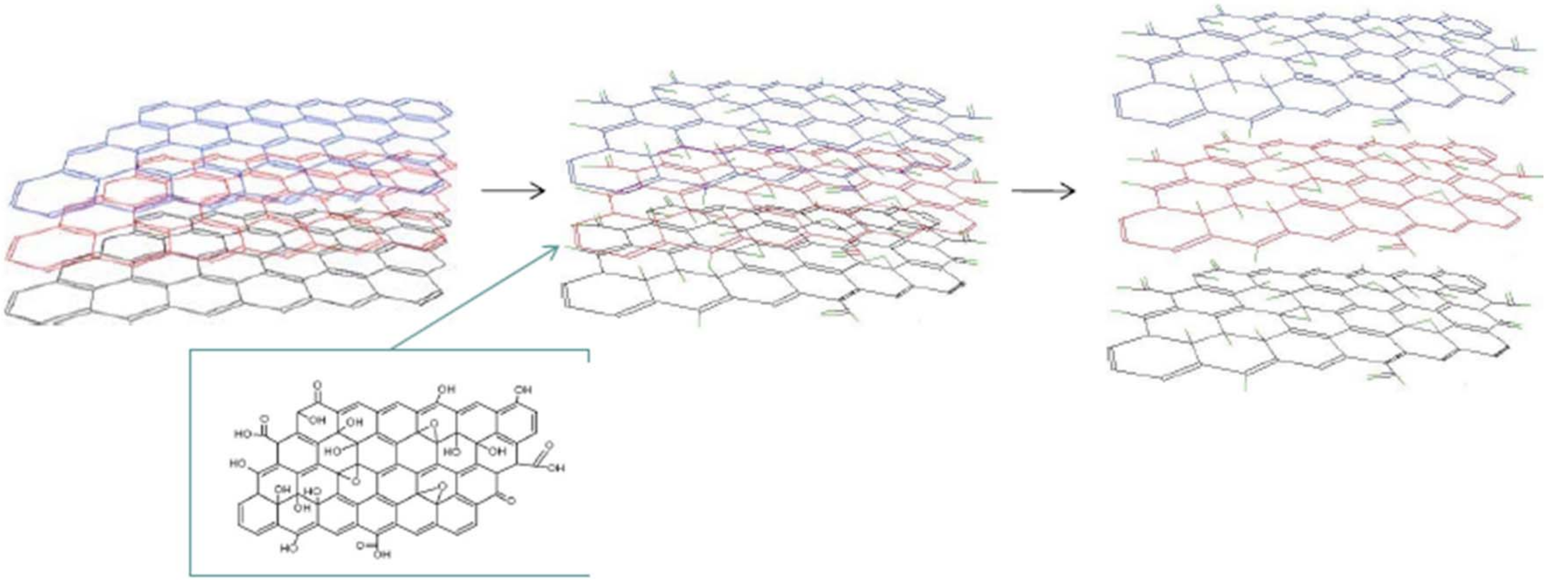


- No graphene of the desired size is possible.
- Difficulty adjusting thickness

Graphene Synthesis – Chemical Exfoliation

- Exfoliation of graphene sheets from graphite powder by chemical oxidation
- It consists in inserting molecules to graphite by chemical treatment to modify the van der Waals forces that hold the single monolayers of carbon together.
- NOT VERY SUCCESSFUL: only restacked and scrolled graphene sheets are obtained



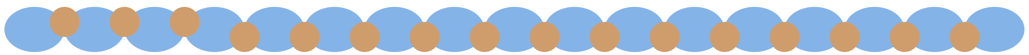


Graphene Synthesis – thermal decomposition

SiC heat treatment

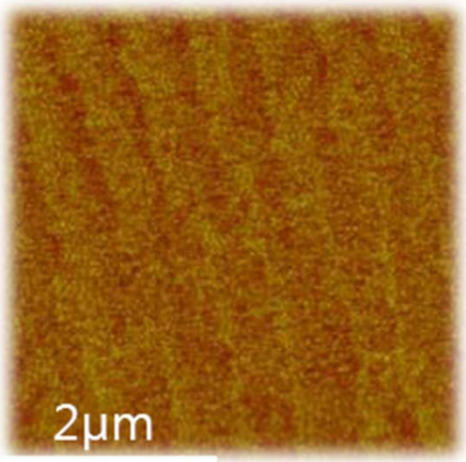
Si

Graphene layer



SiC

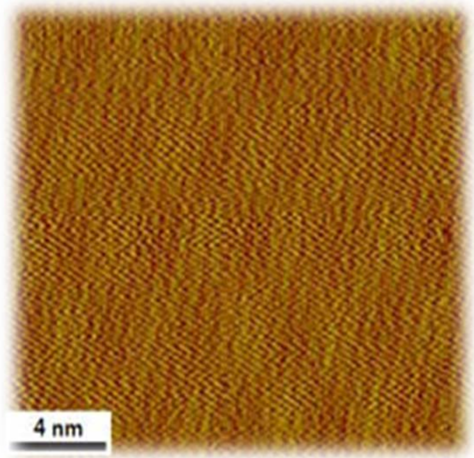
Poor electrical properties
Relatively expensive costs



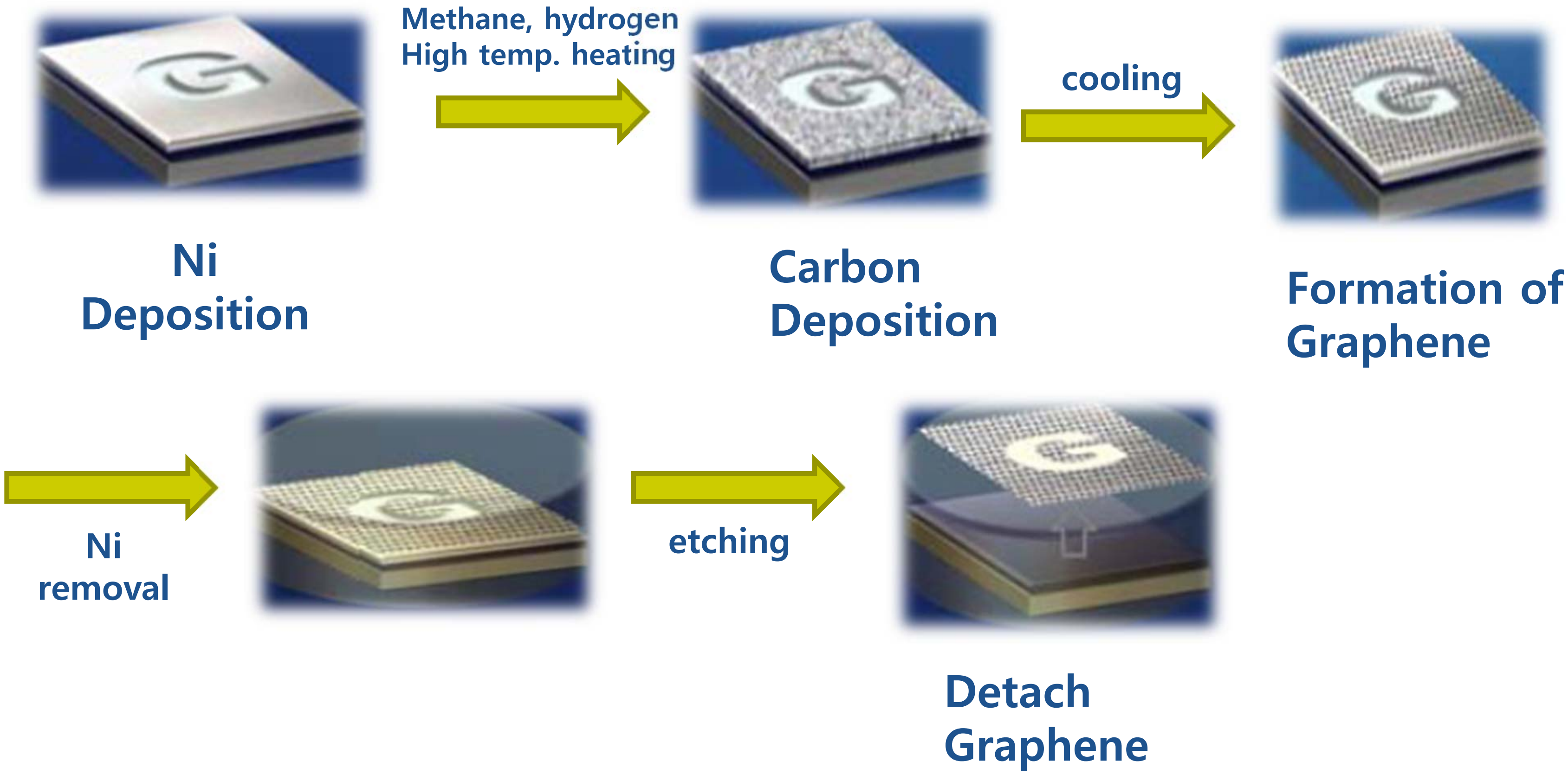
High vacuum

(2x 10^{-6} Torr)

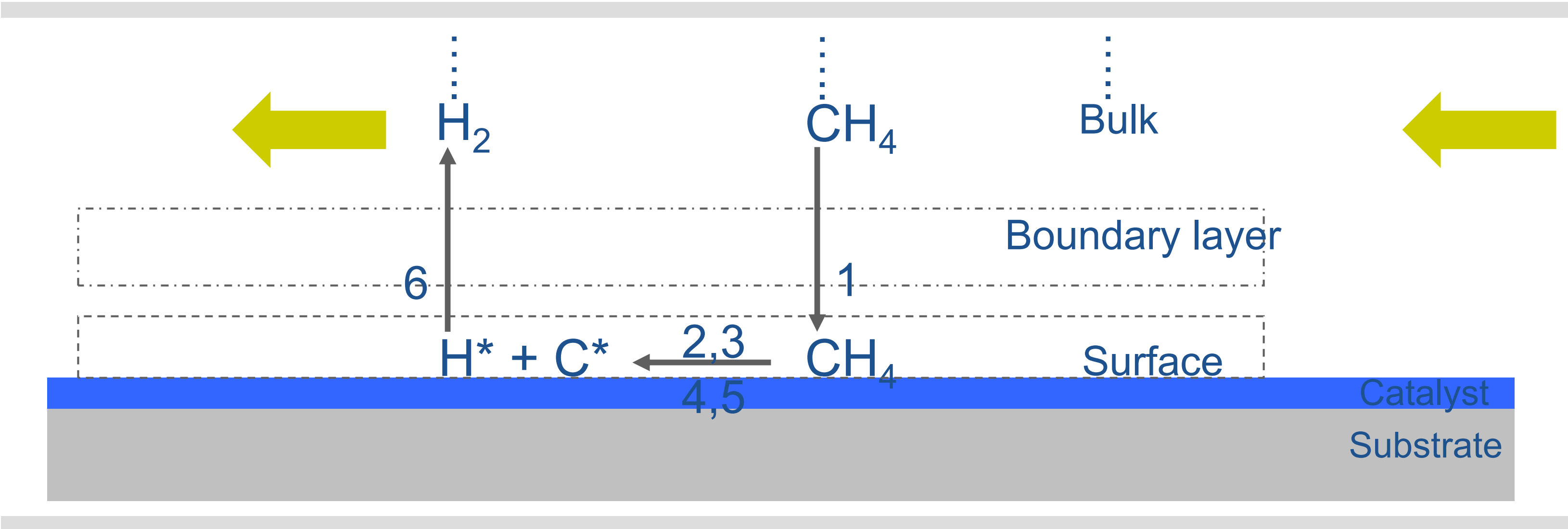
~1700K ~10 min



Graphene Synthesis – CVD Synthesis



Chemical Vapor Deposition



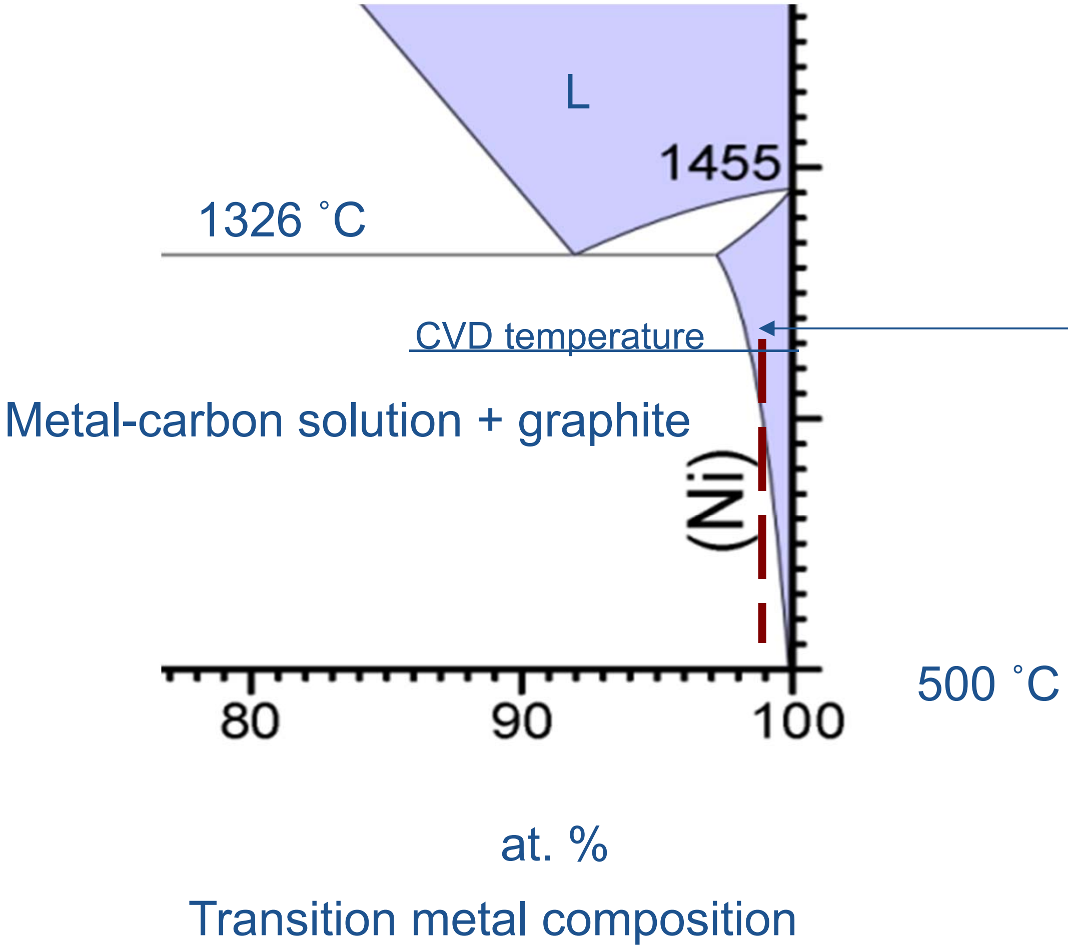
I Mass Transport controlled regime (diffusion through boundary layer)

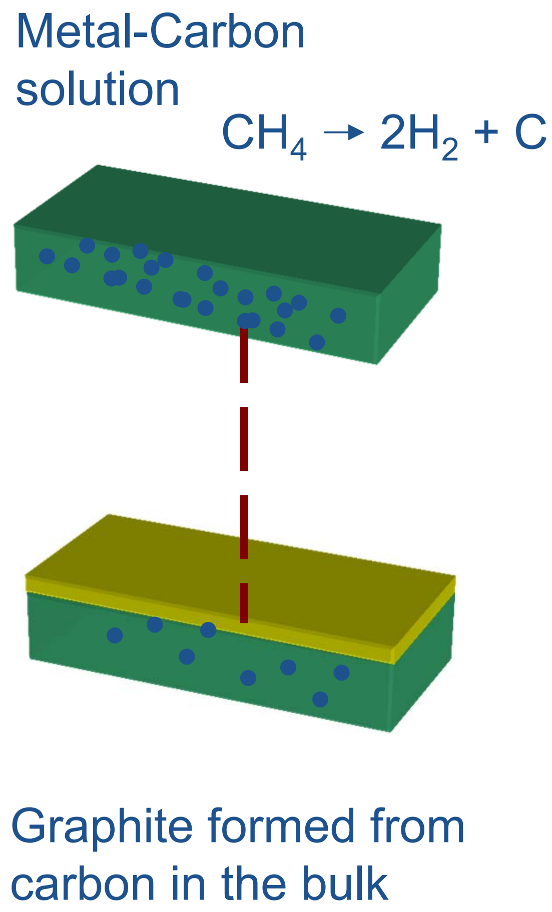
1. Diffusion of methane through the boundary layer
6. Diffusion of Hydrogen away from the surface through the boundary layer

II Surface reaction controlled regime (substrate temperature)

2. Adsorption of methane on surface
3. Decomposition of methane on surface
4. Diffusion of active carbon on the surface to form graphene/graphite
5. Desorption of hydrogen

Carbon Segregation from Nickel



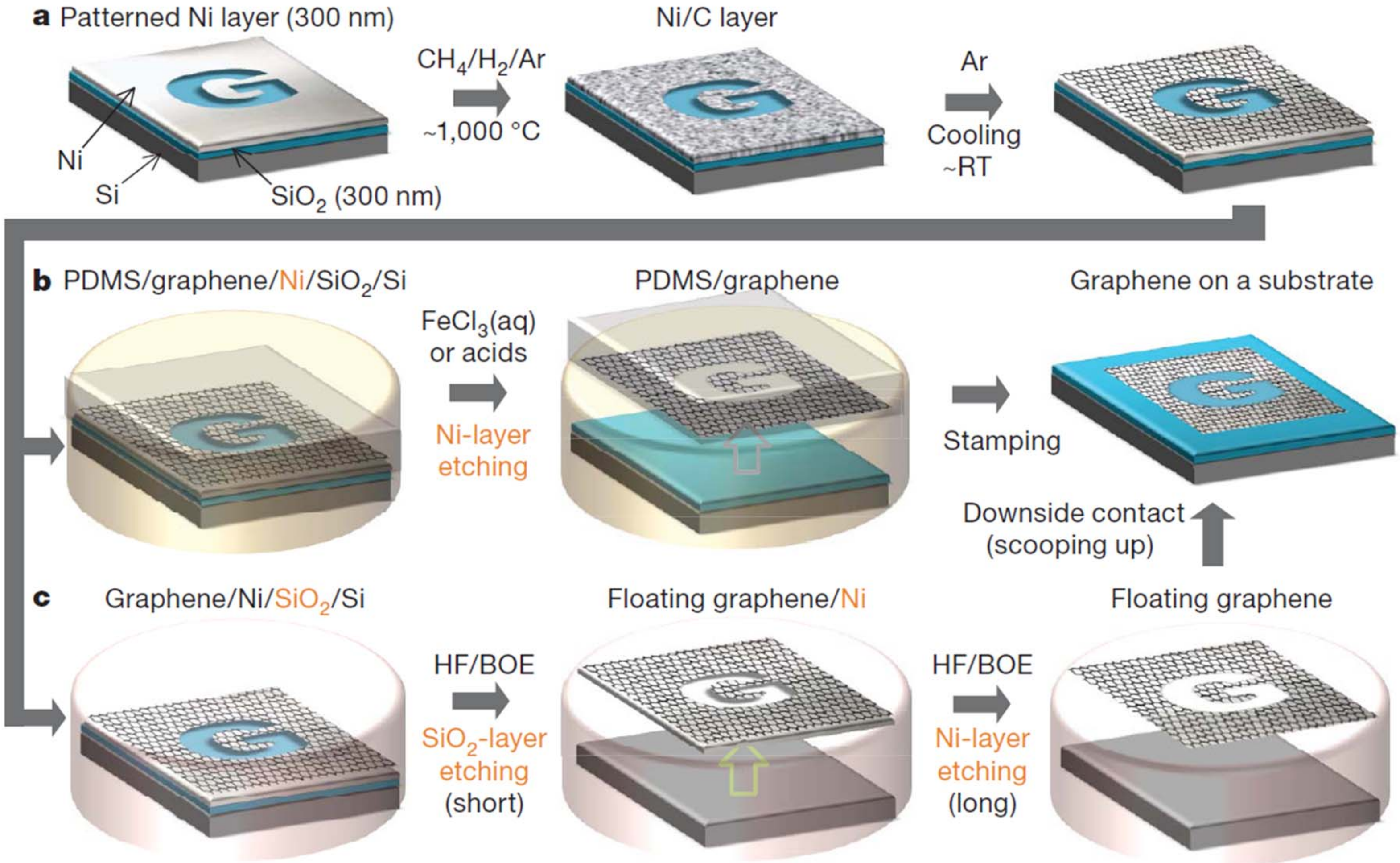


there is finite solubility (1-2%) of carbon inside the Ni

Singleton M.F., and Nash P., C-Ni (Carbon-Nickel), Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski, Vol. 1, 1990, p 866

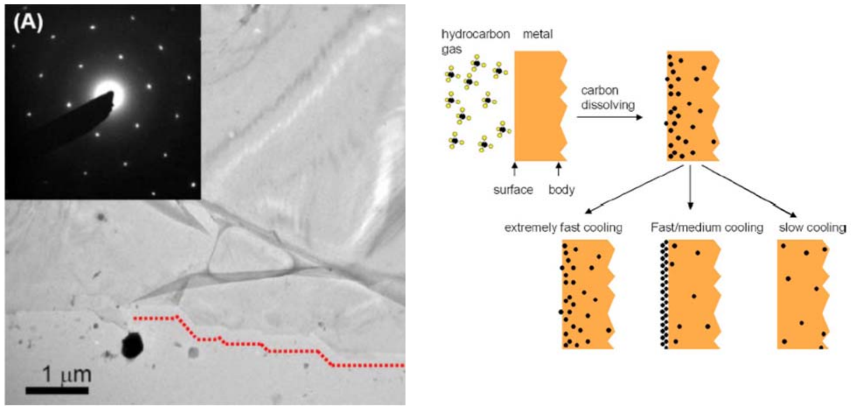
Graphene Synthesis – CVD Synthesis

Synthesis, etching and transfer processes
for the large-scale, patterned graphene films

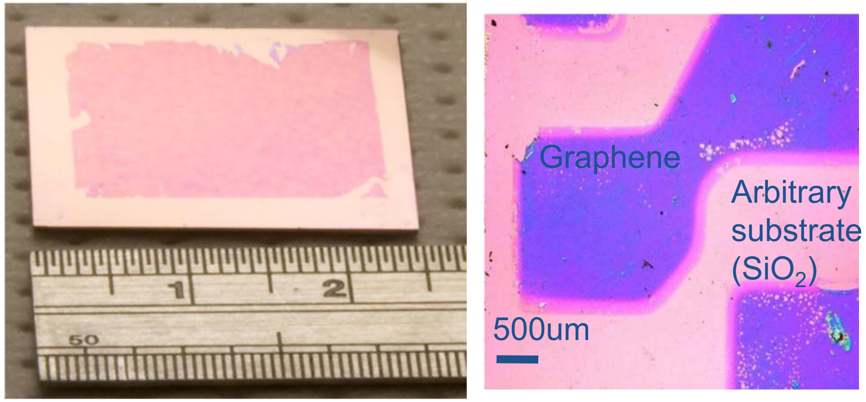


K. Kim et al, *Nature* 2009, 457, 706

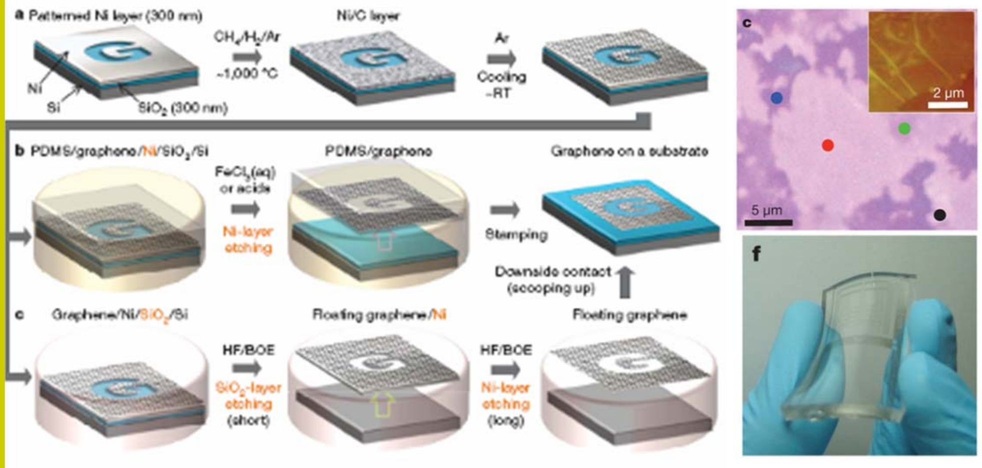
Graphene by carbon segregation enabled by APCVD



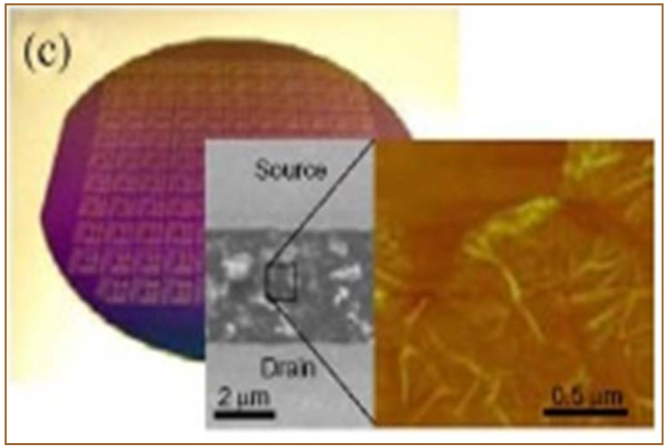
Q. Yu et al, *APL* 2008, 93, (11) 113103-3



A. Reina et al., *Nano Letters* 2009, 9, (1), 30



K. Kim et al, *Nature* 2009, 457, 706



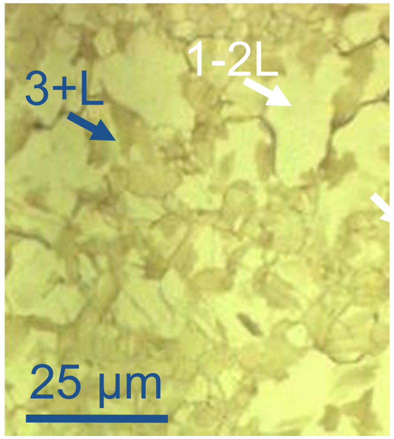
L. Gomez De Arco, et.al., *IEEE Trans. Nano*, 8, 135, (2009)

Controlling graphite precipitation on Ni

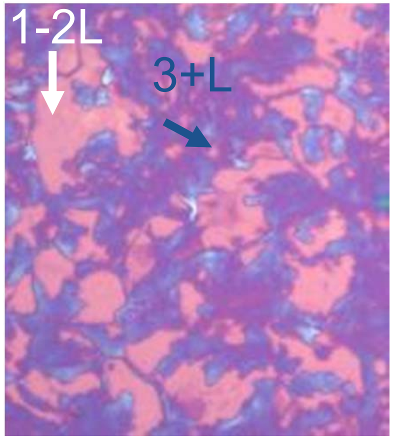
Cooling rate

Fast segregation (150 ˚C/min)

On Ni

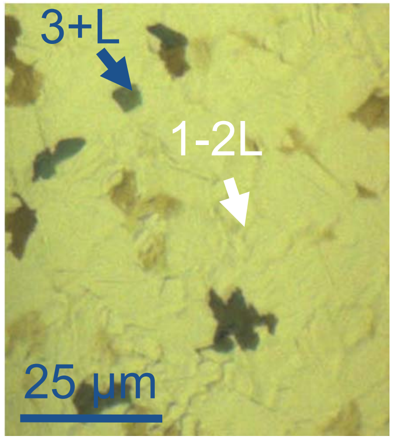


On SiO_2/Si

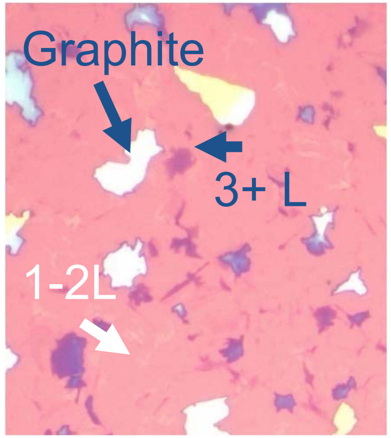


Slow segregation (4-10 ˚C/min)

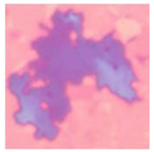
On Ni



On SiO_2/Si



1-2 LG = 1 to 2 graphene layers



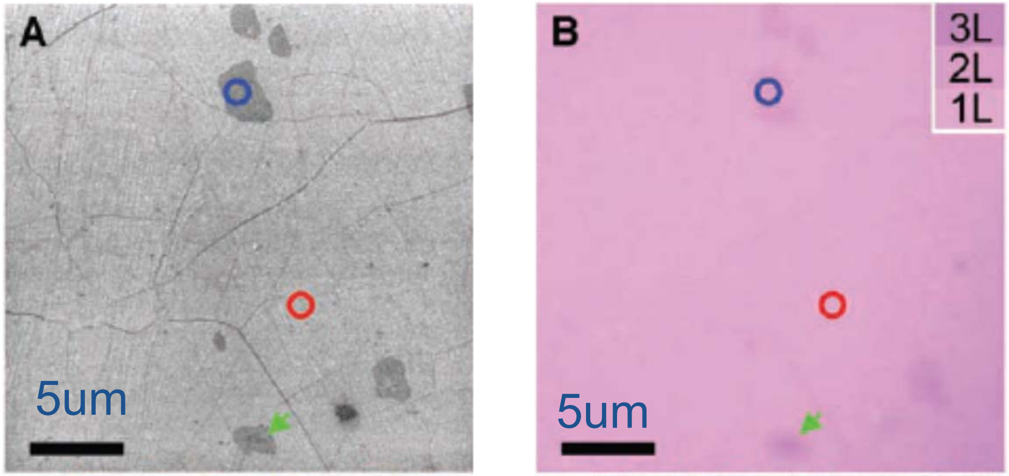
3+ LG = 3 or more graphene layers

A. Reina et. al., Nano Research, 2009

Non-carbon segregation growth of graphene by CVD on Cu

As grown on Cu

Transferred to SiO_2



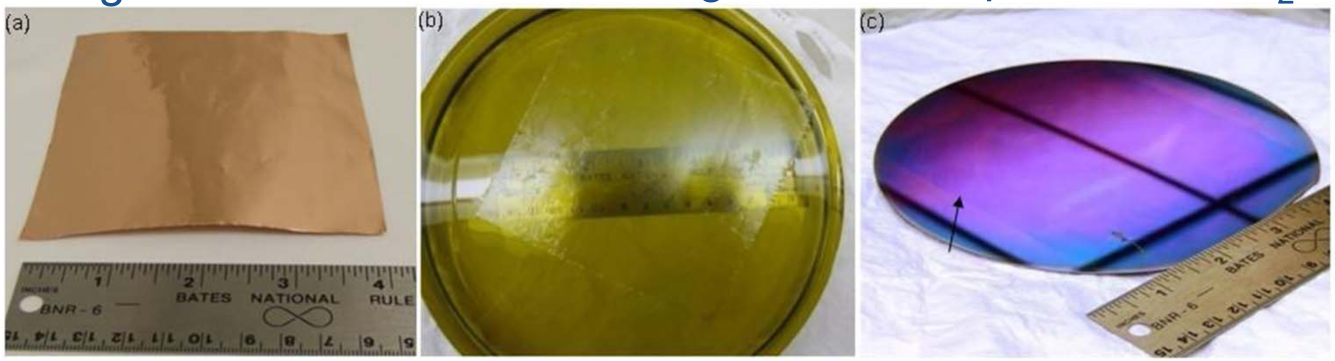
X. Li et. al., Science, 324, 1312 2009

Process yields 95 % monolayer coverage

As grown on Cu

Foil etching

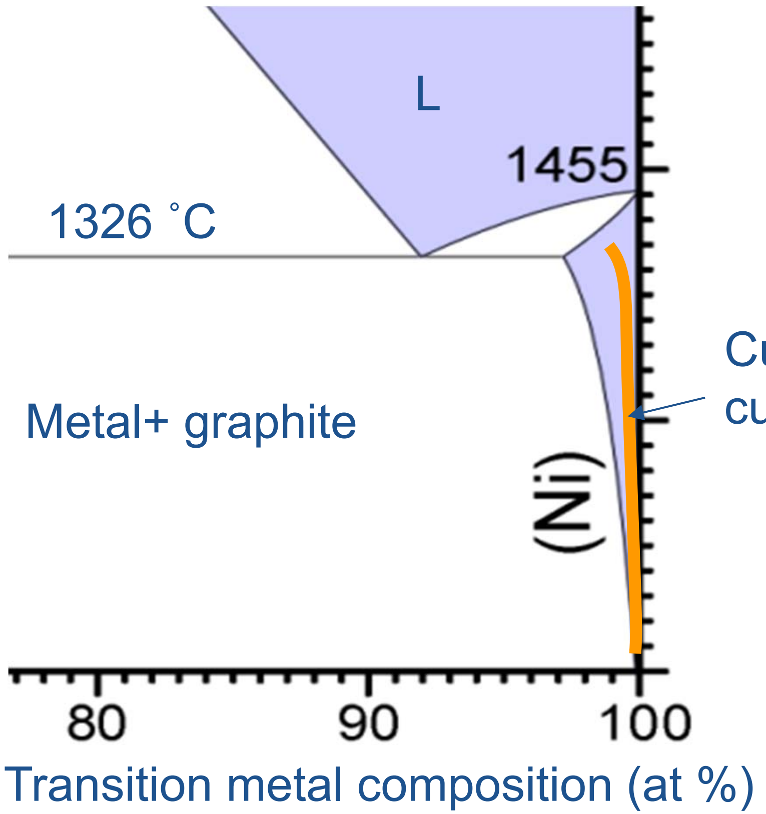
Graphene on SiO_2

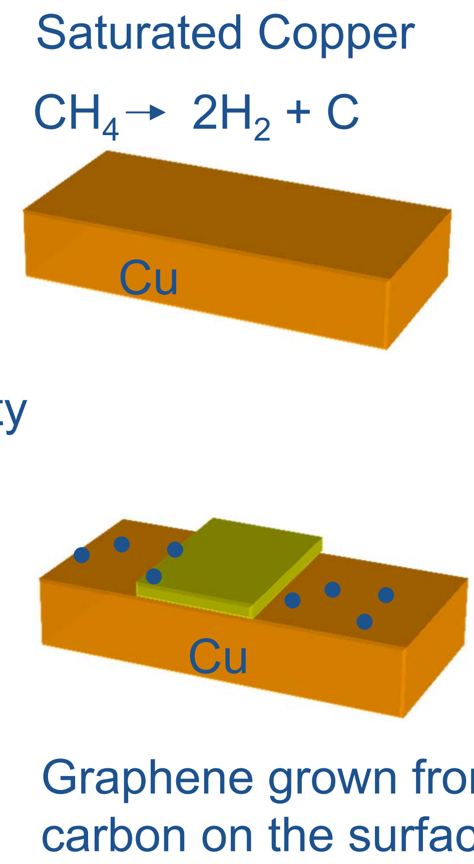


H. Cao et. al., Appl. Phys. Lett 96, 122106 (2010)

Low solubility catalyst: Cu

Graphene growth is limited to surface of the catalyst due to low carbon solubility



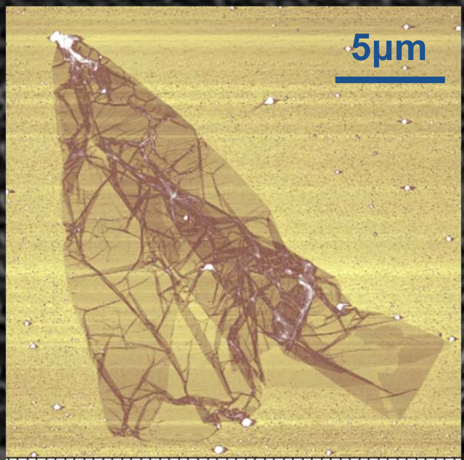


Carbon solubility @ 1000˚C: < 0.0001 at.%

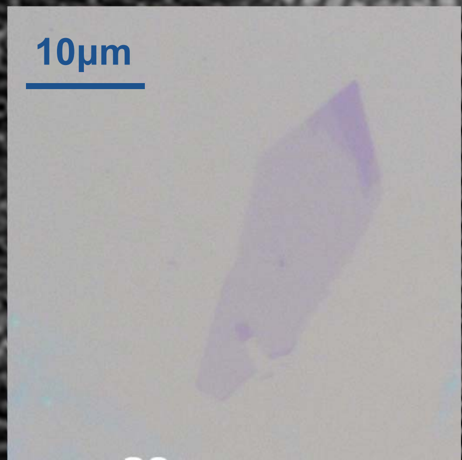
X. Li et al. Nano letter 9 (2009) 4268


2010 Nobel Prize in Physics

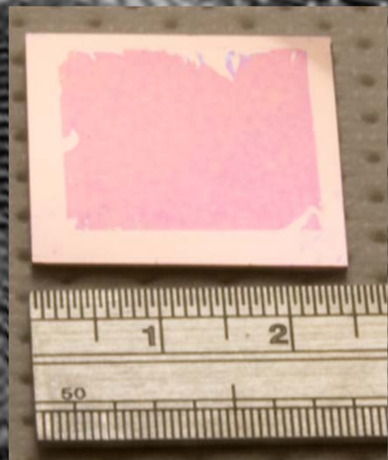
- Counterparts of CNTs
- Can solve the problem of chirality dependence of m- or sc-nature of CNTs
- High carrier mobility ~2,000,000 cm^2/Vs
- High current carrying capability (higher than Cu)
- Transparent & Mechanically strong
- Can precisely control electronic state by chemical functionalization
- Can be compatible with existing Si technology



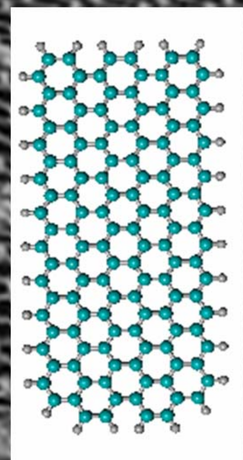
Graphene Oxide

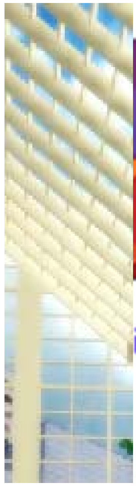


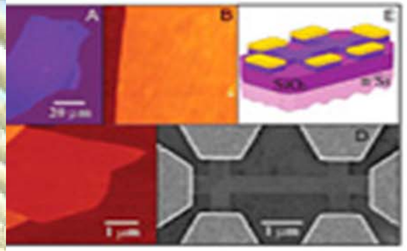
Graphene from HOPG



Graphene from CVD


Graphene Nanoribbon



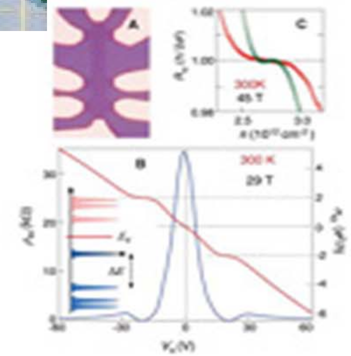


iscovery of Graphene
2004 SCIENCE

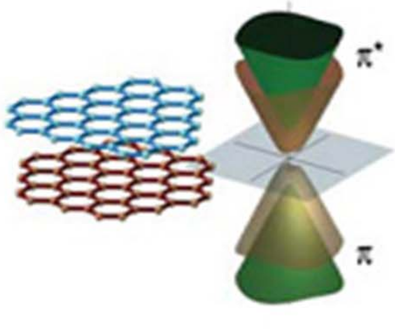
Graphene

High Conductivity
Ultra Stiffness
Quantum Hall Effect
Easier Nano-Fabrication

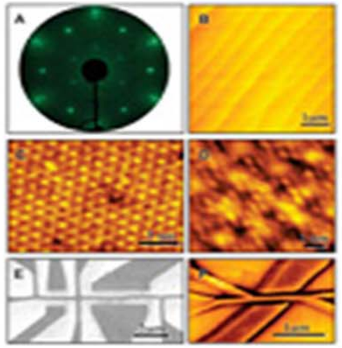
Graphen, 2008



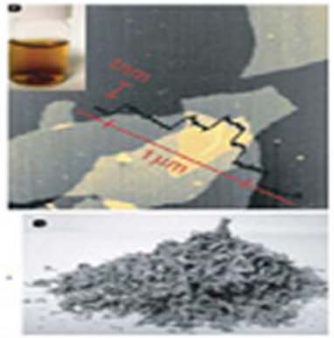
Quantum Hall Effect
2005 SCIENCE



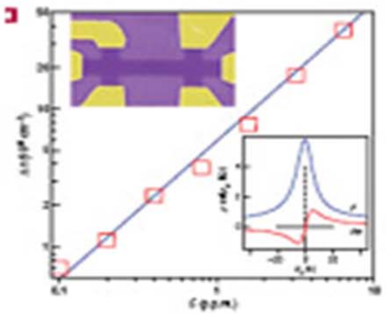
Bilayer Electronics
2006 SCIENCE



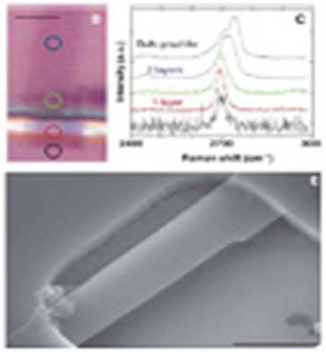
Epitaxial Graphene
2006 SCIENCE



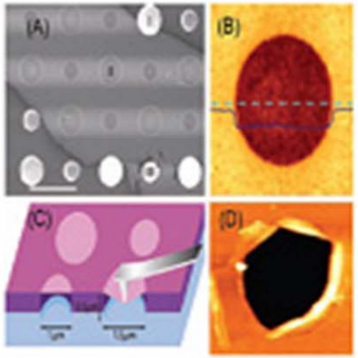
Nano-Composite
2006 NATURE



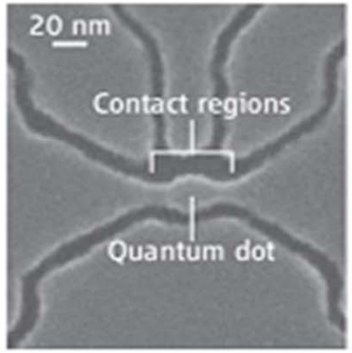
Gas Sensing
2007 NATURE



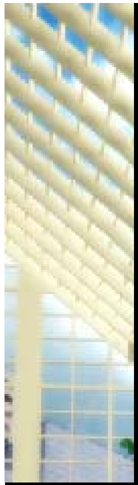
Nano-Resonator
2007 SCIENCE

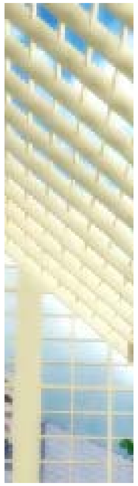


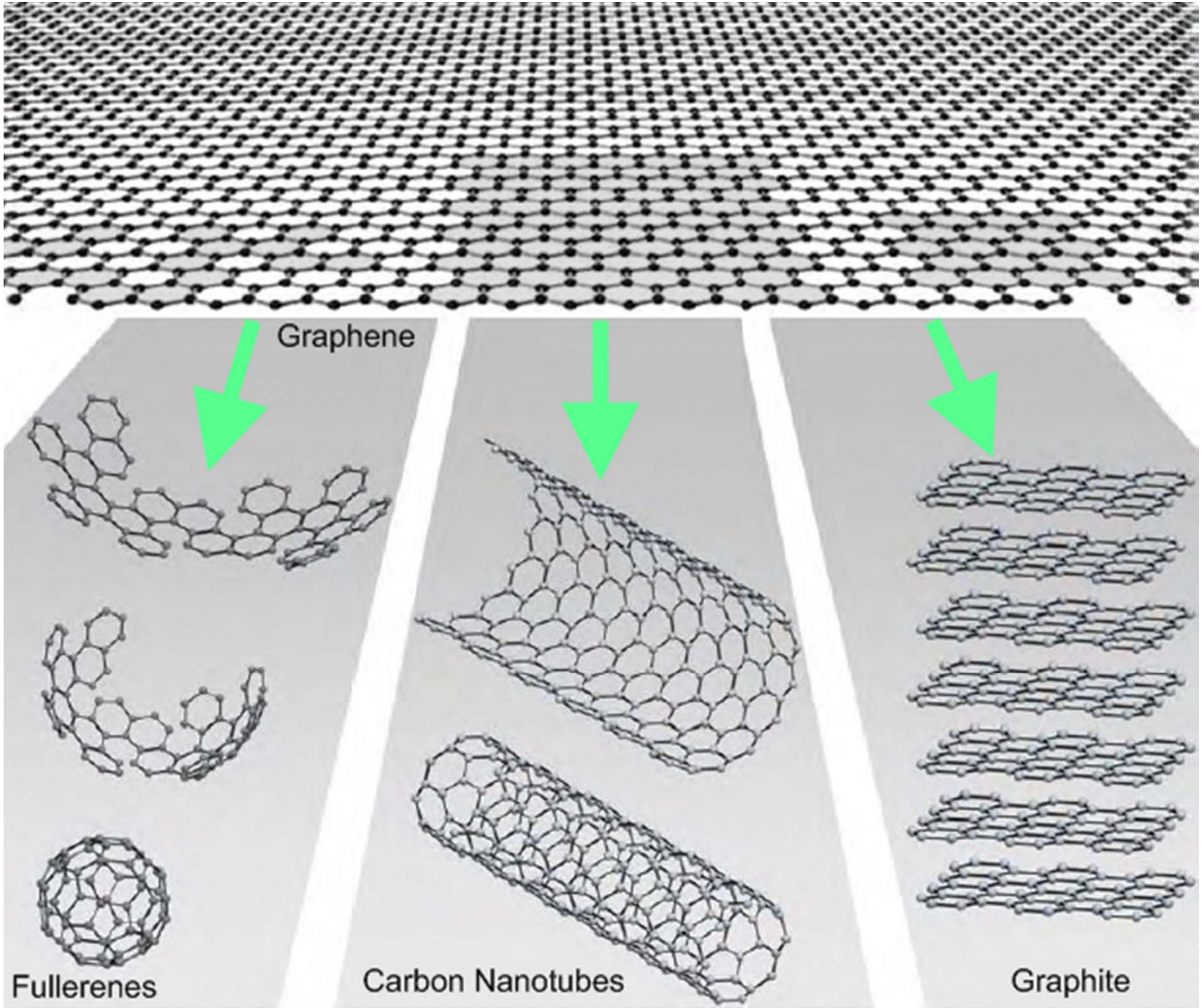
Elasticity
2008 SCIENCE



Nano-Transistor
2008 SCIENCE







Andre K. Geim and K.S. Novoselov, "The rise of graphene." cond-mat/0702595

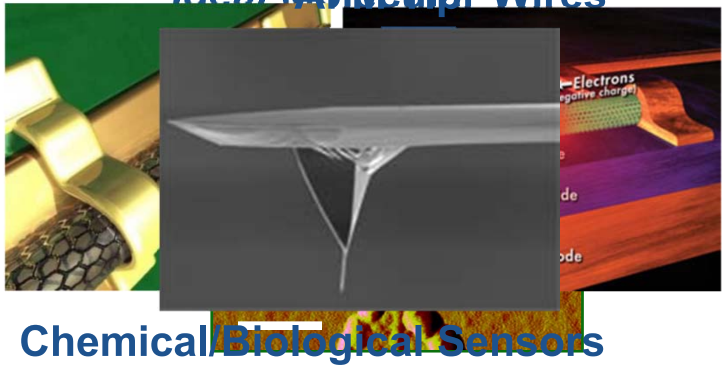
Carbon Family: Nanomaterials

allic Properties

- allistic conductor: 1 defect in 10^{12} C atoms
- igh current density of 10^9 A/cm^2
- (10^3 times higher than that of noble metals)
- ighly transparent & flexible: replacement for ITO

V. Perebeinos, et al., Phys. Rev. Lett. 2005
Wu et al., Science 2004
C.Y. Lee, M. S. Strano et. al, Langmuir 2005

FET   Ideal Molecular Wires   AFM Tip   LED



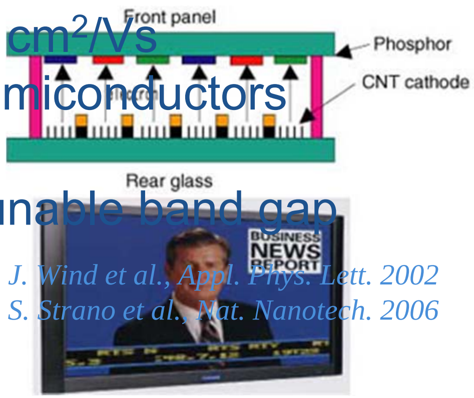
Chemical/Biological Sensors

Space Elevator

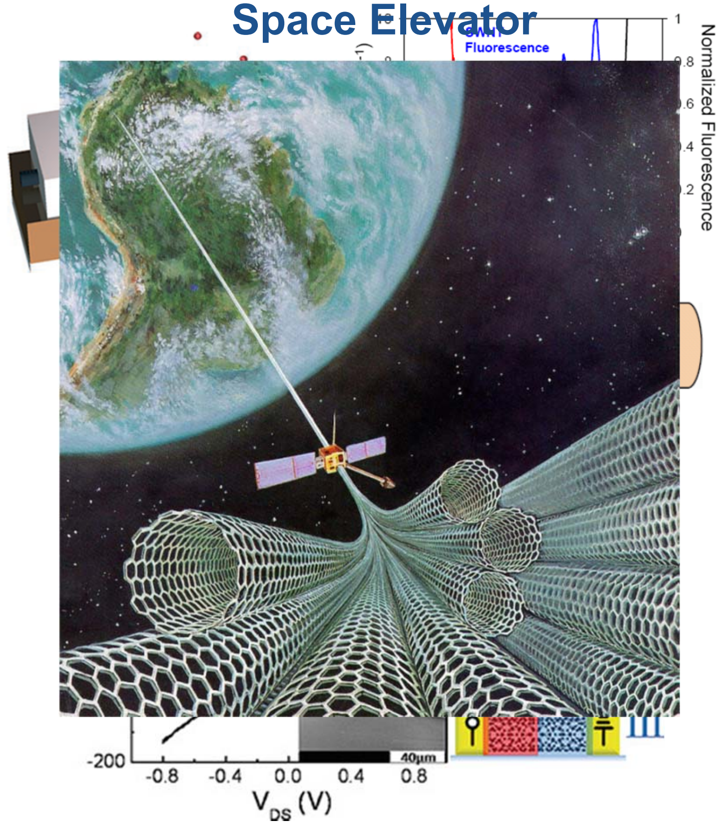
Semiconducting Properties

Interconnection   Field Emission Device   Tra

- High mobility of 100,000 cm^2/Vs
- Stable single electron semiconductors
- Near IR light emission
- Exciton generator with tunable band gap



S. J. Wind et al., Appl. Phys. Lett. 2002
P. Barone, M. S. Strano et al., Nat. Nanotech. 2006



Structural Properties

- High elastic modulus 1 TPa
- Highest strength to weight ratio

J. P. Salvetat, et. al. Phys. Rev. Lett. 1999