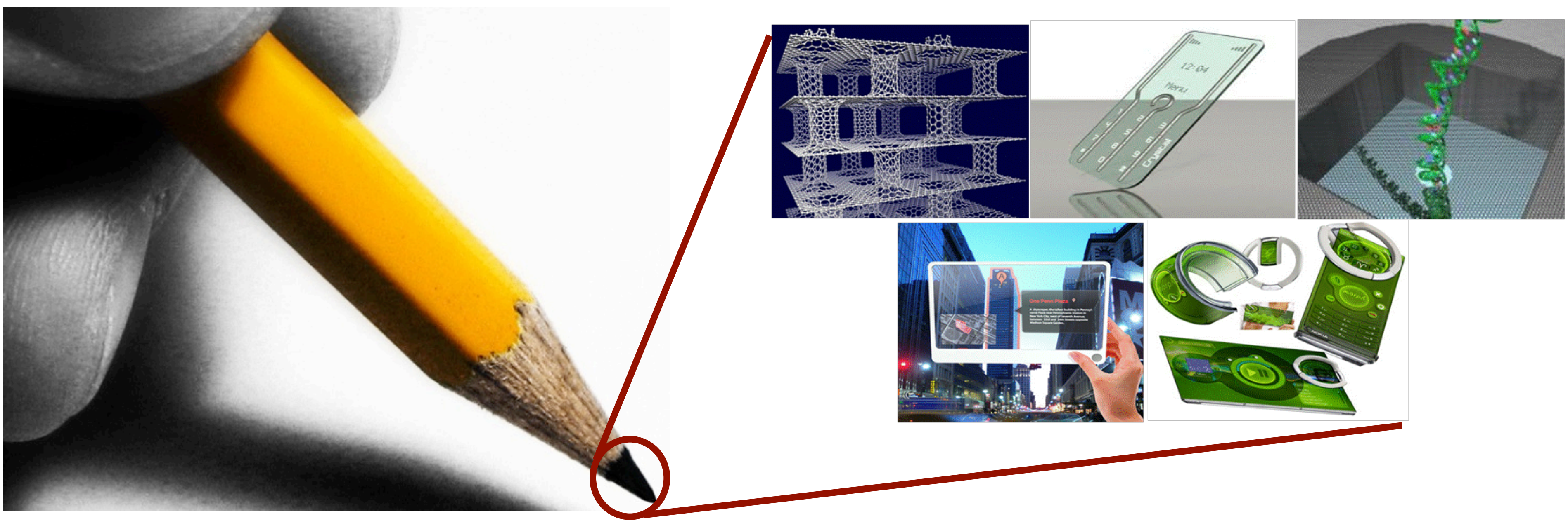
Graphene and other 2D materials:
New Opportunities in Flatland

Tomás Palacios

Department of Electrical Engineering and Computer Science

Massachusetts Institute of Technology



MIT-Japan Conference

Electronics has transformed our world…

Tremendous growth opportunities…

Electronic wall-paper and desks to charge objects wirelessly

Transparent displays embedded in windows

Photoluminescent ceilings

Internet of the things

Ubiquitous sensors/displays

Large area distributed speakers

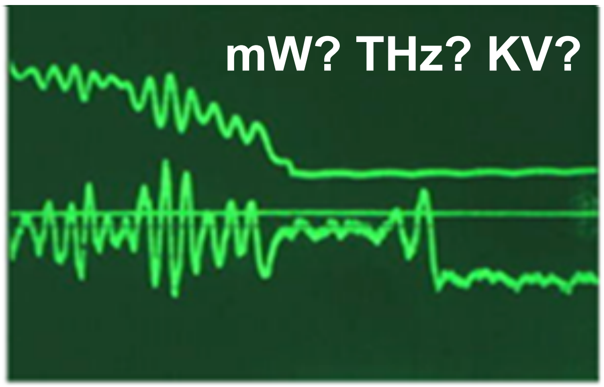
Ubiquitous energy harvesting

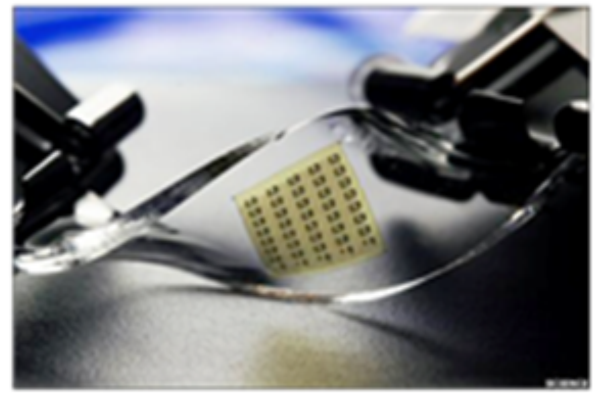
….

Is electronics ready for the required 1000-fold increase in throughput?

It will be very difficult to use today's manufacturing model to provide the large area devices needed by future generations of electronic opportunities

New Paradigm/Market for Electronics





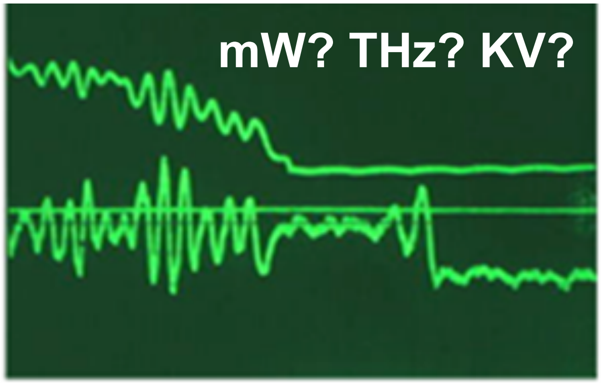
High frequency/ (low) power applications

Flexible electronics

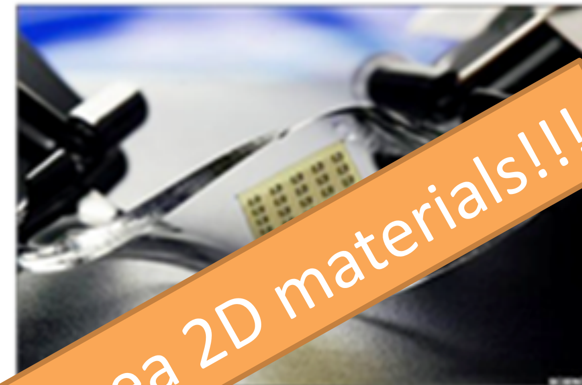
Transparent electronics

Large area electronics

New Materials + New Applications:
The most exciting time for electronics in 30 years



High frequency/(low) power applicati



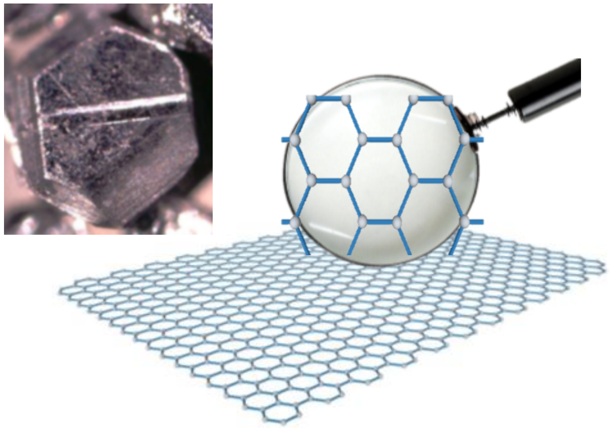
exible electronics

We need a new generation of large-area 2D materials!!!

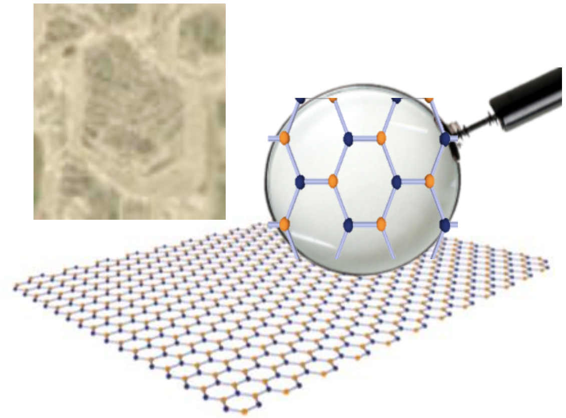
Transparent electronics

Large area electronics

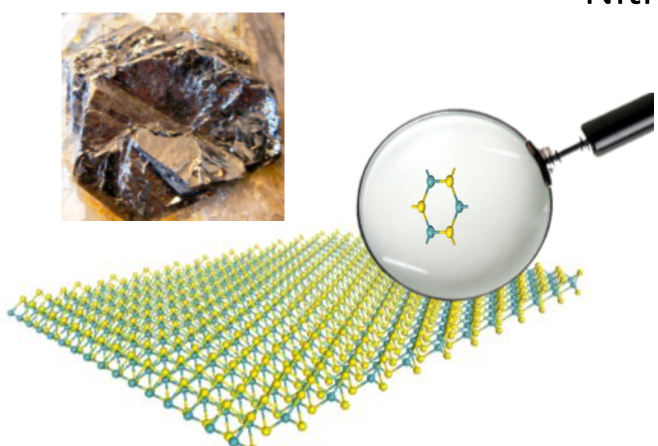
New 2D materials



Graphene (G)



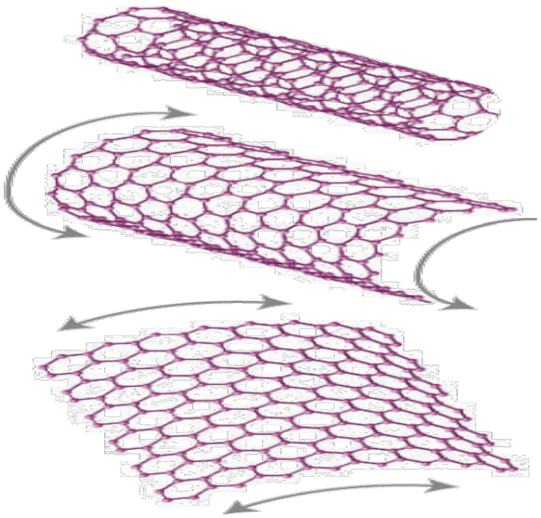
Hexagonal Boron Nitride (hBN)

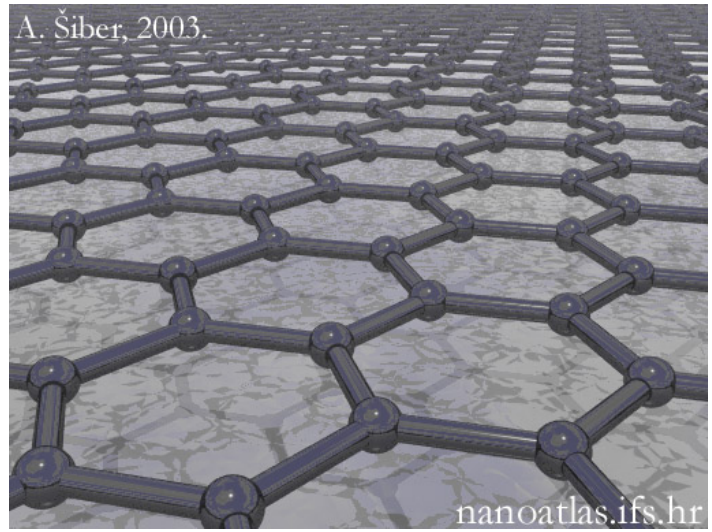


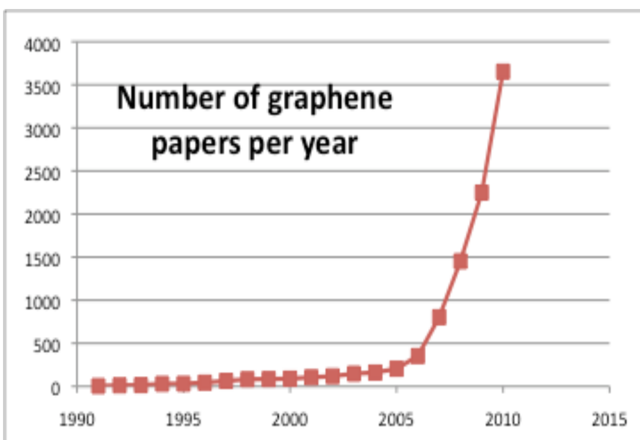
Molybdenum Disulphide (MoS_2) and other related materials

The first atom-thick material… graphene

Graphene is a two-dimensional layer of sp^2-bonded carbon atoms with amazing properties…

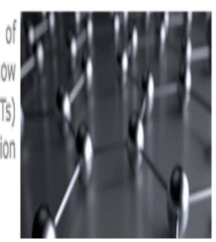






Important investments all-around the world

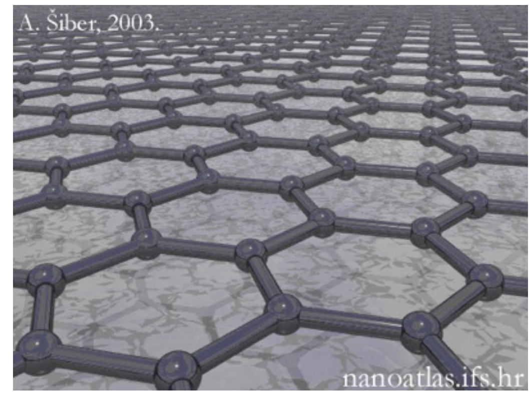
Graphene, a new substance coming from the world of atomic scale manipulation of matter, could be the wonder material of the 21st century. Discovering just how important this material will be for information and communication technologies (ICTs) is the main focus of the Seventh Framework Programme (FP7) Coordination Action GRAPHENE-CA, funded under the 'Ideas' Theme.



Graphene: *the amazing nanomaterial*

✓ Thinnest material sheet imaginable…yet the strongest!
(5 times stronger than steel and much lighter!)

✓ Graphene is a semimetal: it conducts as good (in fact better!) than the best metals, yet its electrical properties can be modulated (it can be switched ON and "OFF")



✓ Record electron and hole mobilities (>×100 than Si)

✓ Superb heat conductor (>x40 than Si)

✓ Very high current densities (~4-8 mA/μm, equivalent to 10^9 A/cm^2)

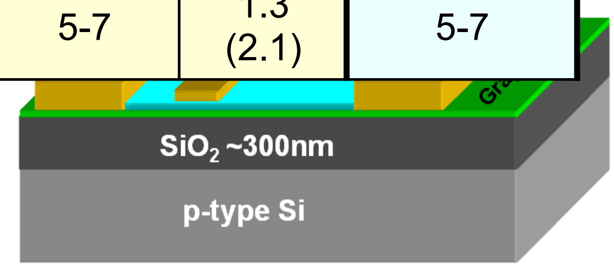
✓ Vast new physics for advanced devices… (e.g. it may become superconductor)

Graphene has the potential to revolutionize numerous fields:
Electronics, materials science, chemistry, …

“Unique” Properties of Graphene for EE

-New devices due to ambipolar transport
-Excellent electrostatic confinement
-Simple integration with Si…
-… or with flexible/transparent substrates
-And in addition… Excellent transport properties

Characteristic	Silicon	AlGaAs /InGaAs	InAlAs/ InGaAs	InSb	AlGaN/ GaN	Graphene
Electron mobility at 300K ($cm^2/V\cdot s$)	1500	8500	5400	80000	1500-2200	> 100,000
Peak electron velocity ($\times 10^7$ cm/s)	1.0 (1.0)	1.3 (2.1)	1.0 (2.3)	5-7	1.3 (2.1)	5-7

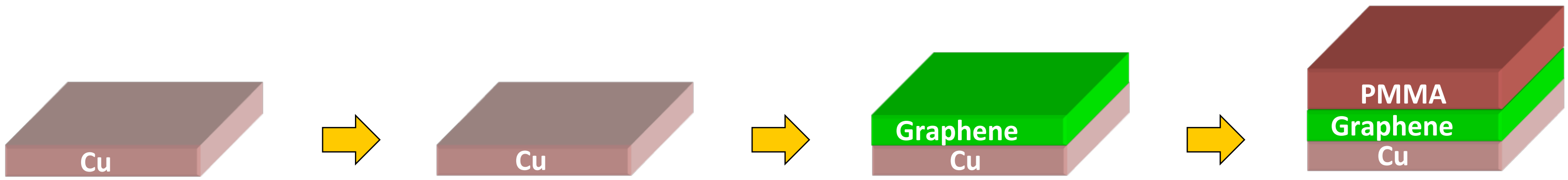


Outline

- Why graphene?
- Growth and fabrication technology
- Some applications:
  - High performance electronics
  - Chemical sensors
- Beyond graphene…
- Conclusions and outlook

CVD Growth of Graphene on Metal

Metal Deposition | **Annealing of Metal** | **CVD Growth** | **Metal Etching**

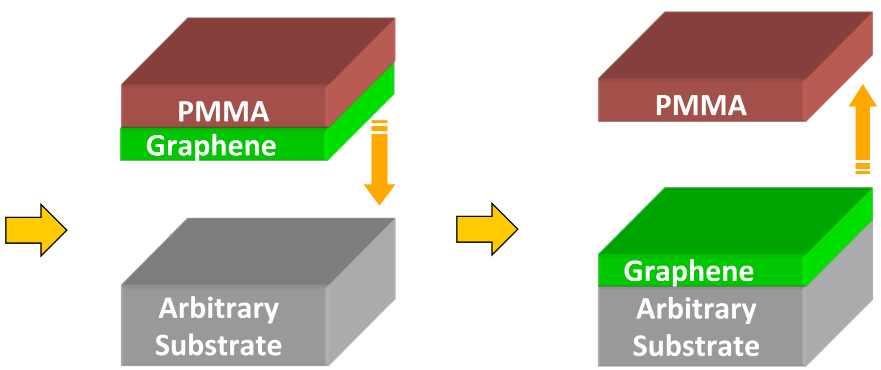


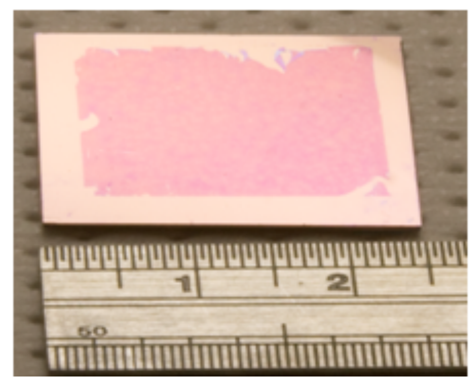
Annealing of Metal: 10-20min at 900-1000C, 600 sccm Ar, 500 sccm H_2

CVD Growth: 5-10min at 1000C, 5-25 sccm CH_4, 1500 sccm H_2

Metal Etching: Cu Etching

Transfer | **PMMA Removal by Acetone**



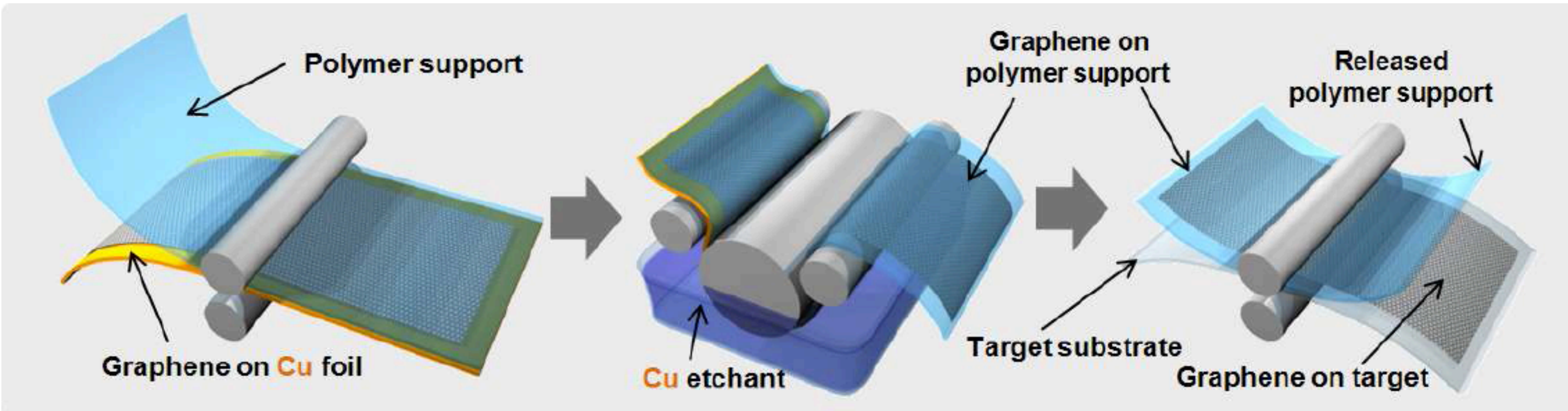


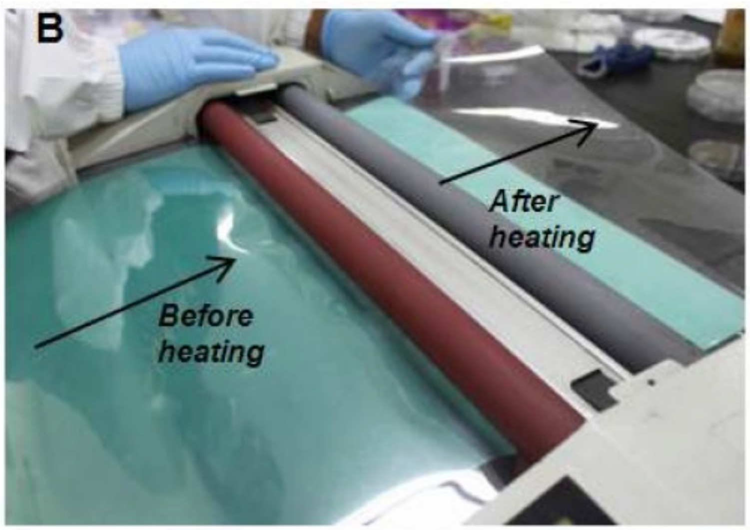
A. Reina et al, NanoLetters (2008) 30

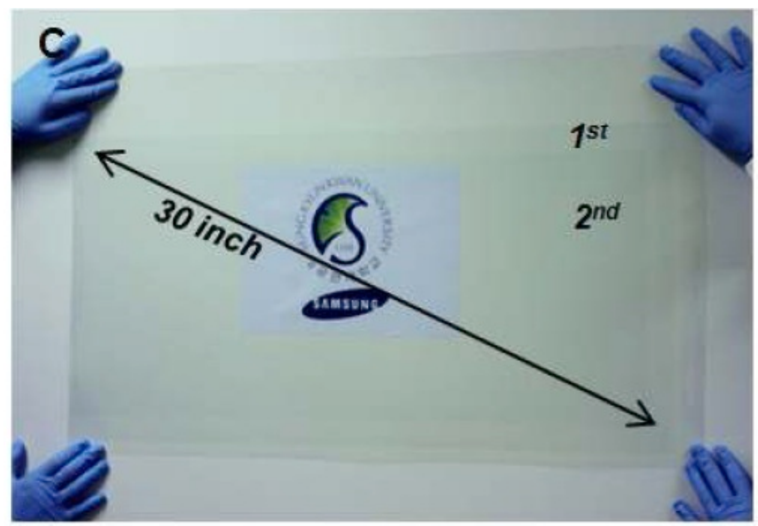
X. Li et al. Science 324, 1312 (2009)

Large-Scale CVD Growth

(Samsung Electronics)



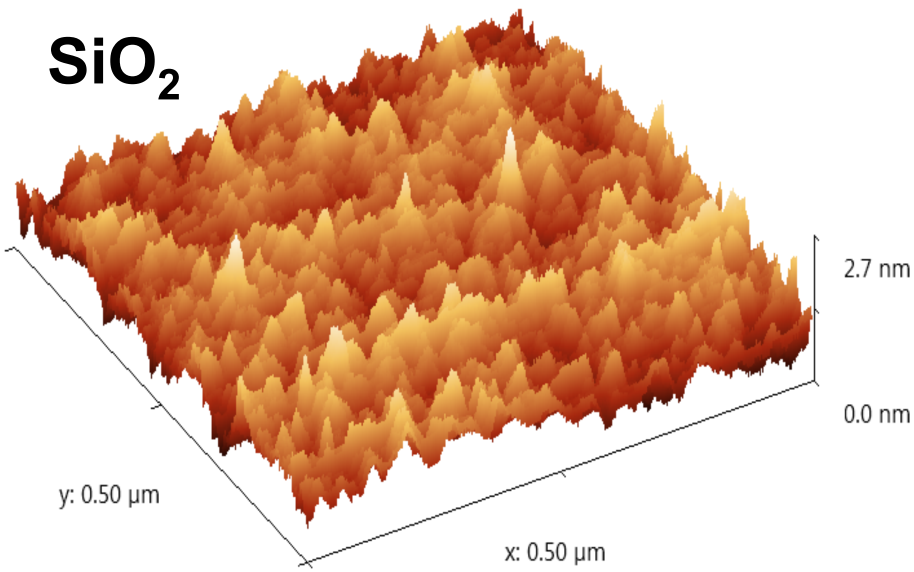




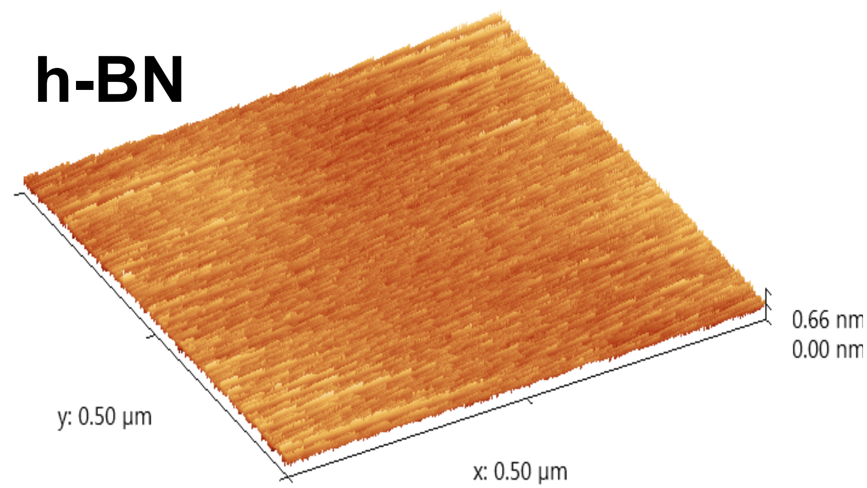
Bae et al, Nature Nanotechnology, 5, 574-578 (2009)

Influence of the substrate

SiO_2



h-BN



SiO_2 Substrate:

Single Layer Graphene
mobility ~ 5000-10,000 cm^2/V.s

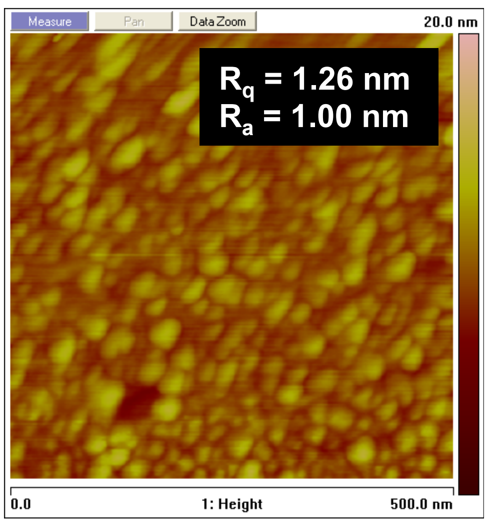
hBN Substrate:

Single Layer Graphene
mobility ~ 20,000-200,000 cm^2/V.s

Hexagonal Boron Nitride From Dr. Taniguchi (NIMS- Tsukuba, Japan)

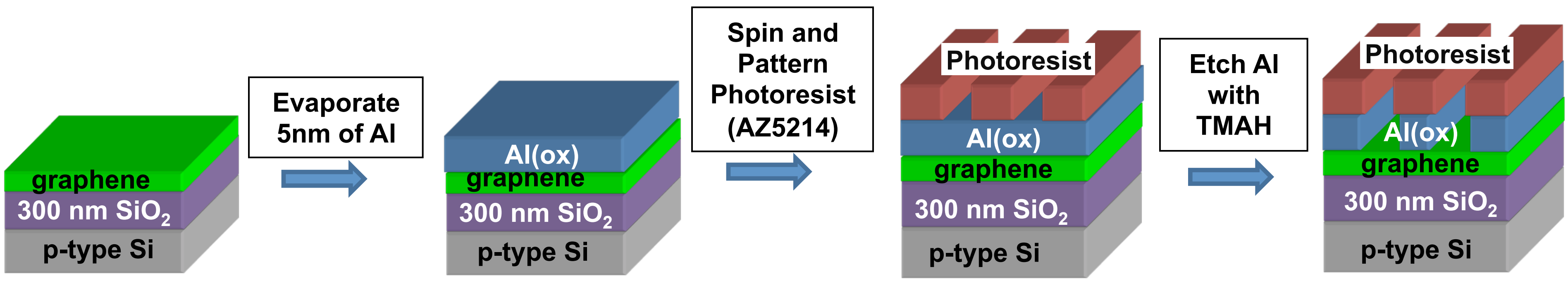
Ohmic Contacts

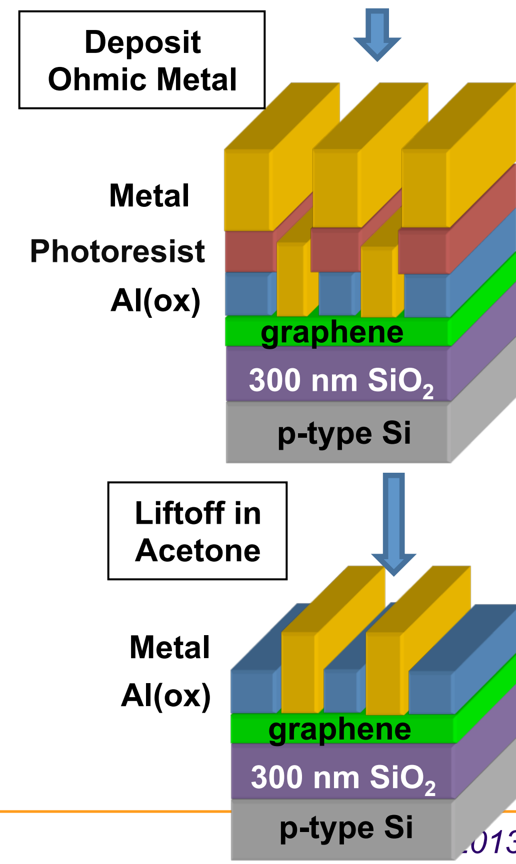
Standard



$R_c \sim 1000\text{-}3000\ \Omega.\mu m$

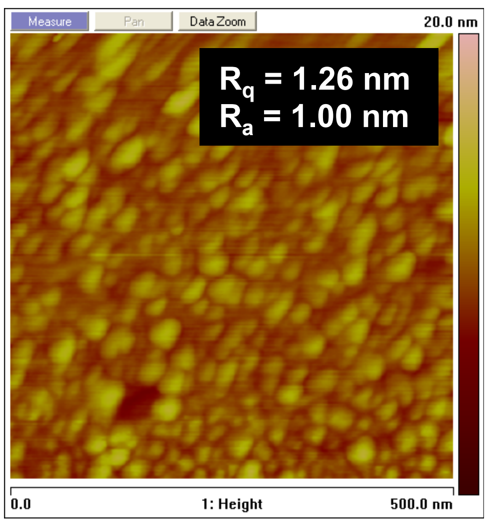
Ohmic Contacts



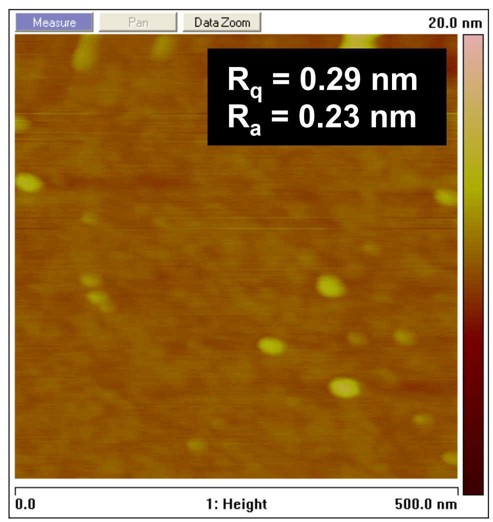


Pre-Ohmic Interface Quality

Standard



Improved



$R_c \sim 1000\text{-}3000\ \Omega.\mu m$

$R_c \sim 100\text{-}500\ \Omega.\mu m$

Outline

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- Some applications:
  - High performance electronics
  - Chemical sensors
- Beyond graphene…
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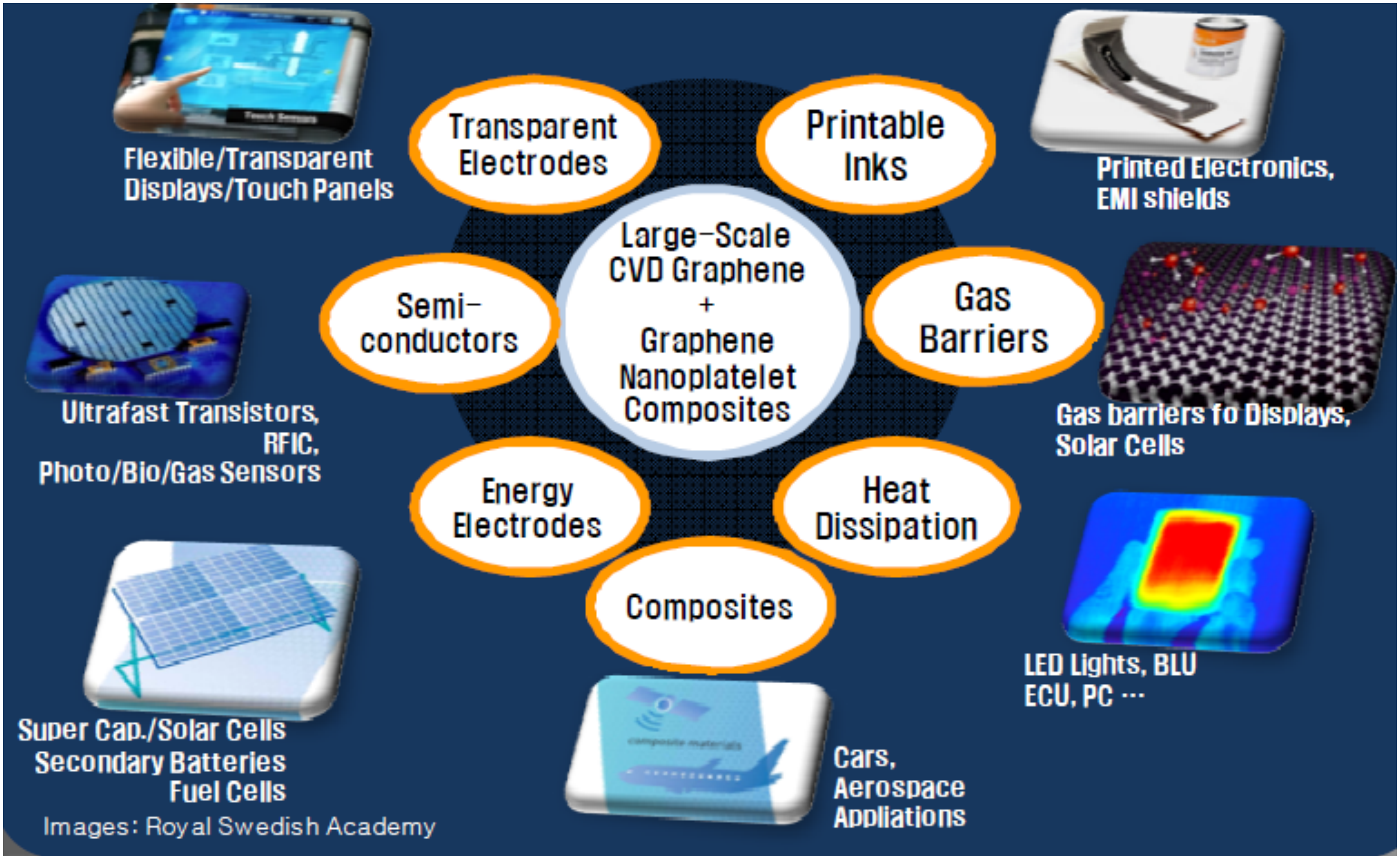
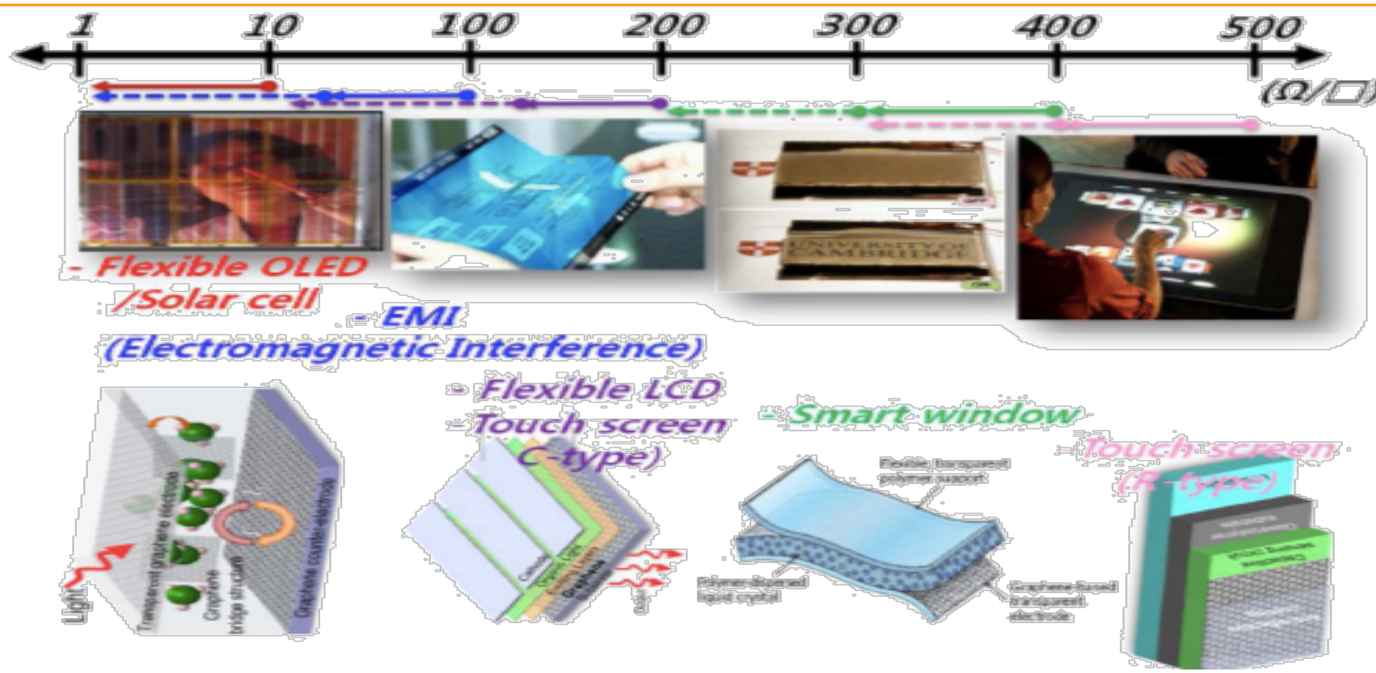
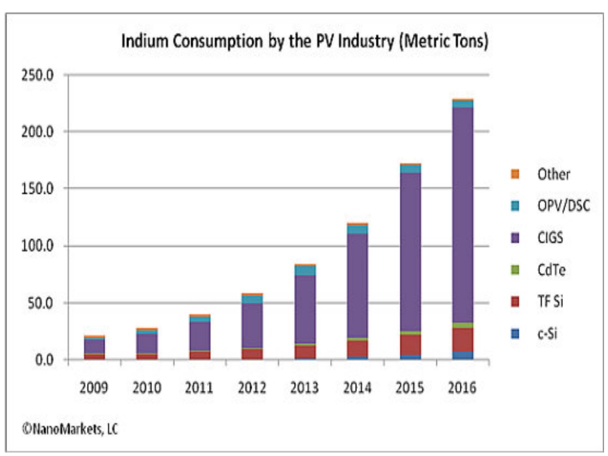
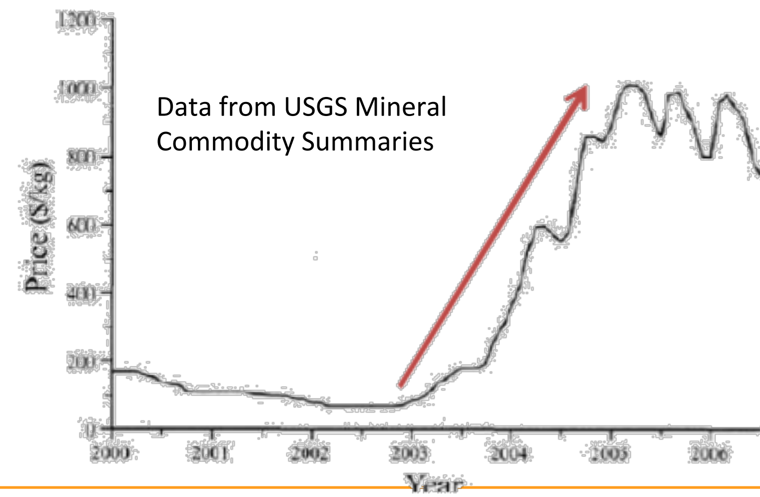
Some applications for graphene



Semitransparent electrode
(solar cells, LEDs, displays, touch screens…)







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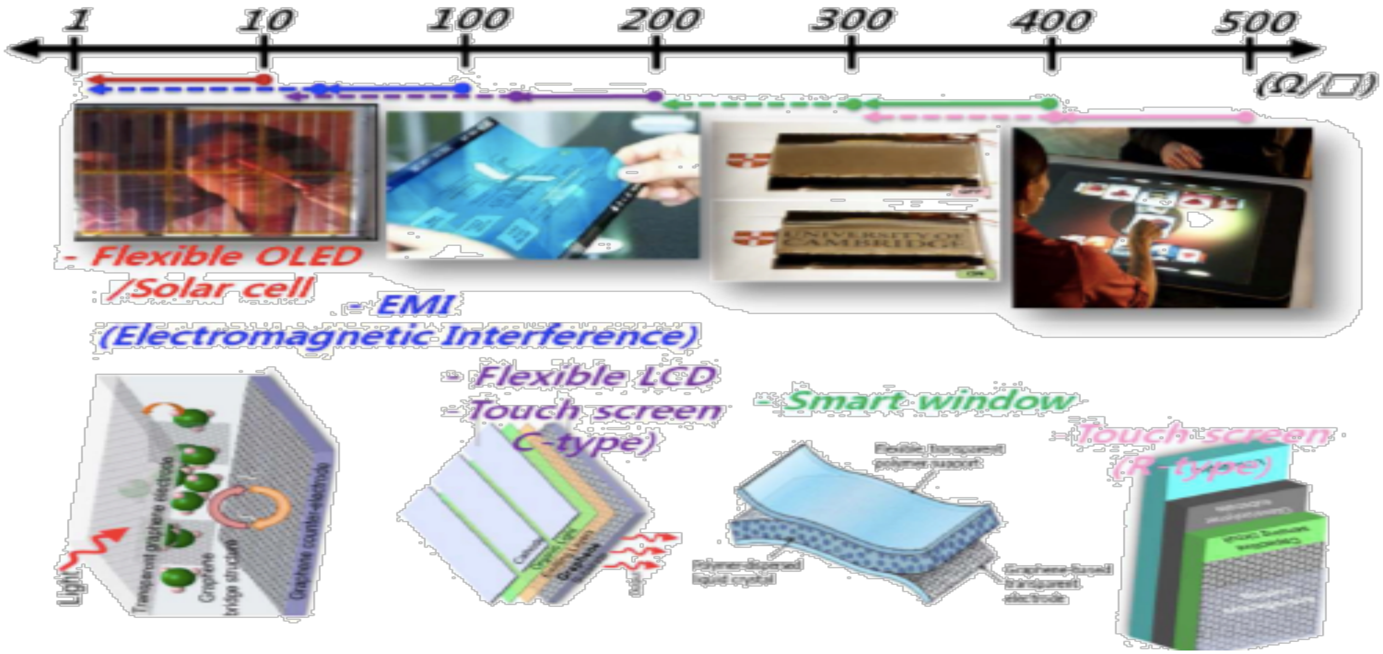
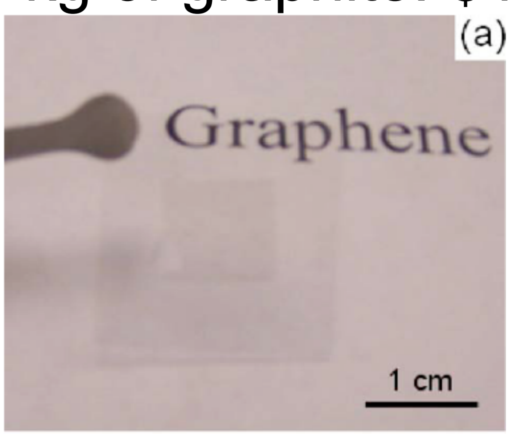
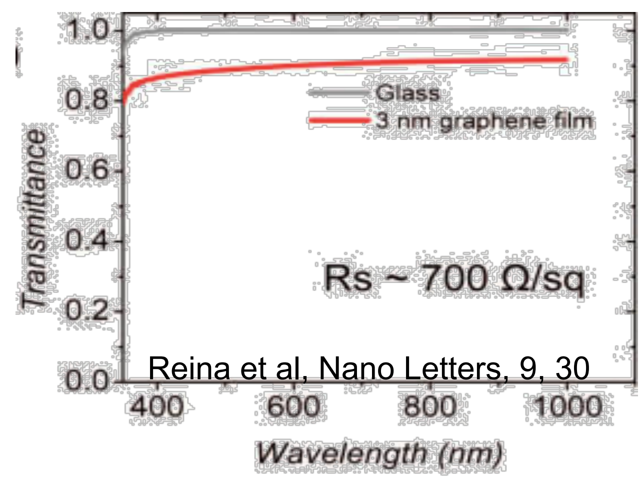
(solar cells, LEDs, displays, touch screens…)



1 kg of graphite: $1.5





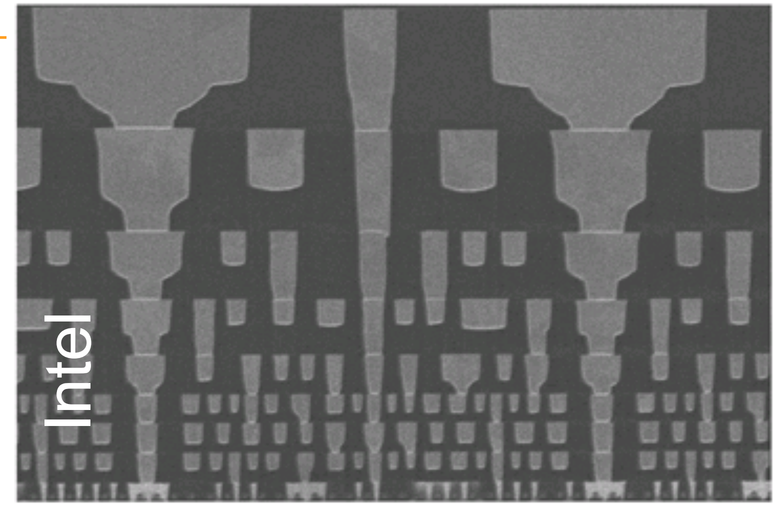
Nano-interconnections

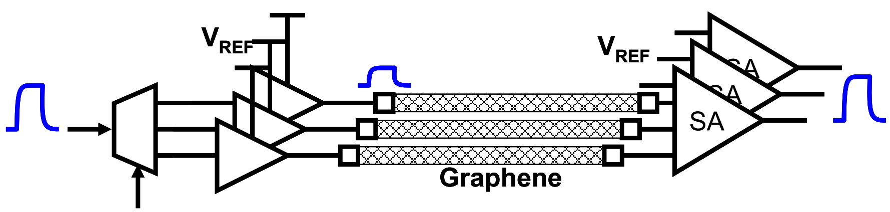
1.) Scaling of width of interconnect vs Cu – GNR Issues – Impurity Scattering, Line Edge roughness (LER)

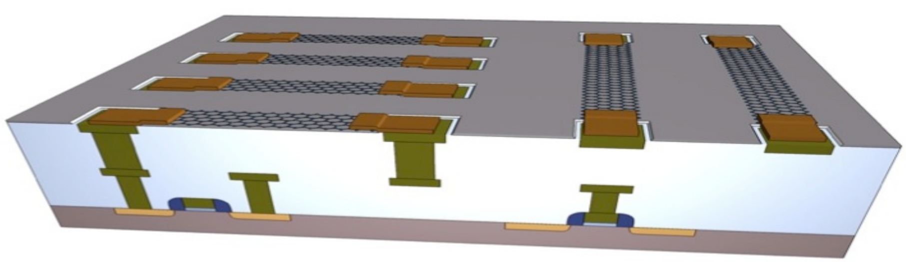
2.) Low Noise – Reduce Capacitance between interconnects

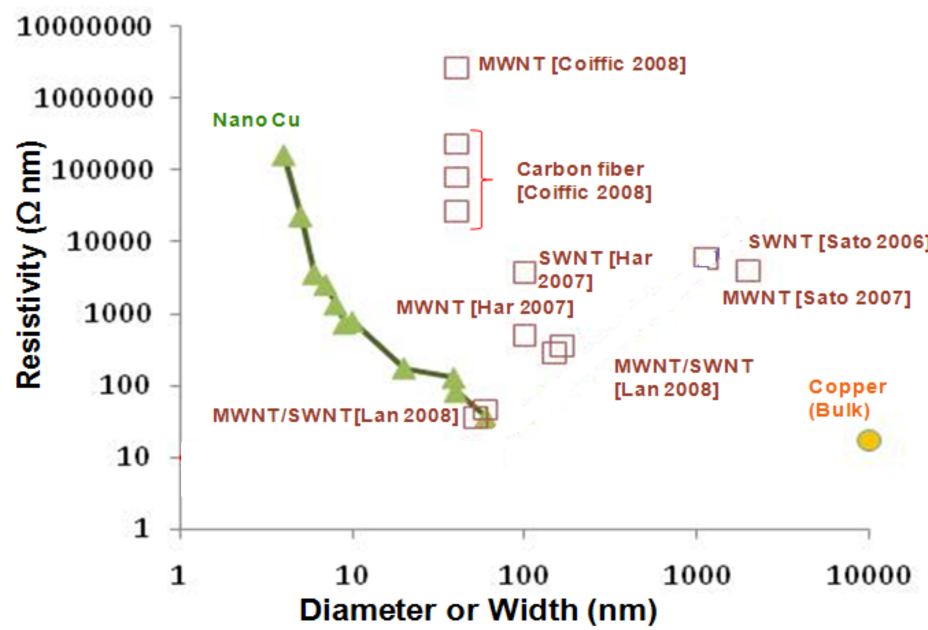
3.) Next Steps – Doping, Multilayer, High Mobility, Substrate Choice – screening to lower scattering

4.) Resistivity Quenching due to higher T – Increase carrier concentration



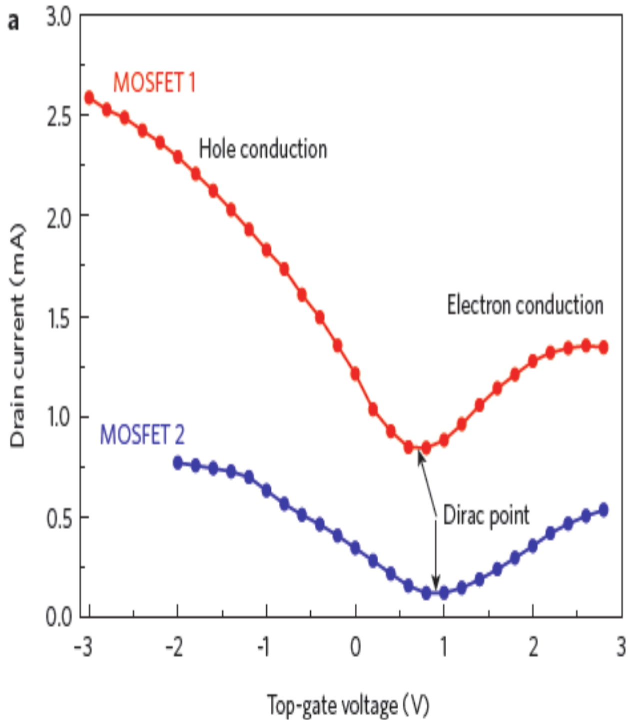


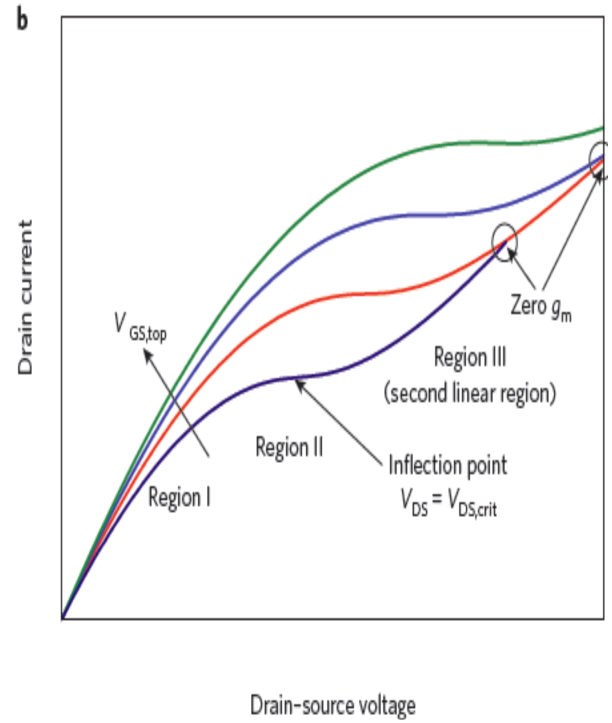


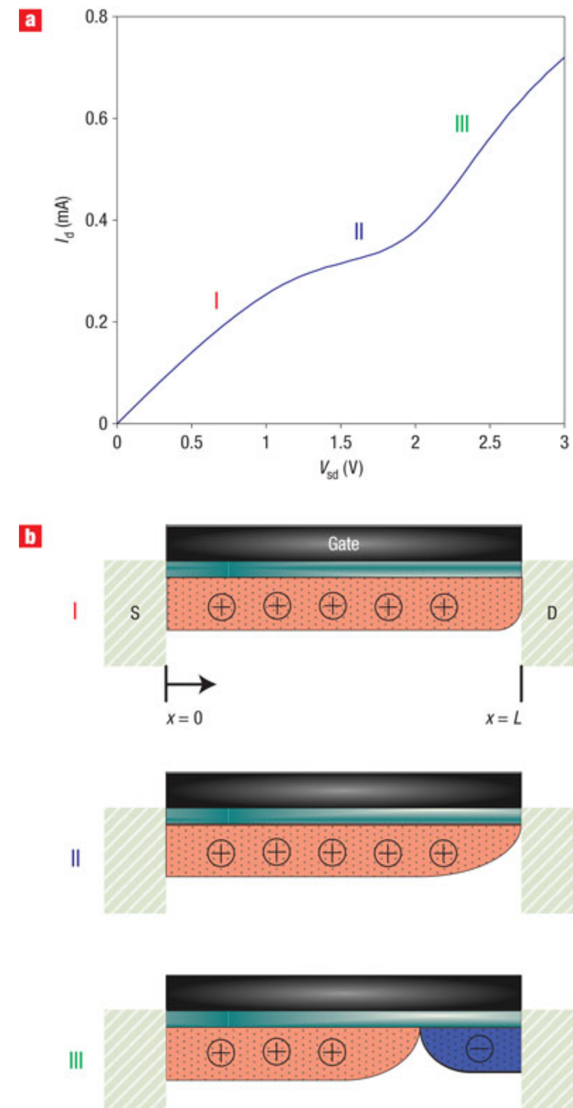


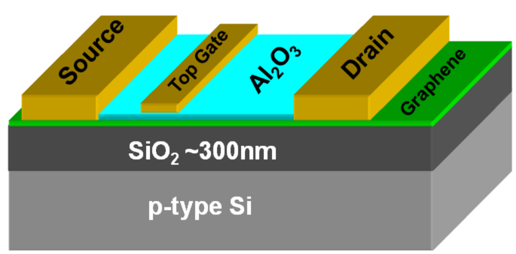
Graphene Transistors

Graphene Transistors



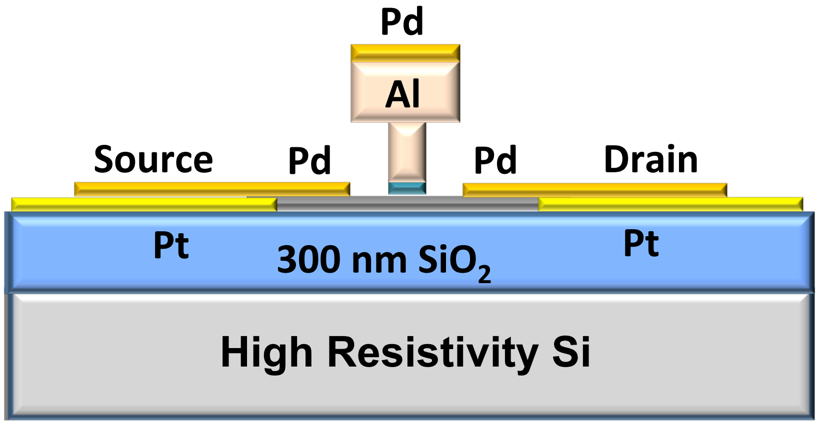


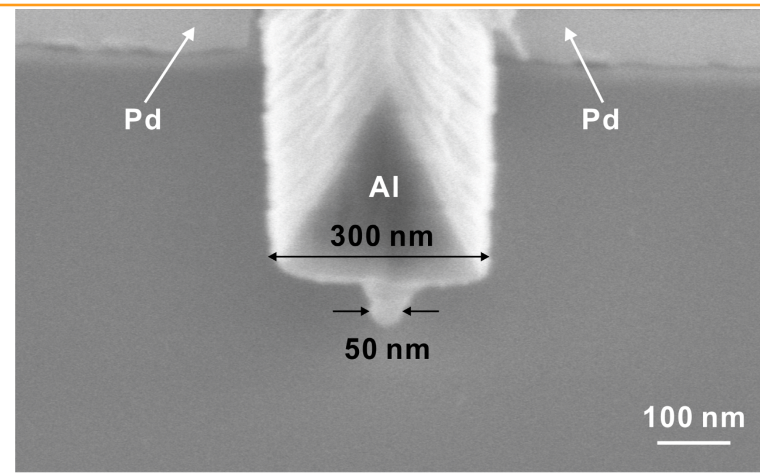


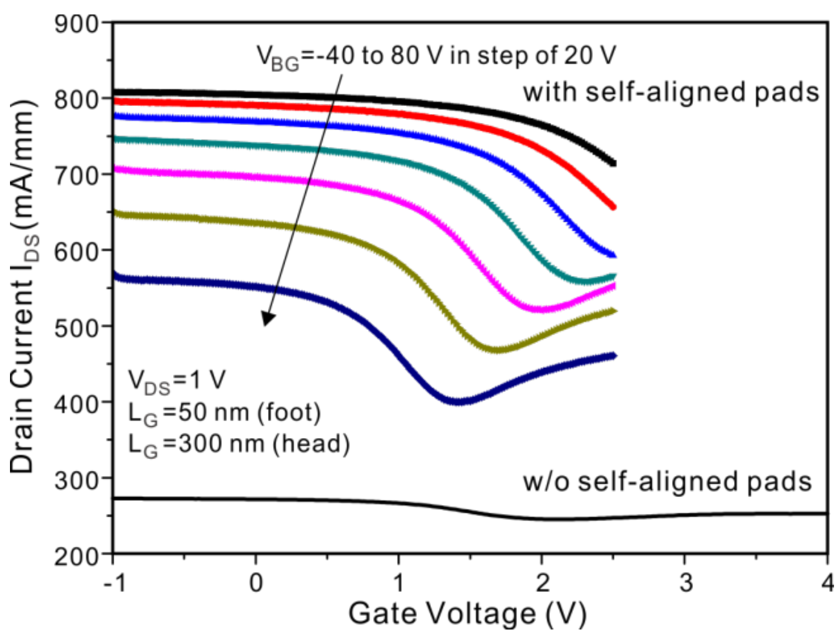


Frank Schwierz, Nature Nanotechnology, vol. 5, July 2010, pp. 487-496
Ken Shepard et al, Nature Nanotechnology, vol. 3, Sept. 2008, pp. 654-659

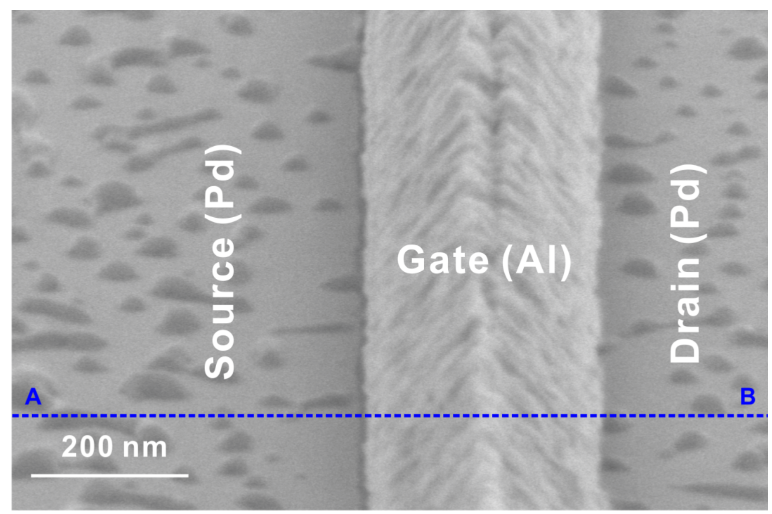
T-Gate Self-aligned GFETs



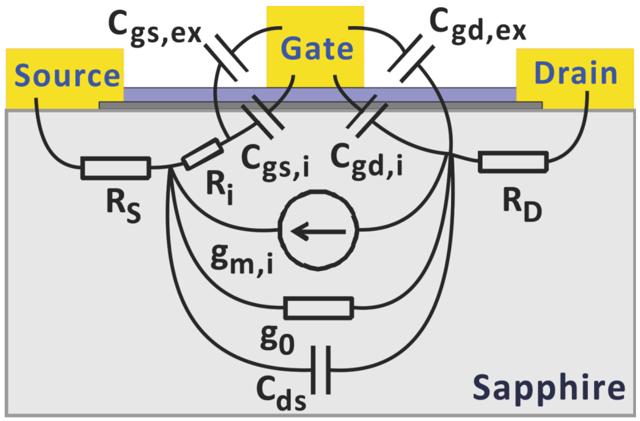




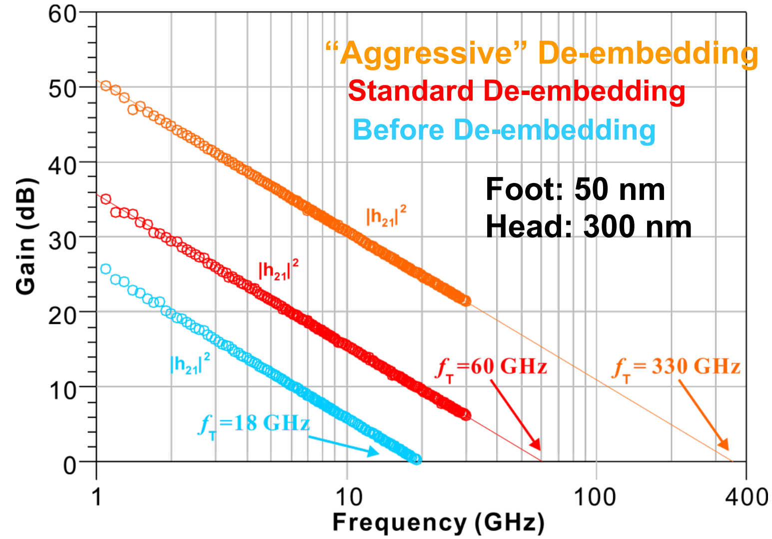
Pd metal stops right at the edge of the gate



Issues with De-embedding and High Frequency…



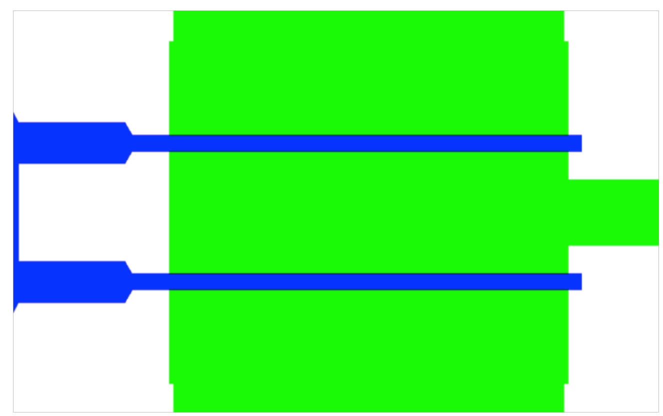
$$f_T = \frac{g_{m,i}/(2\cdot\pi)}{[C_{gs}+C_{gd}]\cdot[1+\frac{R_S+R_D}{R_{ds}}]+C_{gd}\cdot g_{m,i}\cdot(R_S+R_D)}$$



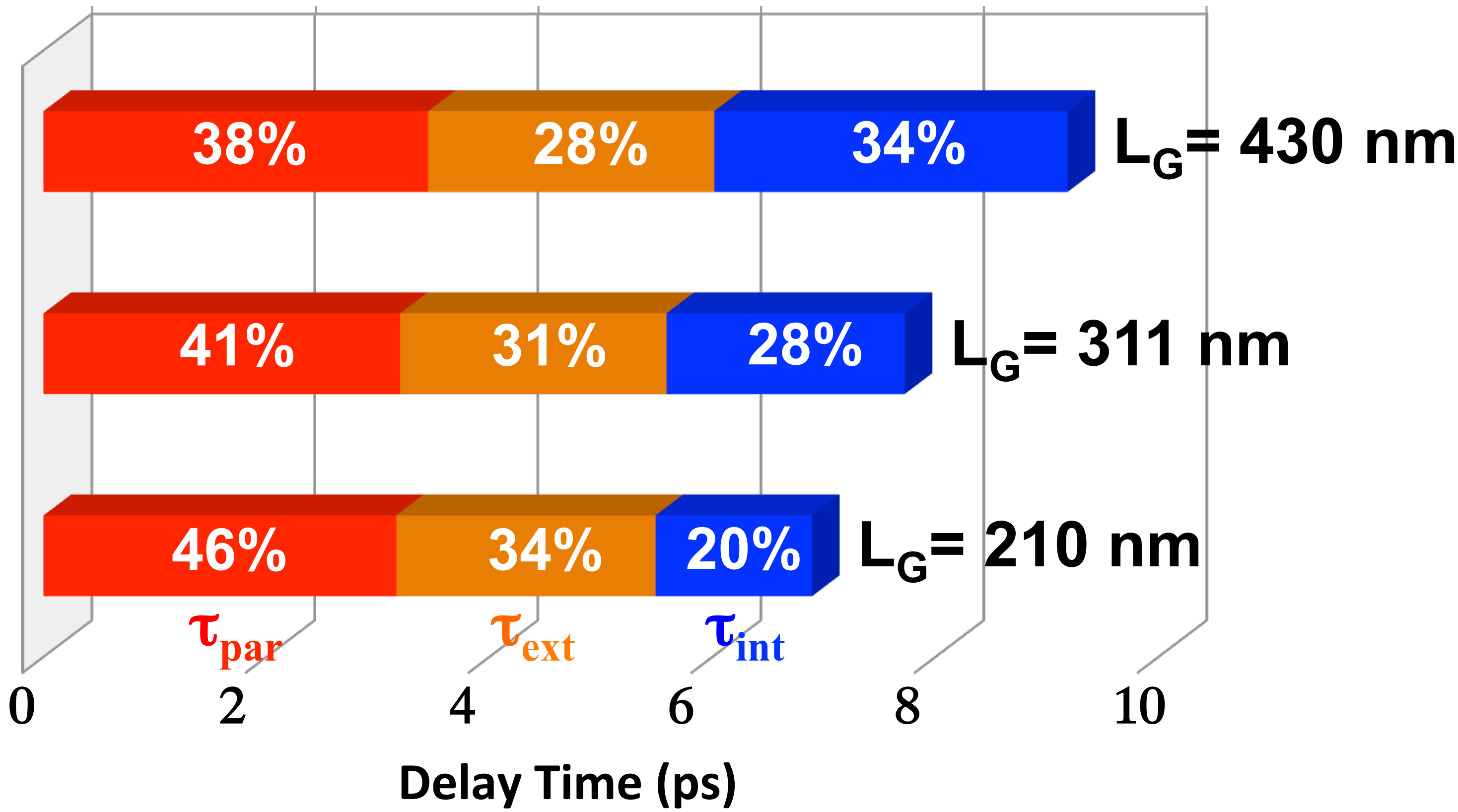
Open Structure

Standard De-embedding

"Aggressive" De-embedding



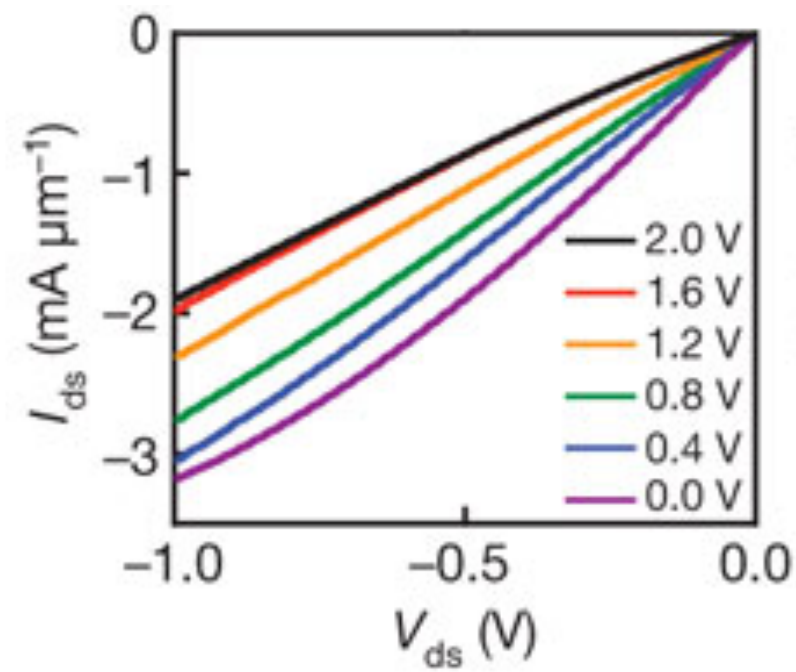
Delay Analysis of Graphene Field Effect Transistors



H. Wang, A. Hsu, D. S. Lee, K. K. Kim, J. Kong and T. Palacios, IEEE EDL, vol. 33, no. 3, 2012

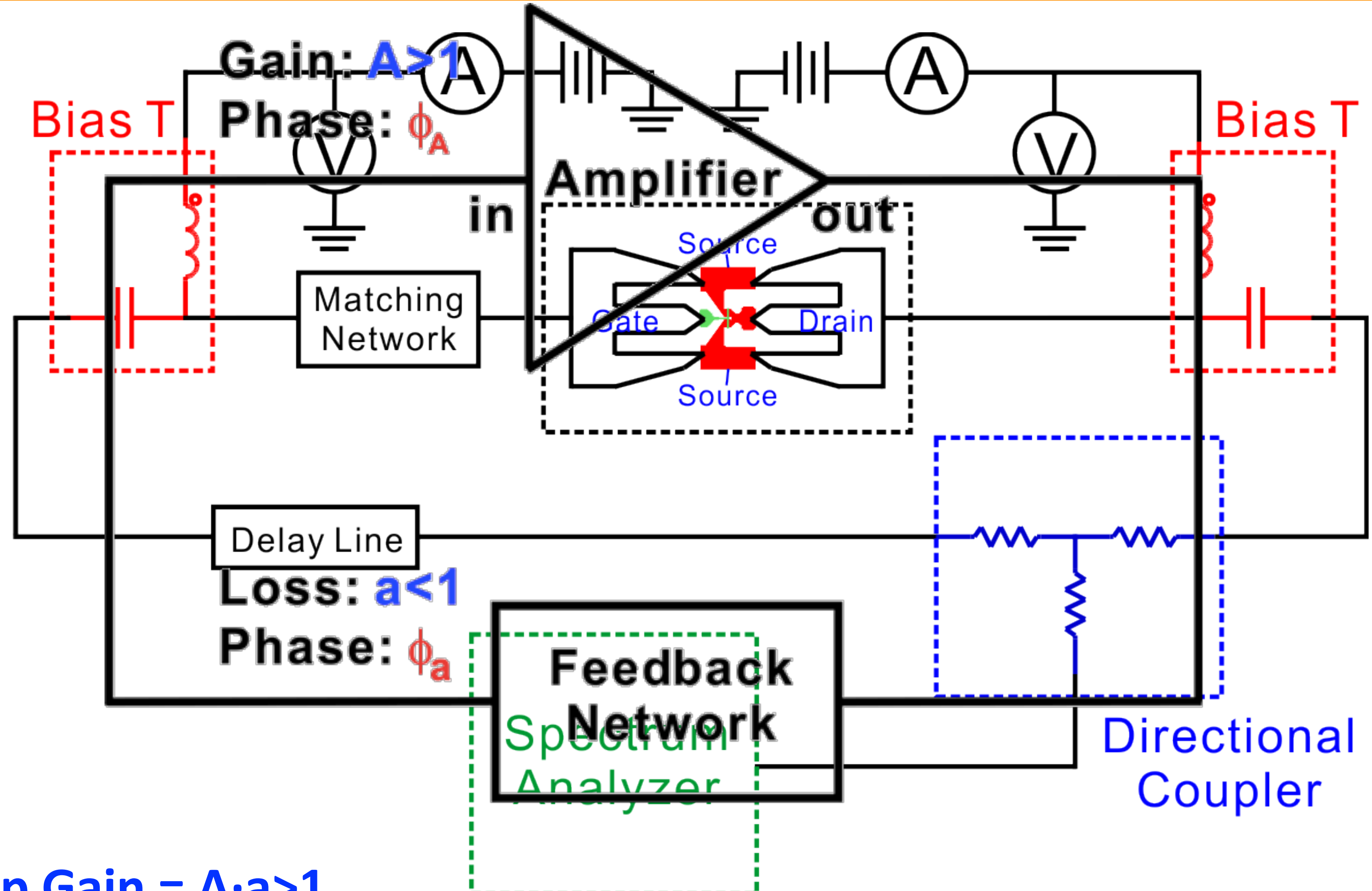
Where to use graphene transistors?

Not in digital electronics (at least not yet)!!



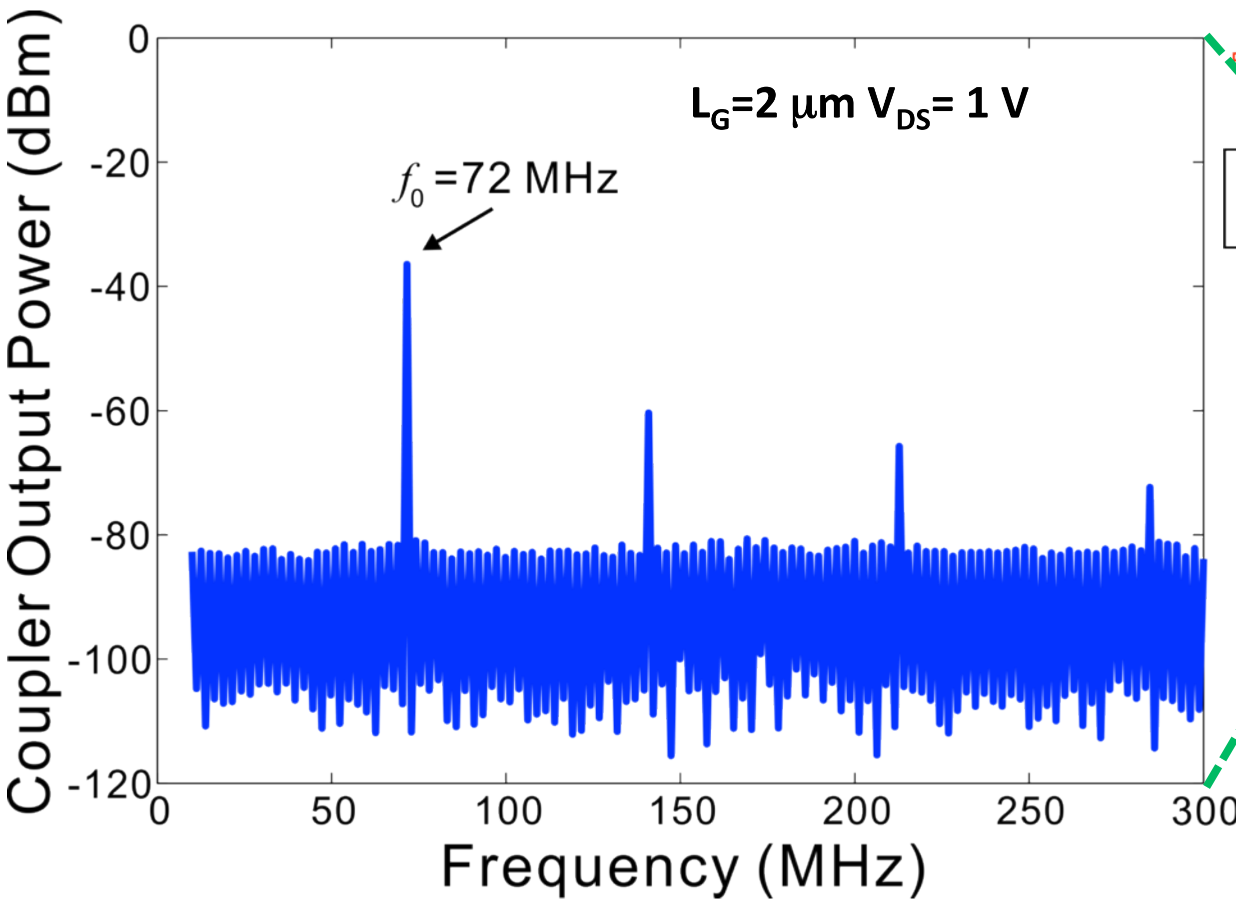
Liao et al., Nature 467, 305-308 (2010)

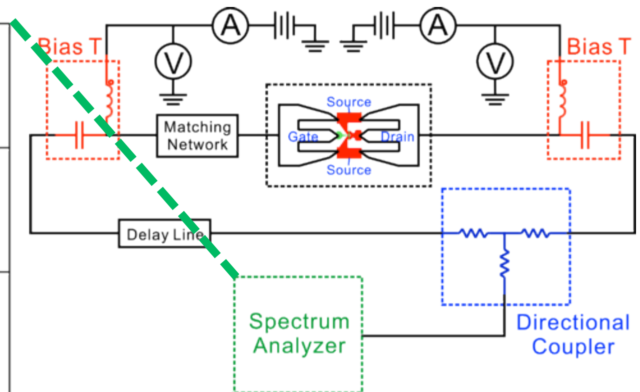
Graphene Oscillator



1. **Loop Gain = A·a>1**
2. **Loop Phase Shift = $\phi_A + \phi_a = m \cdot 2\pi$**

Graphene Oscillator

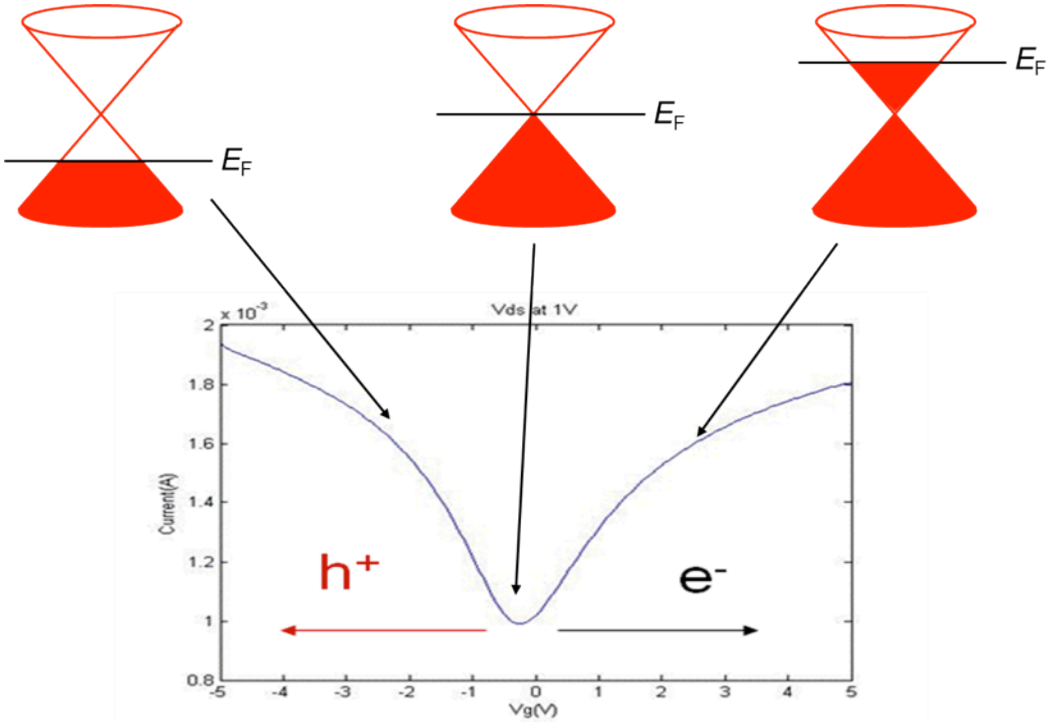


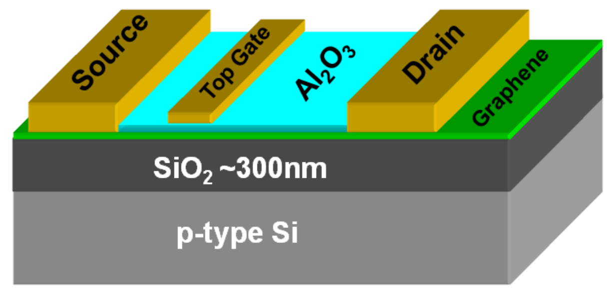


Oscillation frequency tuned by the matching network (not limited to 72 MHz).

First graphene electrical oscillator and
First circuit level demonstration of power gain in graphene transistors.

Ambipolar Electronics





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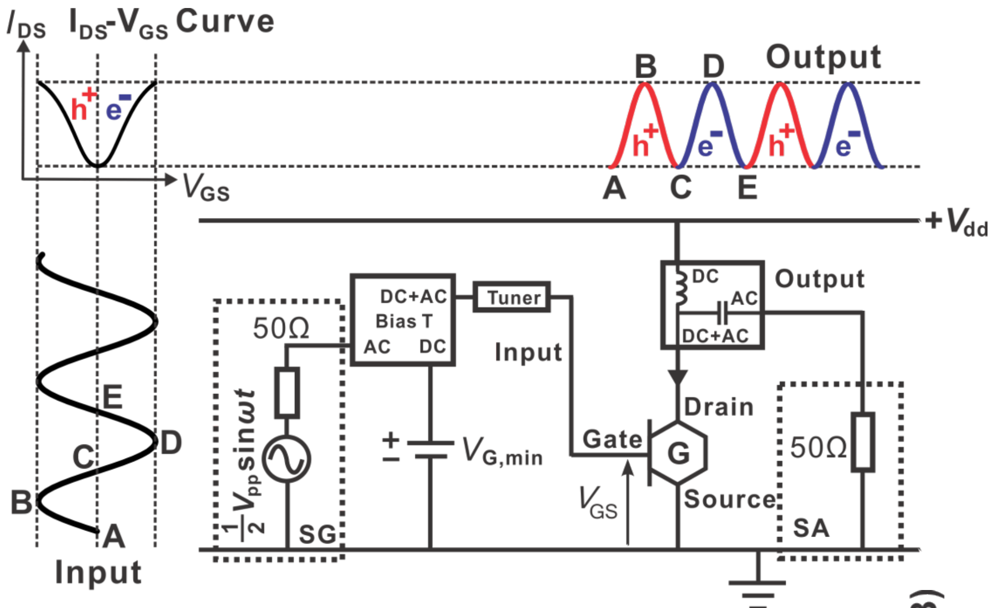
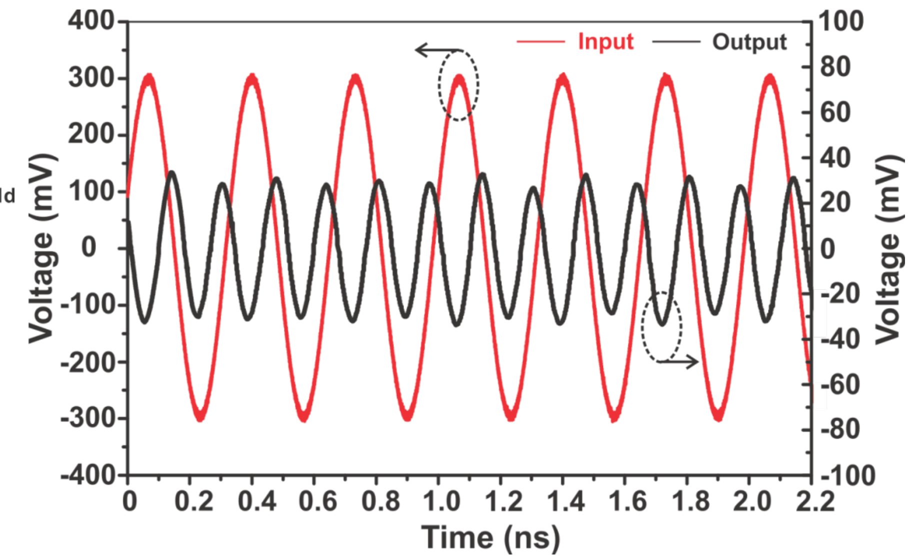
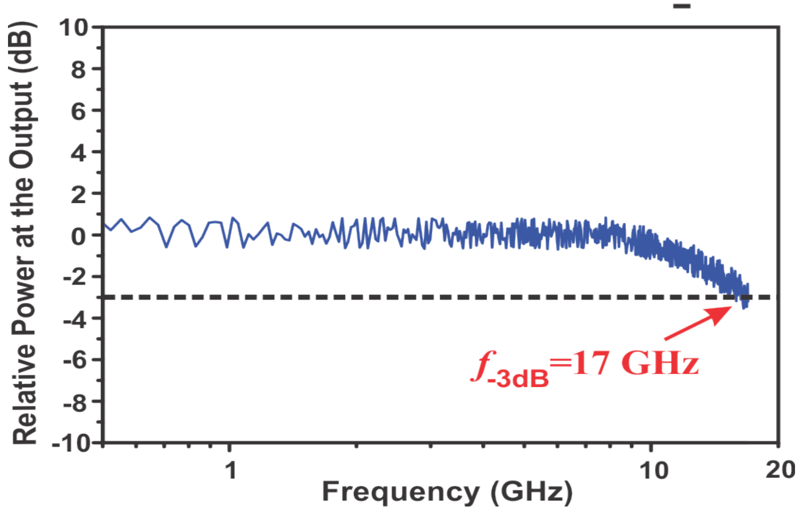
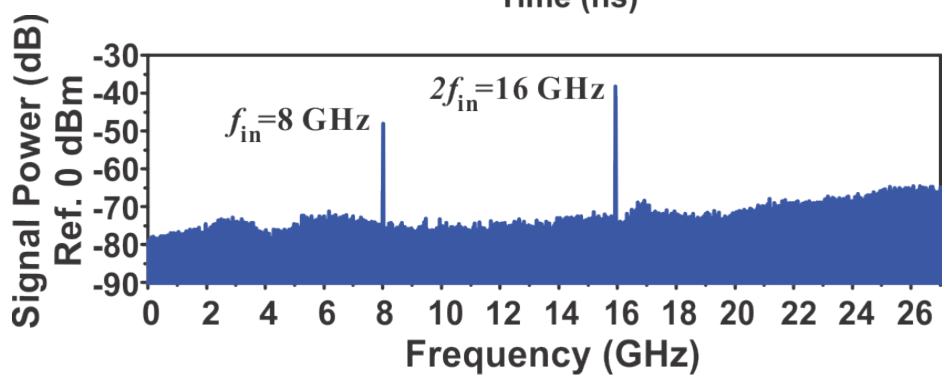
tpalacios@mit.edu

Ambipolar Electronics: Frequency Multiplier with f_{-3dB}=17 GHz





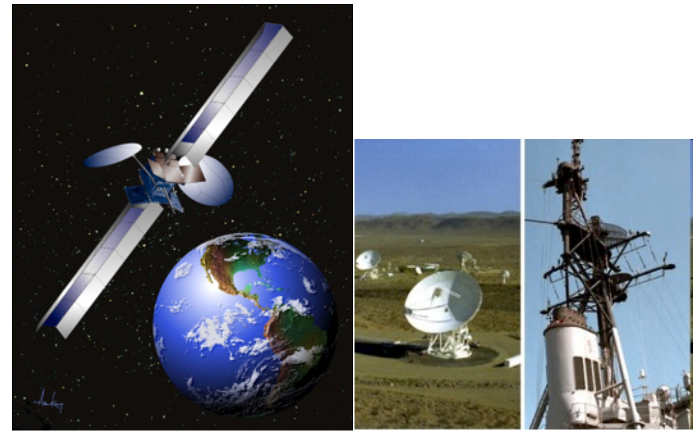




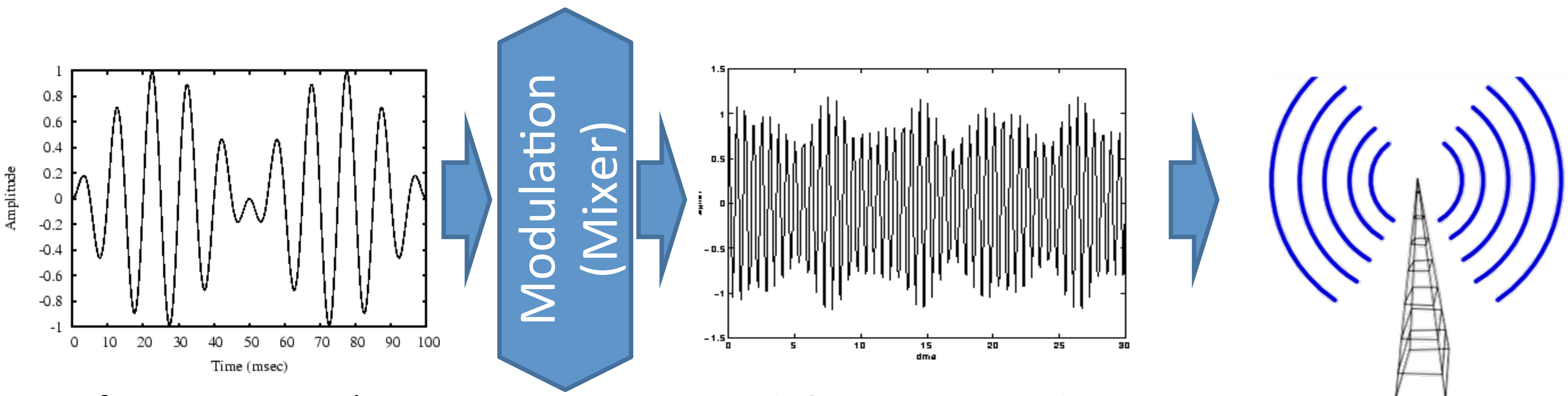
>93% output RF power at 16 GHz without any filtering elements

High Frequency Mixers

Mixers are key elements of virtually all modern RF communication systems:



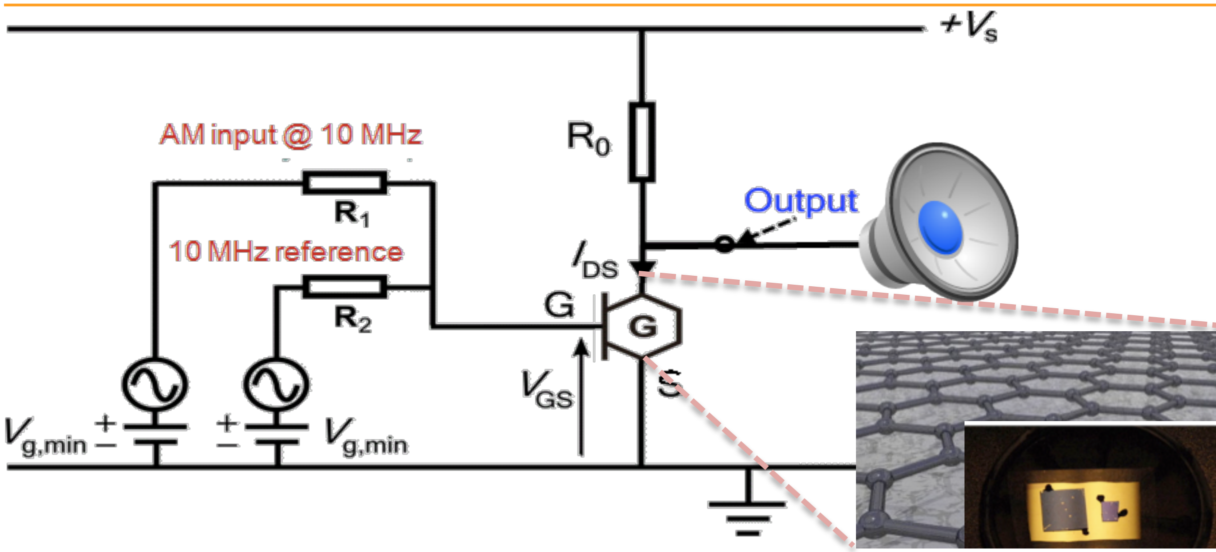
- Modulation and demodulation
- Jamming
- Detectors

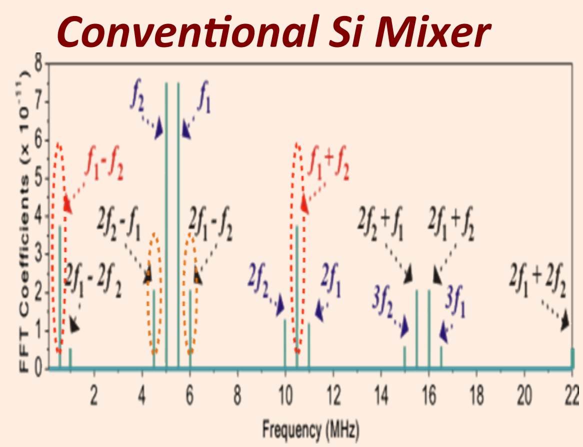


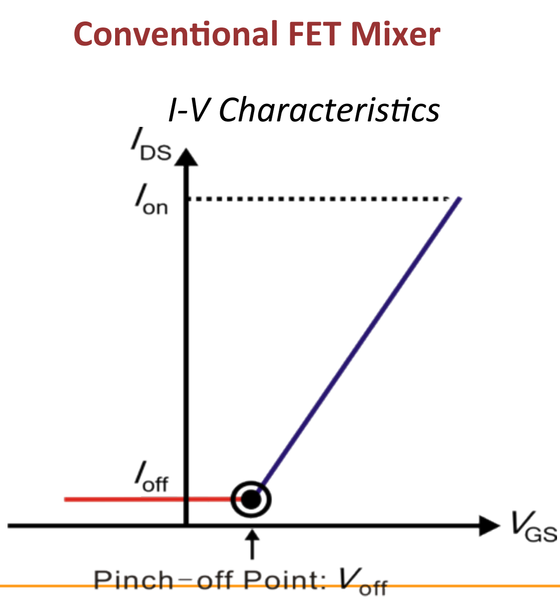
Low frequency signal (information, eg. Voice)

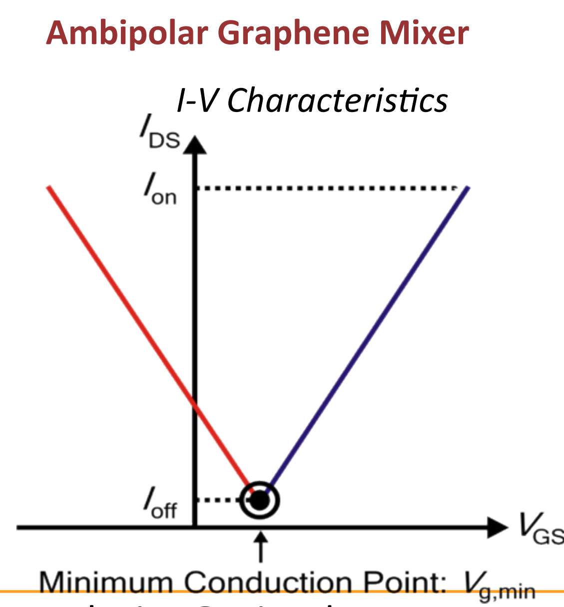
High frequency signal (modulated signal)

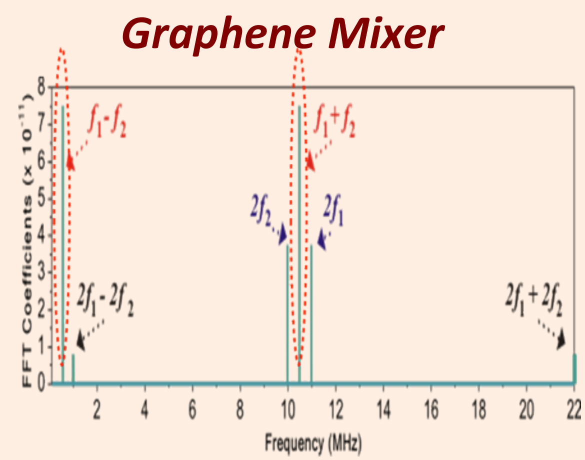
GFET Mixers











Much cleaner spectrum: higher bandwidth efficiencies and lower noise

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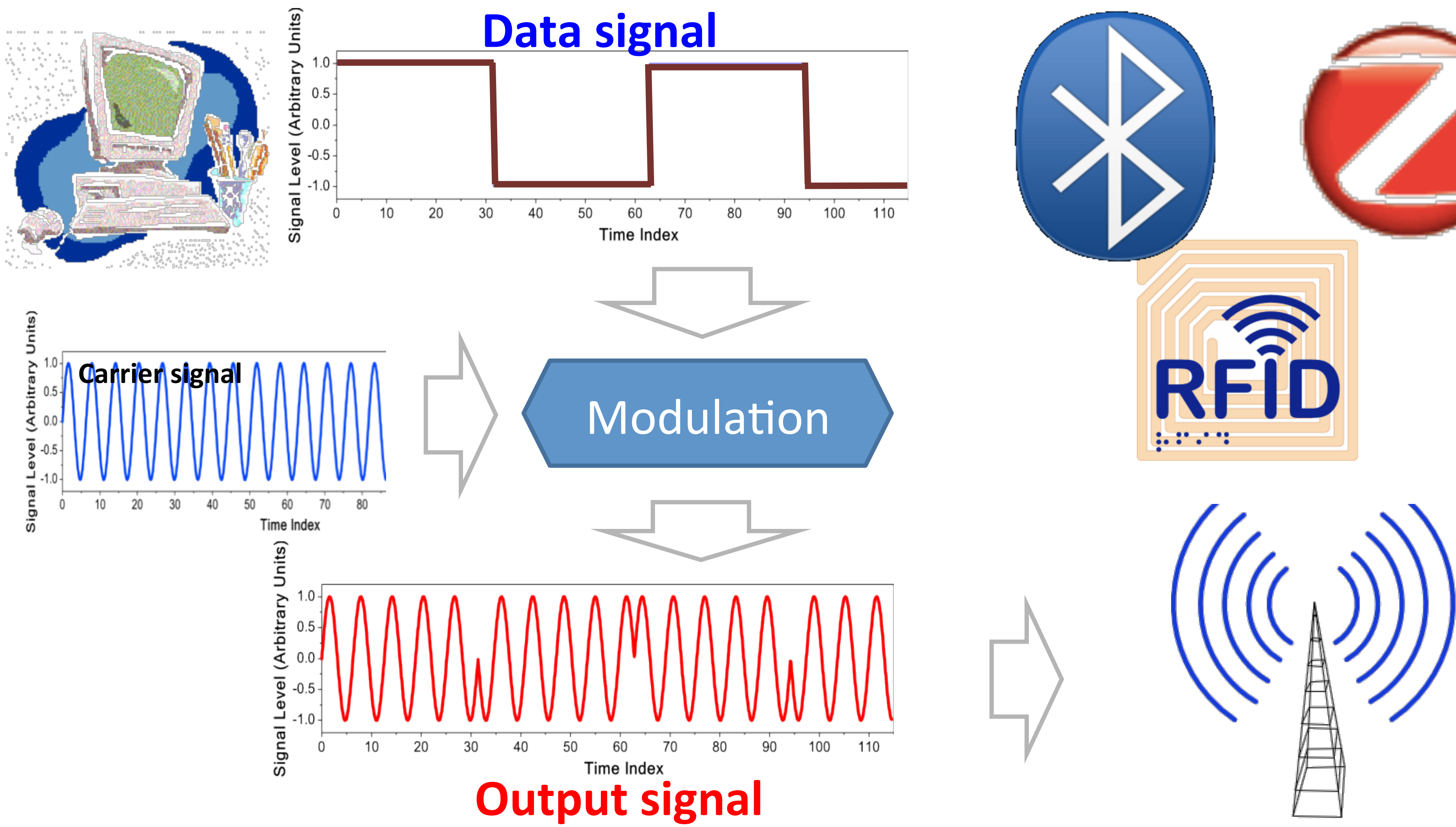
Phase Shift Keying (PSK)

•Phase Shift Keying is one of the most popular digital modulation schemes



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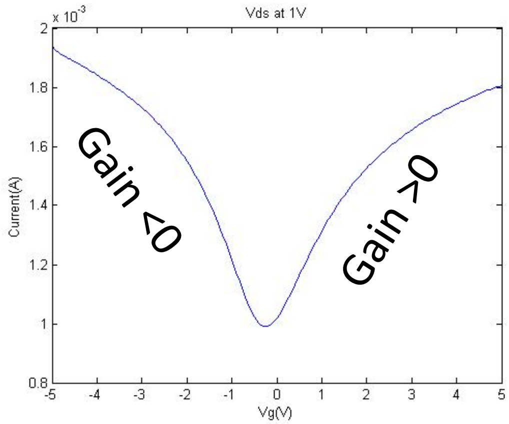
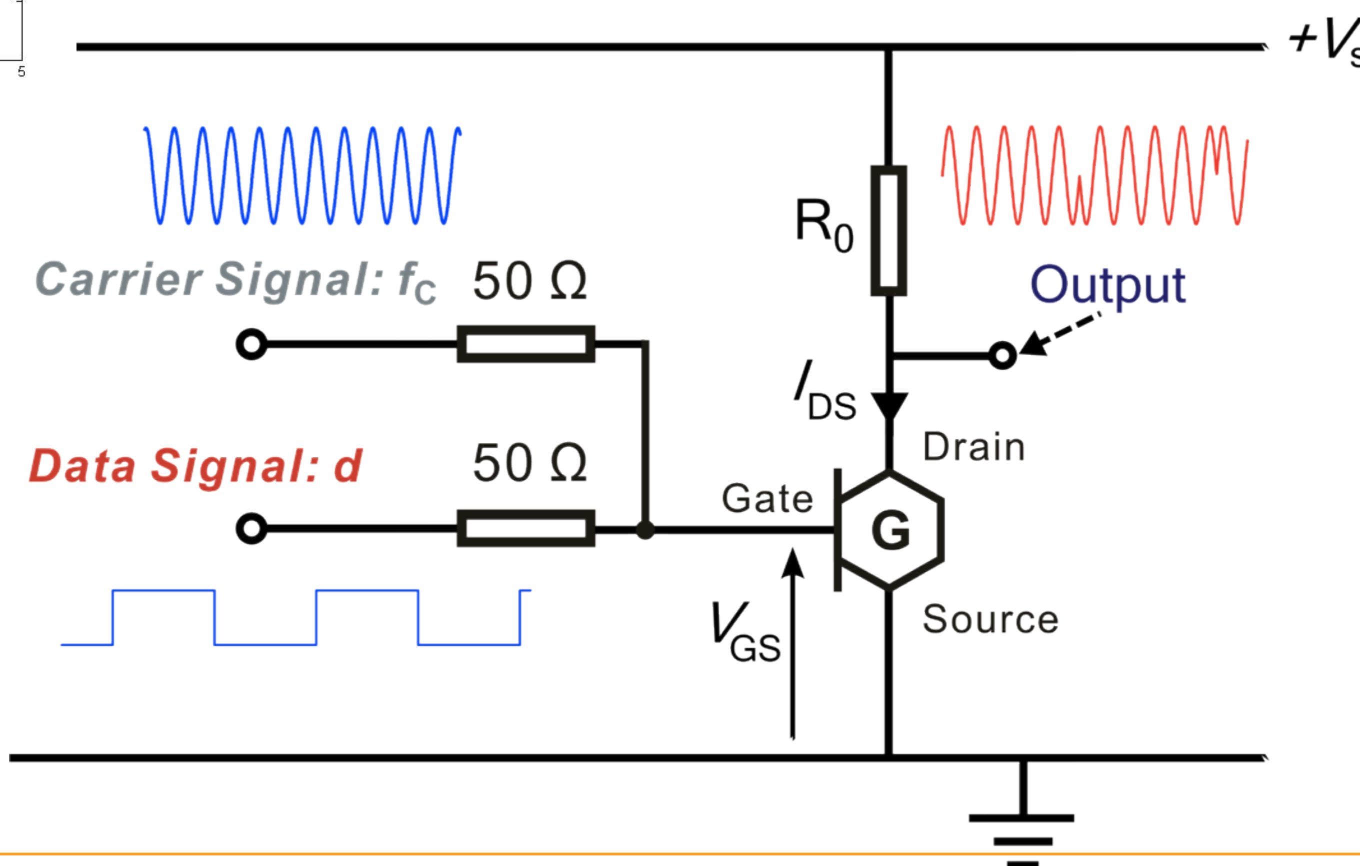
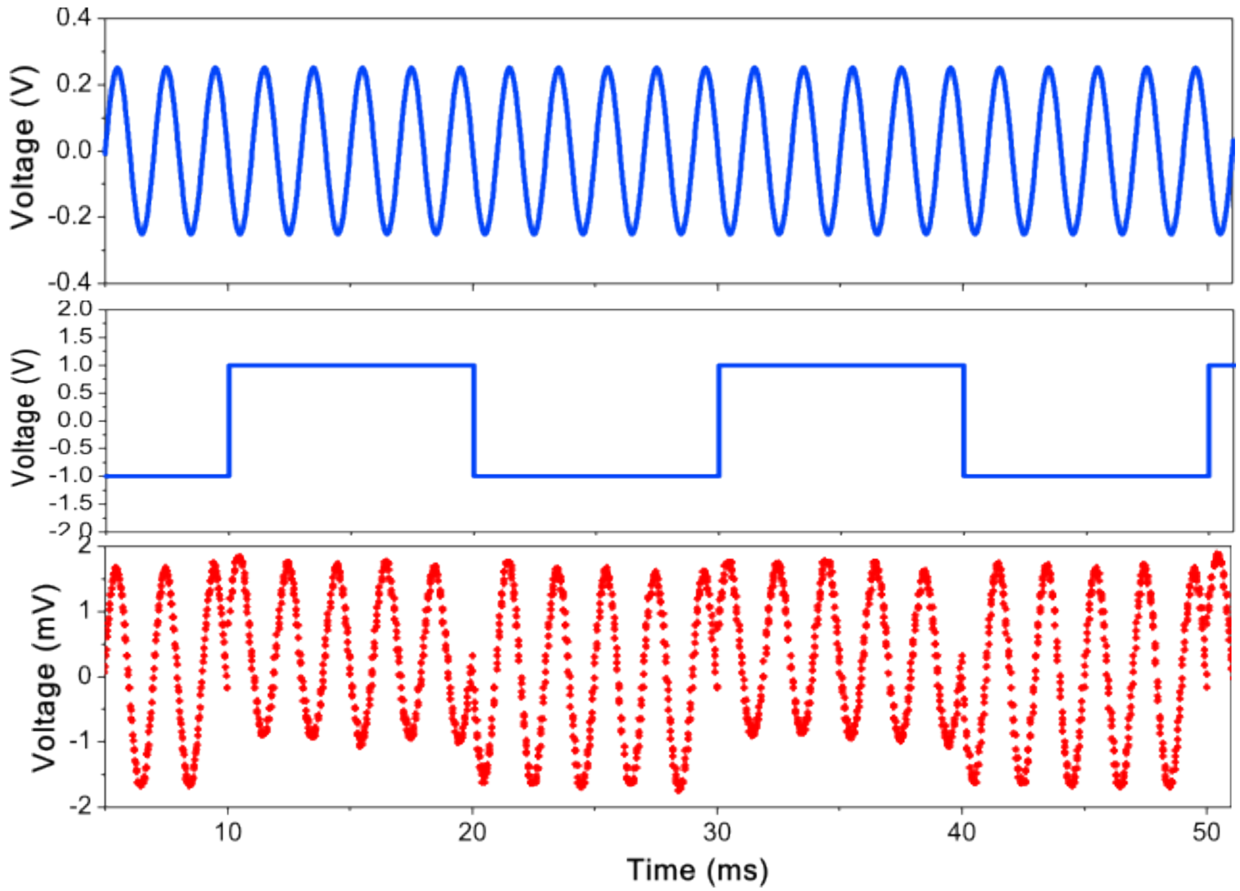
Graphene Phase Shift Keying





Experimental Demonstration

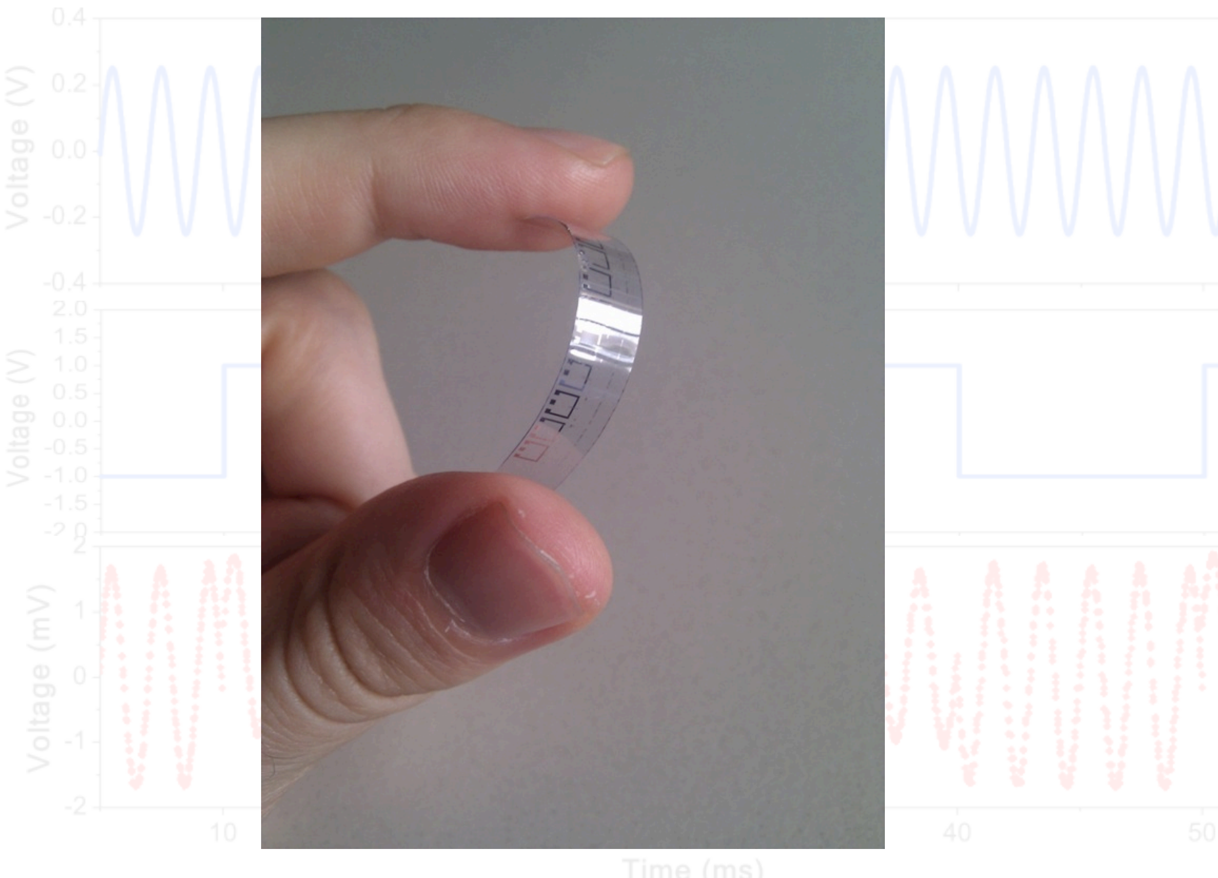


BPSK has been demonstrated, but the idea can be expanded to other forms of PSK such as quadrature PSK (QPSK) as well.

Wang, Palacios, et al., IEEE Communications Magazine (June 2010)

Experimental Demonstration

And many more circuits…



…in a completely new form factor, with fewer components and higher frequencies

Outline

- Why graphene?
- Growth and fabrication technology
- Some applications:
  - High performance electronics
  - Chemical sensors
- Beyond graphene…
- Conclusions and outlook

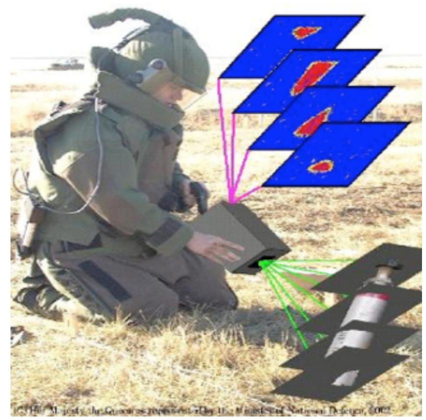
Chemical Sensors

Food monitoring

Biosensors

Industrial processes

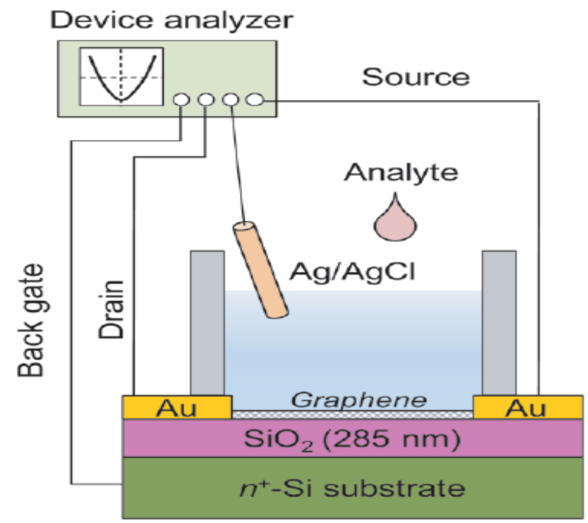
Environmental safety

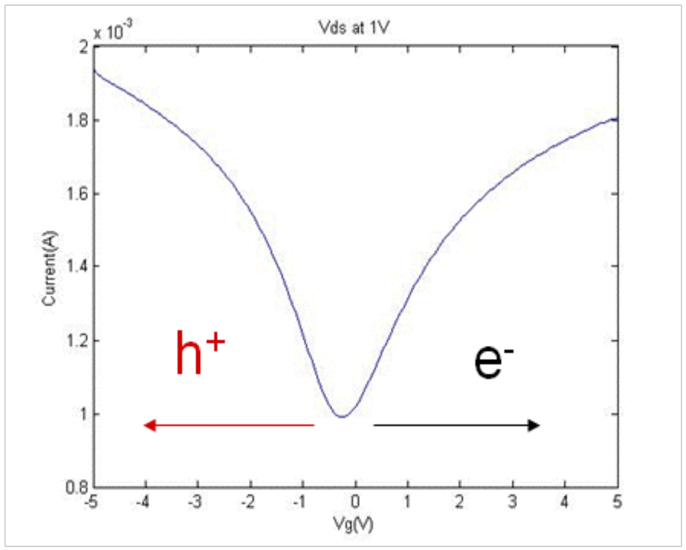


Explosive detection

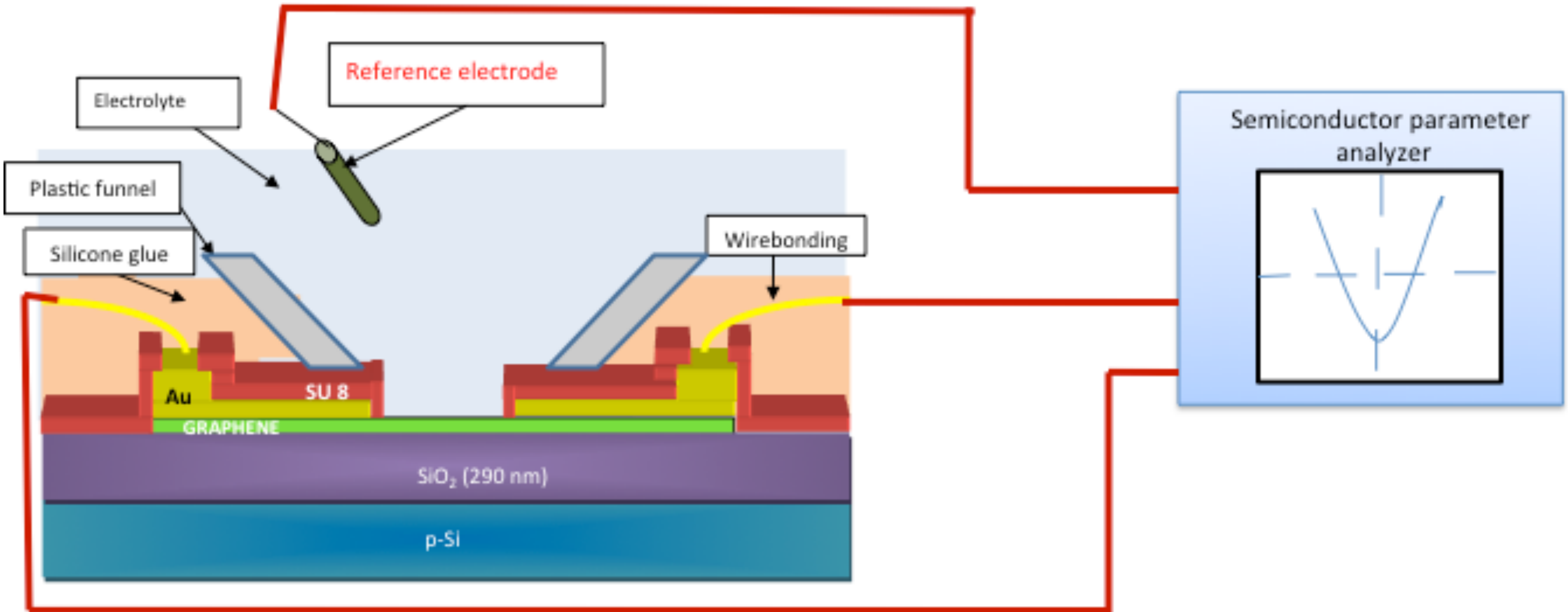
Graphene: *The Ultimate Electronic Sensor?*

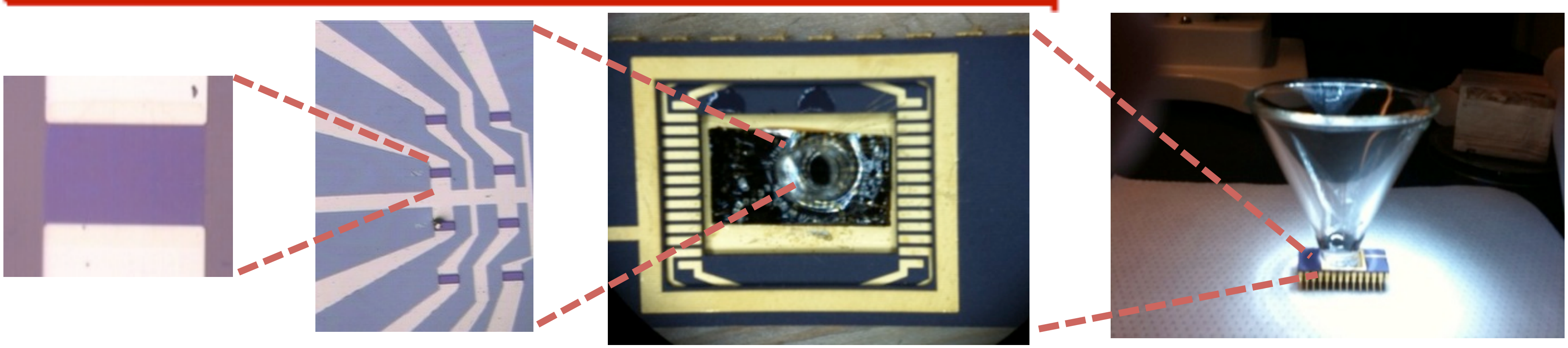
- High sensitivity → One atom thick
- Functionalization chemistry already developed in CNTs
- Lower noise → Reduced carrier scattering and very high transconductance (noise ~ $1/g_m^2$)
- Biocompatible
- High chemical stability
- Transparent → Integration of electrical and optical measurements
- Can be transferred to plastic and paper-based substrates
- Ambipolar transport → Detection of + / - analytes





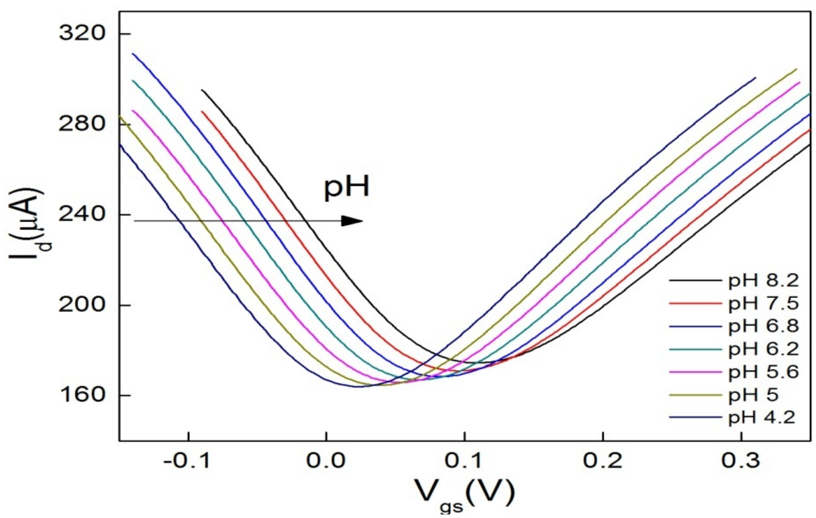
Graphene Electronic Sensor

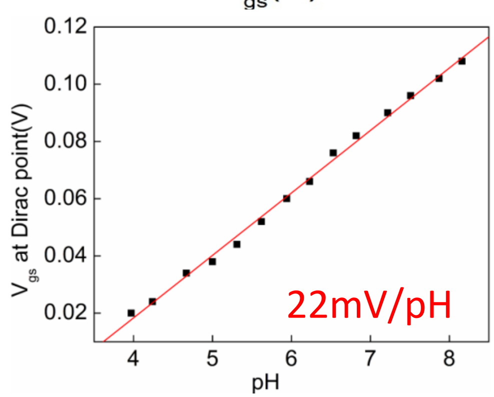




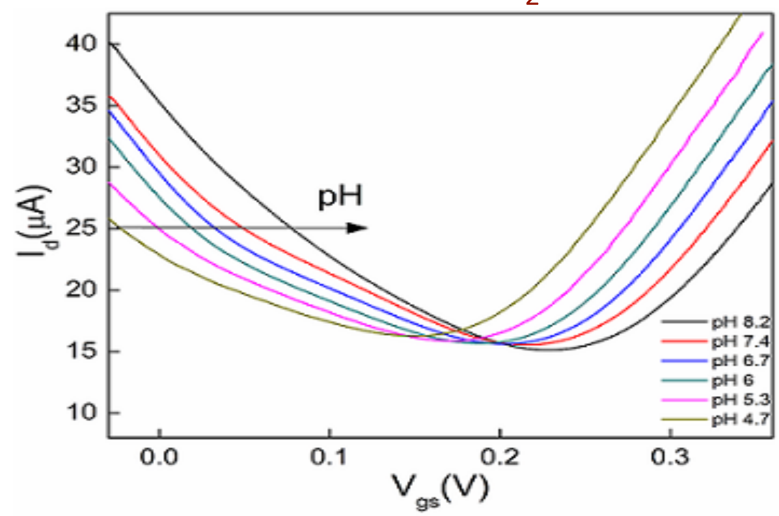
Dirac Point Shift with pH

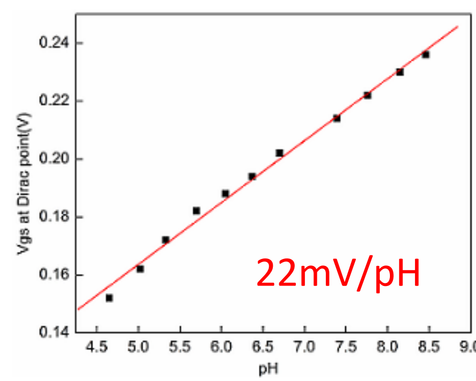
Device on PEN





Device on SiO_2

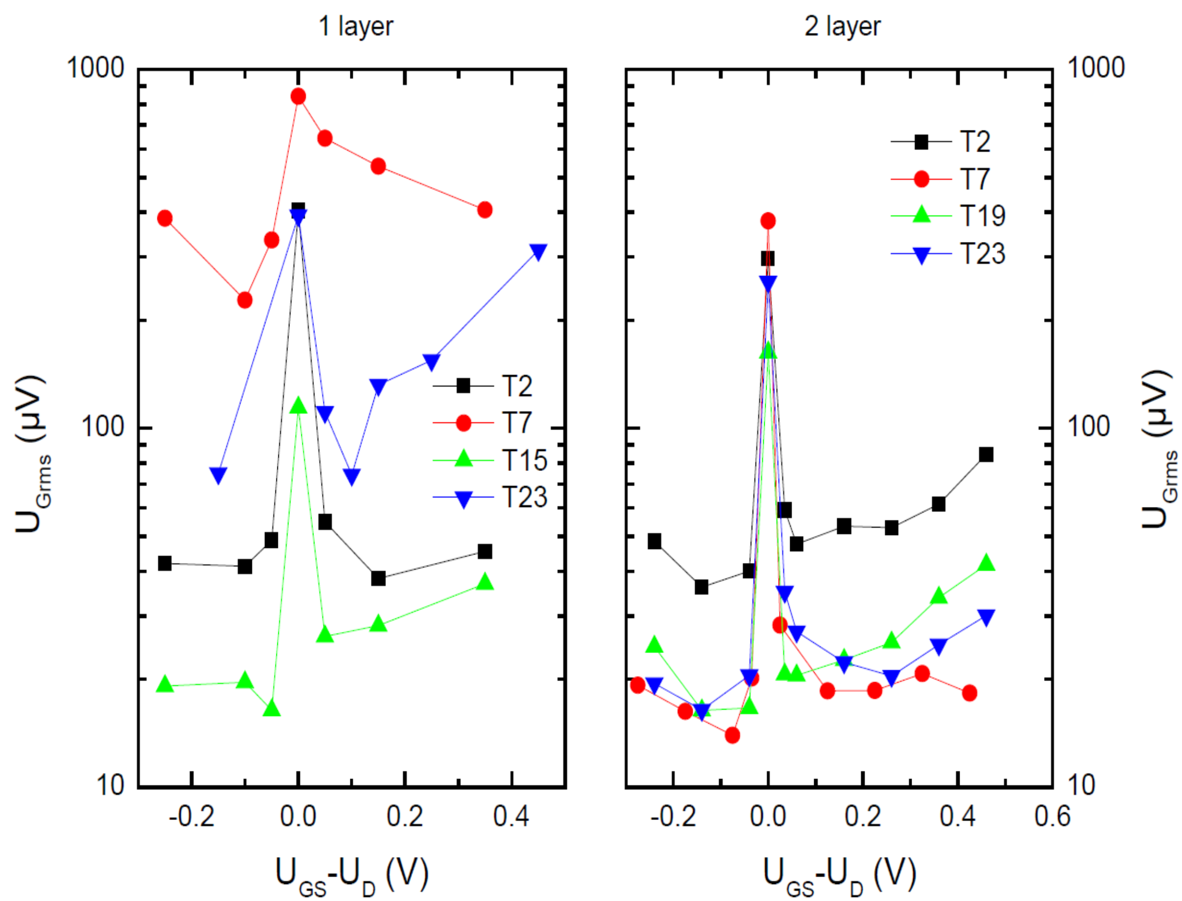




- pH increases → Dirac point shifts towards positive V_g
- Linear relationship with same pH sensitivity : 22 mV/pH

RMS of gate noise spectra density

Gate noise spectra density= minimum gate signal detected by the device



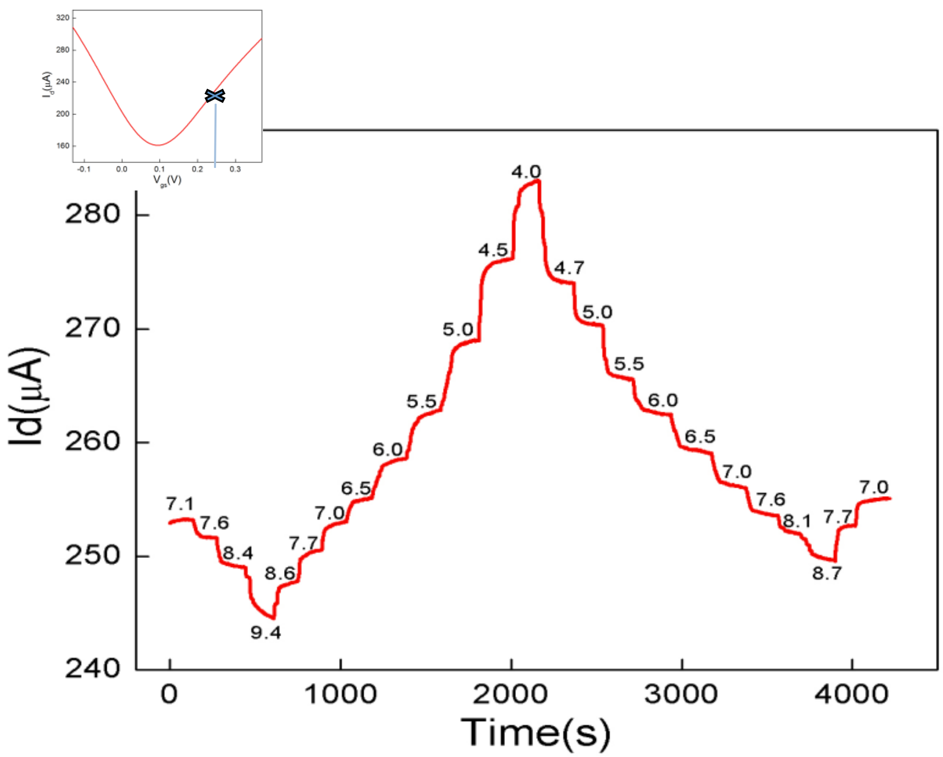
• Single layer devices are not very uniform, although the bes device has a gate noise of 20 µV

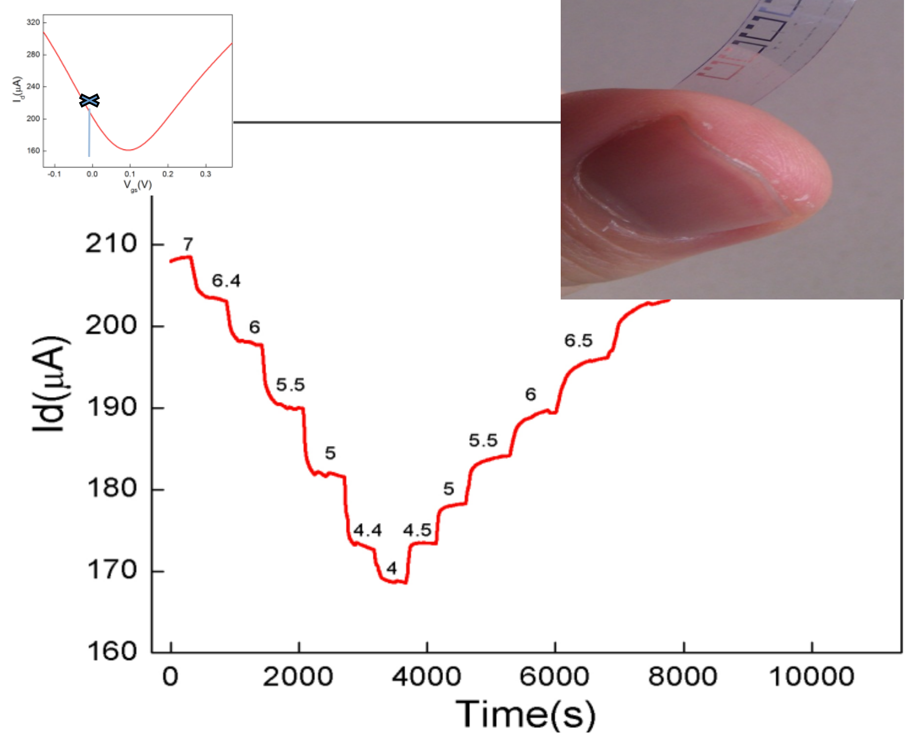
• Nearly all bilayer devices achieve a noise around 15 µV

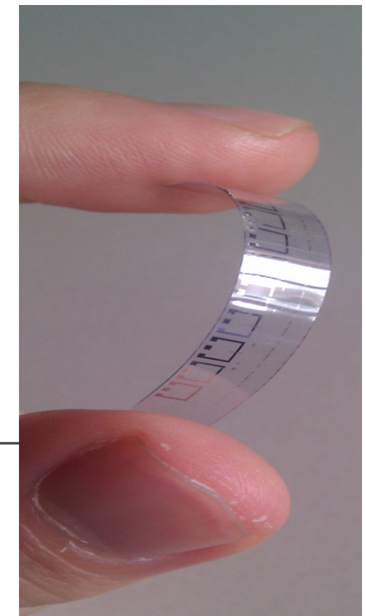
• An order of magnitude lower than in standard Si SGFET's and 50% lower than very-low-noise Si SGFET

pH monitoring

Sensor on PEN, 1000x50μm^2 in size

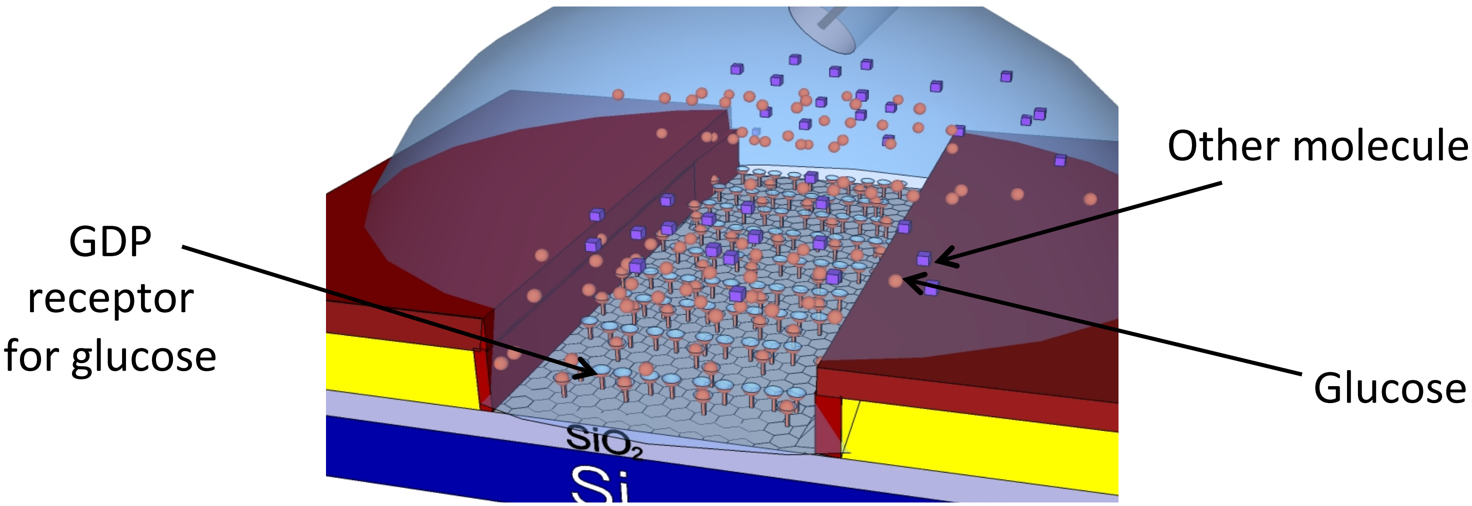


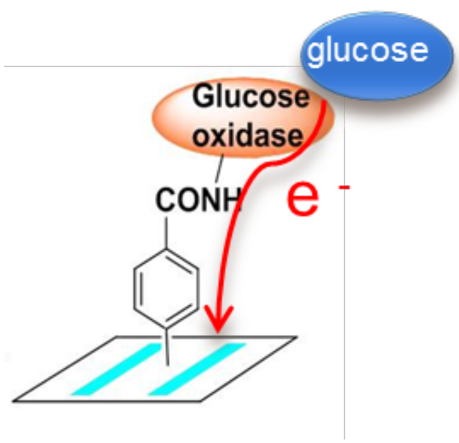


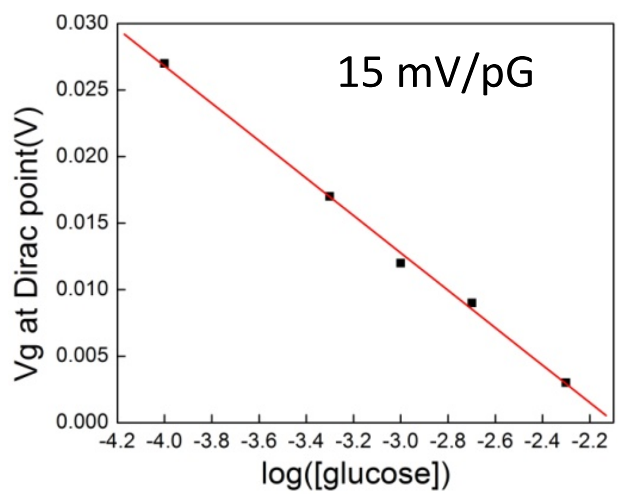


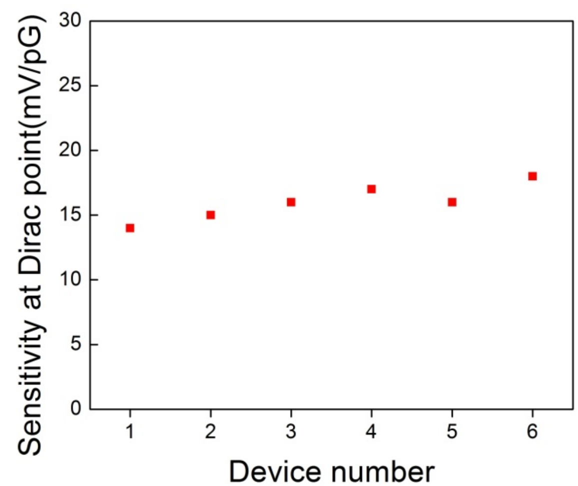
Graphene Glucose Sensors

Functionalization with Guanosine 5′-diphosphoglucose (GDP)









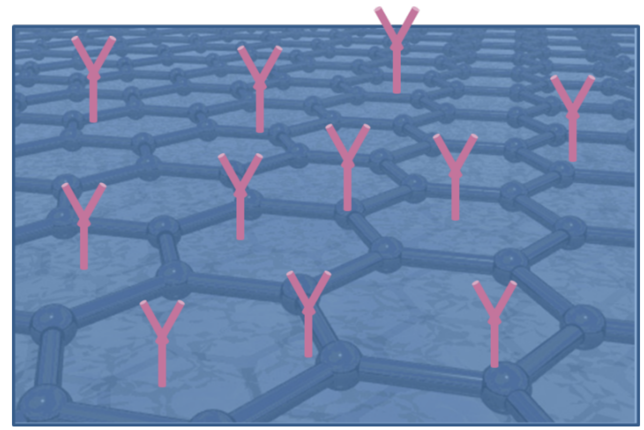
tpalacios@mit.edu

Detection of food-borne pathogens

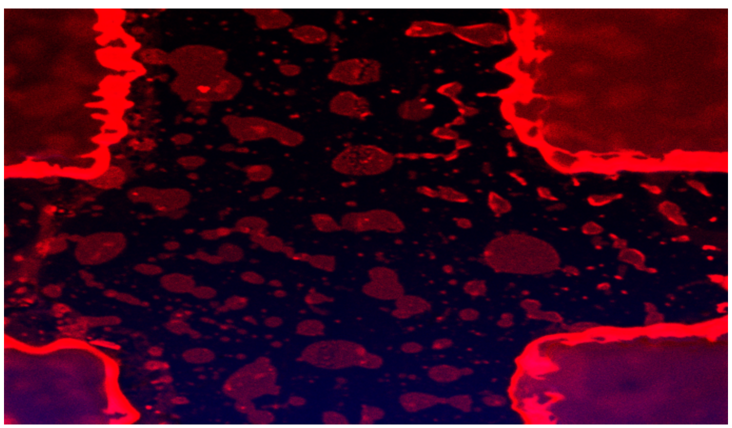
Goal: detection of e-coli in food supply

TWO APPROACHES

- Functionalization of native graphene
- Functionalization of Al_2O_3-coated graphene

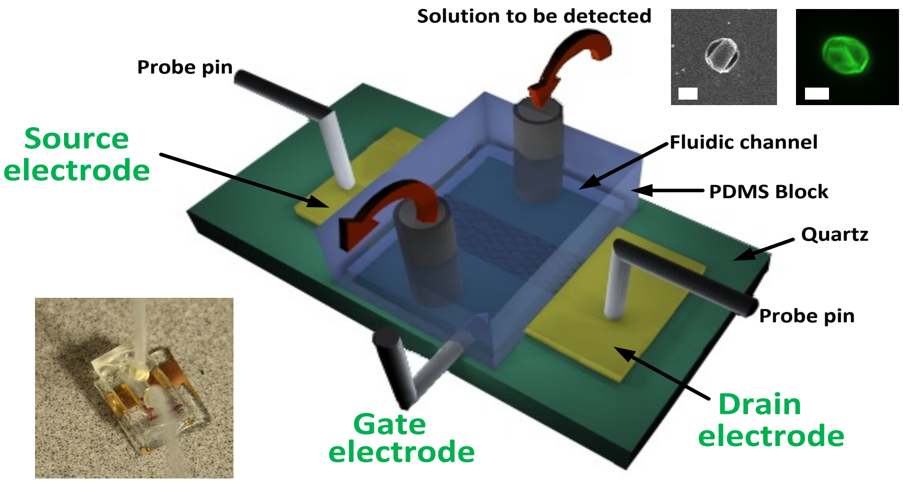


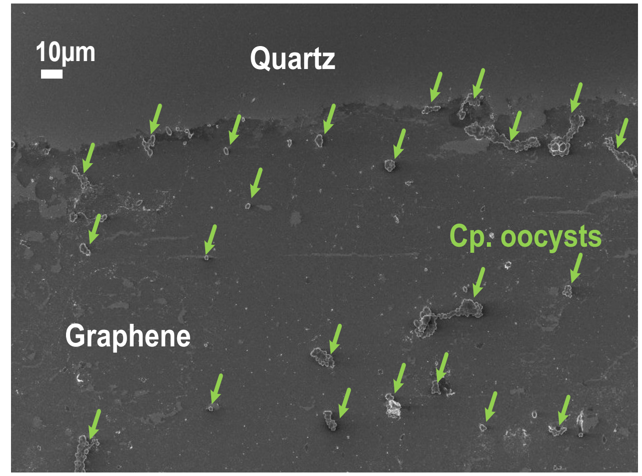
False-colored confocal microscope images of graphene field effect transistor gate regions (red= antibody; blue= reflection)

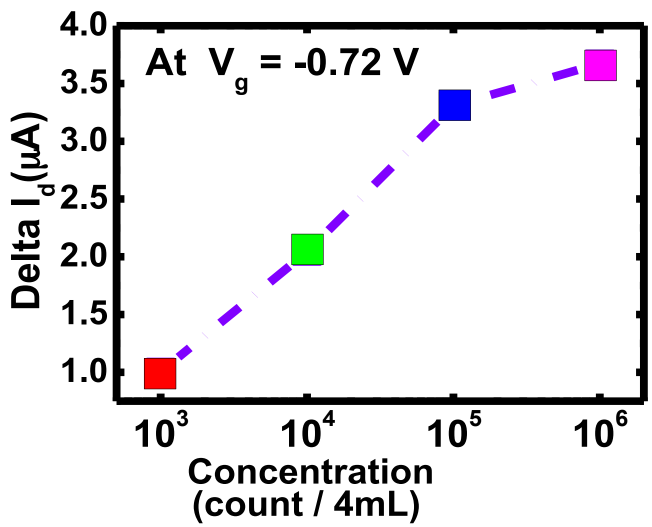


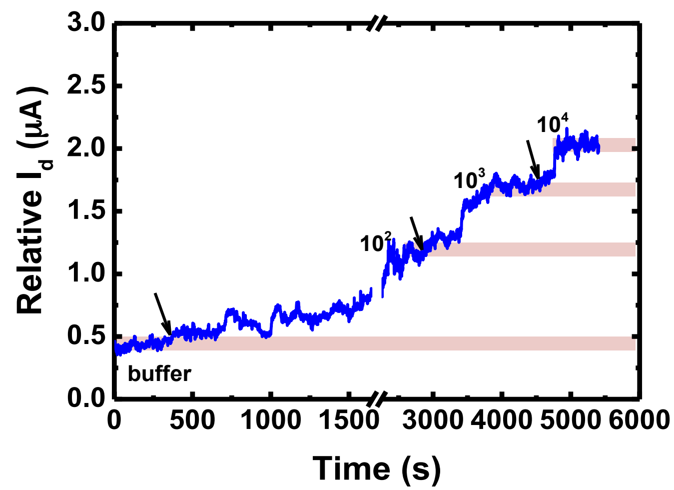
In collaboration with Dr. Dawn Nida (Natick Army Lab)

Detection of Cryptosporidium parvum oocysts









In collaboration with Dr. Lu Wang (*Singapore University of Technology and Design*)

Graphene is an amazing material…

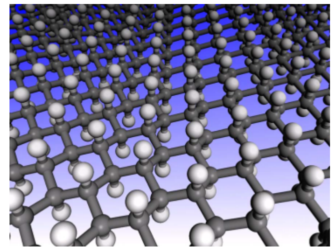
…However many applications need a bandgap

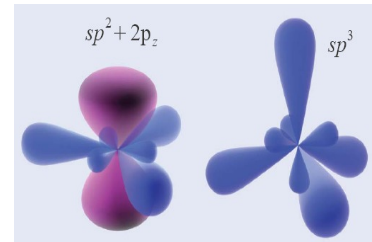
Approaches to open a bandgap:

- Surface functionalization
- Vertical electric field in bilayer graphene
- New materials

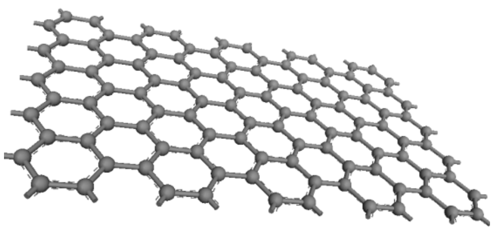
Surface functionalization

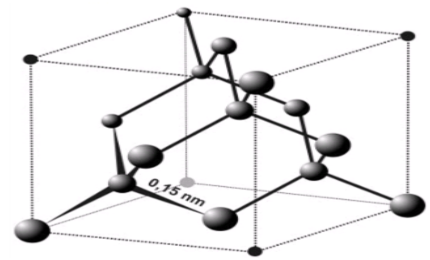
Bandgap Engineering





Graphene





Diamond

Pure sp^2 System

Pure sp^3 System

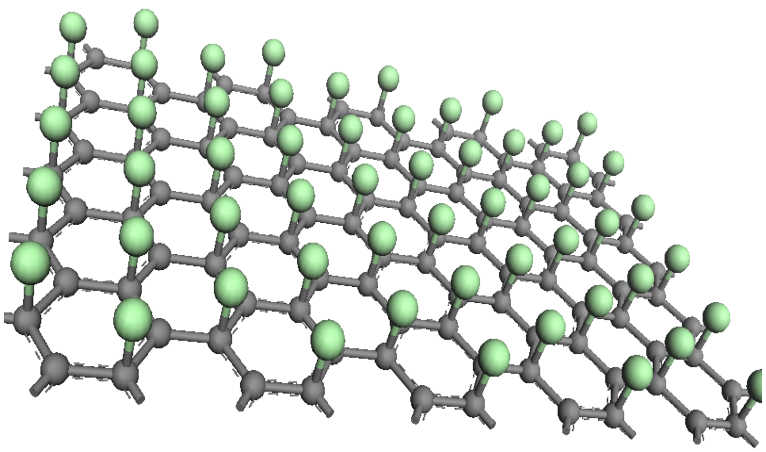
Band gap = 0 eV

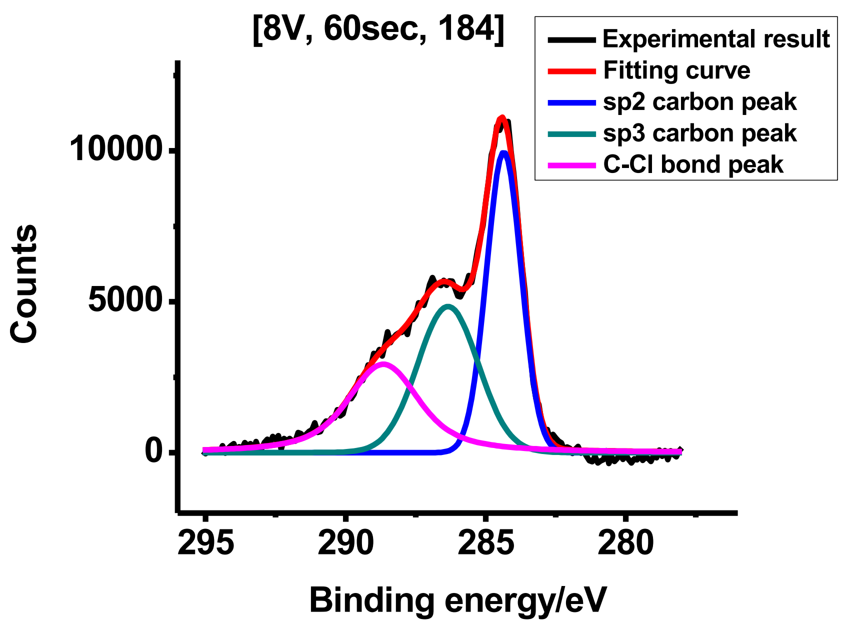
Band gap = 5.5 eV

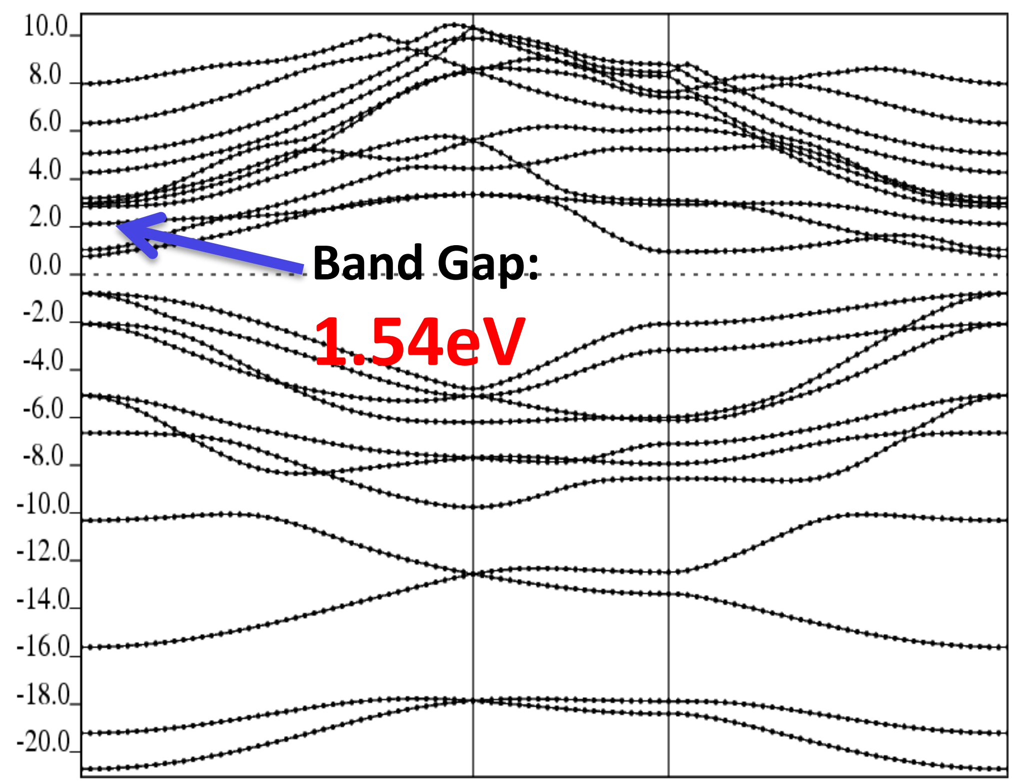
By engineering the sp^3/sp^2 ratio in graphene, we can tune its bandgap.

D.C.Elias et al., Science, 323 (2009)

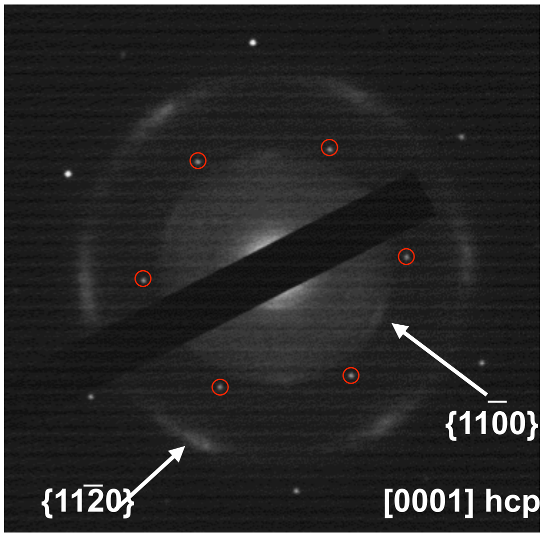
Chlorine-based Surface functionalization

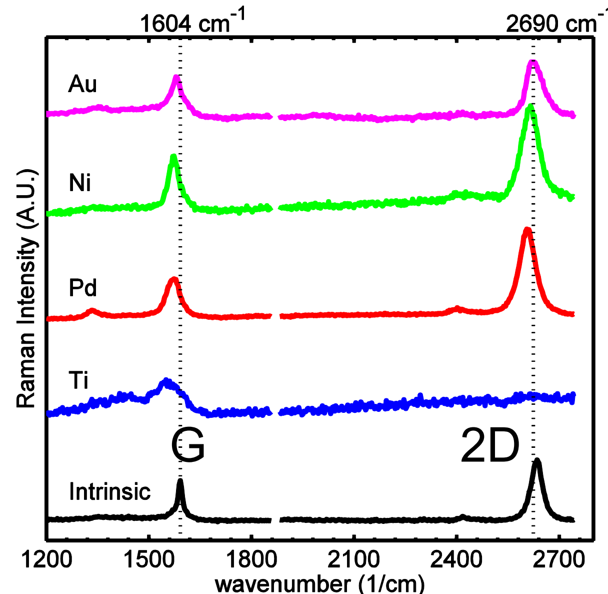


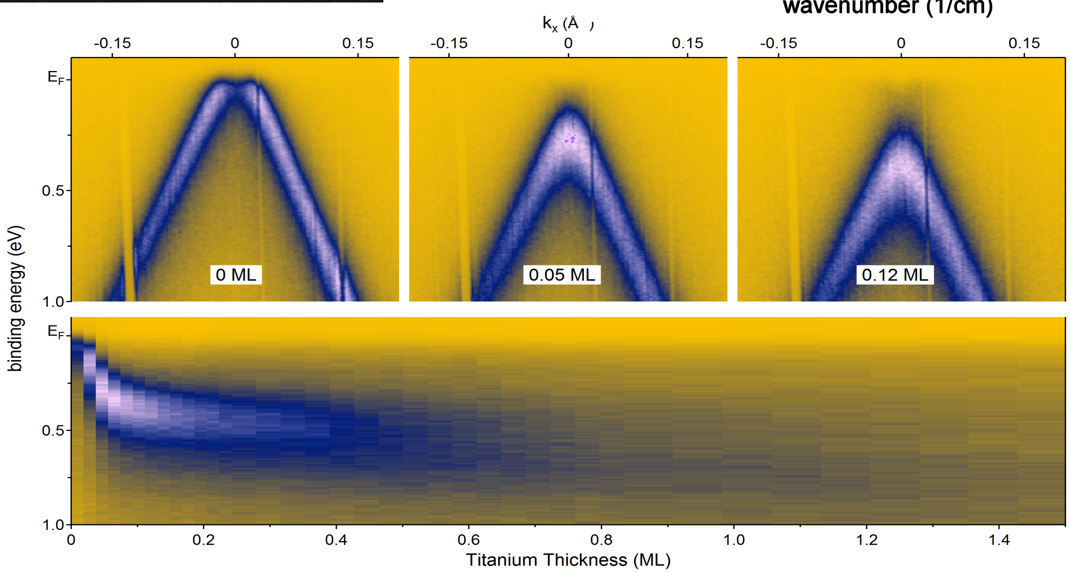




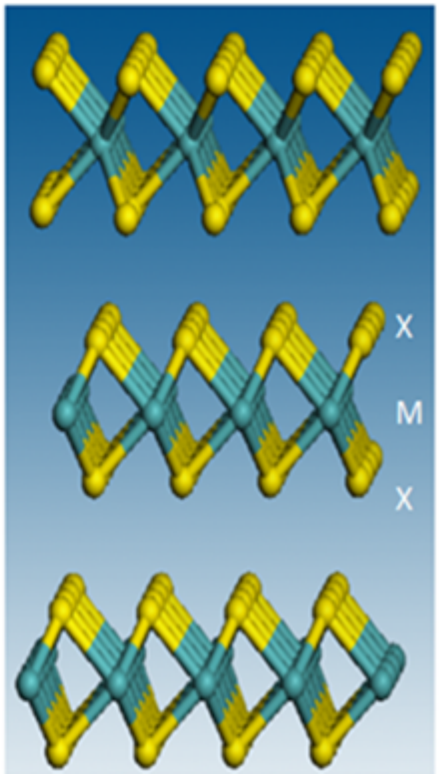
Ti-based Surface functionalization







Graphene is not the only 2-D Material…



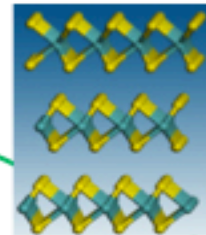
M	- S2	-Se2	-Te2
Ti	1.95(D),0.3(I)	1.55(D),0.15(I)	1.00(D),Semi-metal
Zr	1.68(D),2.10(I)	1.20(D), 1.61(I)	
Hf	2.7(D),1.93(I)	1.77(D),1.18(I)	Semi-metal(-0.4)
V	Metal	Metal	Semi-metal
Nb	Metal	Metal	Metal
Ta	Metal	Metal	Semi-metal
Mo	1.8(SL), 1.72(D),1.2(I)	1.49(SL), 1.38(D), 1.1(I)	1.13(SL), semi-metal
W	1.93(SL), 1.77(D),1.35(I)	1.60(D),1.1(I)	Semi-metal

D: direct bandgap, I:inderect bandgap, SL: single-layer bandgap

Material Synthesis

weak force
between layers

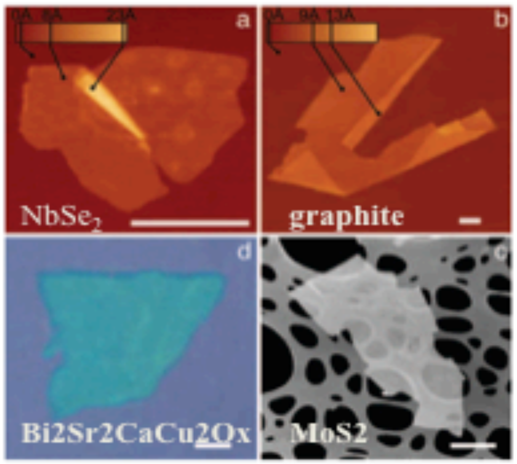
Top-Down



anisotropic structure
2D Van der Waals growth

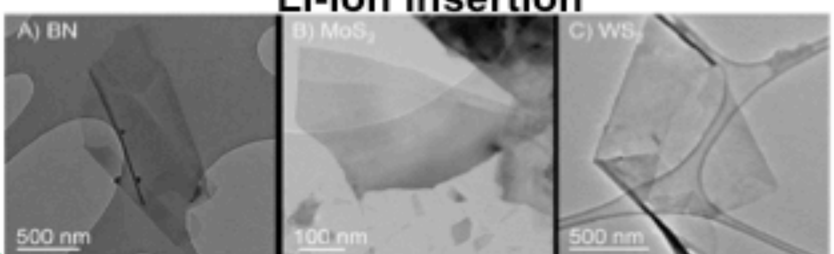
Bottom-Up

Micro-mechanism exfoliation



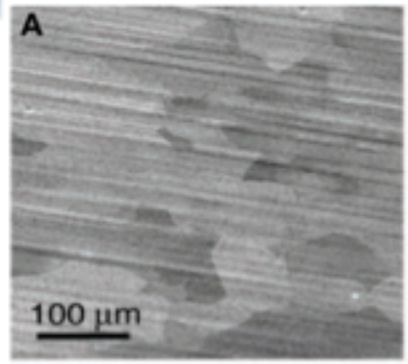
A. K. Geim *PNAS* 102,10451 (2005).

Liquid exfoliation, Solution sonication, Li-ion insertion



Jonathan N. Coleman, et al. *Science* 331, 568 (2011).

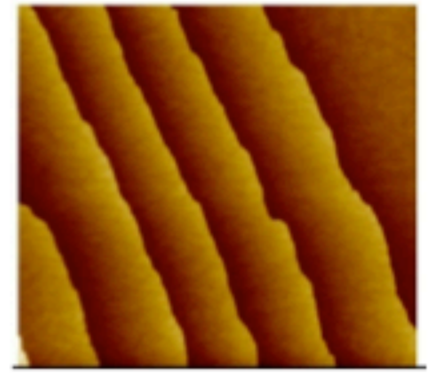
CVD growth



widely used for graphene

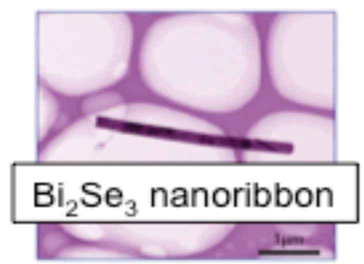
Xuesong Li, et al.,
Science, 324, 1312 (2009).

Epitaxial growth



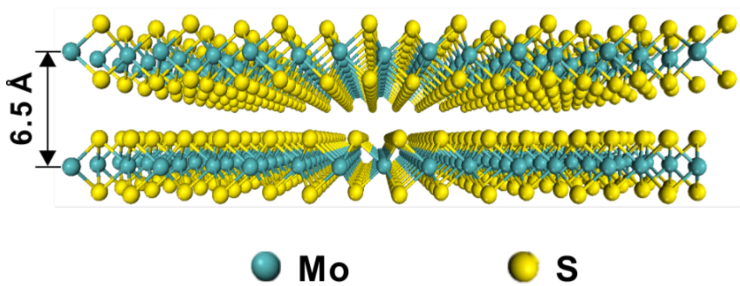
Qi-Kun Xue et al.,
Nature physics, 6,584-588 (2010).

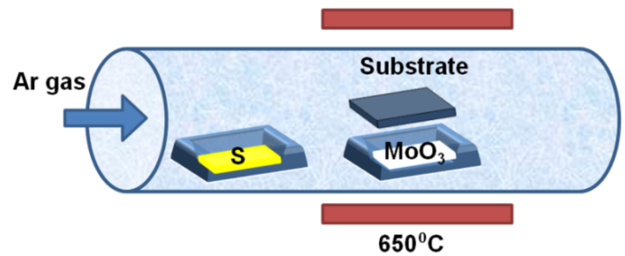
Solution synthesis

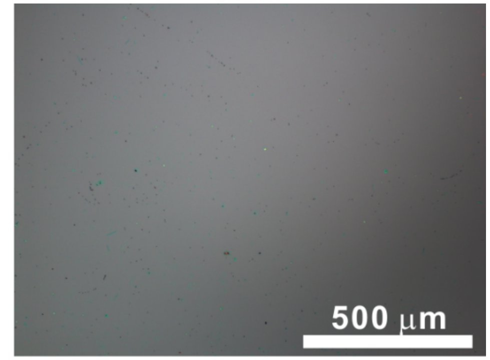


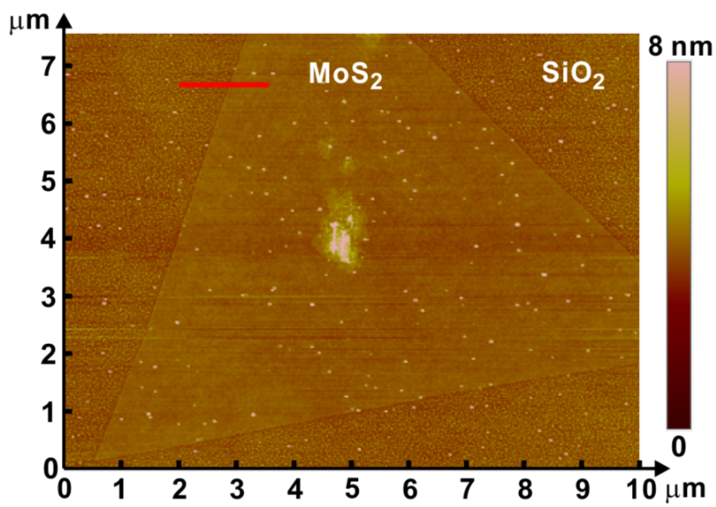
Kang L.Wang et al *Nature nanotechnology*, online (2011).

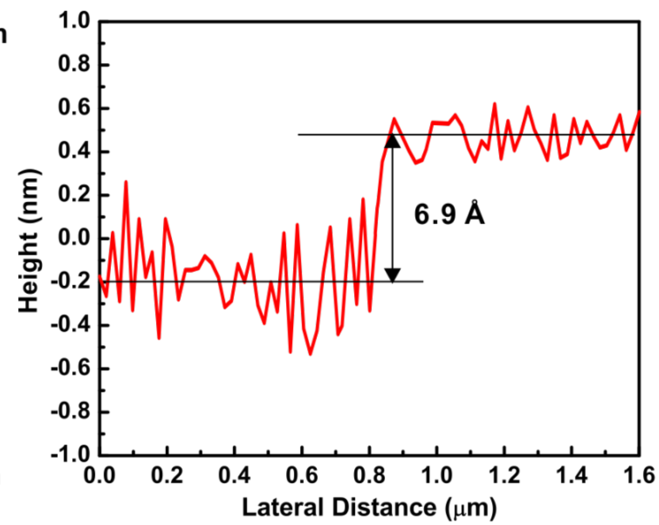
CVD Growth of Single-layer MoS_2





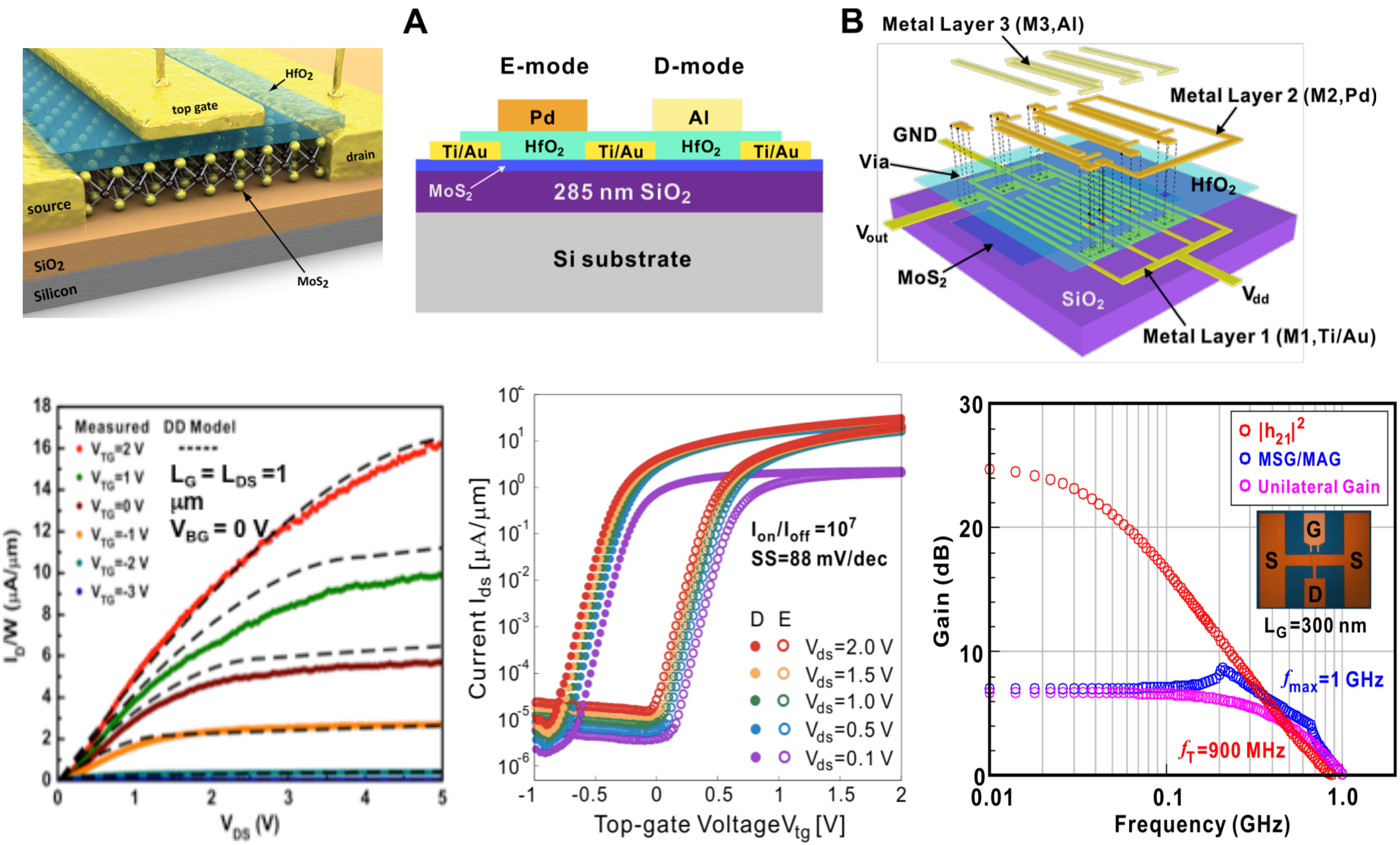






PTAS: perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt

MoS_2 Transistor Technology



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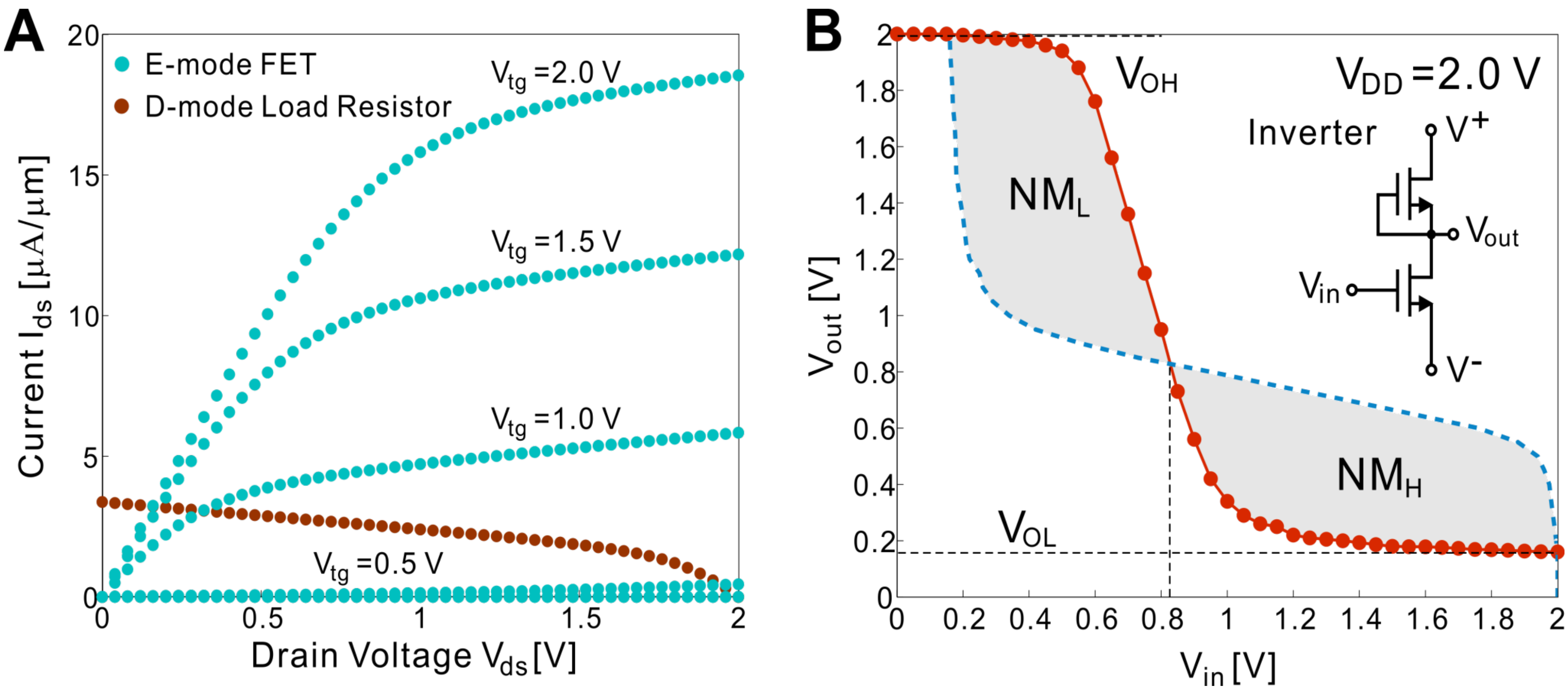
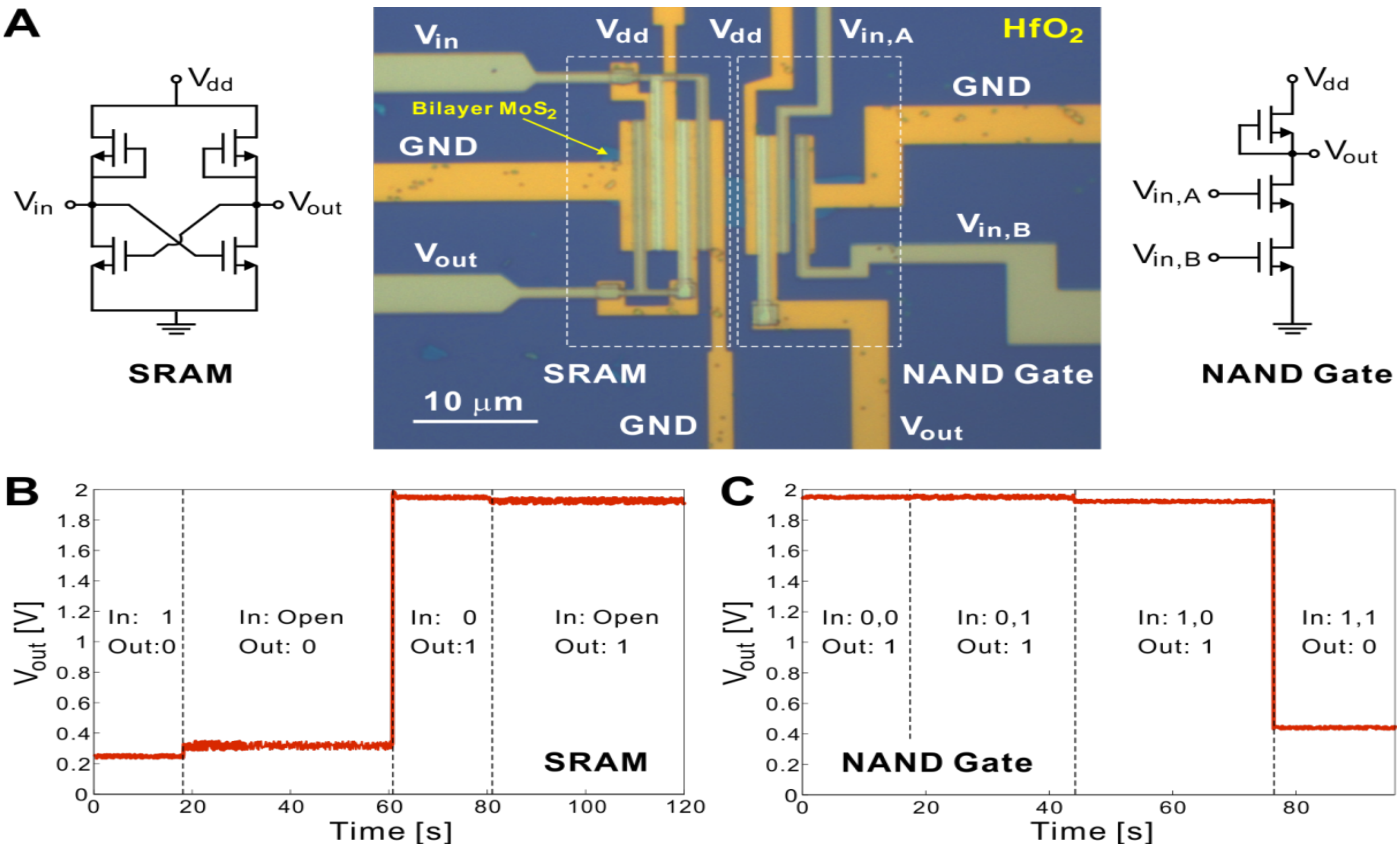
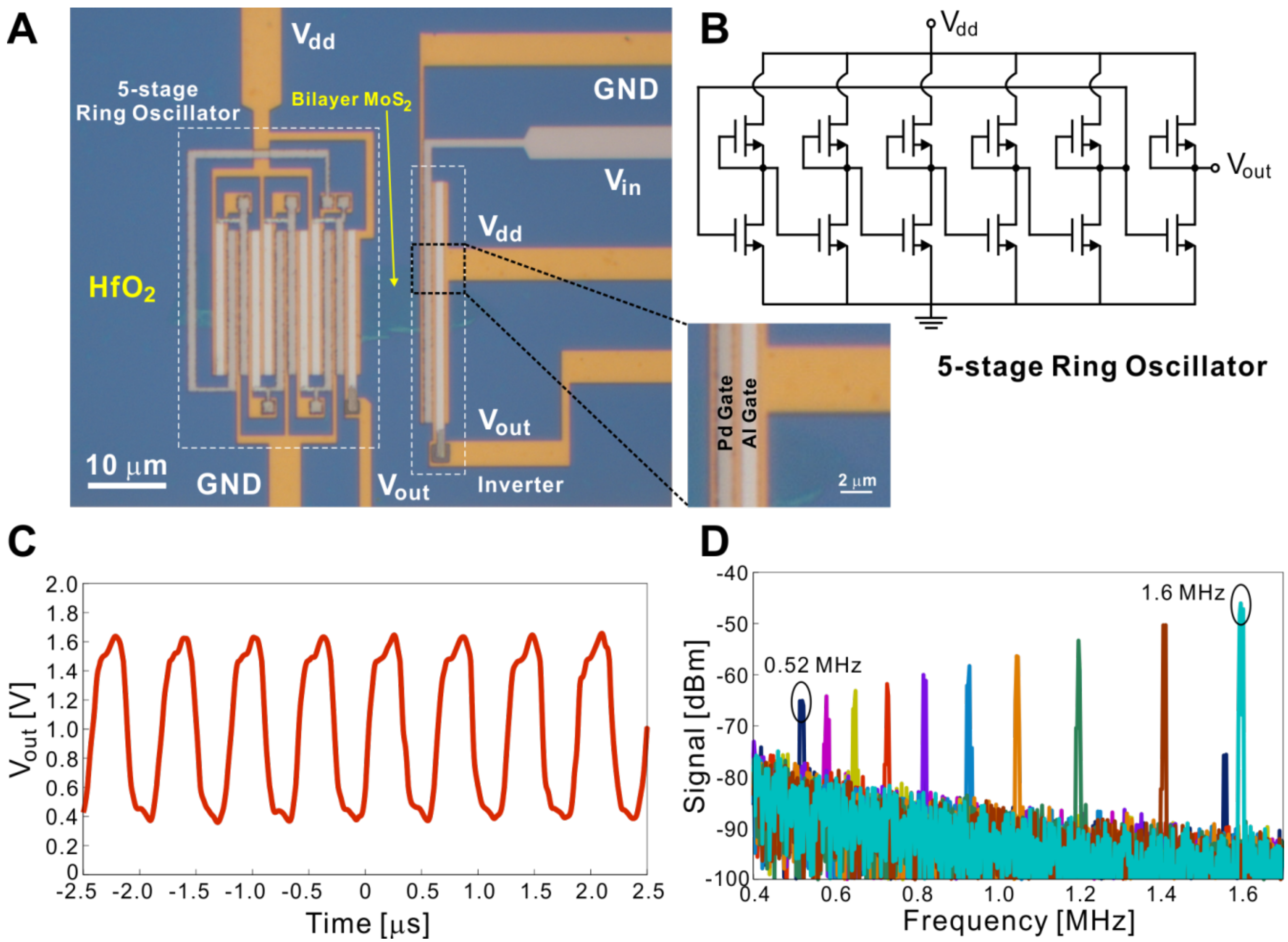
MoS_2 digital circuits



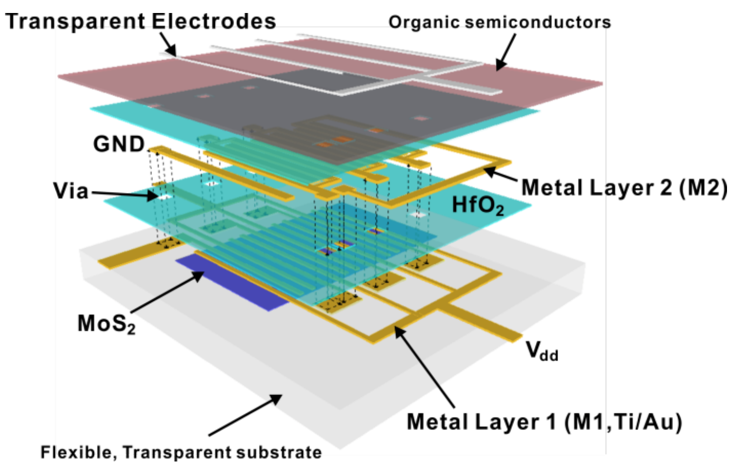
MoS_2 digital circuits

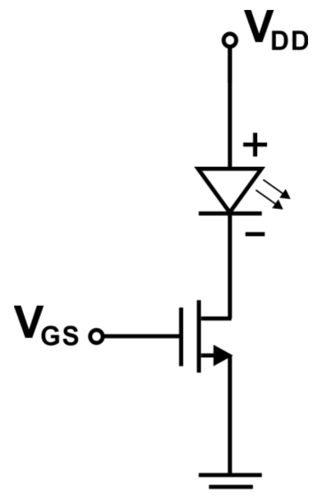


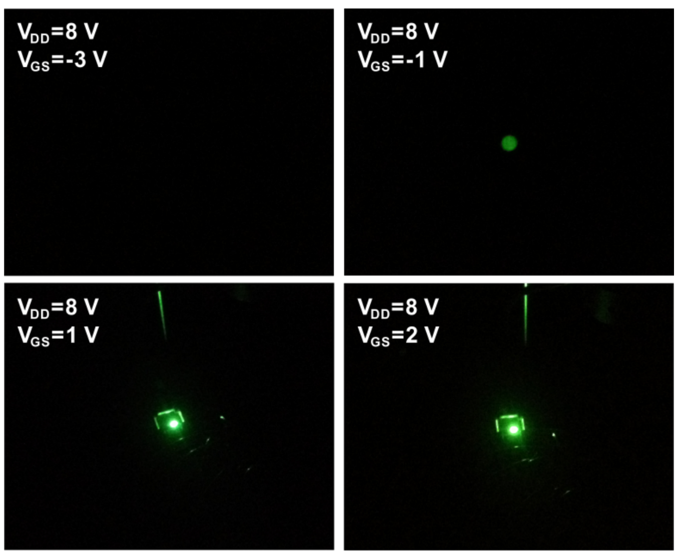
MoS_2 digital circuits

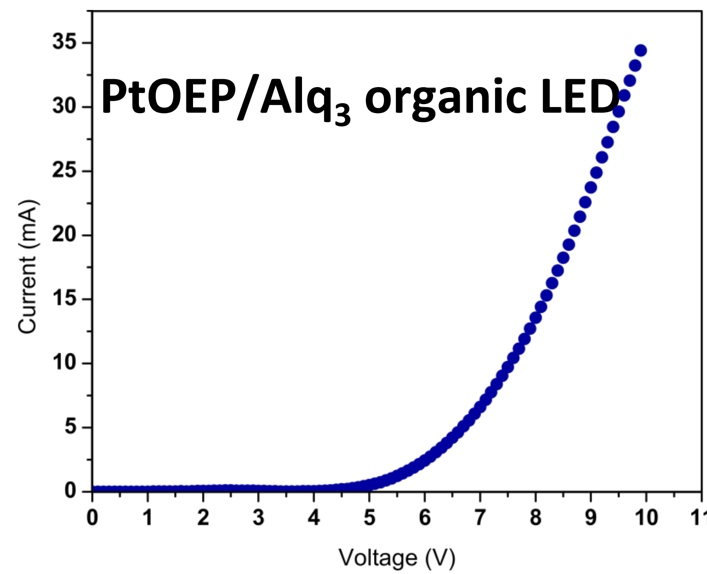


MoS_2 Driving Circuitry for Flexible OLED Displays



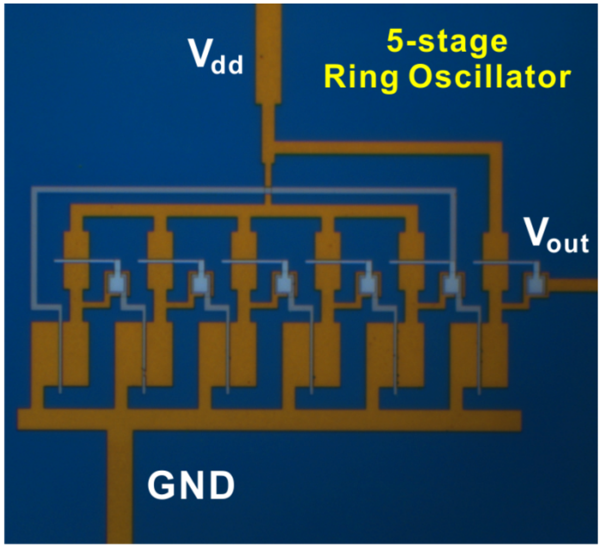


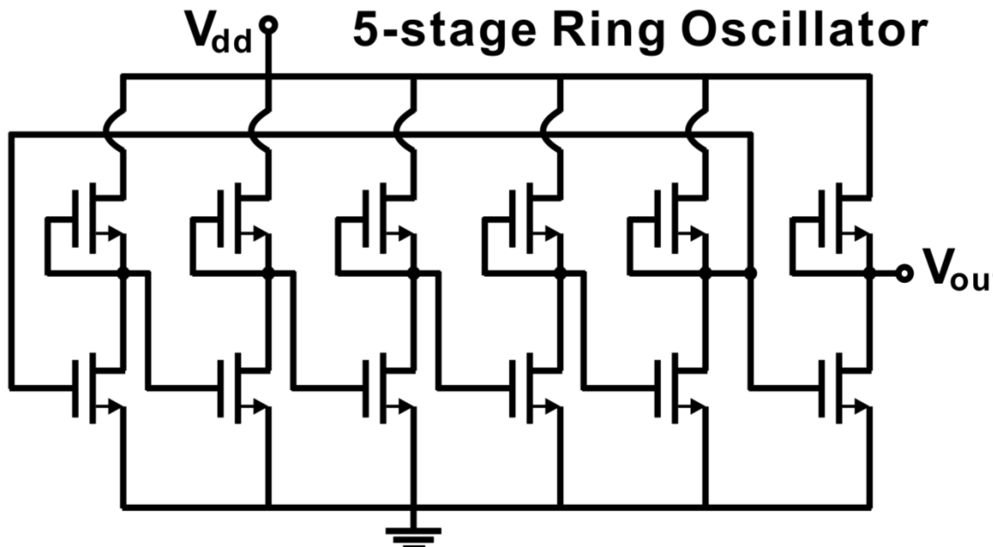


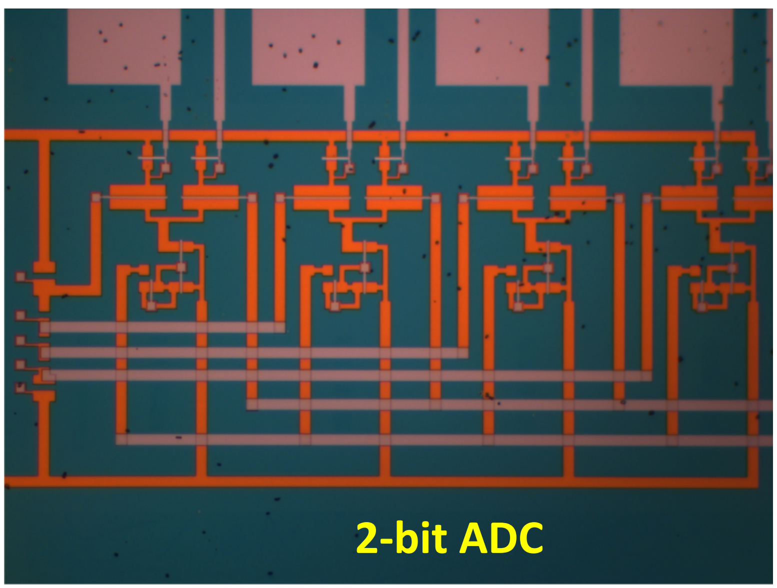


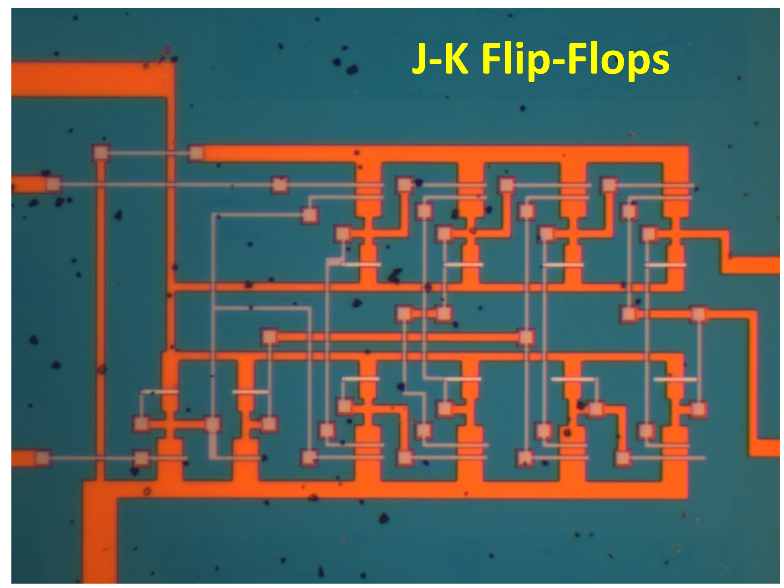
Work in collaboration with Prof. Bulovic

Large-scale MoS_2 Circuits
Ring Oscillators, 2-bit ADC and J-K Flip-Flops

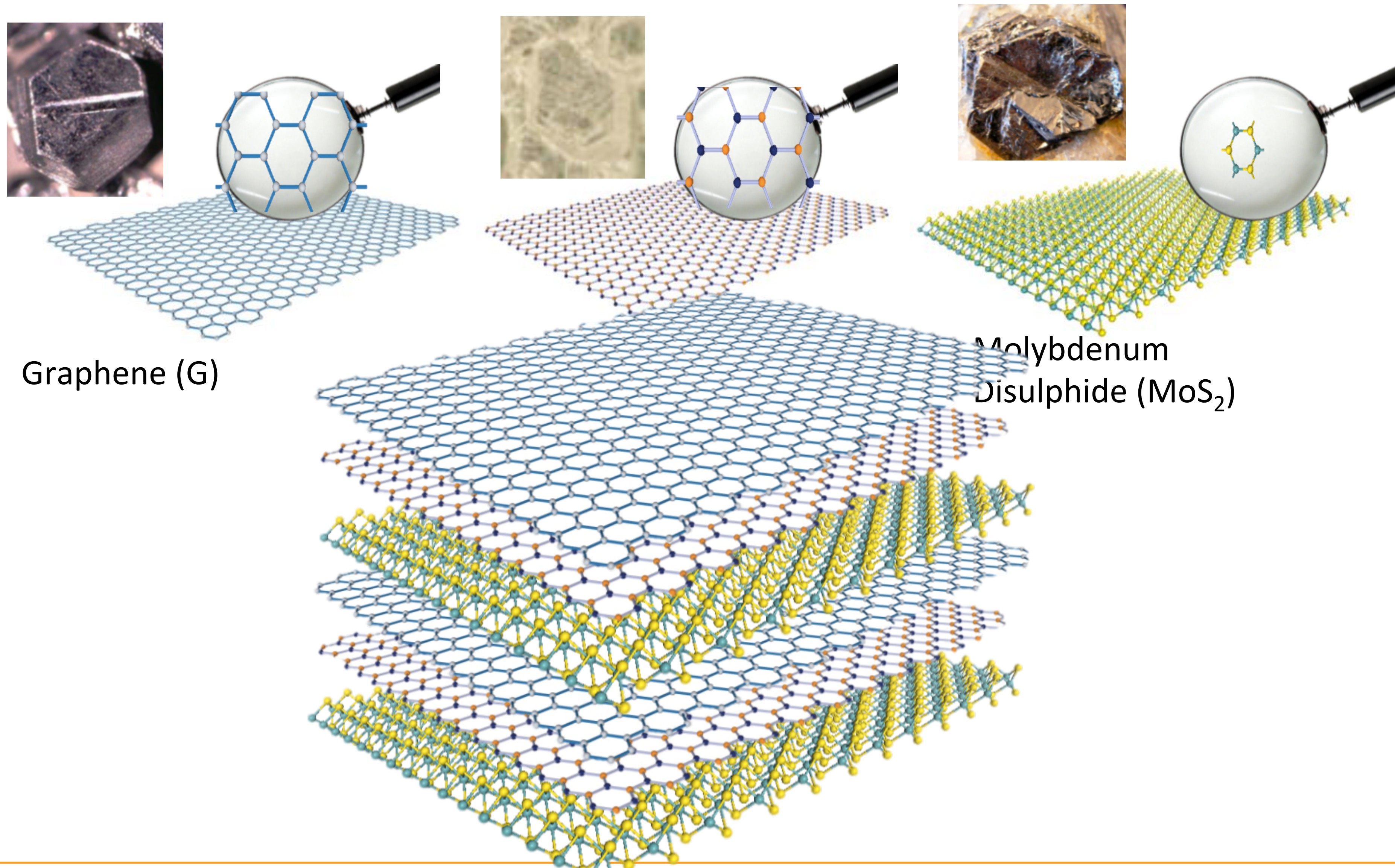








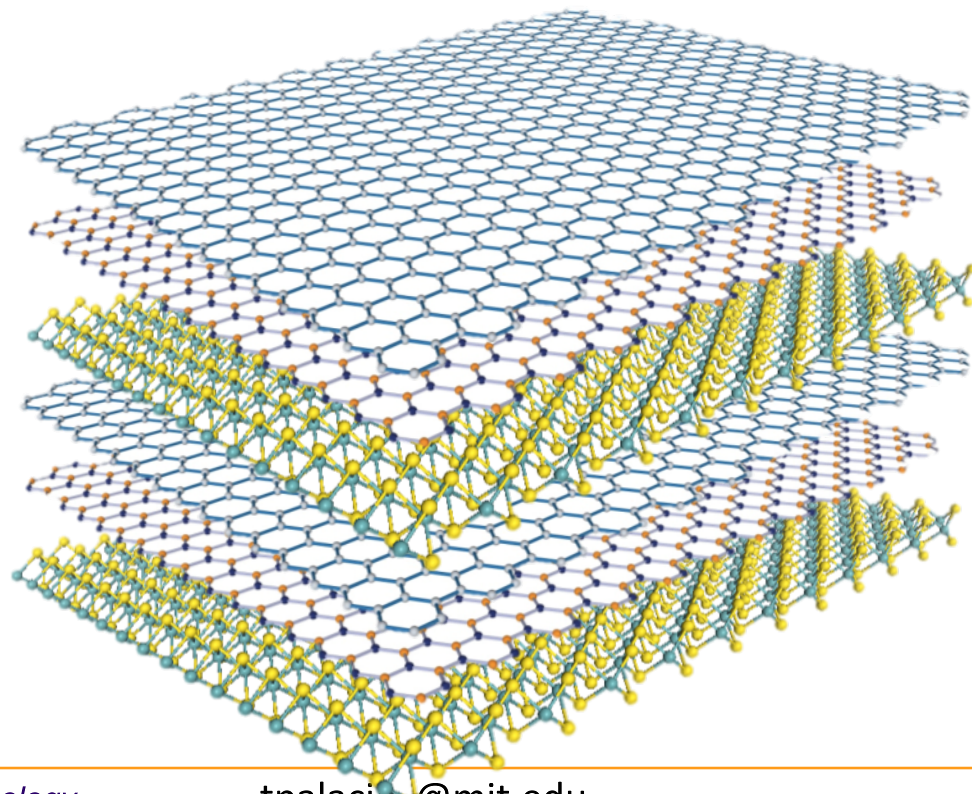
Atom-thick Electronics



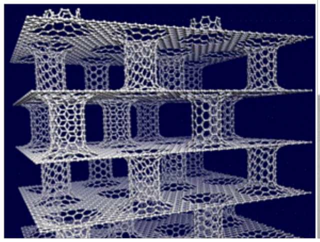
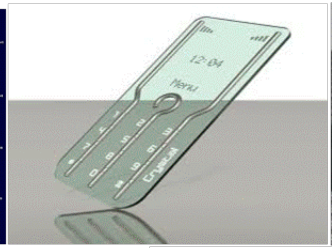
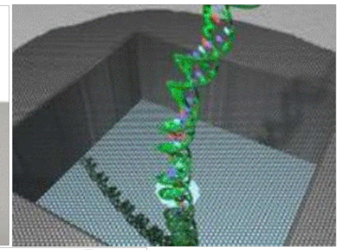
Atom-thick Electronics

Tremendous opportunities for layer-by-layer stacking of electronic devices…

Ultimate heterostructure technology!!

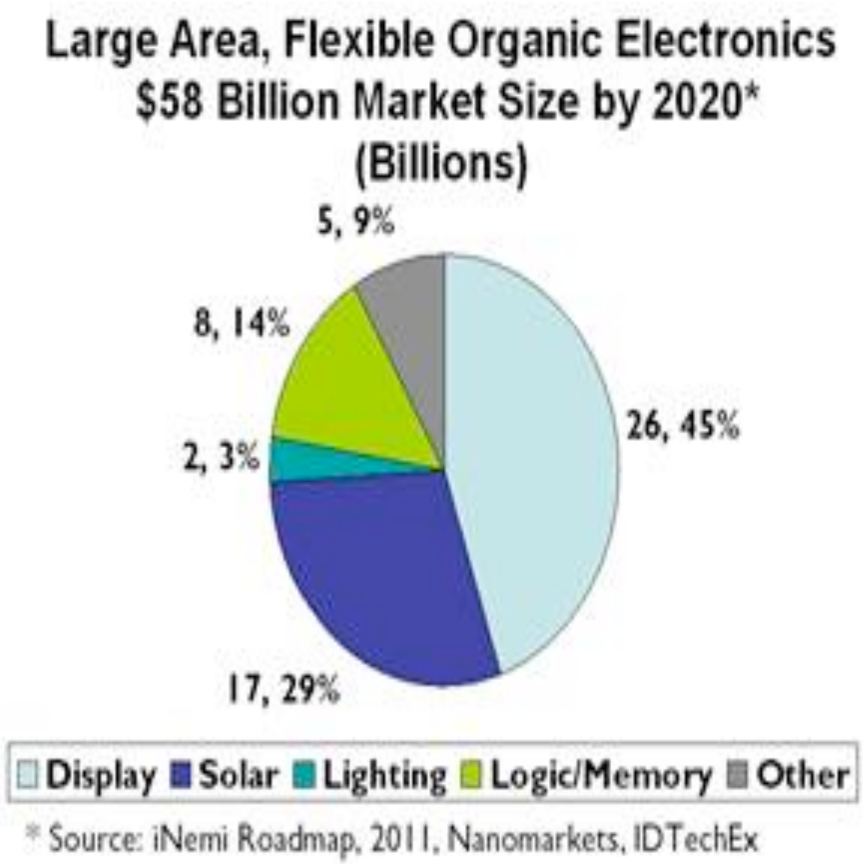


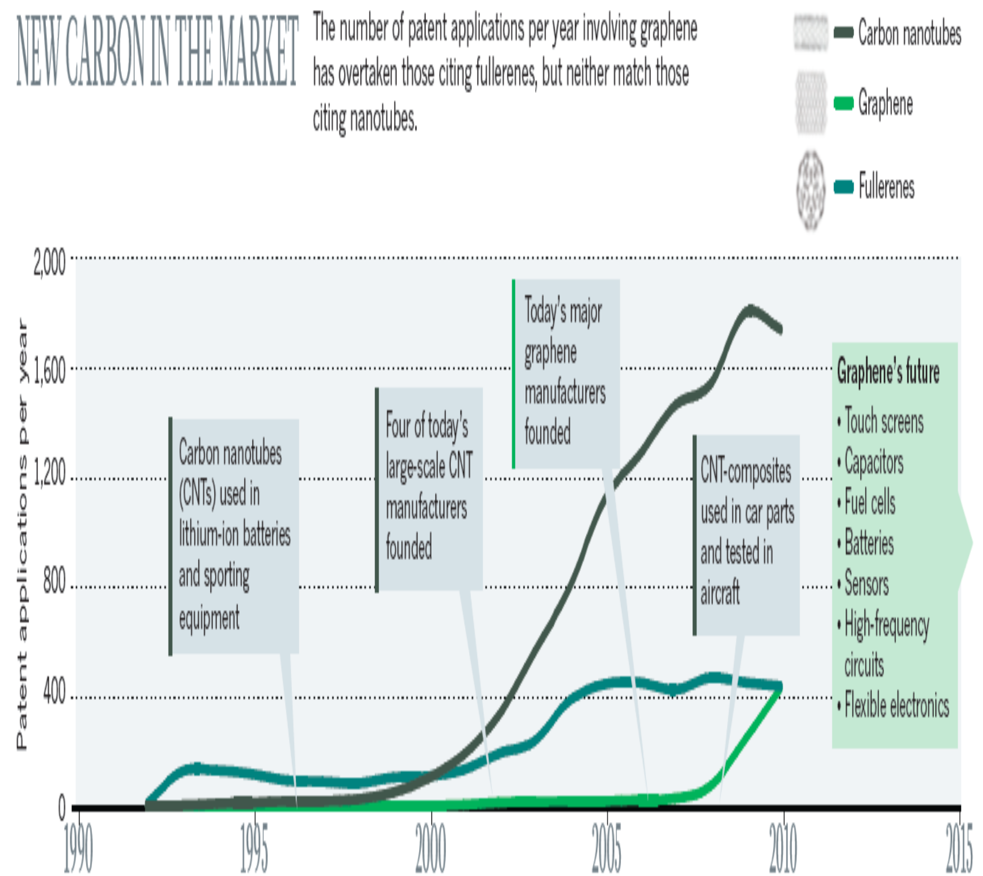
A New Era for Electronics…




Economics of 2D materials?





Future Research Funds(2012-2018)

South Korea (source: B. H. Hong)

- Ministry of Economy

	R&D				Commercialization				Total
	2012	2013	2014	**Sum**	2015	2016	2018	**Sum**	
CVD Graphene	20	21	21	**62**	21	21	21	**63**	**125**
Graphene Flake	20	21	21	**62**	21	21	21	**63**	**125**
Total	40	42	42	**124**	42	42	42	**126**	**250**

Million USD

United Kingdom

NATURE | NEWS

Britain's big bet on graphene

Manchester institute will focus on commercial applications of atom-thick carbon sheets.

$80M already committed

Graphene+ @ MIT

From new carbon science, to devices and systems…

DEVICES AND APPLICATIONS

- Advanced devices for communications
- Ambipolar and non-linear electronics
- Advanced chemical and biological sensors
- IR detection, photodetectors
- Solar cells and semitransparent electrodes
- Supercapacitors and energy harvesting

EPITAXIAL MATERIAL GROWTH

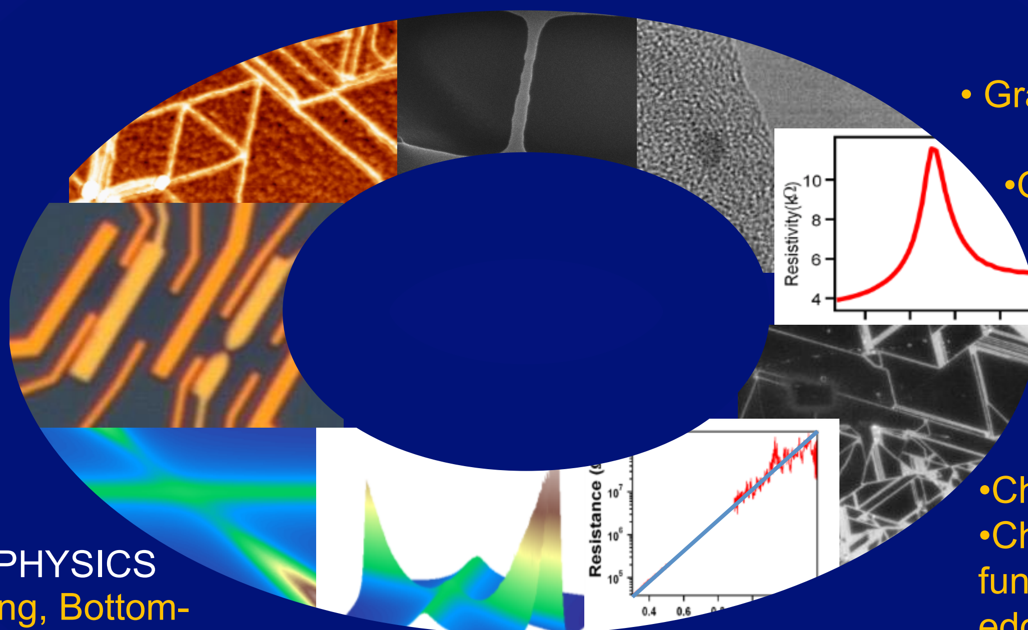
- Growth by CVD
- TEM & Raman characterization
- Crystallographic etching of edges
- Defect reduction by high temperature annealing

CIRCUITS

- Graphene for programmable interconnections
- Graphene/Si integration

CARBON PHYSICS

- Theory and Raman
- DFT Simulations
- Band diagram
- Effect of edges
- Advanced TEM and thermal issues



CHEMISTRY

- Chemically-grown graphene
- Chemical reactivity & functionalization of graphene edges
- Graphene passivation
- Doping
- Conductive inks and smart materials

TECHNOLOGY AND PHYSICS

- Graphene nanostructuring, Bottom-up and Top-Down fabrication
- Quantum nanoelectromechanical and superconducting devices
- Bilayer and Band gap engineering
- Crystallographic etching

<u>Joint monthly meetings</u>

- BACON seminars

(Boston-Area CarbOn Nanoscience Seminars)

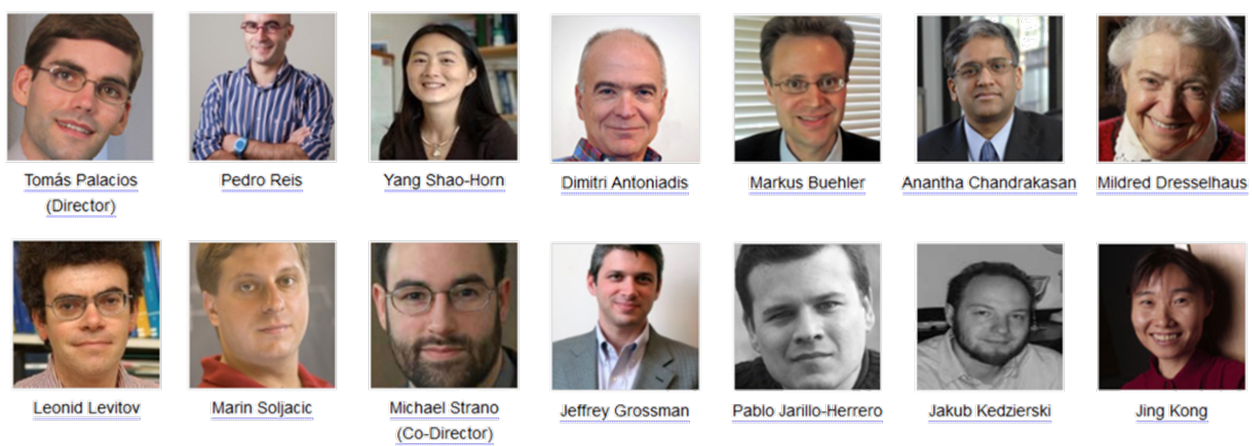
- Graphene Nanofabrication Seminars

MIT Center for Graphene Devices and Systems

Mission:

- The *MIT Center for Graphene Devices and Systems* (MIT-CG) explores advanced technologies and strategies that enable graphene-based materials, devices and systems to provide discriminating or break-through capabilities for a variety of system applications ranging from energy generation and advanced fabrics, to communications and sensing.

- The MIT–CG supports the development of the science, technology, tools and analysis for the creation of a vision for the future of graphene-enabled systems.



From Novel 2D Science to Devices and Systems

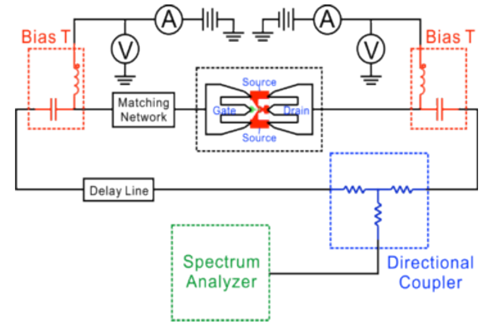
- We are the beginning of a new era for electronics

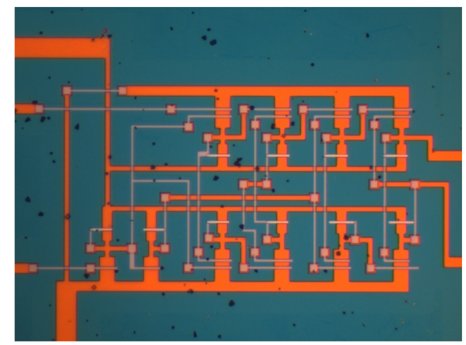
- A multidimensional approach is needed to demonstrate the full potential of 2D materials:
    - High quality material
    - Advanced processing technology
    - New device ideas

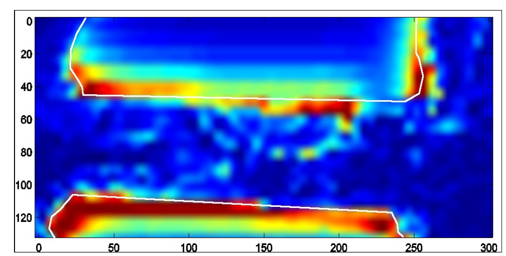
- We shouldn't fight (too much) against nature

- Many applications are quickly becoming competitive:
    - RF transistors with record extrinsic performance
    - First GHz frequency multiplier, mixer and PSK modulator
    - First circuits with real gain: RF oscillators
    - Advanced chemical sensors and IR detectors

- Graphene and other 2D materials will enable ubiquitous electronics and much more…







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  - Xu Zhang
  - Sunghae Ha
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  - Rachel Luo
  - J. M. Tirado

- Dawn Nida and Lu Wang
- M. Dresselhaus' group
- J. Kong's group
- P. Jarillo-Herrero's group
- T. Swager's group
- M. Strano's group
- V. Bulovic's group

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