

Graphene: From fundamental to future applications

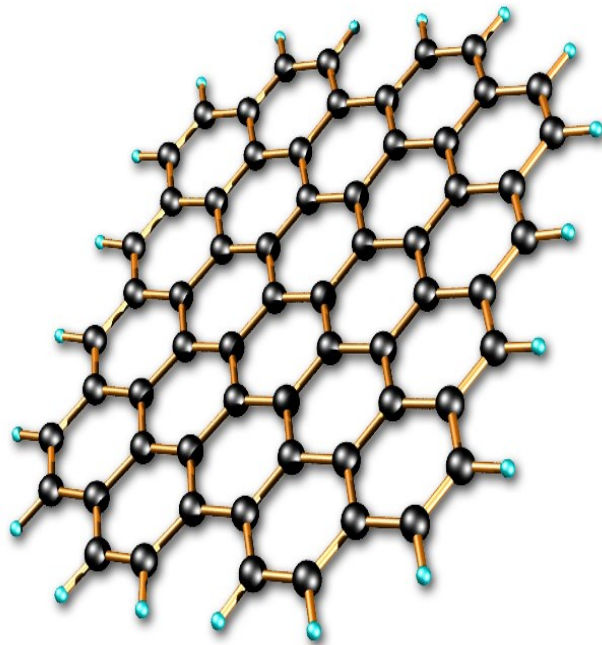
Content

- Introduction to graphene.
- Preparation and characterization graphene
- Potential application of graphene
- Conclusions

What is graphene?

In late 2004, graphene was discovered by Andre Geim and Kostya Novoselov (Univ. of Manchester).

- 2010 Nobel Prize in Physics



Q1. How thick is it?

→ a million times thinner than paper
(The interlayer spacing : 0.33~0.36 nm)

Q2. How strong is it?

→ stronger than diamond
(Maximum Young's modulus : ~1.3 TPa)

Q3. How conductive is it?

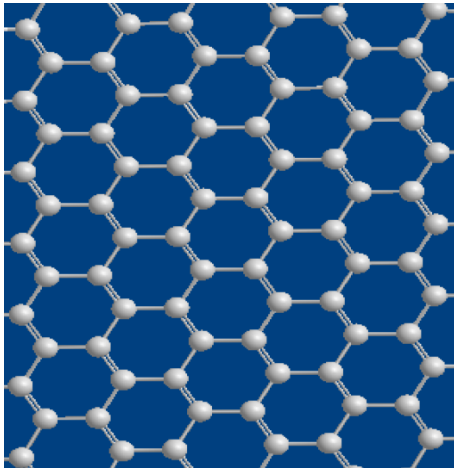
→ better than copper
(The resistivity : $10^{-6} \Omega \cdot \text{cm}$)
(Mobility: $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)

But, weak bonding between layers
Separated by mechanical exfoliation of 3D graphite crystals.₃

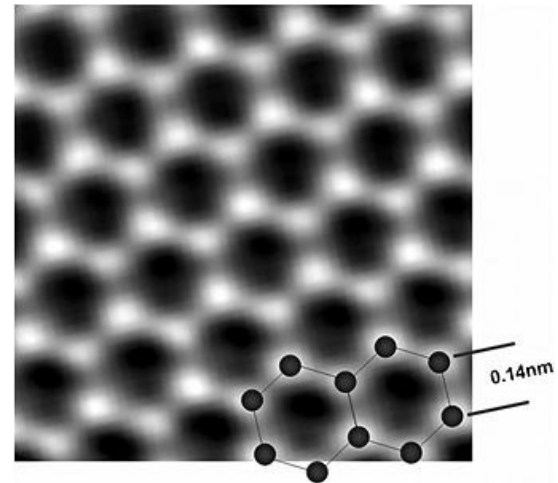
Introduction to graphene

Graphene is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice

The name 'graphene' comes from graphite + -ene = graphene



Molecular structure of graphene



High resolution transmission electron microscope images (TEM) of graphene

Material	Electrical Conductivity (S·m ⁻¹)	Notes
Graphene	$\sim 10^8$	
Silver	63.0×10^6	Best electrical conductor of any known metal
Copper	59.6×10^6	Commonly used in electrical wire applications due to very good conductivity and price compared to silver.
Annealed Copper	58.0×10^6	Referred to as 100% IACS or International Annealed Copper Standard. The unit for expressing the conductivity of nonmagnetic materials by testing using the eddy-current method. Generally used for temper and alloy verification of aluminium.
Gold	45.2×10^6	Gold is commonly used in electrical contacts because it does not easily corrode.
Aluminium	37.8×10^6	Commonly used for high voltage electricity distribution cables [citation needed]
Sea water	4.8	Corresponds to an average salinity of 35 g/kg at 20 °C. [1]
Drinking water	0.0005 to 0.05	This value range is typical of high quality drinking water and not an indicator of water quality
Deionized water	5.5×10^{-6}	Conductivity is lowest with monoatomic gases present; changes to 1.2×10^{-4} upon complete de-gassing, or to 7.5×10^{-5} upon equilibration to the atmosphere due to dissolved CO ₂ [2]
Jet A-1 Kerosene	$50 \text{ to } 450 \times 10^{-12}$	[3]
n-hexane	100×10^{-12}	
Air	$0.3 \text{ to } 0.8 \times 10^{-14}$	

Thermal properties

<u>Material</u>	Thermal conductivity <u>W/(m·K)</u>
Silica <u>Aerogel</u>	0.004 - 0.04
<u>Air</u>	0.025
<u>Wood</u>	0.04 - 0.4
Hollow Fill Fibre Insulation	
<u>Polartherm</u>	0.042
<u>Alcohols</u> and <u>oils</u>	0.1 - 0.21
<u>Polypropylene</u>	0.25 ^[6]
<u>Mineral oil</u>	0.138
<u>Rubber</u>	0.16
<u>LPG</u>	0.23 - 0.26
<u>Cement</u> , Portland	0.29
<u>Epoxy</u> (silica-filled)	0.30
<u>Epoxy</u> (unfilled)	0.59
<u>Water</u> (liquid)	0.6
<u>Thermal grease</u>	0.7 - 3
Thermal <u>epoxy</u>	1 - 7
<u>Glass</u>	1.1
<u>Soil</u>	1.5
<u>Concrete</u> , stone	1.7
<u>Ice</u>	2
<u>Sandstone</u>	2.4
<u>Stainless steel</u>	12.11 ~ 45.0
<u>Lead</u>	35.3
<u>Aluminium</u>	237 (pure) 120—180 (alloys)
<u>Gold</u>	318
<u>Copper</u>	401
<u>Silver</u>	429
<u>Diamond</u>	900 - 2320
<u>Graphene</u>	(4840±440) - (5300±480)

Graphene's Superlatives..

Thinnest Imaginable Material

Largest Surface Area (3000 m^2 per gram)

Strongest Material (>Diamond; Theoretical Limit)

Stiffer than Diamond

Most Stretchable and Pliable Material (up to 20% elastically)

Record Thermal Conductivity (outperforming Diamond)

Highest Current Density at Room Temperature (1000 times of Cu)

Completely impermeable to gases (even does not allow He atoms)

Highest Intrinsic Mobility (100 times that of Si)

Conducts even if there are no electrons

Lightest Charge Carriers (Zero Rest Mass)

Longest Mean Free Path at Room Temperature (Micron Range)

And Many More.....

Introduction

Properties of graphene

Mechanical properties

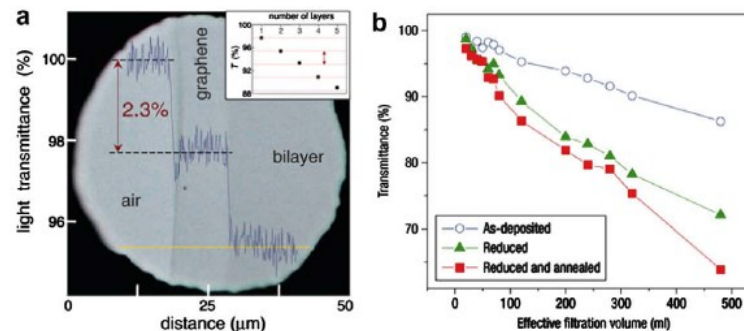
- High Young's modulus ($\sim 1,100$ GPa)
High fracture strength (125 GPa)
- Graphene is as the strongest material ever measured, some 200 times stronger than structural steel



A representation of a diamond tip with a two nanometer radius indenting into a single atomic sheet of graphene (*Science*, **321** (5887): 385)

Optical properties

- Monolayer graphene absorbs $\pi\alpha \approx 2.3\%$ of white light (97.7 % transmittance), where α is the fine-structure constant.



Preparation and characterization graphene

Preparation methods

Top-down approach (From graphite)

- Micromechanical exfoliation of graphite (Scotch tape or peel-off method)
- Creation of colloidal suspensions from **graphite oxide** or graphite intercalation compounds (GICs)

Bottom up approach (from carbon precursors)

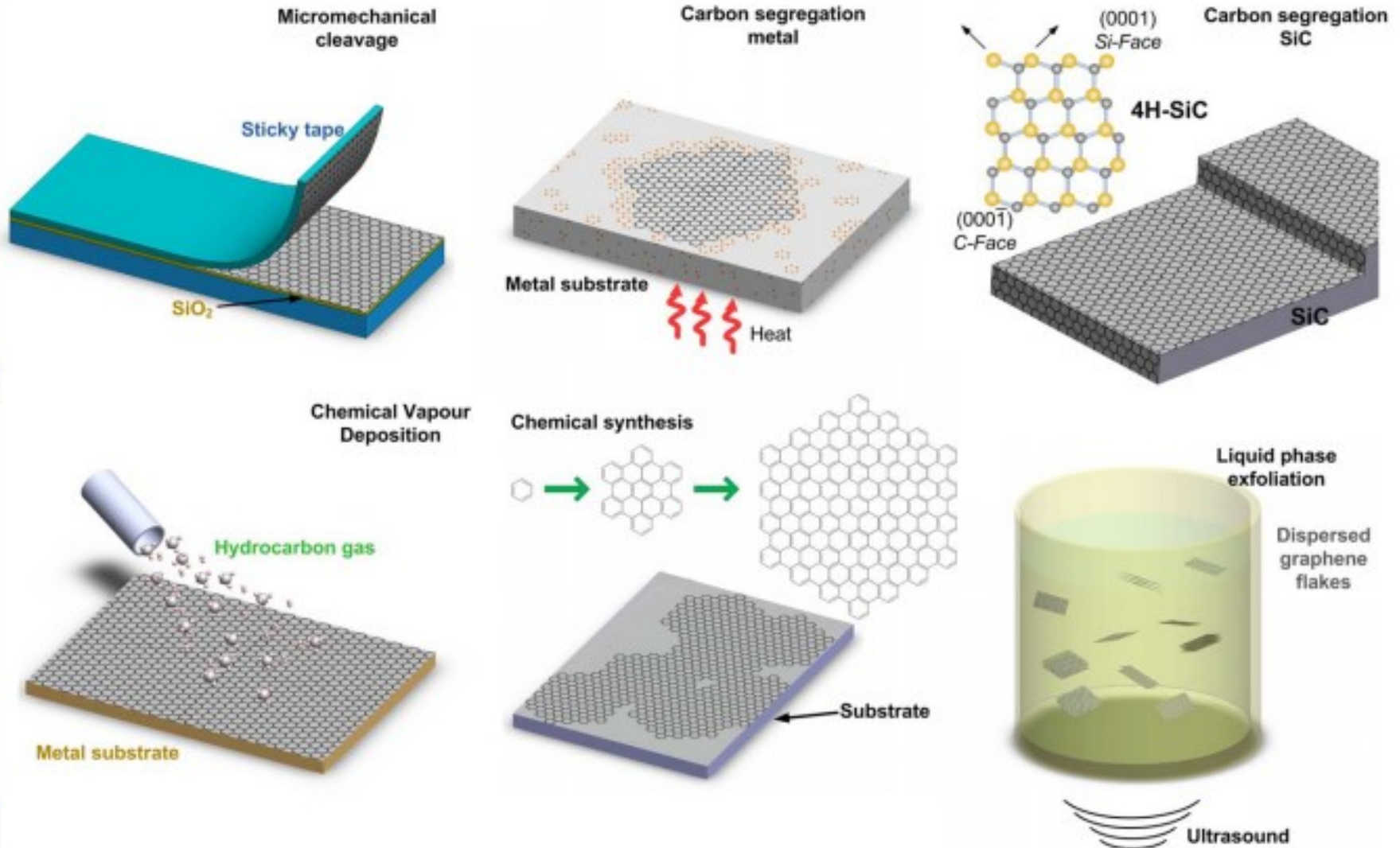
- By chemical vapour deposition (CVD) of hydrocarbon
- By epitaxial growth on electrically insulating surfaces such as SiC
- Total Organic Synthesis

Table 1 – Advantages and disadvantages for techniques currently used to produce graphene.

	Advantages	Disadvantages
Mechanical exfoliation	Low-cost and easy No special equipment needed, SiO ₂ thickness is tuned for better contrast	Serendipitous Uneven films Labor intensive (not suitable for large-scale production)
Epitaxial growth	Most even films (of any method) Large scale area	Difficult control of morphology and adsorption energy High-temperature process
Graphene oxide	Straightforward up-scaling Versatile handling of the suspension Rapid process	Fragile stability of the colloidal dispersion Reduction to graphene is only partial

Ref: Carbon, 48, 2127–2150 (2010)

Graphene Production



Growth on SiC

Both surfaces (Si(0001)- and C(000-1)-terminated) annealed at high T (>1000 °C) under ultra-high vacuum (UHV) graphitize due to the evaporation of Si. Thermal decomposition is not a self-limiting process, and areas of different film thicknesses may exist on the same SiC crystal.

Growth on metals by precipitation

Carbon can be deposited on a metal surface by a number of techniques: flash evaporation, physical vapor deposition (PVD), chemical vapor deposition (CVD), spin coating, etc. In the case of a pure carbon source, flash evaporation or PVD, can be used to deposit carbon directly on the substrate of interest.

Photographs of the roll-based production of graphene films.

(a) Copper foil wrapping around a 7.5-inch quartz tube to be inserted into an 8-inch quartz reactor. The lower image shows the stage in which the copper foil reacts with CH_4 and H_2 gases at high temperatures.

(b) Roll-to-roll transfer of graphene films from a thermal release tape to a PET (Poly Ethylene Terephthalate) film at 120 degree C.

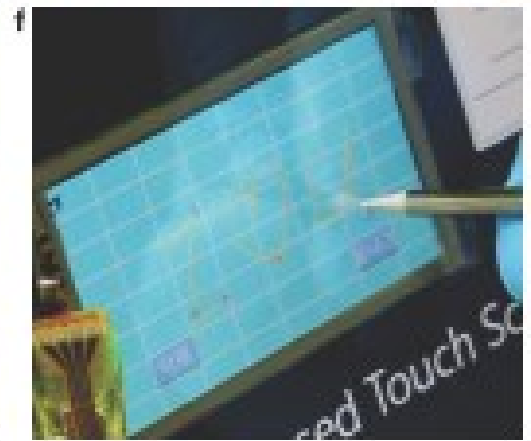
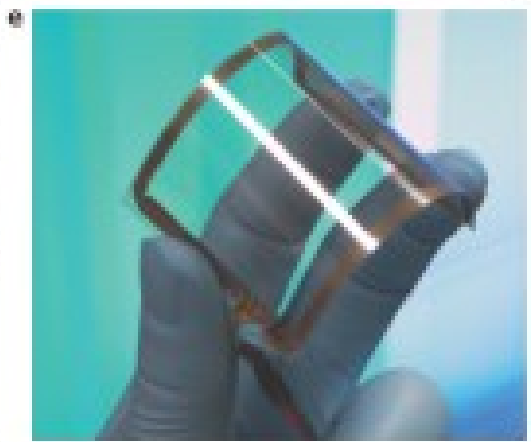
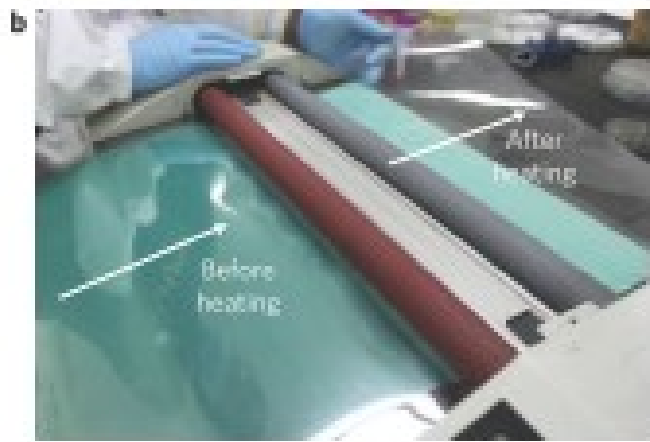
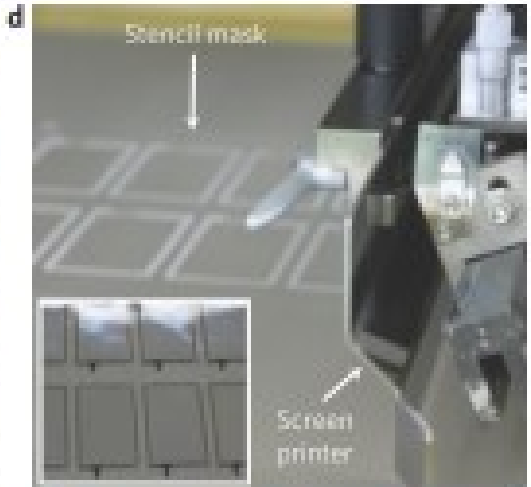
(c) A transparent ultralarge-area graphene film transferred on a 35-inch PET sheet.

(d) Screen printing process of silver paste electrodes on graphene film. The inset shows 3.1-inch graphene panels patterned with silver electrodes before assembly.

(e) An assembled graphene touch panel showing outstanding flexibility

(f) A graphene-based touch-screen panel connected to computer with control software. For a movie of its operation see Supplementary Information.

SKKU Process
Bae Nature Nano (2010)



Characterization methods

Scanning Probe
Microscopy (SPM):

Raman
Spectroscopy

Transmission electron
Microscopy (TEM)

X-ray diffraction
(XRD)

- Atomic force microscopes (AFMs)
- Scanning tunneling microscopy (STM)

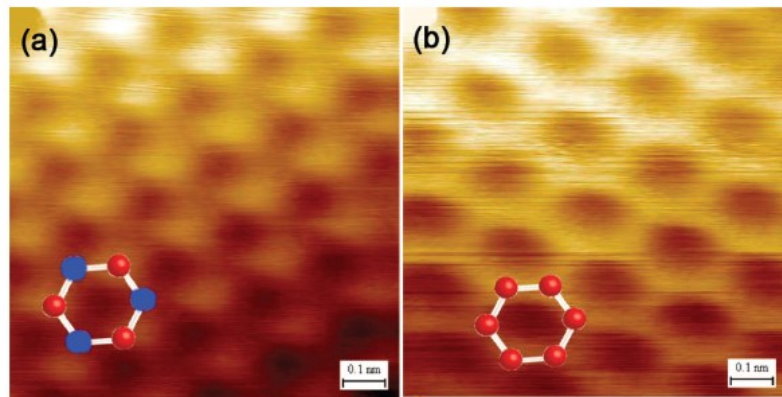
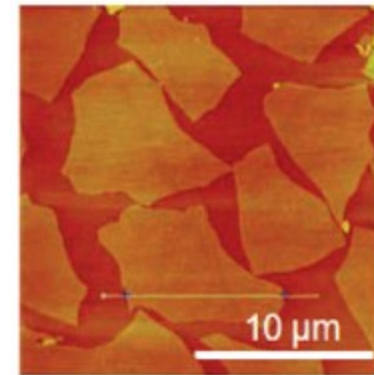


Figure 7. (a) STM image of graphite showing only the three carbons that eclipse a neighbor in the sheet directly below. (b) In contrast, all six carbons are equivalent and thus visible in mechanically exfoliated single-layer graphene. (Reprinted with permission from ref 79. Copyright 2007 PNAS.)



Atomic force microscopy images of a graphite oxide film deposited by Langmuir-Blodgett assembly

Potential application of graphene

- **Single molecule gas detection**
- **Graphene transistors**
- **Integrated circuits**
- **Transparent conducting electrodes**
- **Ultracapacitors**
- **Graphene biodevices**

Graphene FET

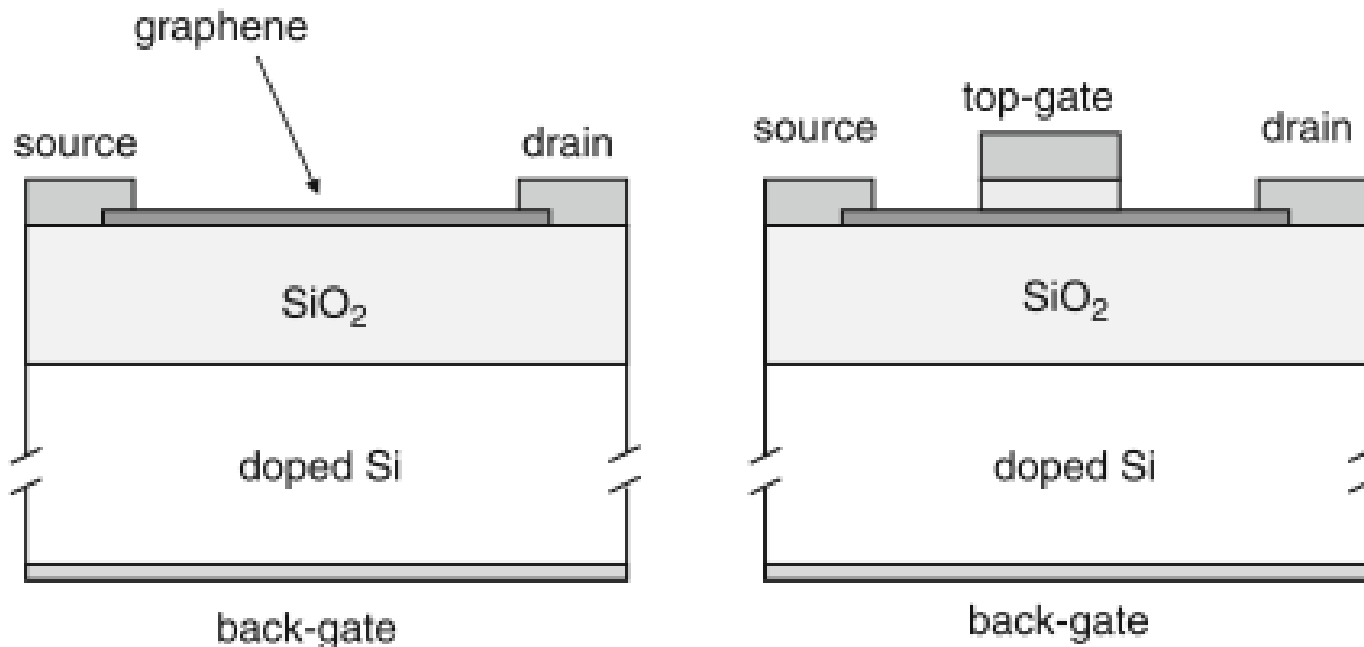


Fig. 3.1 Back-gated and top-gated Graphene FETs are shown in (a) and (b) respectively. Exfoliated and CVD graphene are usually on 300 nm or 90 nm SiO₂ substrate on doped Si. The doped Si allows for backgating

Graphene Atomic Switch

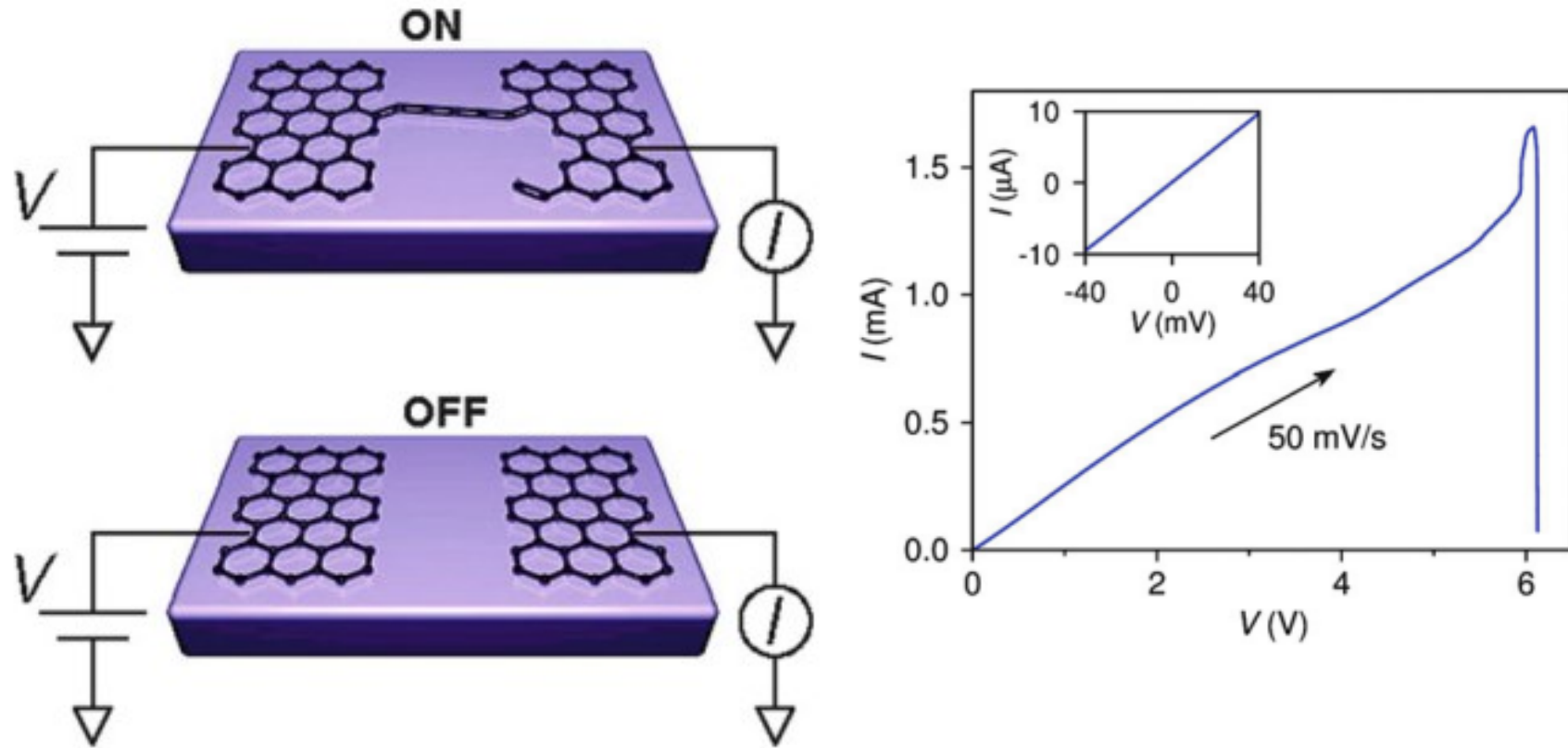

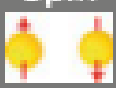

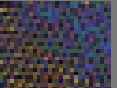








Fig. 4.3 Atomic-scale switch based on graphene (Reproduced with permission from [35]. © 2008 American Chemical Society)

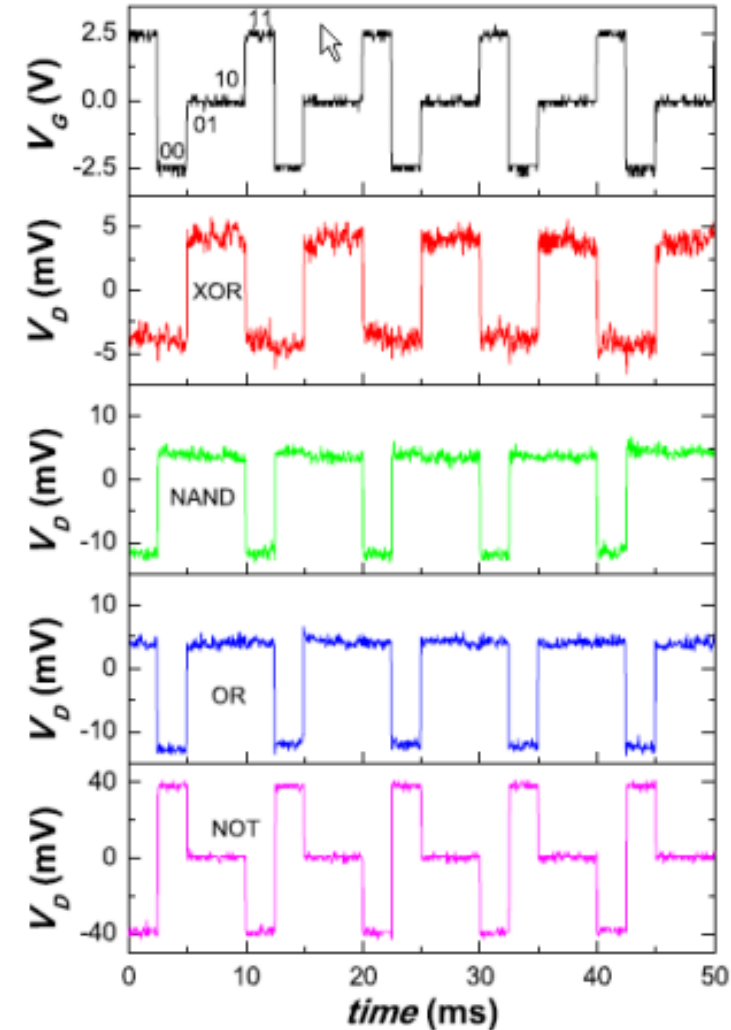
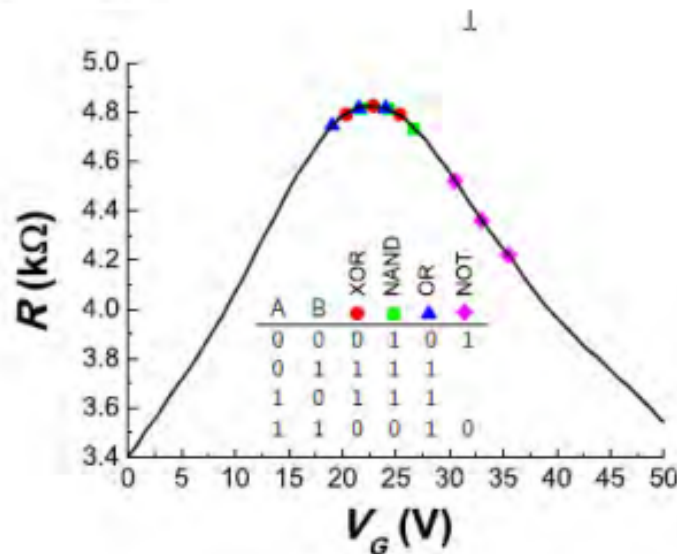
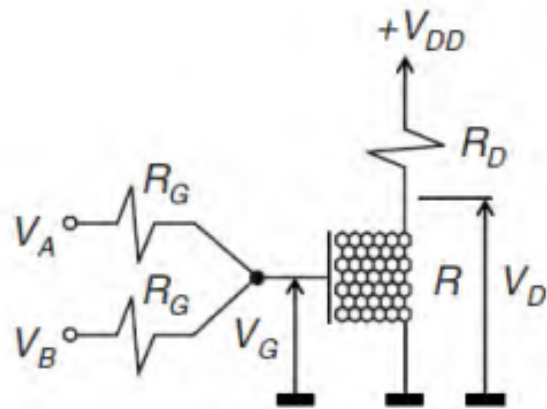
B. Standley, W. Bao, H. Zhang, J. Bruck, C. Lau, and M. Bockrath, "Graphene-based atomic-scale switches," *Nano Lett*, vol. 8, pp. 3345–3349, 2008.

<u>State Variable</u>	Electron 	Spin 	Pseudo Spin 	Phonon 	Molecular Motion 
Device Implementation	FET 	SpinFET 	BiSFET 	Thermal Logic 	Atomic Switch 
Fastest Switching Speed	~1ps energy relaxation time	~1ps precession frequency	~1ps recombination time, RC time constant	~5ns phonon group velocity	1ns vibrational speed
Energy	0.05eV $3kT \ln 2$ (1 electron)	0.05eV $3kT \ln 2$ (1 spin)	0.05eV $3kT \ln 2$	0.02eV $kT \ln 2$	577 eV
Smallest Device Footprint	1nm x 1nm (2 carbon atoms)	0.5nm x 0.5nm (1 carbon atom)	20nm x 20nm	1nm x 1nm (2 carbon atoms)	0.2nm x 75(0.2nm) chain of 75 carbon atoms
Modulation Method -on/off	field effect modulation	magnetic field, spin orbit coupling	carrier densities n and p via electric field control	temperature or voltage via thermoelectrics	capacitive and elastic forces
Advantages	electron based devices well understood	mono -atom operation	low power consumption	Ideal for phonon directional control	extremely good "off" properties (not leaky)
Challenges	bandgap control, static power, edge state control	isolation and single spin addressing	transistional temperature sensitivities T_c	phonons travel relatively slowly	high energy to break C=C covalent bonds

Summary of graphene based state variable performance estimates.

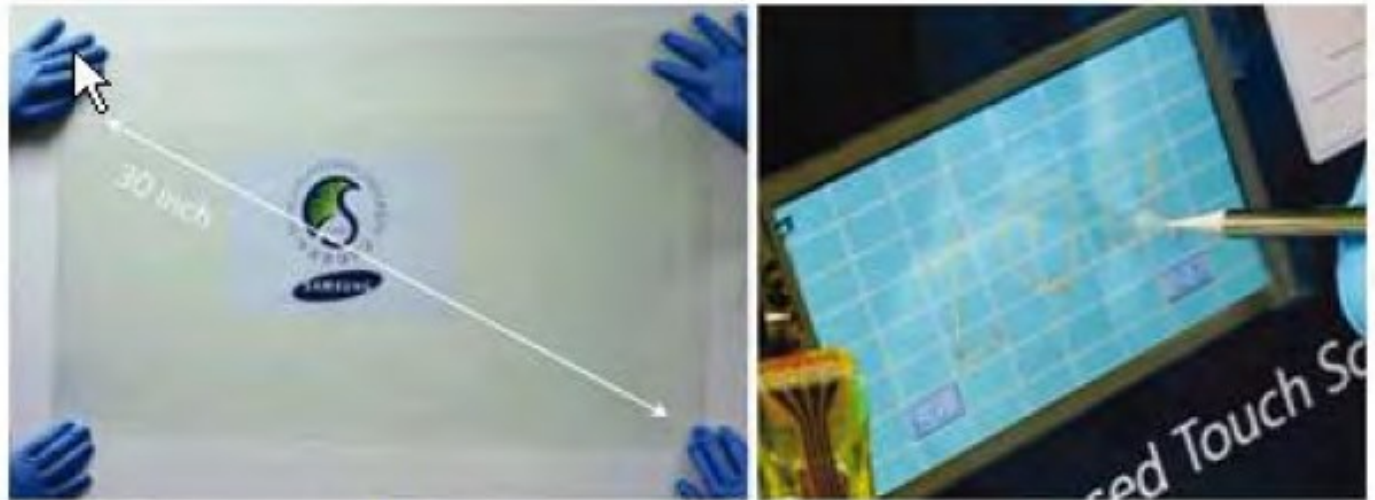
Logic gates with a single graphene transistor

Roman Sordan, Floriano Traversi and Valeria Russo



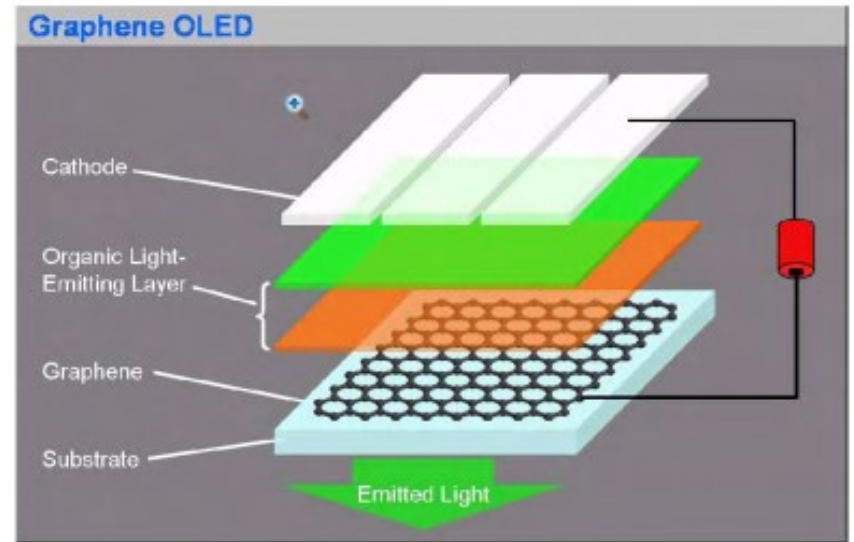
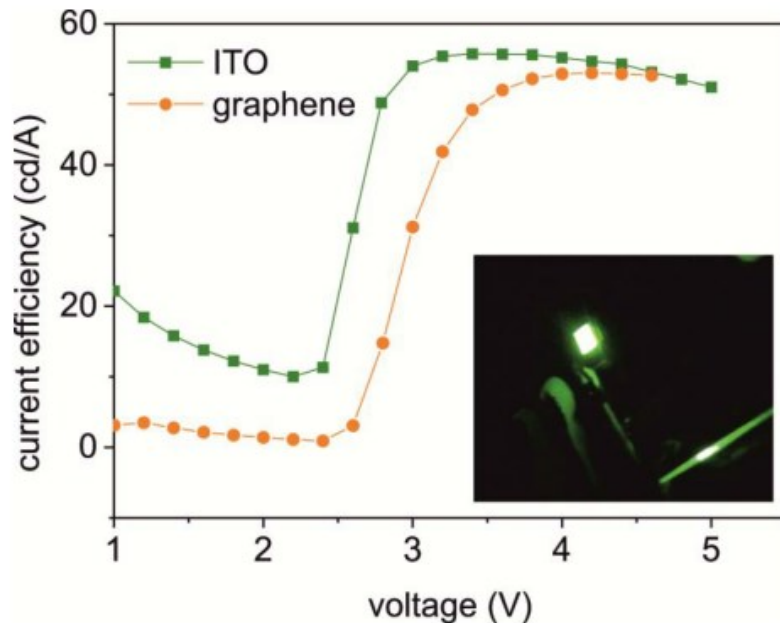
Capacitive touch screen demonstration by KIST/Samsung

- CVD grown graphene



Left: A transparent graphene film transferred on a 35-inch PET sheet. Right: A graphene-based touchscreen panel connected to a computer

OLED displays with graphene electrodes



Current efficiency vs. voltage characteristics of OLEDs with ITO and graphene electrode.

Wu & al **ACS Nano** 2010 4 (1), 43-48

THz – what and why?

- “THz gap” lies between the RF microwave and optical IR domains
 - From 300-GHz to 10+ THz (1mm to 10 μm)
- Very interesting interactions with matter
 - Very rich spectral signature information at this part of EM spectrum (molecular resonances)
- Faster electronics
 - Compared to RF frequency electronics, wider bandwidths, component compactness and improved spatial resolution are possible
- Some applications for sources and detectors of terahertz radiation
 - Security and defence
 - Terahertz radiation penetrates many materials (except metals) and so can be used to “see” through packages at airports, for example – “T-rays”
 - Spectroscopic detection of biological agents (difficult, but doable)
 - Medicine & pharmaceuticals
 - imaging cancer tumors for early disease diagnosis, especially for skin tumors (THz is non-ionizing radiation)
 - identification of fake drugs, polymorphic structures
 - Astronomy
 - For example the cosmic microwave background includes a terahertz component
 - Molecular analysis of gases etc.
 - Material analysis
 - For ex. semiconductor materials
 - Biological research
 - Non-invasive monitoring of binding processes of biomaterials
 - Communications
 - Most suitable for for satellite/high altitude communications
 - 10-100 m range only at sea level due to atmospheric attenuation
 - Very well focused beams possible due to small antenna size (easy to use large antenna arrays..)
 - No working systems at sea level yet due to lack of reasonable transceiver structures...



Note: Research concept

Energy solutions

Flexible battery with higher power density and faster charging time, **photovoltaics**

Functional surface materials

Toughness, dirt repellency, **antenna integration**, **EM shielding**, haptics

Transparency and compliancy

Stretchable electronics, flexible displays

Integration and customization

Printable electronics, reel-to-reel

Integrated sensors

Chemical and bio-chemical sensors

Energy efficient computing

Distributed processors & **local high speed computing**, **radio solutions**, low cost electronics

