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Part 1: A brief Introduction to Graphene Properties, Synthesis, and Applications

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Materials Science and Engineering

Global Energy Outlook

(adapted from A. Majumdar, U.S. and Japan Seminar on Nanoscale Heat Transfer, 2007)

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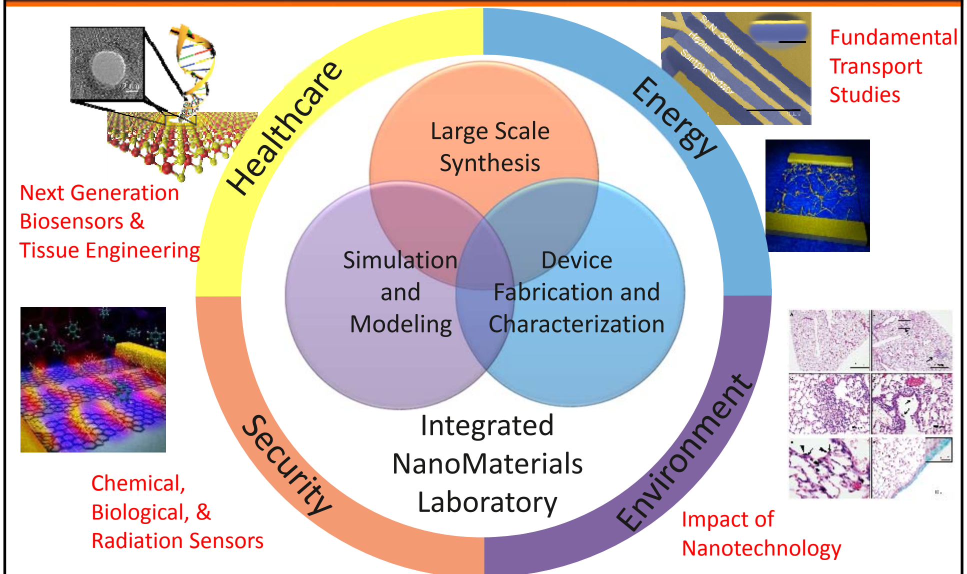
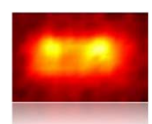
Integrated NanoMaterials Laboratory



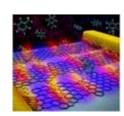
http://coen.boisestate.edu/inml

Outline of the talk

Part 1: A brief Introduction to Graphene Properties, Synthesis, and Applications

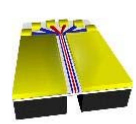


- Review of bonding and structure
- Energy Bands in Solids
- Microscopy Techniques
- Graphene Synthesis and Applications



Part 2: Atomic Layer Research in the INML

- Carbon nanotube transistors
- Role of defects in graphene sensing and transport
- Biomolecules to Tissue Engineering in the INML



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Atomic Structure

- electron 9.11×10^{-31} kg
  proton 1.67×10^{-27} kg
  neutron 1.67×10^{-27} kg
- Atomic # = number of protons in the nucleus or atom
  = of electrons in a neutral species
- Isotope: Determined by number of neutrons in atom
- Ion: Charged atom, unequal number of electrons and protons
- amu = 1/12 mass of ^{12}C isotope
- Atomic wt = wt of 6.023×10^{23} molecules or atoms, weighted average of all isotopes
- 1 amu/atom = 1 g/mole

Atomic Number	14
Symbol	Si
Atomic Weight	28.08

$$\overline{A}_M = \sum_i f_{i_M} A_{i_M}$$

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Valence Electrons

- Valence Electrons determine all of the following properties
  - Chemical
  - Thermal
  - Optical
  - Electrical
- Valence electrons – those in unfilled shells
  - Filled shells are more stable
- Valence electrons are most available for bonding
- Example: Carbon (atomic number = 6)
  - $1s^2$ $2s^2\,2p^2$

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- Most elements: Electron configuration not stable.

Element	Atomic #	Electron configuration
Hydrogen	1	$1s^1$
Helium	2	$1s^2$ (stable)
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
...		...
Neon	10	$1s^2 2s^2 2p^6$ (stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
...		...
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$ (stable)
...	...	...
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ (stable)

Adapted from Table 2.2, *Callister & Rethwisch 9e.*

- Why? Valence (outer) shell usually not filled completely.

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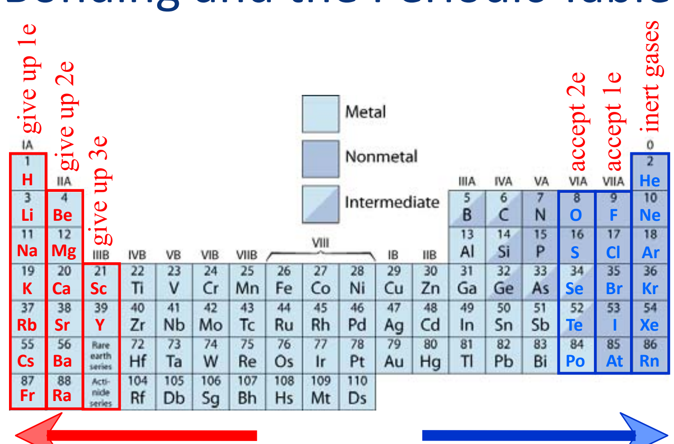
Bonding and the Periodic Table



Electropositive elements: Readily give up electrons to become + ions.

Electronegative elements: Readily acquire electrons to become - ions.

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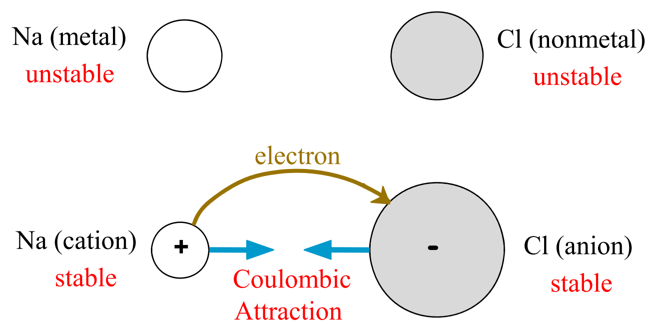
Ionic Bonding

- Large difference in electronegativity is required
- Occurs between + ions and – ions
- Requires electron transfer



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Covalent Bonding

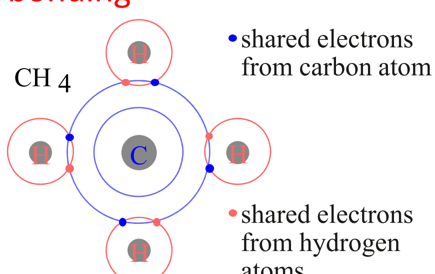
- Sharing of electrons results in strong bonds
- Similar electronegativity ∴ share electrons
- Bonds determined by valence
  - *s* & *p* orbitals dominate bonding

C: has 4 valence e^-, needs 4 more

H: has 1 valence e^-, needs 1 more

- Methane: CH_4

Electronegativities are comparable.



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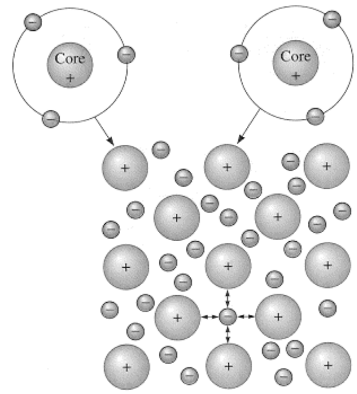
Metallic Bonding

- 80 of the ~109 natural elements are metals
- Valence electrons are released from the atom leaving behind a positively charged ion core, called a “cation”
- Cations are held together by a sea of electrons
- the bond occurs because the positive cations are attracted to the negative electrons.



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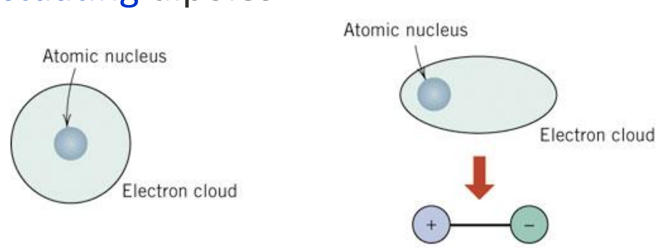
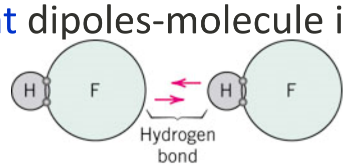
Secondary bonds

- Fluctuating dipoles



- Permanent dipoles-molecule induced



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Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable *large-Diamond* *small-Bismuth*	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable *large-Tungsten* *small-Mercury*	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

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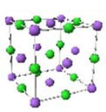
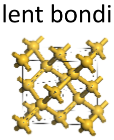
Ceramics and Semiconductors

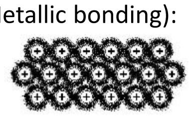
(Ionic & covalent bonding):





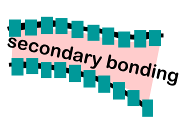
Metals

(Metallic bonding):



Polymers

(Covalent & Secondary):



Large bond energy

large T_m
large E
small α

Variable bond energy

moderate T_m
moderate E
moderate α

Directional Properties

Secondary bonding dominates
small T_m
small E
large α

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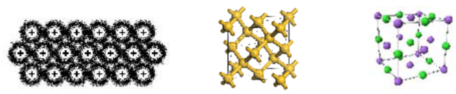
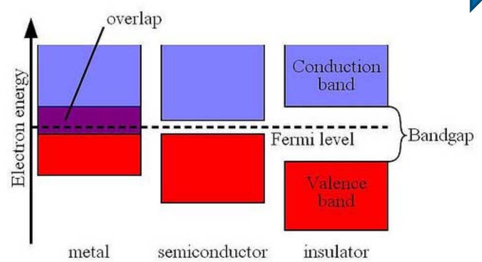
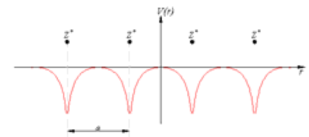
Bonding and Crystal Structure



$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Electrical properties span 20 orders of magnitude!





$$\left(\frac{\hbar^2}{2m}k^2 - E\right)c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0\,.$$

- Properties of a material depend on the crystal structure.
- Electrons in a crystal are subject to periodic potentials.

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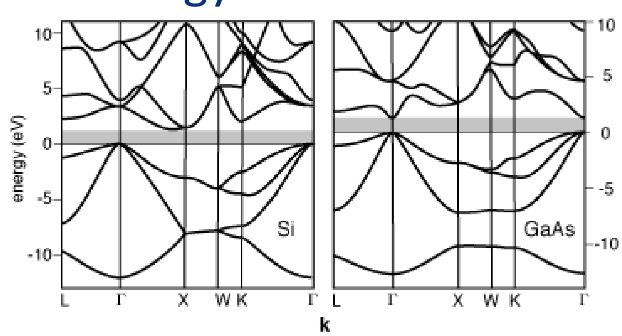
Energy Bands in Solids



$$\left(\frac{\hbar^2}{2m}k^2 - E\right)c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0\,.$$

- Parabolic relation between energy and momentum
- Effective mass of an electron relates to the curvature of the band
- Forbidden energy states!

Microscopy

Optical resolution ~ diffraction limited

For higher resolution need higher frequency

- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.
- Atomic Forces
  - Sensing atomic interactions between a cantilever and a surface allows for direct correlation of structure and properties

Scanning Electron Microscopy

Analysis of scattered electrons can produce images, crystallographic information, and elemental analysis

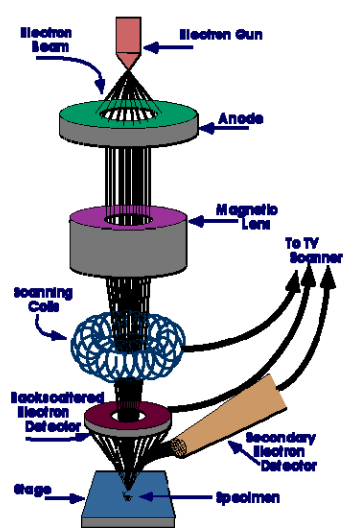


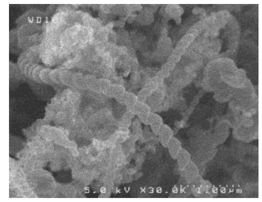
Diagram courtesy of Iowa State University

Scanning Electron Images

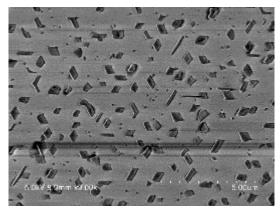
Dislocations

Fig. 4.7, *Callister & Rethwisch 9e.*
(Courtesy of M. R. Plichta, Michigan Technological University.)

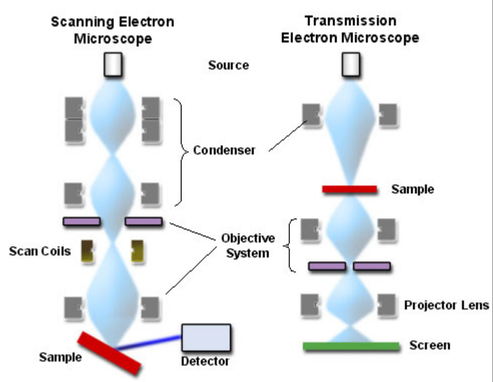
Helical carbon nanotubes



2-D TMDC crystals on sapphire



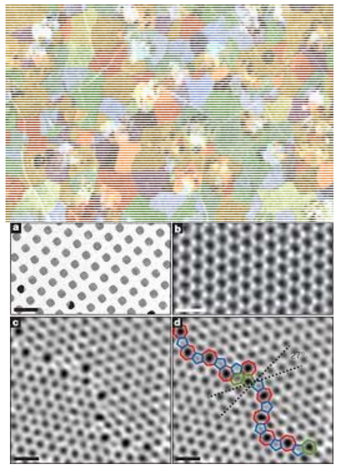
Transmission Electron Microscopy



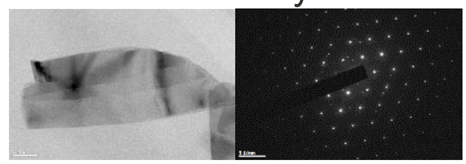
- TEM uses transmitted electrons to produce an image rather than secondary electrons
- Transmission through the sample produces diffraction patterns
- Higher energy → Higher Resolution

Transmission Electron Microscope Images

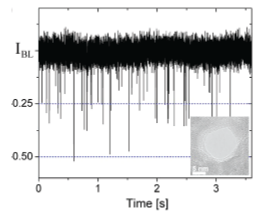
Graphene Grain Boundaries

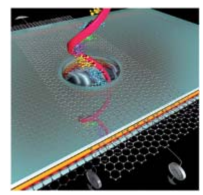


2-D TMDC crystals



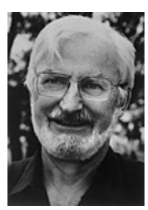
Nanopore Formation





Scanning Tunneling Microscopy

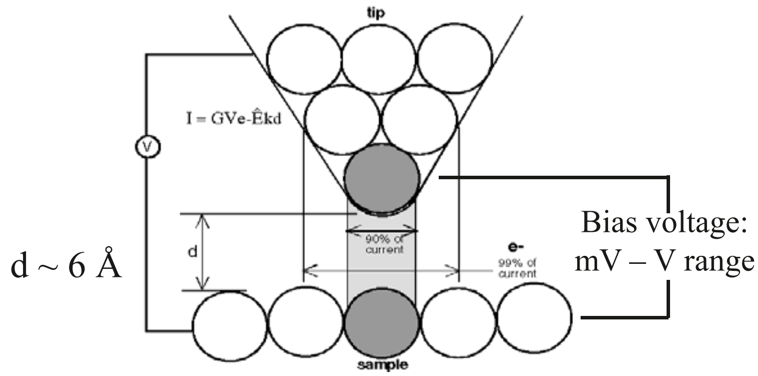
- Developed by Gerd Binnig and Heinrich Rohrer at the IBM Zurich Research Laboratory in 1982.

Binnig   Rohrer

- The two shared half of the 1986 Nobel Prize in physics for developing STM.

- STM has fathered a host of new atomic probe techniques: Atomic Force Microscopy, Scanning Tunneling Spectroscopy, Magnetic Force Microscopy, Scanning Acoustic Microscopy, etc.

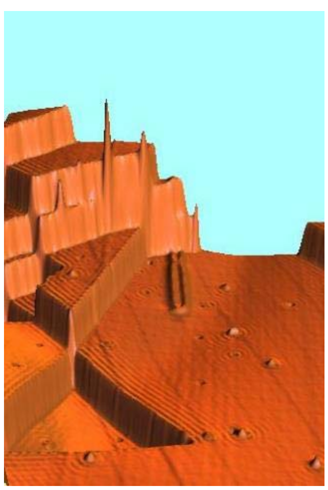
Basic Principles of STM



Electrons tunnel between the tip and sample, a small current I is generated (10 pA to 1 nA).

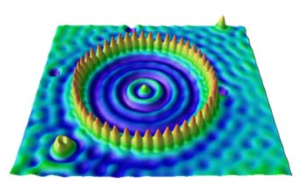
I proportional to e^{-xd}, I decreases by a factor of 10 when d is increased by 1 Å.

Interesting Images with STM



Copper Surface

Carbon monoxide molecules arranged on a platinum (111) surface.



Iron atoms on the surface of Cu(111)

Atomic Force Microscopy

- Developed by Gerd Binnig, Calvin Quate, and Christoph Gerber in 1986

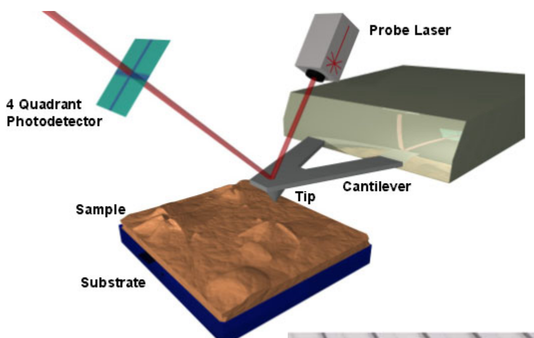
Binnig

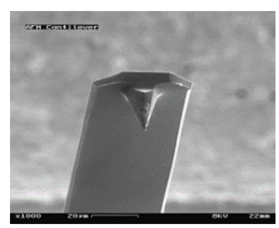
Quate

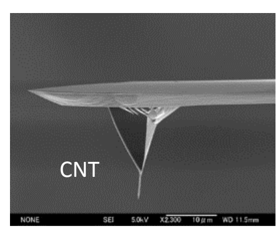
Gerber

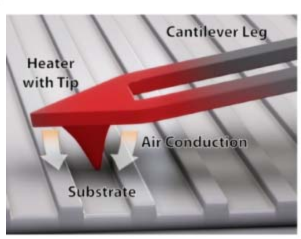
- First commercial AFM was introduced in 1989.
- AFM tips can be “functionalized” to probe a variety of physical properties with nanoscale resolution

Atomic Force Microscopy



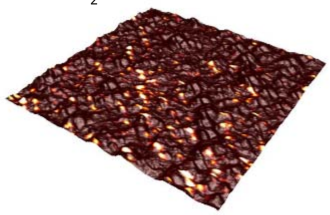




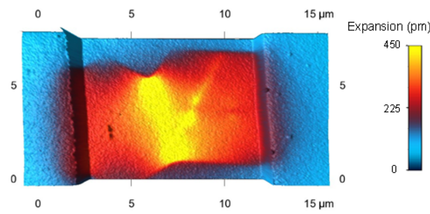


Atomic Force Microscopy

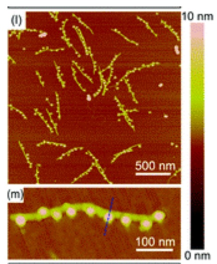
MoS$_2$ 500 nm x 500 nm scan



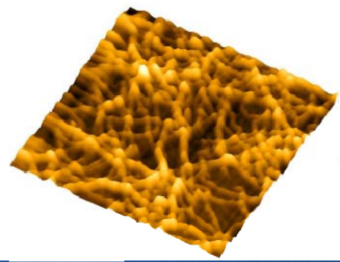
Scanning Joule Expansion Microscopy



DNA Origami with Au NPs (Bui, et al. Nano Lett. 2010)



RecA coated DNA (1 x 1 um scan)



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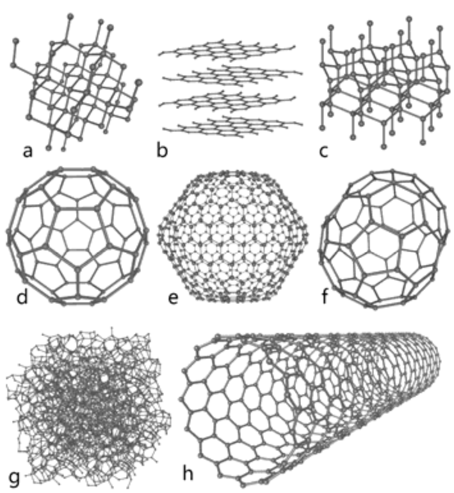
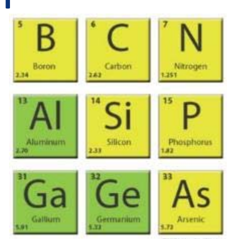
Carbon Allotropes





A. Diamond
B. Graphite
C. Ionsdaleite
D. C60 Buckminster Fullerene
E. C540
F. C70
G. Amorphous Carbon
H. Single-Wall Carbon Nanotube

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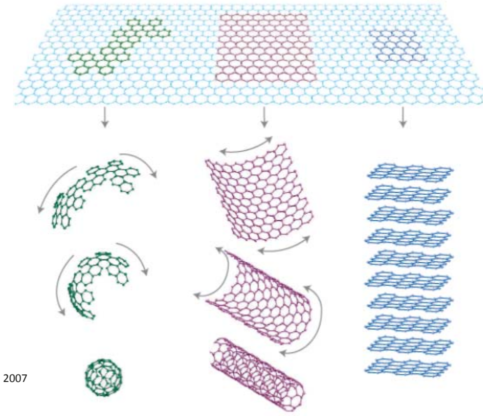
Graphene: A 2D Building Block



Geim and Novoselov, Nature Materials, 2007

- If you can isolate a single sheet from graphite you get graphene.
- Physical properties return to bulk graphite after 10 layers.

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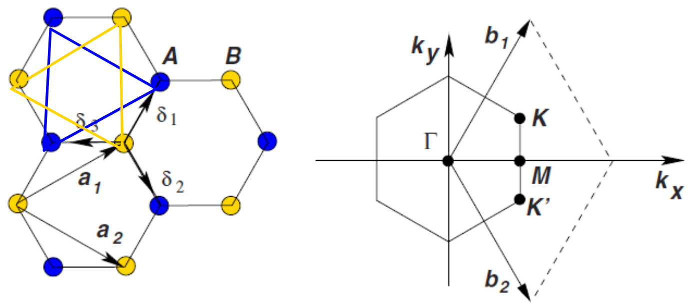
Crystal Structure of Graphene



$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$E(k_x, k_y) = \pm\gamma_0\sqrt{1 + 4\cos\frac{\sqrt{3}k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}$$

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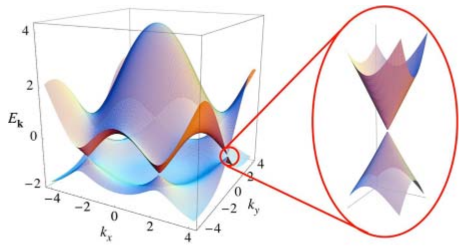
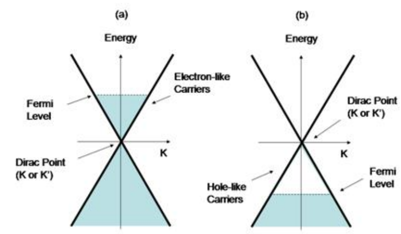
Energy Bands in Graphene





- Energy bands are linear near the K and K' points of the reciprocal lattice.
- Massless Dirac Fermions with a Fermi velocity of c/300 ~1 x 10^6 m/s.
- Energy bands are symmetric → equal electron and hole mobilities.
- Bands touch at the "Dirac Point" → no band gap, zero density of states.
- Graphene is semi-metal or zero-band gap semiconductor.

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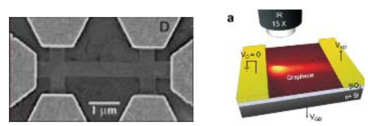
Graphene has great electrical, thermal, mechanical, and optical properties!

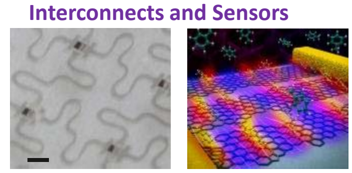
- Symmetric energy band → equal electron & hole mobility, 10-100x higher than Si
- Large optical phonon energy (0.18 eV vs. 0.06 eV in Si)
- Atomically thin → High optical transparency and surface to volume ratio
- Strong σ bonds → high thermal conductivity k ≈ 20 x k_{Si}
- Emerging applications in layer-by-layer (LBL) assembled vdW solids

Field-Effect Transistors



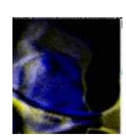
K. Novoselov, et al. Science (2004) M.-H. Bae, et al. Nano Lett. (2012)

Interconnects and Sensors



R.-H. Kim *et al.*, Nano Lett. (2011) Salehi-Khojin, et al., Adv. Mat. (2012)

LBL Assembled vdW Solids



L. Britnell, *et al.*, Science (2012) G. Gao *et al.*, Nano Lett. (2012)

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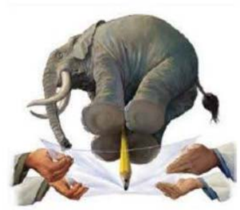
Graphene Superlatives

- Thinnest imaginable material.
- Strongest material ever measured.
- Stiffest material known
- Most stretchable crystal.
- Record thermal conductivity.
- Highest current density at room temperature. (10^6>copper)
- Highest intrinsic mobility. (100 times > Si)
- Lightest charge carriers. (zero rest mass)
- Longest mean free path.
- Most impermeable membrane.



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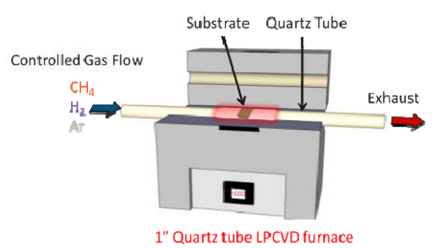
CVD Growth



X.Li, et al, Science (2009)

- Graphene grown directly on Cu foil at 1000 ^oC
- CVD growth of graphene → polycrystalline films
- Graphene is transferred by etching of Cu foil in $FeCl_3$
- Films are annealed in Ar/H_2 at 400 °C to remove residue

A.Salehi-Khojin **/ D. Estrada,** et al., *Advanced Materials* **24**, 53-57 (2012)

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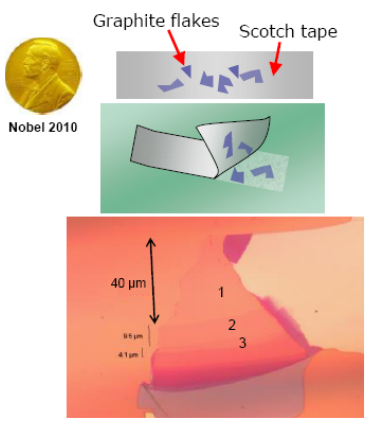
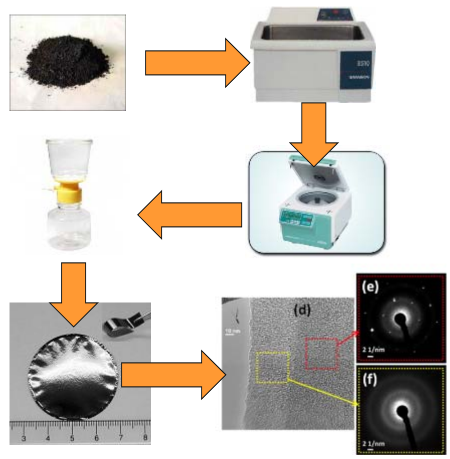
Mechanical Exfoliation



Novoselov, K. S. *et al.* ,*Science* (2004)
Novoselov, X. *et al.* ,*Science* (2009)

Solvent Assisted Exfoliation



Y. Hernadez, et al., Nat. Nano (2008)
D. Li, et al., Nat. Nano (2008)

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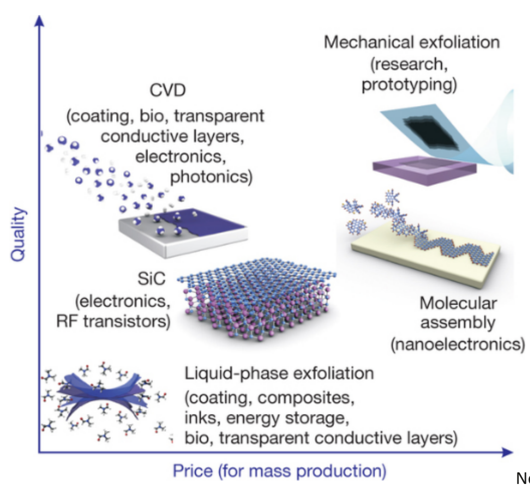
Graphene Quality and Synthesis



Novoselov, Nature (2012)

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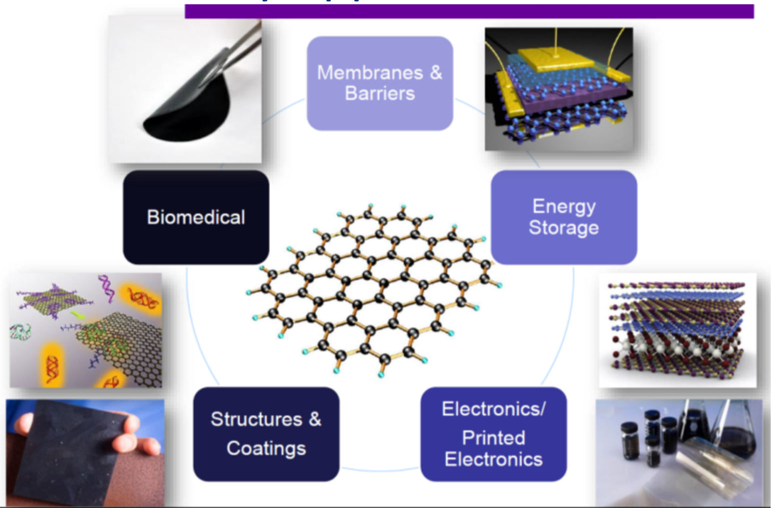
Key Applications



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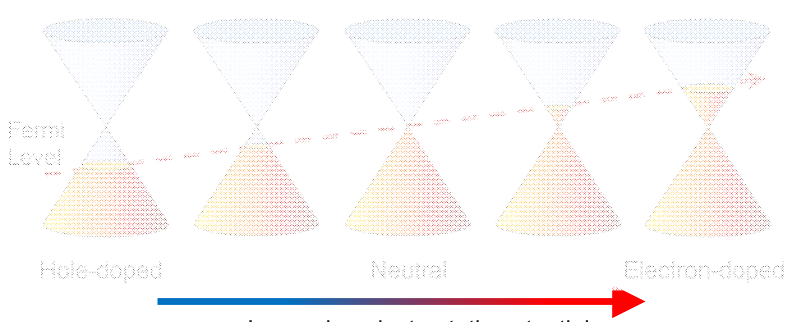
Electrostatic Doping of Graphene

Positive electrostatic potential lowers electron energy (or effectively raises Fermi level).



Local carrier density and type can be changed by applying an electrostatic potential. Use in graphene Field-Effect Transistors (FET).

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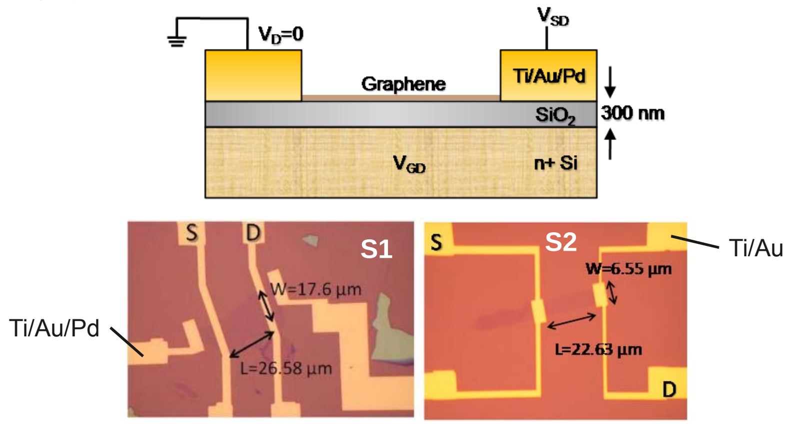
Graphene FETs

- 3-terminal FET fabricated using 'tape' method [1] from natural flake graphite and e-beam lithography.



[1] Novoselov et al., *Science* (2004)

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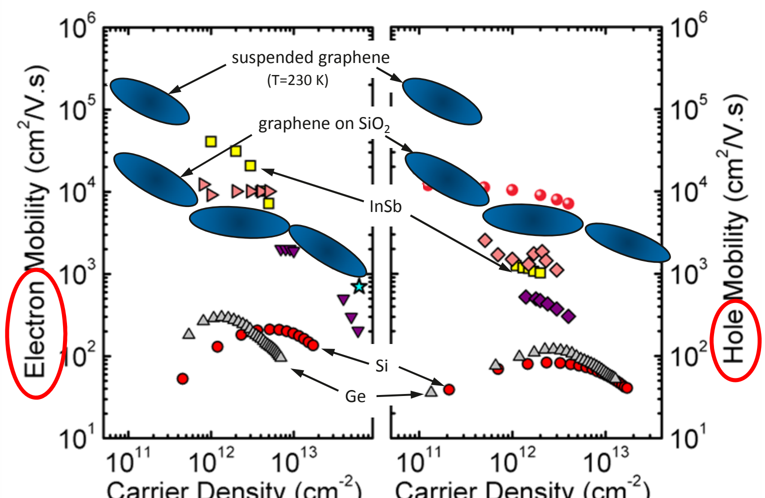
Carrier Mobility in Graphene



Abundance:

#1 O
#2 Si
...
#15 C
...
#35 Ga
...
#53 Ge
#55 As
...
#61 Sb
#67 In

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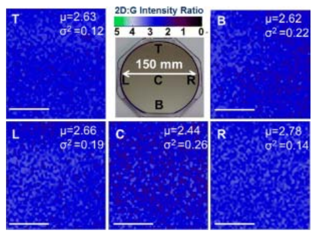
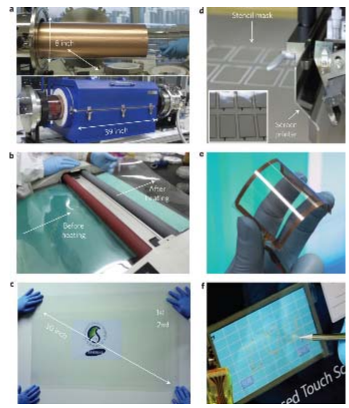
Wafer Scale and Beyond



Rahimi, ACS Nano, 2014

Average mobilities of ~2500 cm^2/V-s with 75% yield.

Roll to roll production on copper foils.



Bae, Nat. Nano. (2010)

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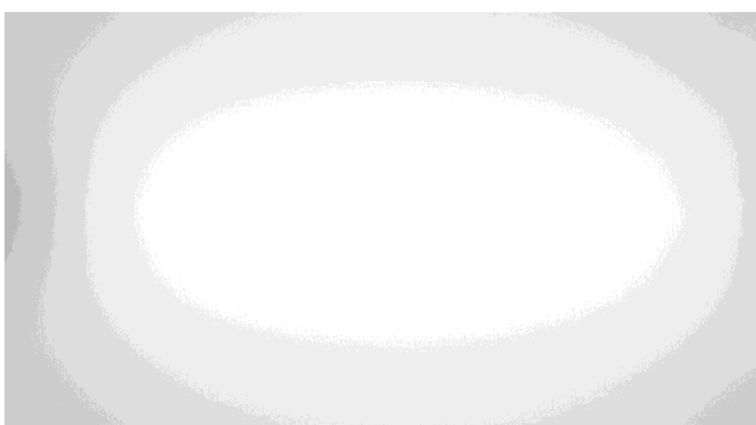
Water Purification



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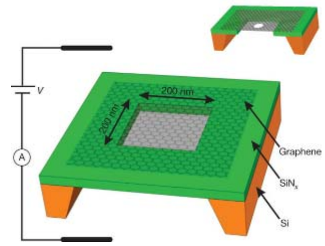
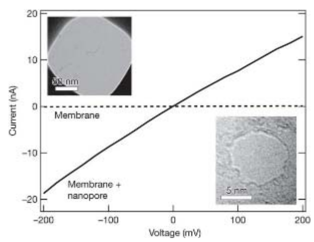
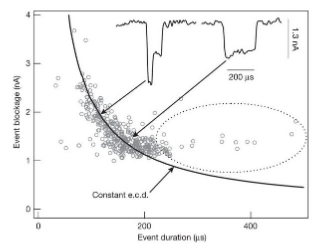
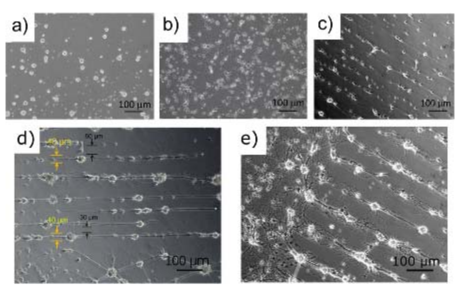
Biomedical



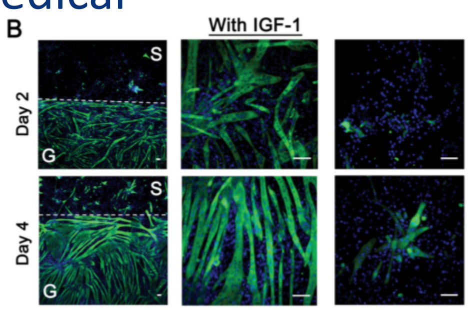




Biomedical



Lorenzoni, Sci. Reports (2013)



Bajaj, Adv. Health. Materials (2013)

Planar graphene has been used to pattern and differentiate stem cells.
Cell growth aligns with graphene patterns.
Graphene enhances differentiation over supporting substrate.
Mechanical crosstalk only investigated mechanism.

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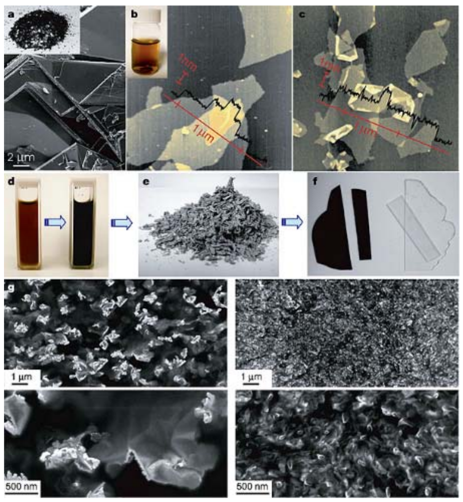
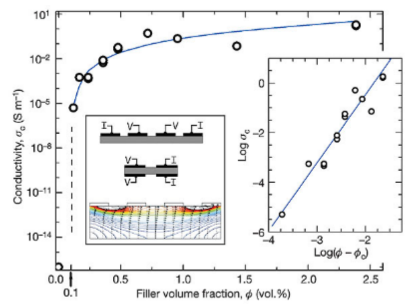
Composites





Large scale exfoliation and reduction of graphene oxide can be used to tune the electrical properties of graphene polystyrene composites.

Stankovich, Nature (2006)

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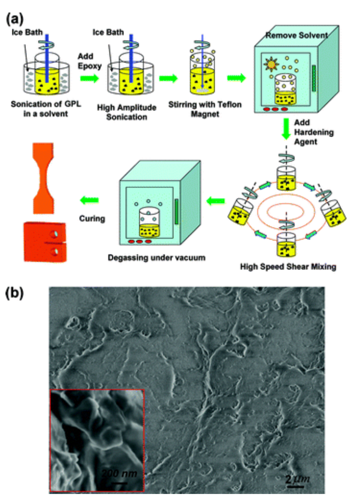
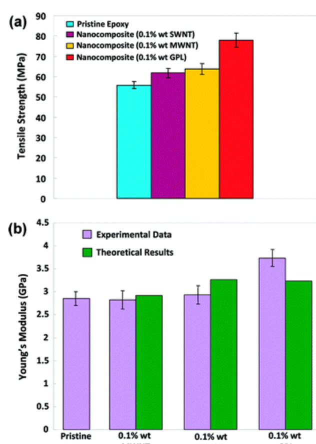
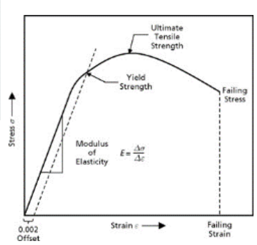
Composites







Rafiee, ACS Nano, 2009

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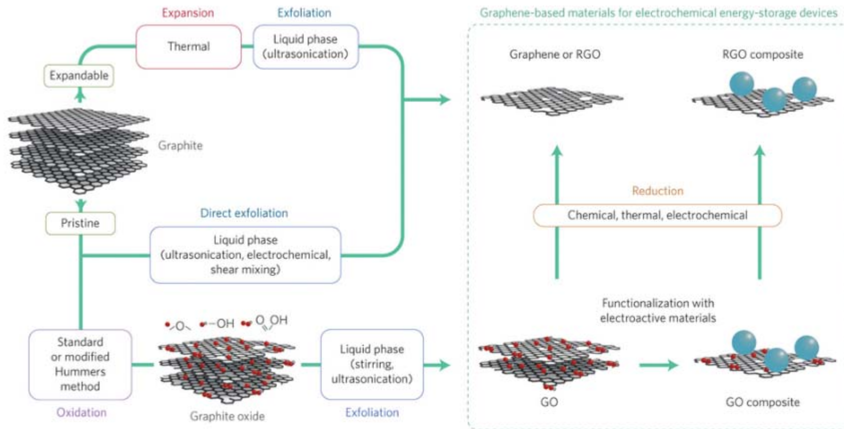
Energy Storage



Raccichini, Nature Materials (2015)

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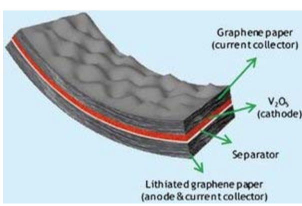
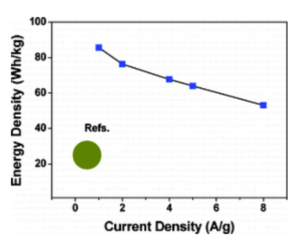
Energy Storage

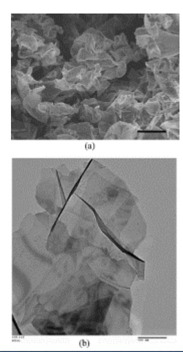


Yakobson, J. Phys. Chem. Lett. (2013)

Randomly stacked layers of graphene nanoplatelets enhance charge storage in Li+, and Na+ batteries. Enable flexible batteries.

Graphene supercapacitors store as much energy as Ni metal hydride batteries (~70 Wh/kg)





Liu, Nano Lett. 2010

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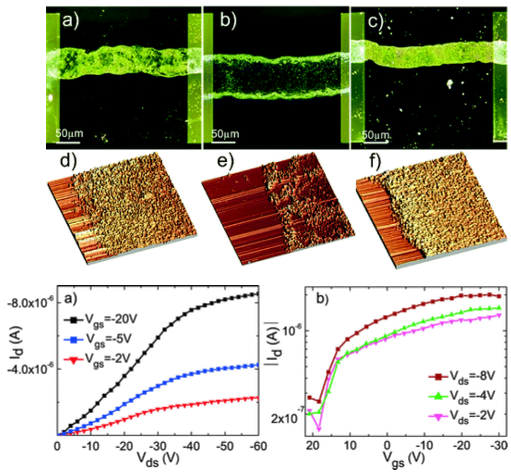
Printed and Electronics



- Graphene inks are now commercially available.
- Device mobilities as high as ~100 cm_2/V-s have been reported for Graphene on SiO_2. and ~1000 cm^2/V-s for graphene on hBN.

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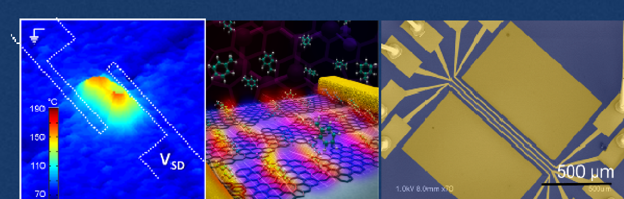
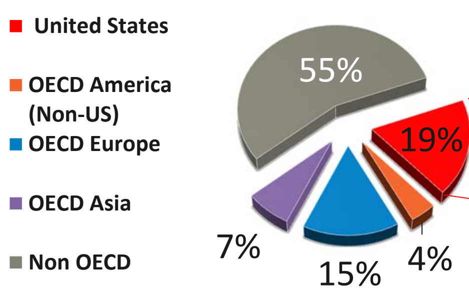
Part 2: Atomic Layer Research in the Integrated NanoMaterials Lab



David Estrada
Assistant Professor
Materials Science and Engineering Department

U.S. Energy Consumption in 2011



Computers and buildings account for almost 50% of U.S. energy use.

E. Pop, *Nano Research* 3, 147 (2010)
http://buildingsdatabook.eren.doe.gov/default.aspx

- Consumed **1/5** of the global energy produced in 2011.
- Consumed more than any other **O**rganization for **E**conomic **C**ooperation and **D**evelopment (OECD) member country.
- 80% of U.S. energy is produced by fossil fuels, and ~ 50% of is rejected before end use. → Heat loss!

U.S. Energy Information Administration (http://205.254.135.7/)

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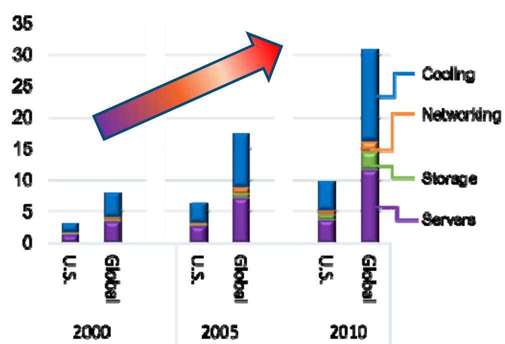
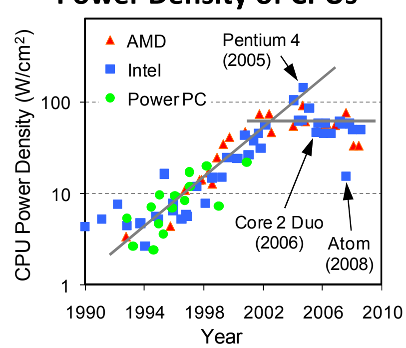
Computer Related Energy Consumption

Data Center Related Power Use (GW)



Power Density of CPUs



- Cloud computing 5th largest energy consumer in the world.
- Power density of CPUs has been increasing, reached air cooling limit of Silicon.
- Data centers + 100 million PCs + displays <u>+ cooling</u> = 5 % of nation-wide power budget in 2007 → 1/3 by 2025.

E. Pop, *Nano Research* 3, 147 (2010)
http://www.energystar.gov/
Green Peace, Climate Report (2012)

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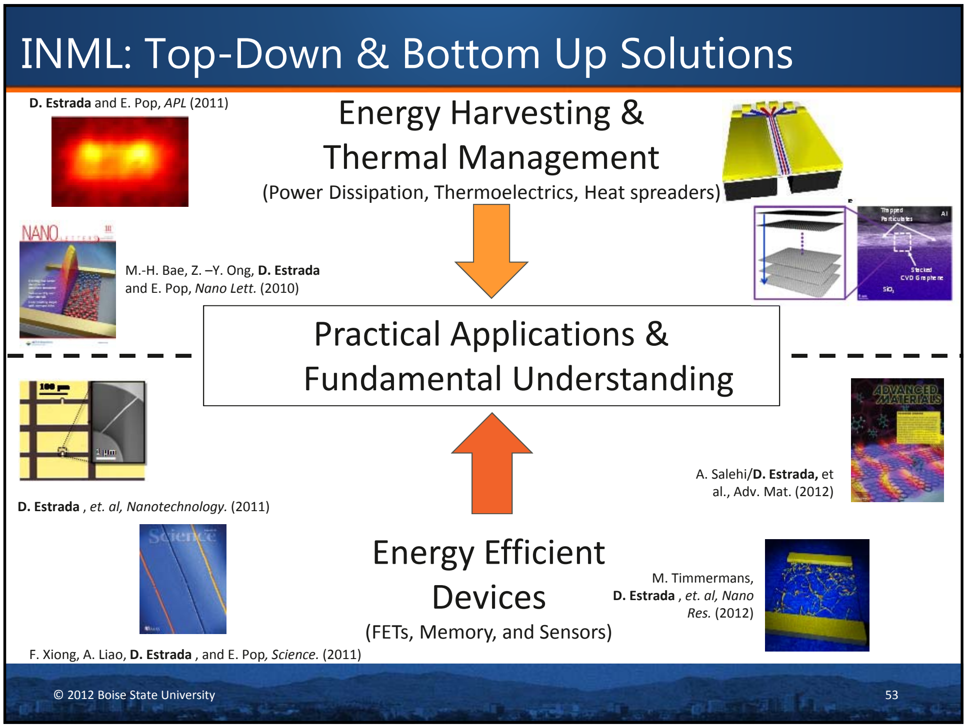
INML: Top-Down & Bottom Up Solutions
D. Estrada and E. Pop, APL (2011)
Energy Harvesting &
Thermal Management
(Power Dissipation, Thermoelectrics, Heat spreaders)
M.-H. Bae, Z. –Y. Ong, D. Estrada and E. Pop, Nano Lett. (2010)
Practical Applications &
Fundamental Understanding
D. Estrada , et. al, Nanotechnology. (2011)
A. Salehi/D. Estrada, et al., Adv. Mat. (2012)
Energy Efficient
Devices
(FETs, Memory, and Sensors)
M. Timmermans, D. Estrada , et. al, Nano Res. (2012)
F. Xiong, A. Liao, D. Estrada , and E. Pop, Science. (2011)
© 2012 Boise State University
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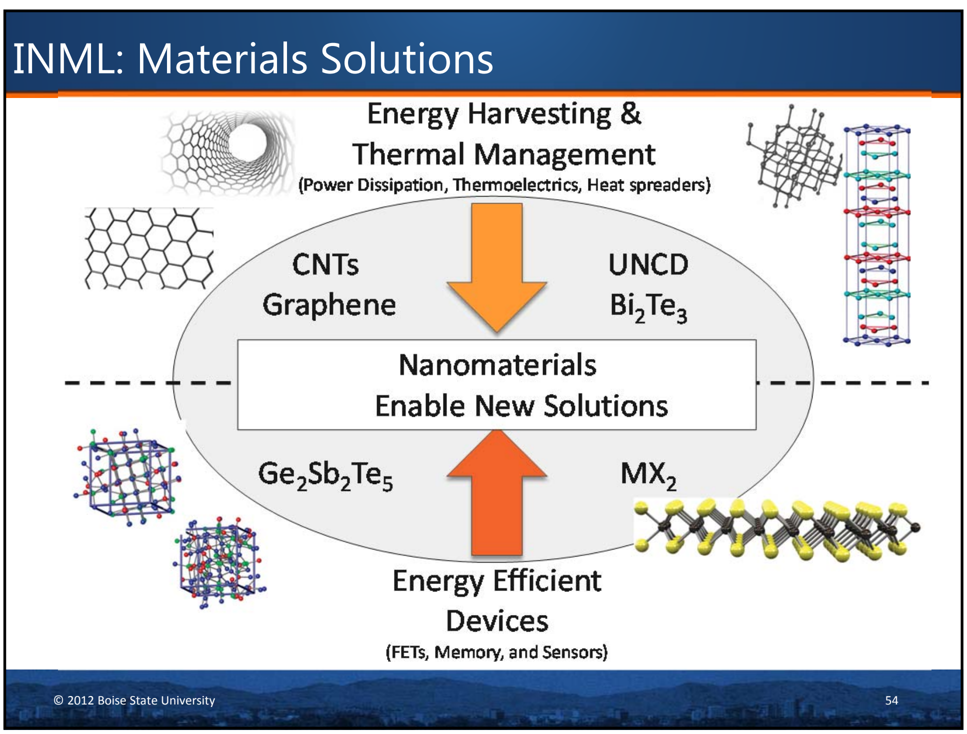
INML: Materials Solutions
Energy Harvesting &
Thermal Management
(Power Dissipation, Thermoelectrics, Heat spreaders)
CNTs
Graphene
UNCD
Bi_2Te_3
Nanomaterials
Enable New Solutions
$Ge_2Sb_2Te_5$
MX_2
Energy Efficient
Devices
(FETs, Memory, and Sensors)
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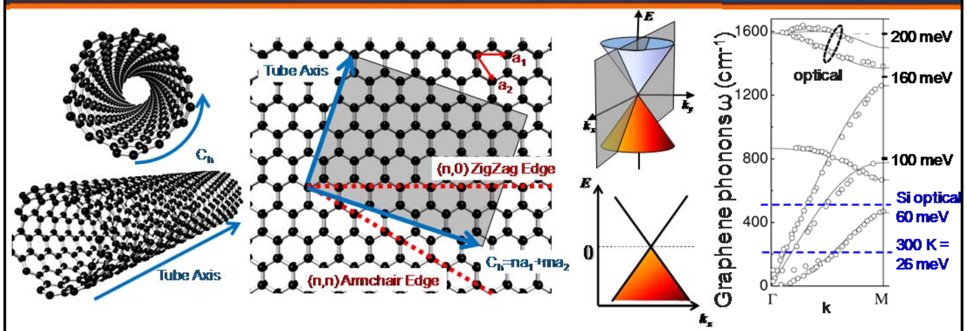
Properties of Carbon Nanomaterials

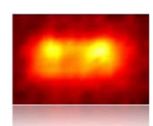


- Great electrical and thermal properties → low power dissipation!
  - Symmetric energy band, equal electron & hole mobility, 10-100x higher than Si: less scattering
  - Large optical phonon energy (0.18 eV vs. 0.06 eV in Si) : less scattering
  - Strong σ bonds → high thermal conductivity $k \approx 20 \times k_{si}$
- Gate tuning of carrier density and power dissipation

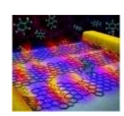
I α nμE

Outline of Part 2

Carbon Nanotube Thin-Film Transistors
- Direct Imaging of Power Dissipation
- Effects of CNT-CNT Junctions on Reliability

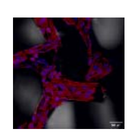


Graphene Chemical Sensitivity
- Graphene Growth by Chemical Vapor Deposition
- Role of Linear Defects in Sensing

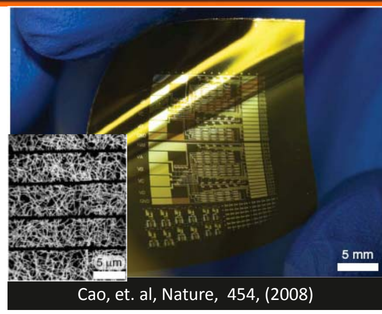


Thermal Transport in CVD Graphene
- Suspended Thermometry Platform
- In-plane and cross-plane thermal conductivity measurements

Nanobiotechnology Research in the INML
- Nanopores and graphene bioscaffolds

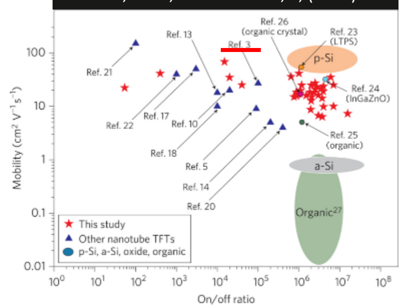


Carbon Nanotube Network Transistors



Cao, et. al, Nature, 454, (2008)

Sun, et. al, Nature Nano., 6, (2011)

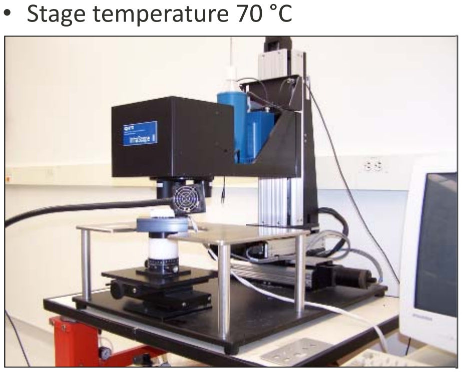


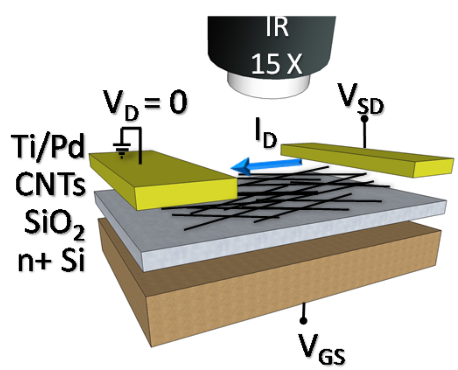
- CNT networks (CNNs) have lower performance than single CNTs (μ, I_{ON}/I_{OFF}).
- CNN thin-film-transistors (TFTs) show promise as energy efficient display drivers.
- Low thermal conductivity substrates affect TFT performance
  → Self heating and reliability.
- IR microscopy and electrical breakdown can be used to investigate power dissipation and reliability in CNN TFTs

IR Imaging of CNN - TFTs

- QFI InfraScope Micro-Thermal Imager
- Specifications:15X objective, spatial resolution 2.8 µm and 0.1 K temperature resolution
- IR radiation of wavelength from 2 to 4 µm
- Stage temperature 70 °C

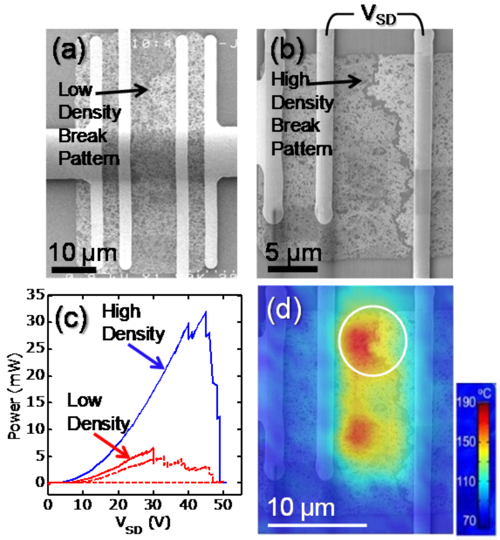
$J \alpha T^4$





D. Estrada and E. Pop, *Applied Physics Letters* **98**, 073102 (2011)

IR Imaging of CNN - TFTs



- Irregular breakdown pattern bears the imprint of the hotspot
- Channel temperature near breakdown << 600 °C
- Large drop in the P-V curve indicates break in the film
- Temperature profile signature of percolation

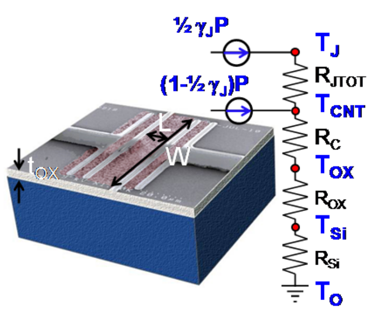
$$T_{BD} - T_0 = P_{BD} \times R_{TH}$$

D. Estrada and E. Pop, *Applied Physics Letters* **98**, 073102 (2011)

Thermal Modeling of CNN-TFT

$$T_{BD} - T_0 = P_{BD} \times R_{TH}$$

g = 0.3 W K^{-1} m^{-1}



$$R_{JTOT} = \frac{(T_{BD} - T_{CNT} - T_{OX} - T_{SI})}{\frac{1}{2}\gamma_J P_{BD}}$$

$$R_C = \frac{1}{g \times L_C}$$

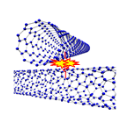
$$R_{OX} = \frac{t_{OX}}{\kappa_{OX} A_C}$$

$$R_{Si} = \frac{1}{2\kappa_{Si}\sqrt{LW}}$$

600 °C
3.49 × 10^7 K/W
104.5 °C
462.9 K/W
101.4 °C
4.46 × 10^3 K/W
71.5 °C
223.6 K/W
70 °C

$R_J \approx R_{JTOT} \times n_J \times A \approx$ **4.4 × 10^{11} K/W** (2.27 pW/K), 2.06 × 10^{-6} m^2 K W^{-1}

$R_{JTOT} \approx$ 3.38–3.50 × 10^7 K W^{-1} for g = 0.05 – 0.6 W K^{-1} m^{-1}

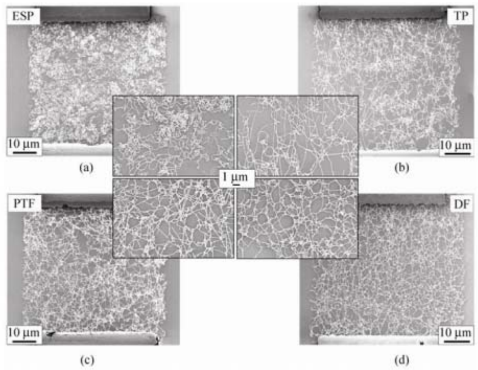


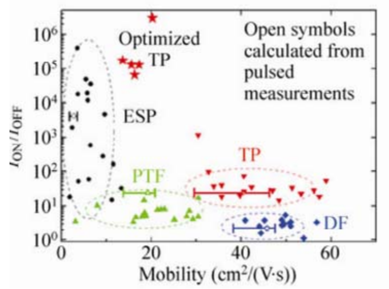
Other work: 3.3 × 10^{11} K W^{-1} (3 pW/K), 1 × 10^{-7} m^2 K W^{-1}

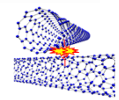
Zhong, et. al, PRB (2006)
Prasher, et al, PRL (2009)

D. Estrada and E. Pop, *Applied Physics Letters* **98**, 073102 (2011)

CNT Network Morphology



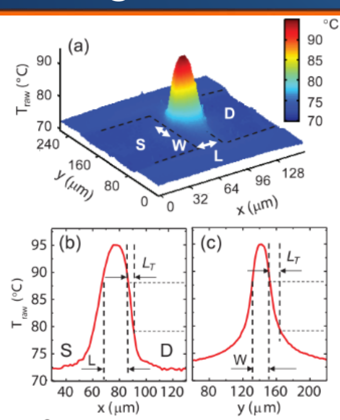


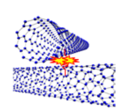


- Aerosol CVD of CNTs and deposition methods can result in drastically different network morphologies.
- Network morphology affects CNT-CNT junction areas → device mobility.
- Greater CNT alignment and reduced junctions areas improve device performance.

M. Timmermans, **D. Estrada,** et. al, *Nano Research* **5**, 307 (2012)

Reducing Junction Resistance





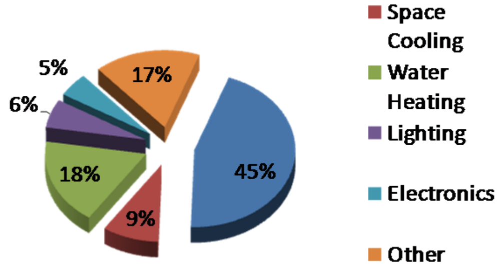
- Use of monodisperse CNTs reduces the number Schottky barriers in the network → reduced resistance and uniform power dissipation.
- Thermal resistance of junctions can be used to solder together CNTs.

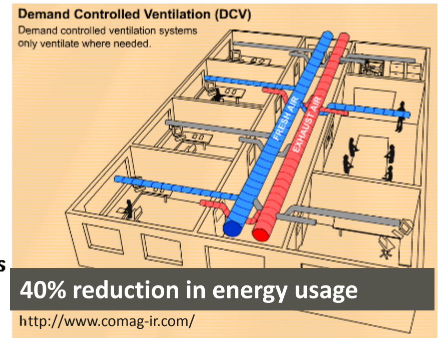
A. Behnam, et al., *ACS Nano* **7**, 482 (2013)

J. W. Do, **D. Estrada**, et al., *Nano Letters* **13**, 5844 (2013)

Building Related Energy Consumption

Residential Energy Consumption By End Use





- U.S. Buildings sector → 7% of global power consumption in 2010.
- 28 % of U.S. CO_2 emissions can be traced to HVAC systems.

http://buildingsdatabook.eren.doe.gov/

- Adjust the ventilation rate based on pollutants level
- Potential to reduce heating & cooling costs
- *Refreshable, sensitive, and cheap, pollutant detectors needed*

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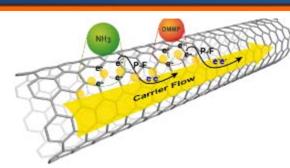
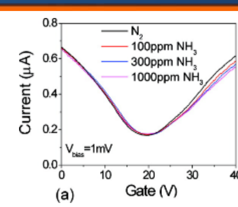
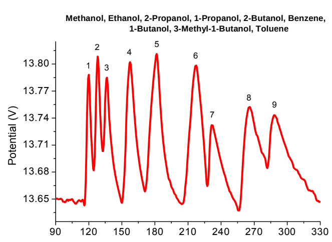
Carbon Based Chemical Sensors



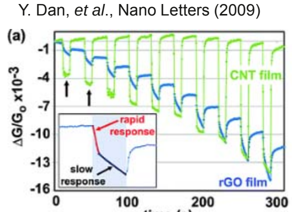
A. Salehi-Khojin, et al., *Science* (2010)



Y. Dan, *et al*., Nano Letters (2009)



A. Salehi-Khojin, et al., *Nanoscale* (2011)



J.T. Robinson, et al., Nano Letters (2008)

- 0-D defects in CNT sensors show to enhance sensitivity/selectivity
  → Physics approach vs. chemical approach
- Graphene intrinsic response below that of CNTs, even for rGO films!

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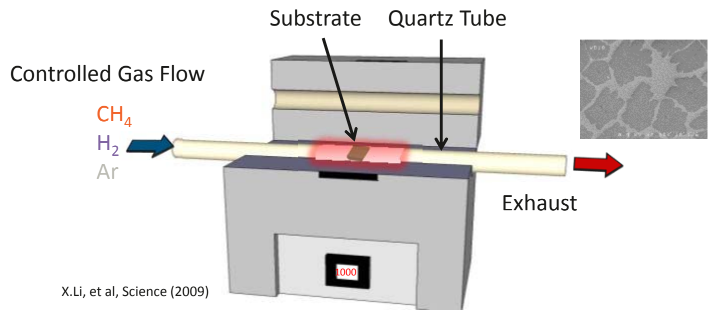
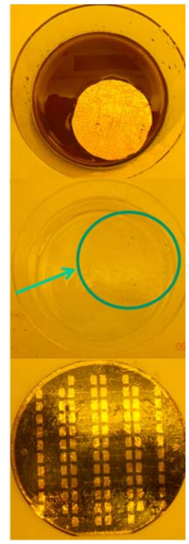
Graphene Growth by CVD



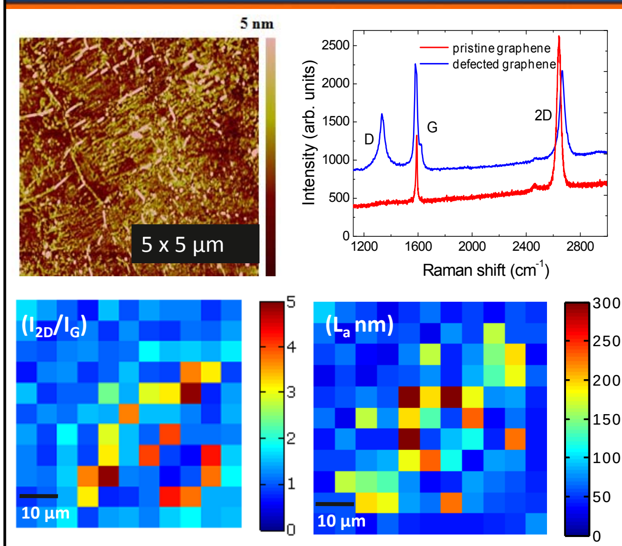


1" Quartz tube LPCVD furnace

- Graphene grown directly on Cu foil at 1000 °C
- CVD growth of graphene → polycrystalline films
- Graphene is transferred by etching of Cu foil in $FeCl_3$
- Films are annealed in Ar/H_2 at 400 °C to remove residue

A.Salehi-Khojin / **D. Estrada,** et al., *Advanced Materials* **24**, 53-57 (2012)

CVD Graphene is Inherently Defective



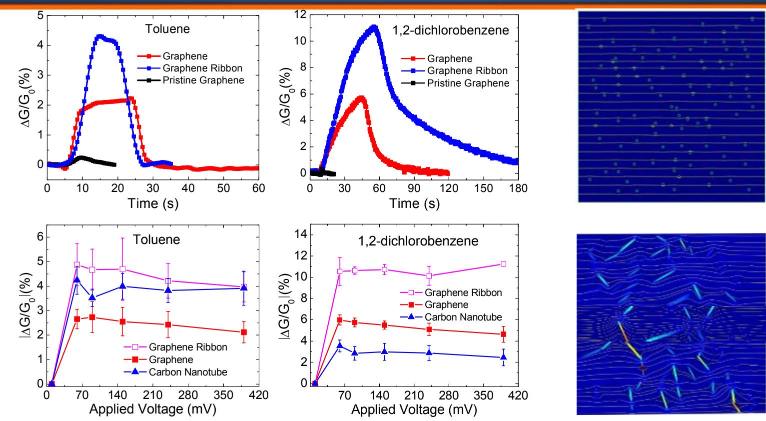
- AFM and Raman Spectroscopy reveal defective nature of CVD graphene
- Raman mapping shows our growth varies between mono and bilayer graphene
- The "crystallite" size is ~ 80 nm
- Can line defects enhance chemical sensitivity?

$L_a \sim I_D/I_G$

$\#Layers \sim I_{2D}/I_G$

A.Salehi-Khojin / **D. Estrada,** et al., *Advanced Materials* **24**, 53-57 (2012)

Sensor Response to Trace Gas Vapors

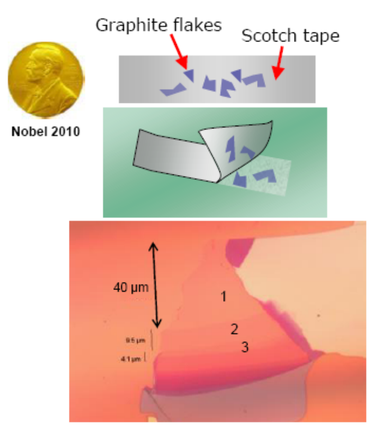


- CVD graphene ribbons show high sensitivity to 10^{14} molecules of toluene and 10^{15} molecules of dichlorobenzene → ppb sensitivity
- Confining current flow through linear defects allows polar molecules to modulate device conductance
- Defects in graphene enhance chemical sensitivity

A.Salehi-Khojin / **D. Estrada**, et al., *Advanced Materials* **24**, 53-57 (2012)

Other Ways of Obtaining Graphene

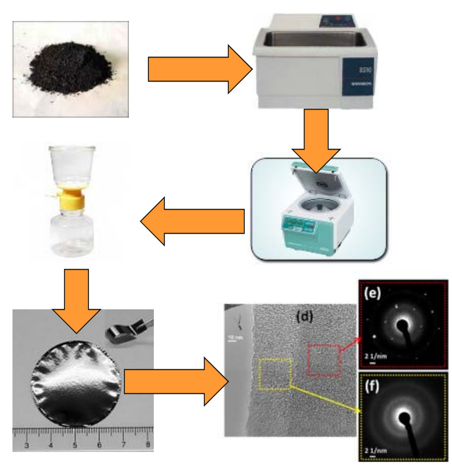
Mechanical Exfoliation



Novoselov, K. S. *et al.* ,*Science* (2004)

Novoselov, X. *et al.* ,*Science* (2009)

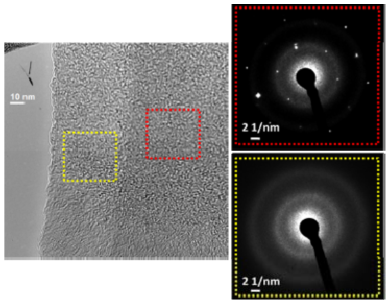
Chemical Assisted Exfoliation



Y. Hernadez, et al., Nat. Nano (2008)

D. Li, et al., Nat. Nano (2008)

Other Graphene Chemical Sensor Studies



APPLIED PHYSICS LETTERS **100**, 033111 (2012)

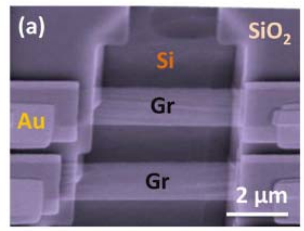
Chemical sensors based on randomly stacked graphene flakes

Amin Salehi-Khojin,[1,7,a)] David Estrada,[2,3] Kevin Y. Lin,[1] Ke Ran,[4,5] Richard T. Haasch,[5] Jian-Min Zuo,[4,5] Eric Pop,[2,3,6] and Richard I. Masel[7,a)]
[1]*Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[2]*Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[3]*Micro and Nanotechnology Lab, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[4]*Department of Material Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[5]*Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[6]*Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*
[7]*Dioxide Materials, 60 Hazelwood Dr., Champaign, Illinois 61820, USA*

NANO LETTERS
Letter
pubs.acs.org/NanoLett

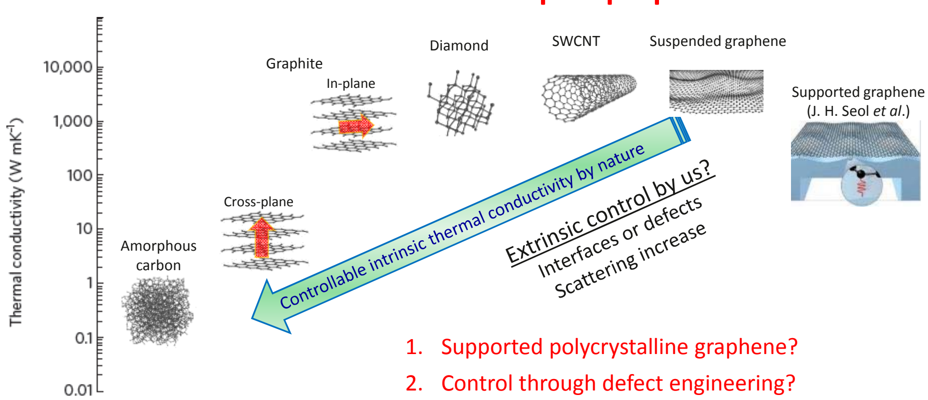
The Role of External Defects in Chemical Sensing of Graphene Field-Effect Transistors

B. Kumar,[†] K. Min,[‡] M. Bashirzadeh,[§] A. Barati Farimani,[‡] M.-H. Bae,[∥,⊥] D. Estrada,[∥] Y. D. Kim,[#] P. Yasaei,[†] Y. D. Park,[#] E. Pop,[∥] N. R. Aluru,[‡] and A. Salehi-Khojin*[,†]



Thermal Conductivity of Carbon Allotropes

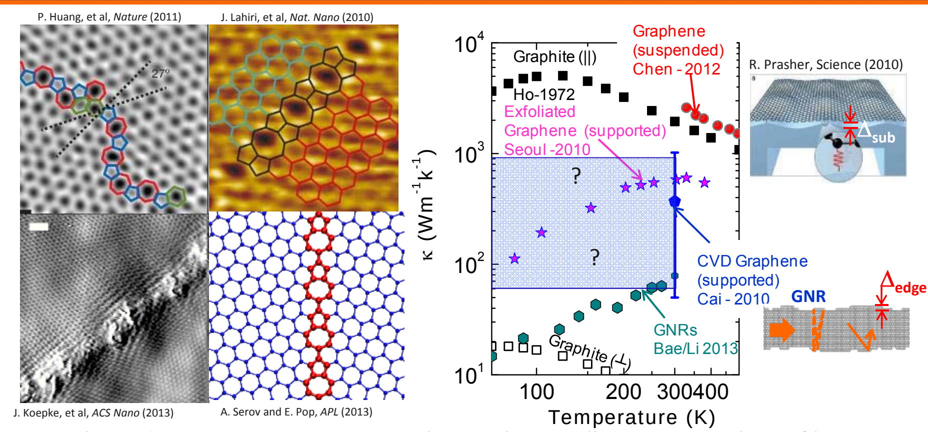
Can we tune thermal transport properties ?



1. Supported polycrystalline graphene?
2. Control through defect engineering?
3. Weaken cross-plane coupling?
4. Tune thermal anisotropy?
5. Transparent heat spreaders?

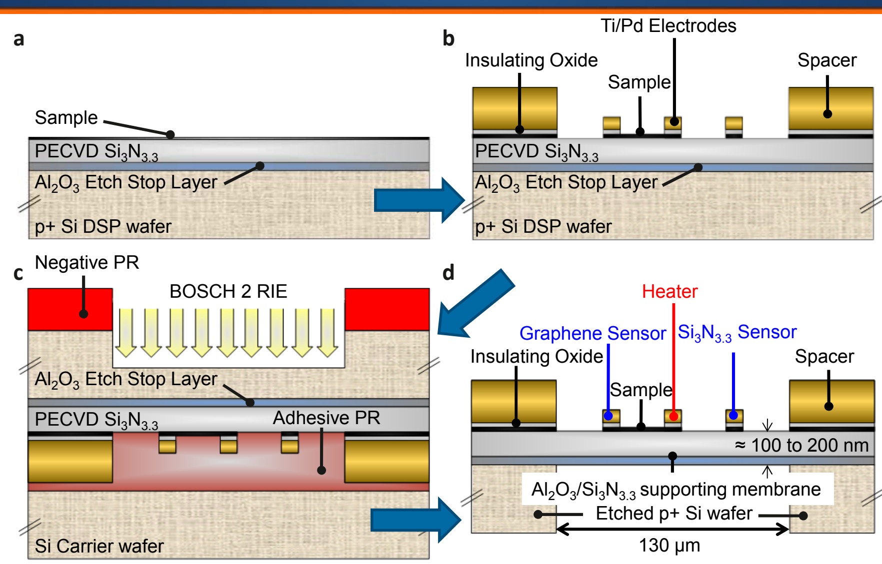
A. A. Balandin Nat. Mater. **10**, 569 (2011)
R. Prasher, Science **328**, 185 (2010)
J. H. Seol *et al.*, Science **328**, 213 (2010)
http://www.chemicool.com/elements/carbon.html

Linear Defects in Large Scale Graphene Films

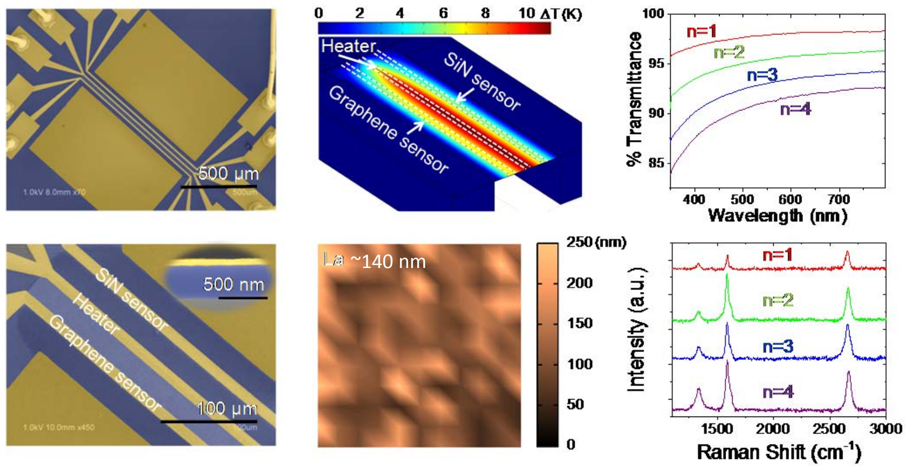


- Grain boundary structure varies greatly in polycrystalline CVD graphene films
- Significant carrier scattering observed by STM at grain boundaries
- Theory predicts significant phonon scattering at grain boundaries (depends on type)
- Extrinsic influences → tunable thermal transport in low-dimensional crystal

Suspended Thermometry Platform Fabrication

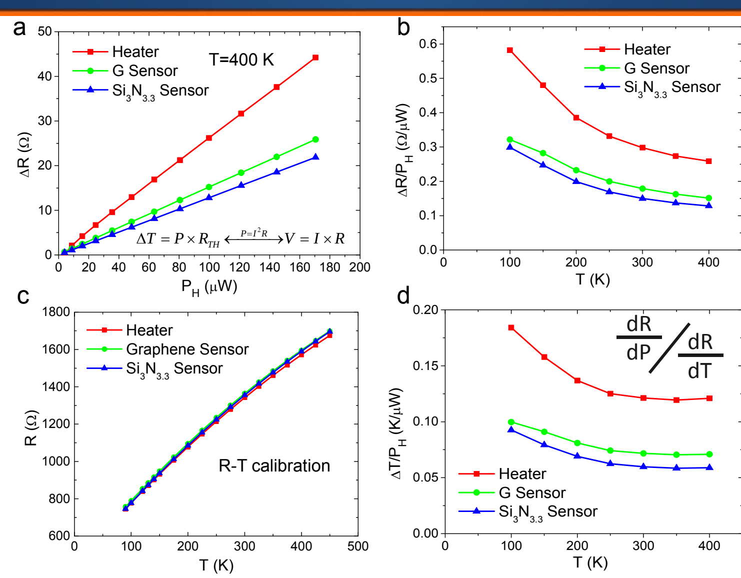


Suspended Electrical Thermometry Platform

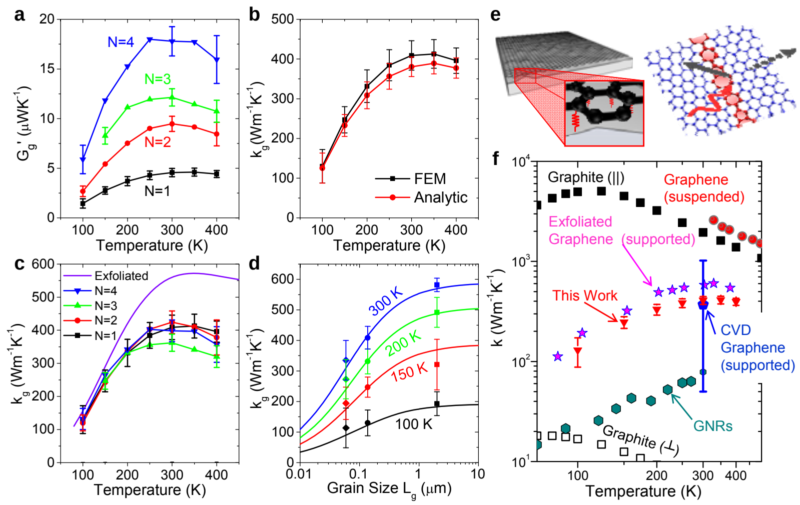


- Devices are wirebonded to a leaded chip carrier and placed inside a Janis VTPS for measurements (80 to 450 K)
- Graphene films are characterized by Raman, absorbance, AFM, and XPS.

Suspended Electrical Thermometry Platform



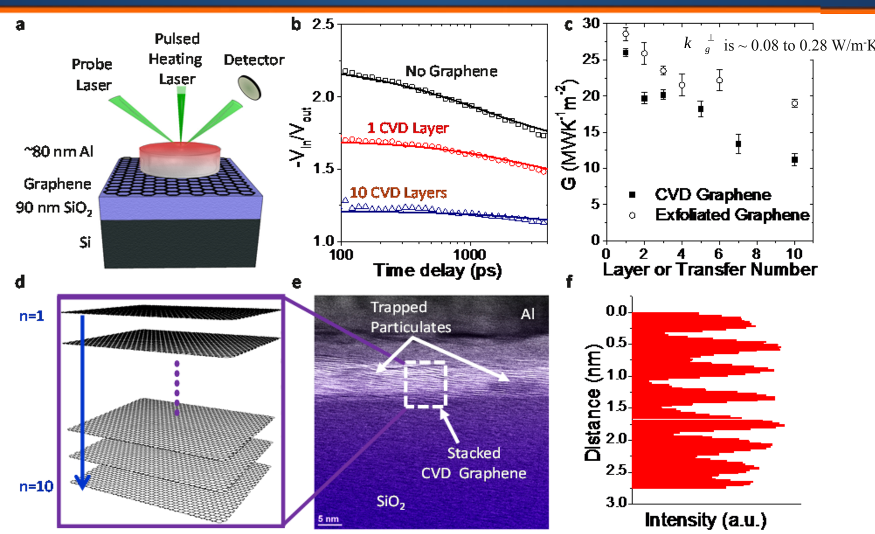
Suspended Electrical Thermometry Platform



Thermal conductivity is limited by grain size and substrate scattering (N<4)

 75

Cross-Plane Thermal Measurements



Cross-plane thermal conductivity is 2x< exfoliated → tunable anisotropy

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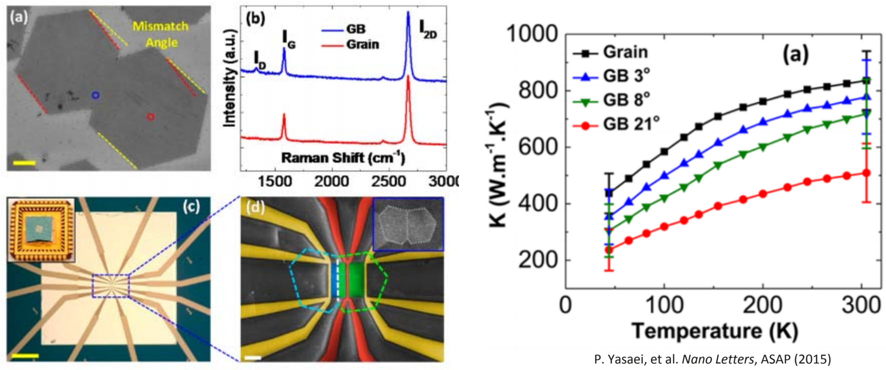
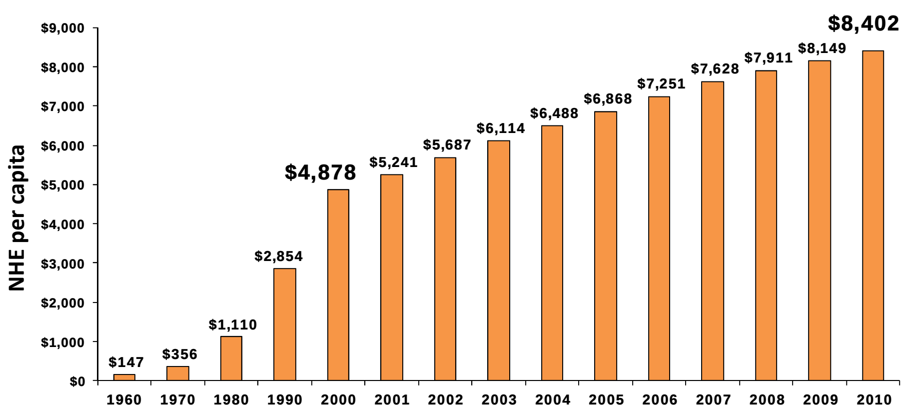
Thermal Transport Across Grain Boundaries



P. Yasaei, et al. *Nano Letters*, ASAP (2015)

- Direct electrical thermometry of CVD graphene with and without a GB reveals strong phonon scattering at GBs.
- Thermal conductivity decreases with increased GB misalignment → increased structural disorder near the GB.

U.S. Healthcare Expenditures



NHE as a Share of GDP

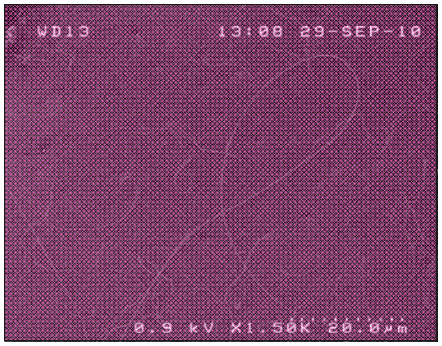
1960	1970	1980	1990	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
5.2%	7.2%	9.2%	12.5%	13.8%	14.5%	15.4%	15.9%	16.0%	16.1%	16.2%	16.4%	16.8%	17.9%	17.9%

Source: Centers for Medicare and Medicaid Services, Office of the Actuary, National Health Statistics Group, at http://www.cms.hhs.gov/NationalHealthExpendData/ (see Historical; NHE summary including share of GDP, CY 1960-2010;

Projected to grow to $13,708 in 2020 (~20% of GDP)

It's not always the economy……

- 7.6 million deaths (around 13% of all deaths) in 2008.
- About 70% of all cancer deaths occurred in low- and middle-income countries
- Deaths projected to continue to rise to over 13.1 million in 2030.
- High chance of cure if detected early and treated adequately



http://www.who.int/

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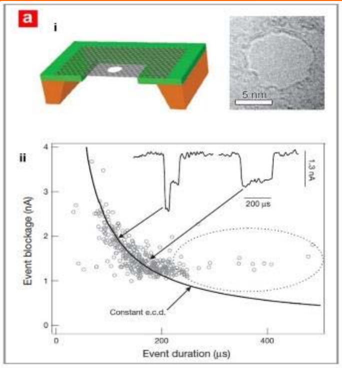
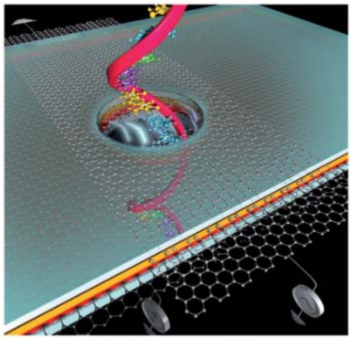
Nanopores in Graphene

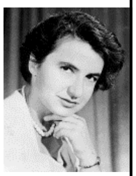


Garaj et al., *Nature*, **2010**



Venkatesan and Bashir, *Nat. Nano* **2011**

- Interlayer spacing of graphite (graphene thickness) ≈ 0.35 nm
- Inter-nucleotide separation in ssDNA ≈ 0.35 – 0.55 nm
- Both were studied by Rosalind Franklin ~60 years ago!
- Electrical access and new 2D materials enables new sensing modalities



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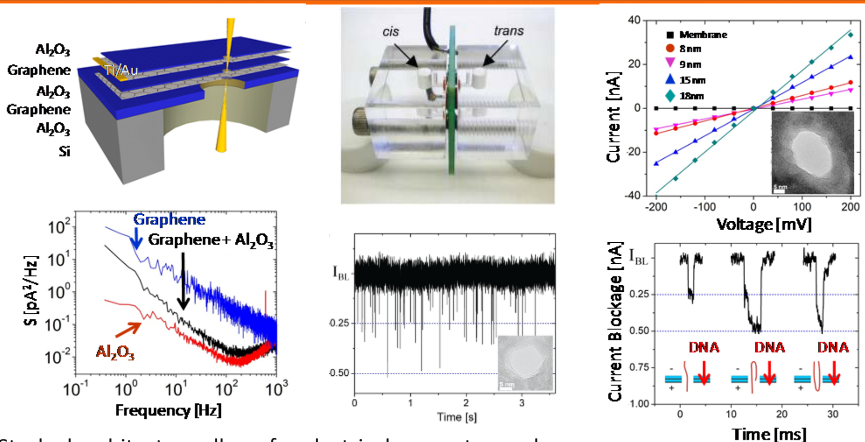
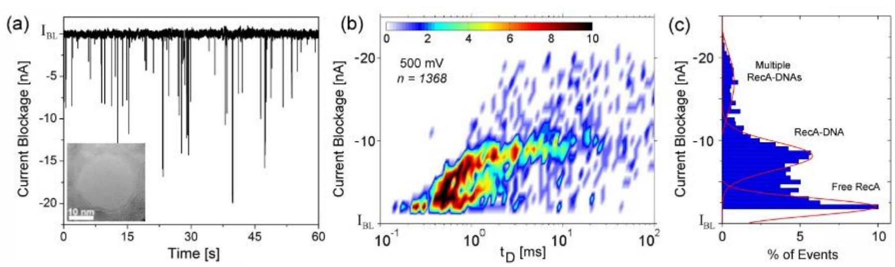
Stacked Dielectric-Graphene Architecture



- Stacked architecture allows for electrical access to graphene
- Pore conductance varies with diameter → lower 1/f than graphene only (1 M KCl, 10 mM Tris, 1 mM EDTA, pH 8)
- λ-DNA translocation and structure detected through ionic current blockades

B.M. Venkatesan, **D. Estrada,** et al., *ACS Nano* **6**, 441 (2012

DNA-RecA Protein Translocation



- Signature current blockades observed during DNA-protein translocation (25 nm pore, 400 mV, 1 M KCl, 10 mM Tris, 1 mM EDTA, pH 8)
- Unique current blockades correspond Free Reca, RecA DNA, and multiple RecA-DNA translocation events
- Proof of principle experiment shows possibility of using MBD proteins for early cancer detection

B.M. Venkatesan, **D. Estrada,** et al., *ACS Nano* **6**, 441 (2012)

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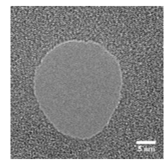
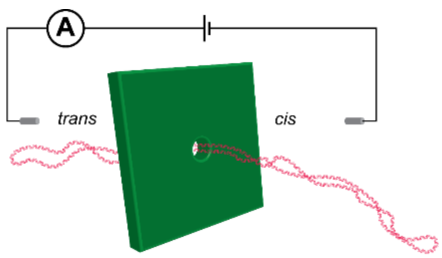
EXPERIMENTAL CONDITIONS

Nanopores:

- Drilled with JEOL 2010F TEM in 20 nm thick suspended Si_3N_4 membrane TEM grid (Norcada)
- ~ 21 nm diameter nanopore sandwiched between two flow cells forming only electrical path between reservoirs



Nanopore TEM image



Translocation:

- Reservoir electrolyte: 1M KCl, 1X TE buffer
- 7.5 kbp circular DNA: pTYB21 (NEB)
- Axopatch 200B amplifier, Digidata 1440 data acquisition system (Molecular Devices)
- 100 mV bias
- 10 kHz low pass hardware filter
- Added 50 μM Ethidium Bromide (EtBr) solution to DNA solution to alter topology

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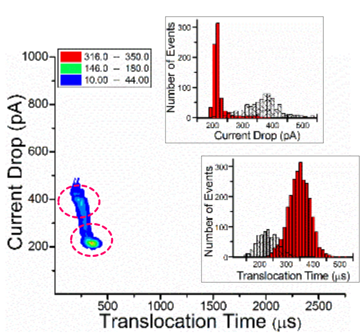
CIRCULAR DNA TRANSLOCATION EVENTS

Translocation of 7.5 kbp circular DNA suggests two distinct molecular conformations:



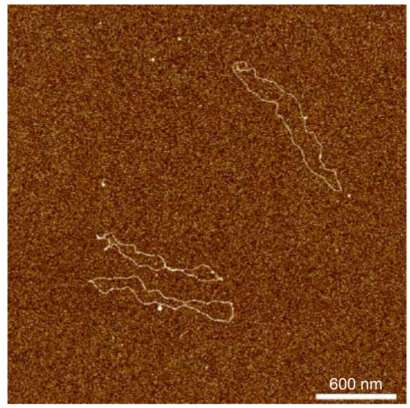
- Data analyzed using custom MATLAB routines and Origin 8.5
- Analyzed ~ 8000 events to determine the maximum current blockade and translocation time
- We can identify 2 distinct regions in the density plot and histograms which suggests 2 molecular conformations

Region 2: supercoiled branched

Region 1: circular covalently closed

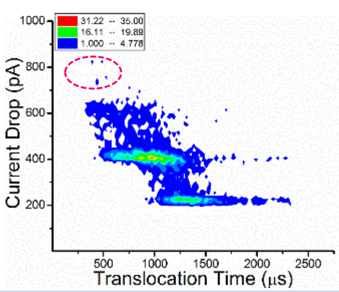
AFM Images Reveal DNA Topology

- Optimized sample preparation
  - DNA incubated with $NiCl_2$ on fresh cleaved mica for 5 minutes
  - Rinsed samples with ultrapure H_2O and gently dried with N_2
- AFM imaging
  - Tapping mode, Bruker MultiMode 8 AFM
  - Image processing with NanoScope Analysis software
- 2D projection of the DNA in solution
- Representative AFM image demonstrate initial circular DNA topology



Some branching, but generally uniform topology

Intercalated Circular DNA Topology: Region 4

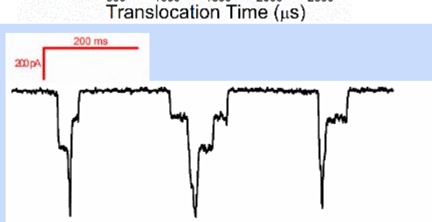


- Small population of events (~ 5%) with higher current drop: > 700 pA
- Multiple identifiable current drops

↓

Further unwinding causing:

- ***additional branched structures***
- ***secondary branching***



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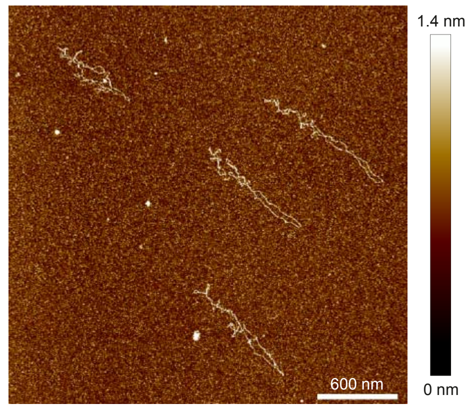
AFM IMAGES OF INTERCALATED DNA

Circular DNA treated with EtBr exhibits significant branching

- Optimized sample preparation
  - DNA incubated with $NiCl_2$ and EtBr on fresh cleaved mica for 5 minutes
  - Rinsed samples with ultrapure H_2O and gently dried with N_2
- AFM imaging
  - Tapping mode, Bruker MultiMode 8 AFM
  - Image processing with NanoScope Analysis software
- Representative AFM image of intercalated circular DNA
- Under identical imaging conditions, observable structural changes to topology



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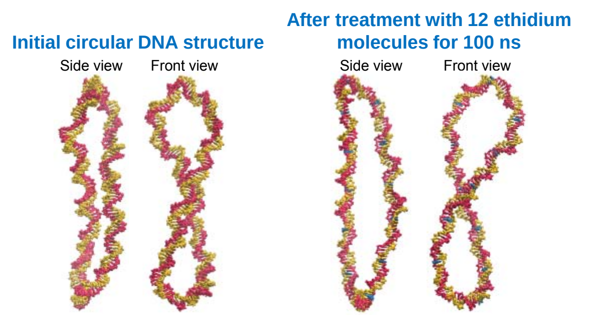
MOLECULAR DYNAMICS SIMULATIONS

All-atom Molecular Dynamics simulations identify unwinding due to intercalation:

BLUE WATERS SUSTAINED PETASCALE COMPUTING

Simulation Conditions:

- 750,000 atoms
- 180 base-pair negatively supercoiled circular DNA (Lk = 14)
- 1M ion concentration



Ethidium initiates a positive supercoiling and unwinding of the circular DNA

Average total twist changes by 160°

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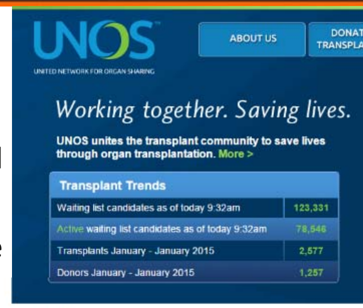
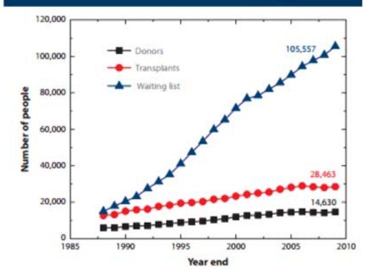
The Need for Tissue Engineering

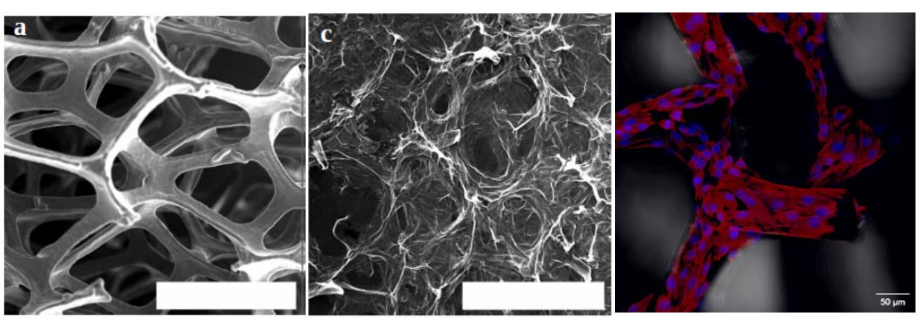
- Current waiting list for organ transplantation exceeds 123,000 (>78,000 active).
- Widening gap between patients and donors.
- Transplantation of vital organs is the only treatment for end stage organ failure.
- No such treatments exist for Traumatic Brain Injury (TBI) or neuromuscular disorders.
- New materials are needed to mimic cell-cell and cell-ECM interactions.





P. Bajaj, Review of Biomedical Engineering (2014)

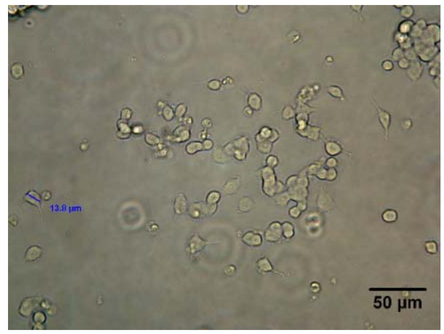
C2C12 Growth on Graphene Foam



- Growth of 2D materials can be extended to 3-dimesions on 3D transition metal foams.
- Selective etching removes metal scaffold → biocompatible 3D scaffold for cell growth
- C2C12 myoblasts can be seeded on laminin coated graphene foam.
- Confocal fluorescence microscopy of C2C12 cells shows high adhesion to foam walls:
  - Red - Alexa Fluor 546 phalloidin (F-actin)
  - Blue – DAPI
- Electrical stimulation and defects could play a role in cell growth and differentiation

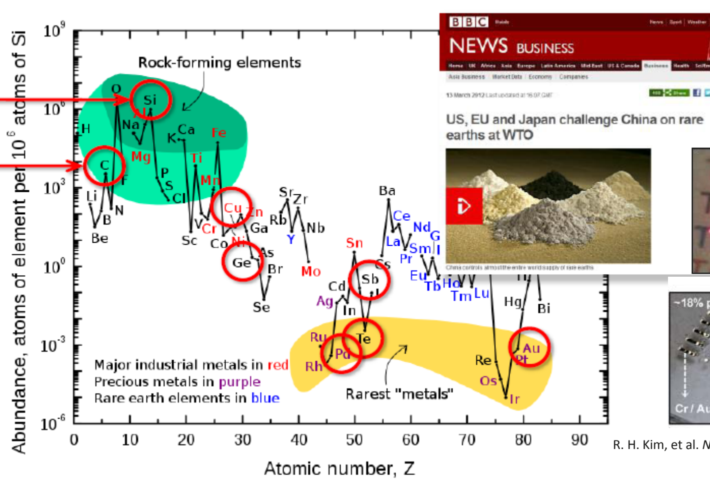
Cell Growth for Neural Network

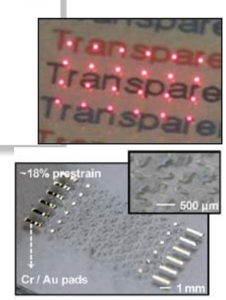
- Culture electrically responsive cells for developing functional engineered neural networks
- PC-12 rat pheochromocytoma cells
- Commonly used to model neurons
- Differentiate into neuron-like cells



Phase contrast image of PC-12 cells in laminin-coated dish.
In media with 100ng/ml nerve growth factor.

Using Carbon makes ene





R. H. Kim, et al. *Nano Letters* **11**, 3881 (2011)

source: http://pubs.usgs.gov/fs/2002/fs087-02

Cost of Indium kg^{-1} has increased from ~$94.00 to ~$850 this decade.

(http://www.metalbulletin.com/)

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Doctoral Committee:

INML Researchers and Staff:

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THANK YOU

http://coen.boisestate.edu/inml/

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