



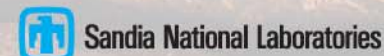
Graphene Nanoelectronics

Project Manager: Carlos Gutierrez
Surface and Interface Sciences Dept.
Sandia National Labs

Principal Investigator: Steve Howell

Co-Investigators: Thomas Beechem, Laura Biedermann, Tom Friedmann, Kevin McCarty, Taisuke Ohta, Wei Pan, Anthony Ross, Cody Washburn and David Wheeler

*This work was supported the LDRD program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.





Outline

- Background About Sandia National Labs
 - What I Sandia National Labs?
 - What does Sandia do?
 - Why does Sandia care about Graphene Nanoelectronics?
- Background About Graphene
- Sandia's Graphene Research Efforts





First...

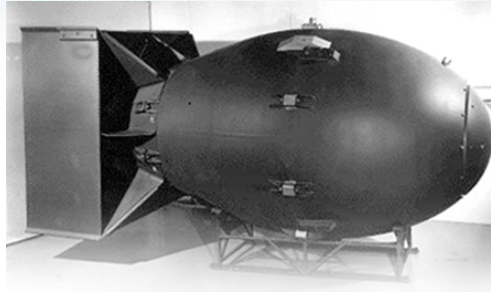
What is Sandia National Labs?

What does Sandia National Labs do?

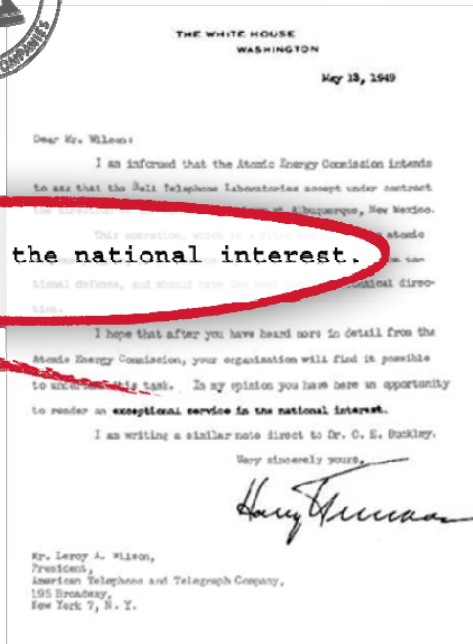
**Why do they care about Graphene
Nanoelectronics?**



Sandia's Beginning: Spin Off from LANL's Z-Division (1949)



exceptional service in the national interest.



Sandia's Governance Structure



Sandia Corporation

- AT&T: 1949–1993
- Martin Marietta: 1993–1995
- Lockheed Martin: 1995–present

Government owned, contractor operated



Federally funded research and development center



Sandia's Sites

**Albuquerque,
New Mexico**



**Livermore,
California**



Tonopah, Nevada



**Waste Isolation Pilot Plant,
Carlsbad, New Mexico**



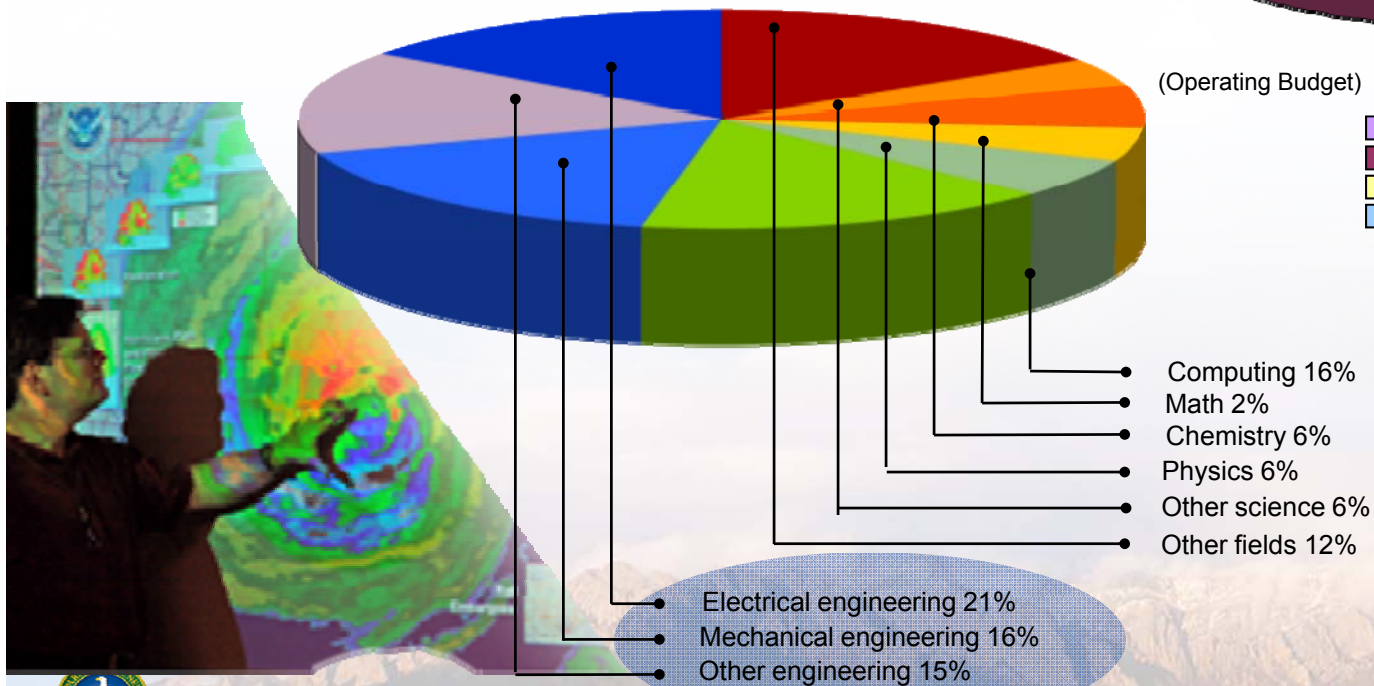
Pantex, Texas



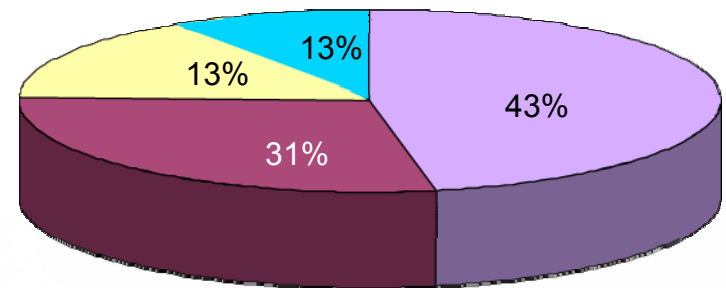
People and Budget (As of October 15, 2010)

- On-site workforce: 11,677
- Regular employees: 8,607
- Gross payroll: ~\$898.7 million

Technical staff (4,277) by discipline:



FY10 operating revenue
\$2.3 billion



(Operating Budget)

- Nuclear Weapons
- Defense Systems & Assessments
- Energy, Climate, & Infrastructure Security
- International, Homeland, and Nuclear Security



The Mission Has Evolved for Decades

1950s

Production
engineering &
manufacturing
engineering

1960s

Development
engineering

1970s

Multiprogram
laboratory

1980s

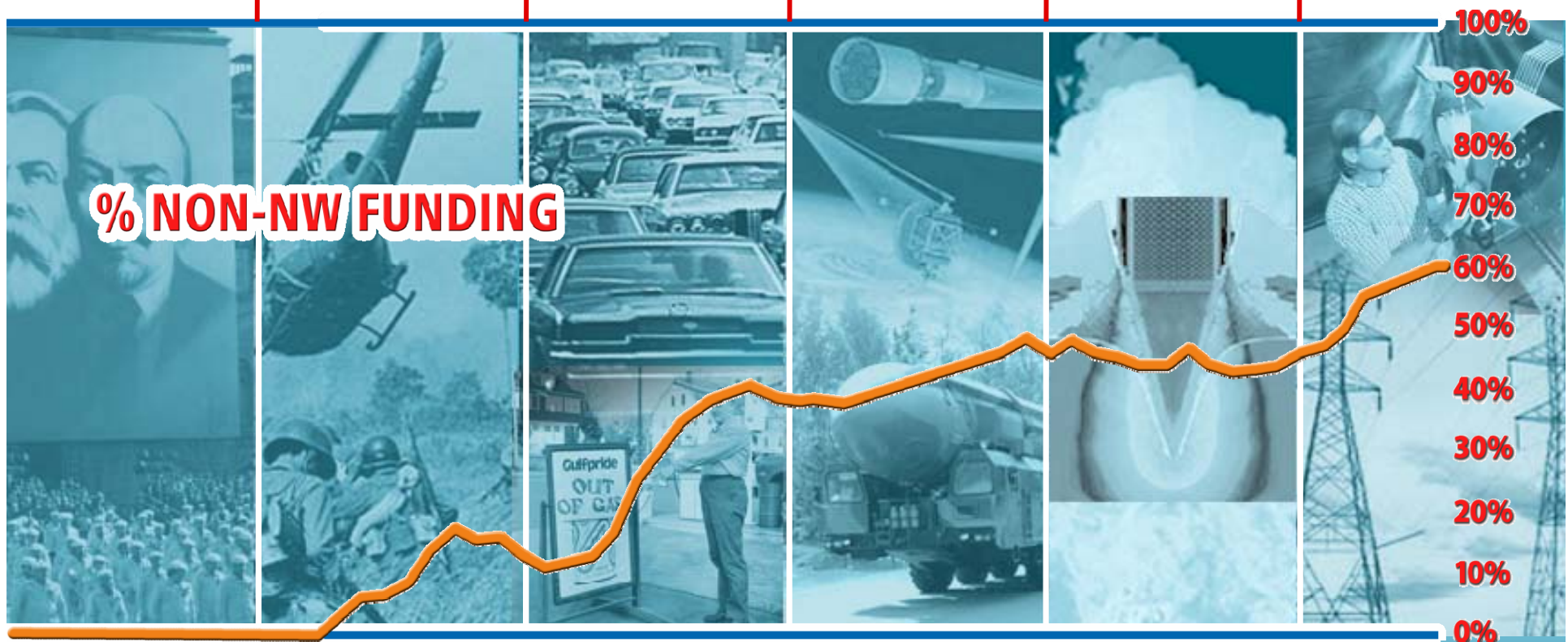
Research,
development and
production

1990s

Post-Cold War
transition

2000s

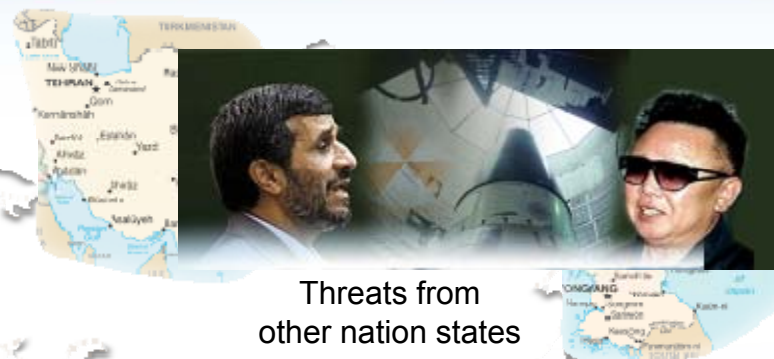
Broader national
security challenges



Addressing Our Evolving National Security Environment is of the Greatest Importance



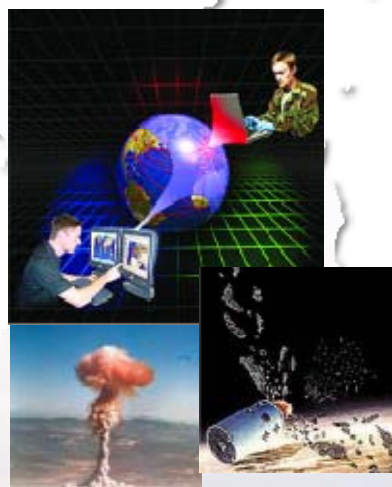
Traditional strategic nuclear threats



Threats from other nation states



Threats from non nation states



Threats of tech surprise



Other threats: natural disasters, climate change, energy supply

Sandia Microelectronics and Microsystems R&D Facilities

The MESA (Microsystems & Engineering Sciences Applications) Complex



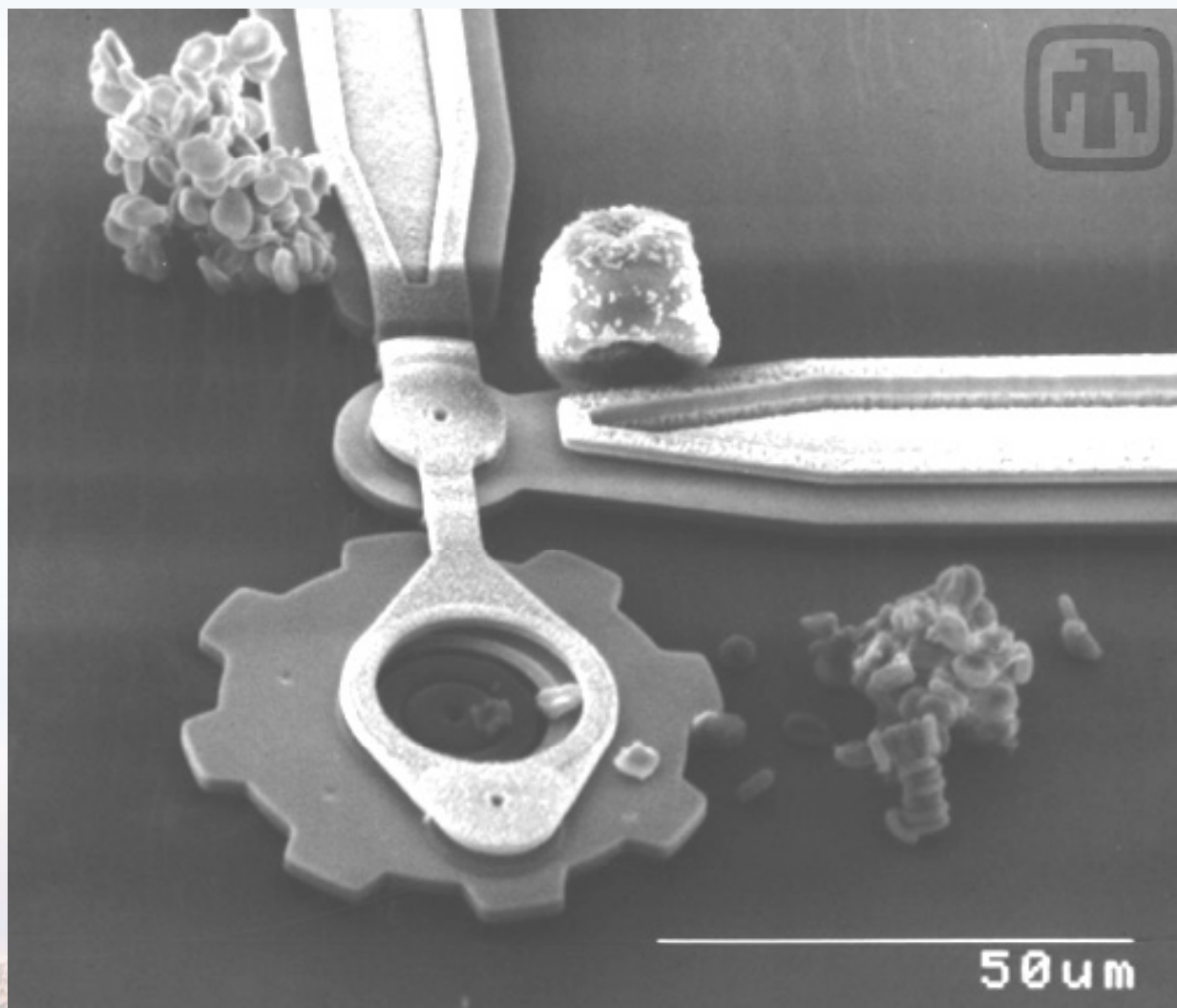
Micromachined Six-gear Chain
(Operation up to 250,000 RPM)



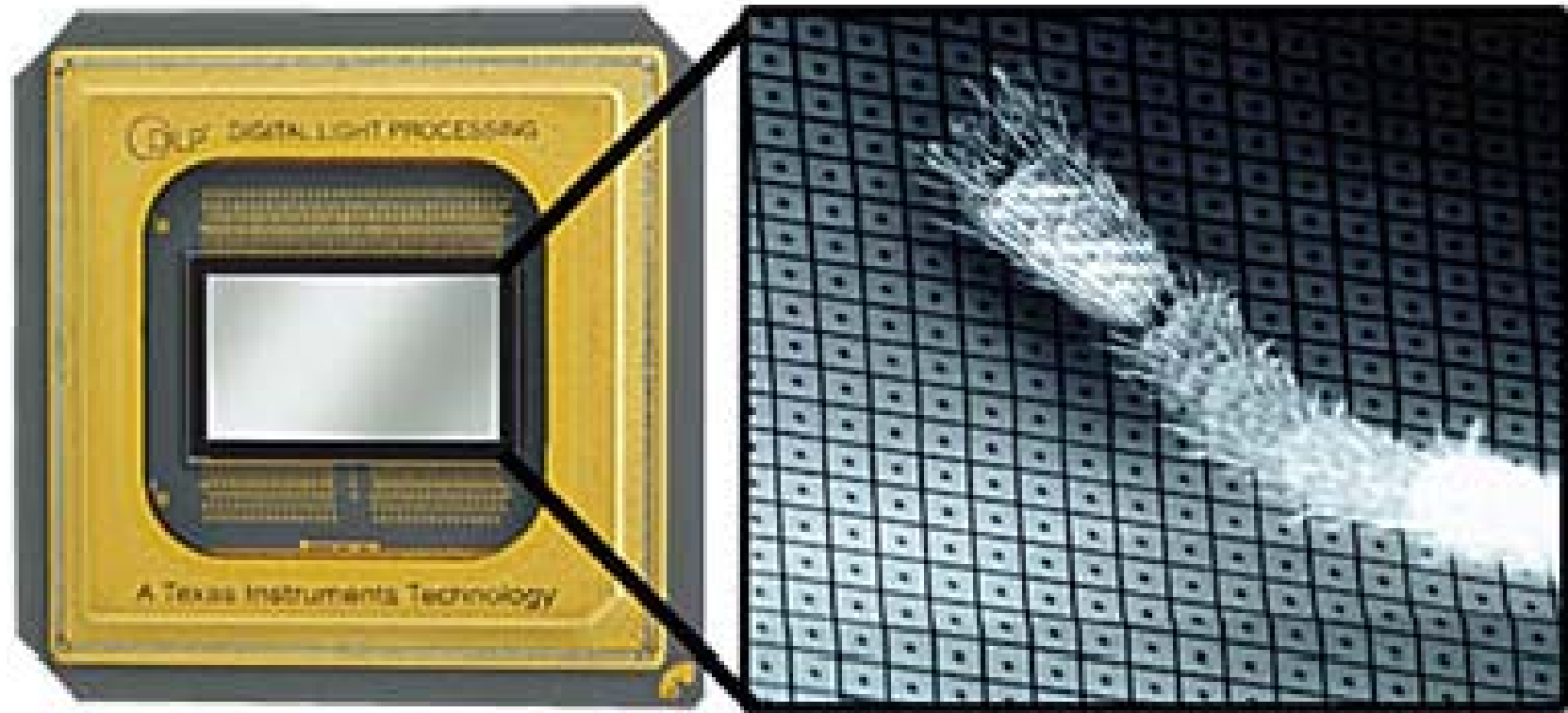
Sandia has made an enormous investment (>\$500M) towards microelectronics and microsystem development (i.e., the MESA complex: www.sandia.gov/mesa/, and MEMS fabrication: mems.sandia.gov/).



A Micro Gear, Red Blood Cells & Pollen



The TI DLP Chip is Based on MEMS Micromirrors

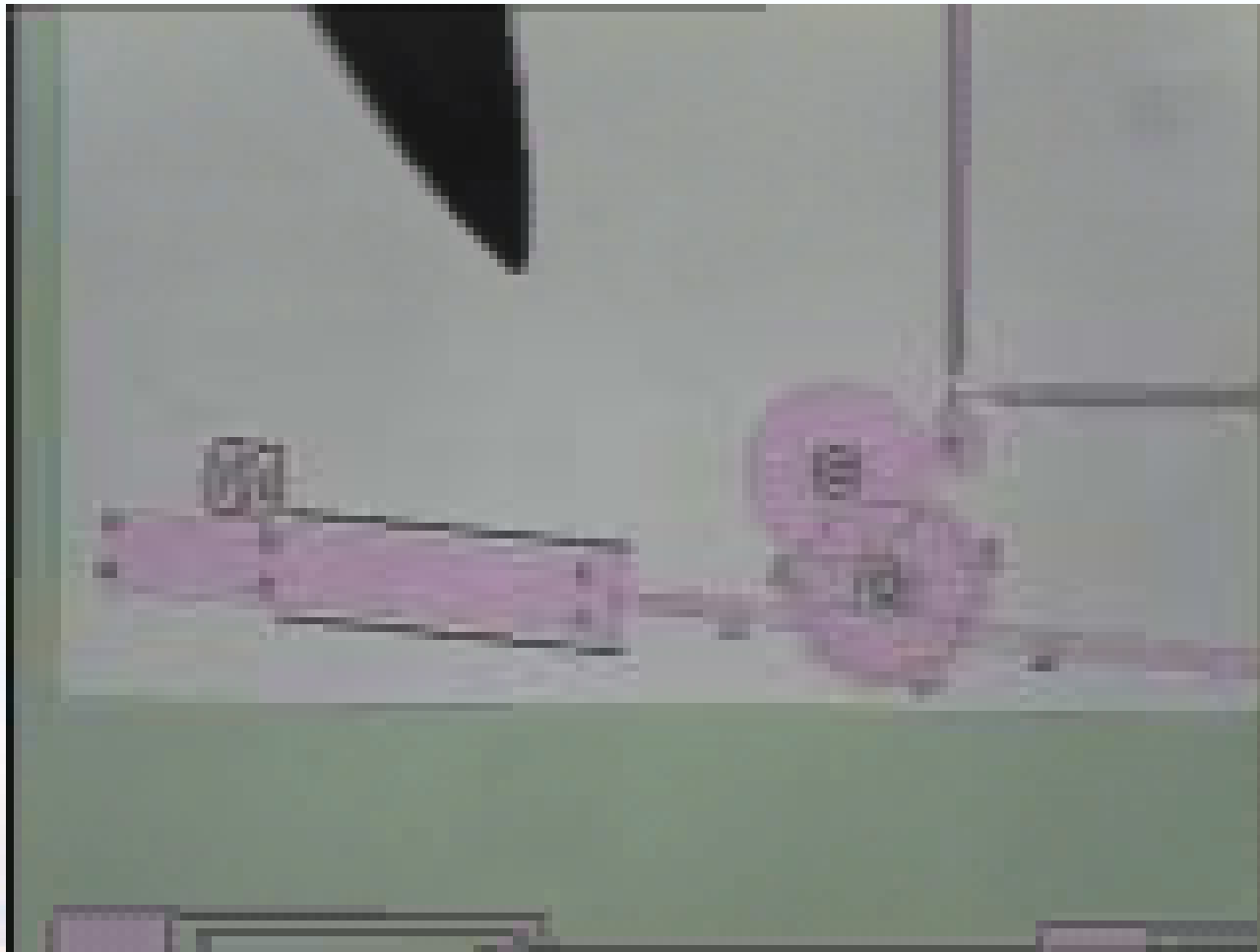


This is used in some movie projectors and some HD TVs





Microgears Drive a Micromirror



A Micromachined Mirror in slow motion



Sandia National Laboratories

Energy, Climate, and Infrastructure Security

Program Areas

- Infrastructure Security
- Energy Security
- Climate Security
- Enabling Capabilities

Areas of Expertise

- Modeling & Analysis, Cyber, Electricity Distribution, and Energy Assurance
- Renewables, Energy Efficiency, Energy for Transportation, and Nuclear Energy Systems
- Sensing & Monitoring, Carbon Capture, Sequestration, Modeling and Analysis, and Water
- Discovery Science & Engineering, Systems Analysis, and Regulatory & Policy



National Laboratories

National Solar Thermal Test Facility at Sandia National Laboratories, NM



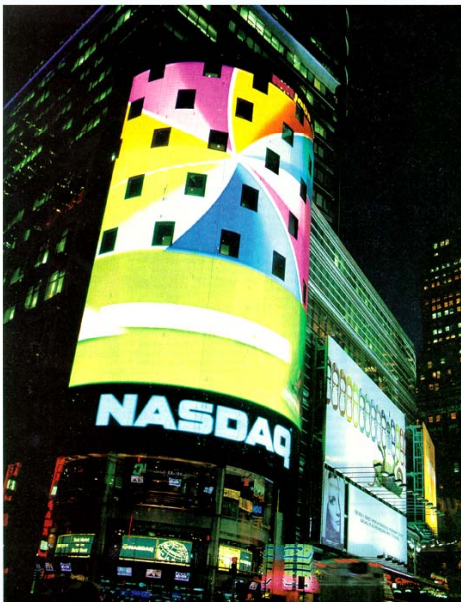
Specifications:

- 5 MW total thermal power
- Peak flux to 260 W/cm^2

The primary goal of the NSTTF is to provide experimental engineering data for the design, construction, and operation of unique components and systems in proposed solar thermal electrical plants planned for large-scale power generation. In addition the facility can provide: high heat flux and temperatures for materials testing or aerodynamic heating simulation; large fields of optics for astronomical observations or satellite calibrations; a solar furnace; a rotating platform for parabolic trough evaluation.



SNL has a major compound semiconductor S&T focus on Solid State Lighting



Advantages of LEDs:

- Compact
- Shock resistant
- Long lifetime (100,000 hours)
- Easily integrated w/ control systems for intelligent lighting

Expected Benefits:

- Significant increases in energy efficiency
- Entirely new ways of integrating and controlling light

LEDs are already superior for monochrome applications.

- Red LEDs are now 10X more efficient than red- filtered incandescents
- Payback time for LED traffic lights is ~ 1 year
- Today, 1/3 of US traffic lights are LED-based



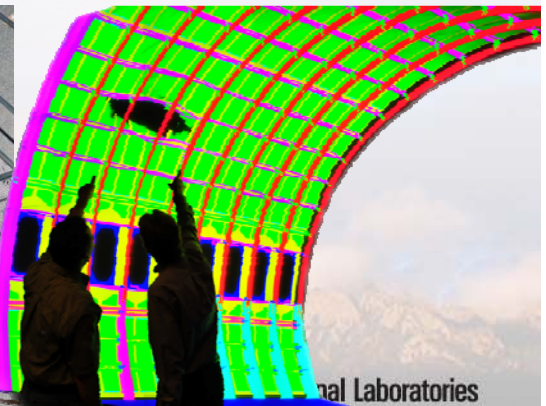
International, Homeland, and Nuclear Security

Program Areas

- Critical Asset Protection
- Global Security
- Homeland Defense and Force Protection
- Homeland Security

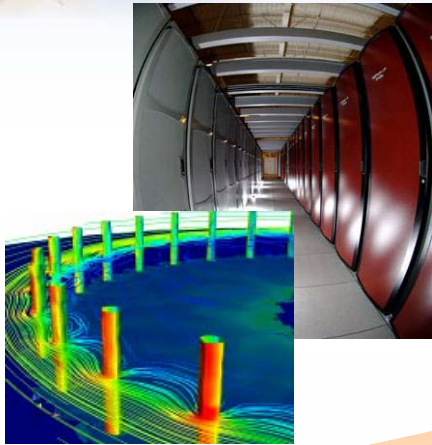
Areas of Expertise

- Countering Bioterrorism
- Nuclear, Radiological, and Chemical Risk Reduction
- Nonproliferation and Arms Control
- Physical Security
- Emergency Response
- Systems Analysis and Engineering
- Border Security
- Aviation and Airworthiness Security

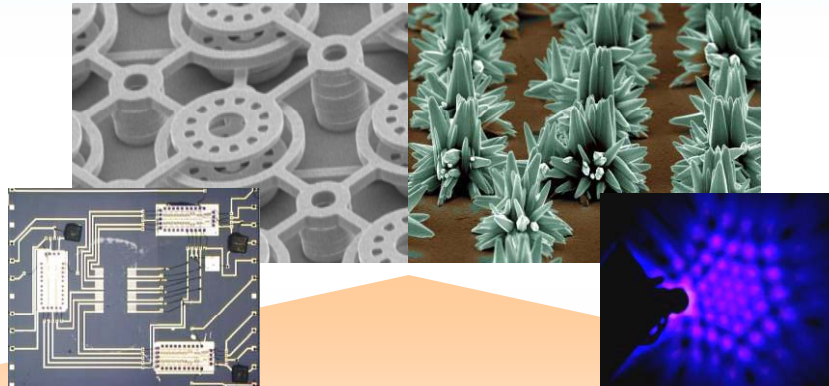


al Laboratories

Research Disciplines Drive Capabilities



**High Performance
Computing**

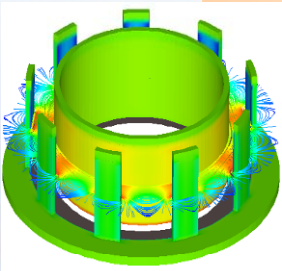


**Nanotechnologies
& Microsystems**

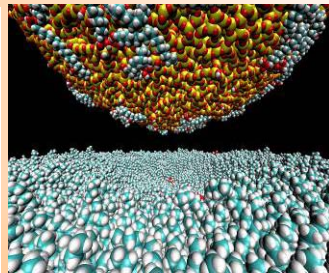


**Extreme
Environments**

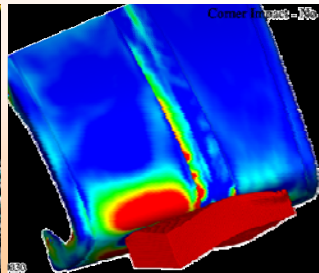
**Computer
Science**



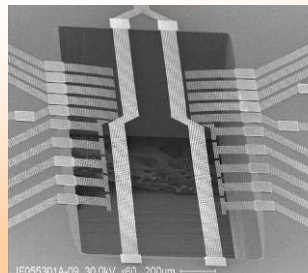
Materials



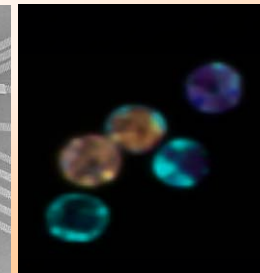
**Engineering
Sciences**



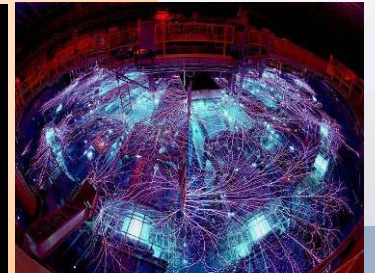
**Micro
Electronics**



Bioscience



Pulsed Power



Research Disciplines



Emerging National Security Thrusts



Nuclear



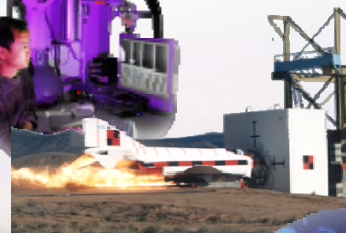
Energy



Cyber



Science & Technology



Joint SNL/LANL CINT is one of five Department of Energy Nanoscience Centers.



Sandia National Laboratories

CINT Core/Gateway model embodied with physical user facilities

Core Facility in Albuquerque



CINT Gateway to Sandia
Nanomaterials/Microfabrication

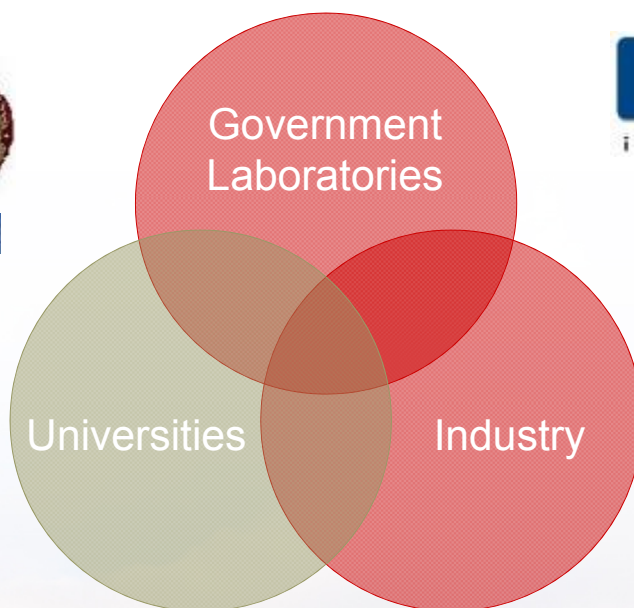


CINT Gateway to Los Alamos
Nanomaterials/Biosciences

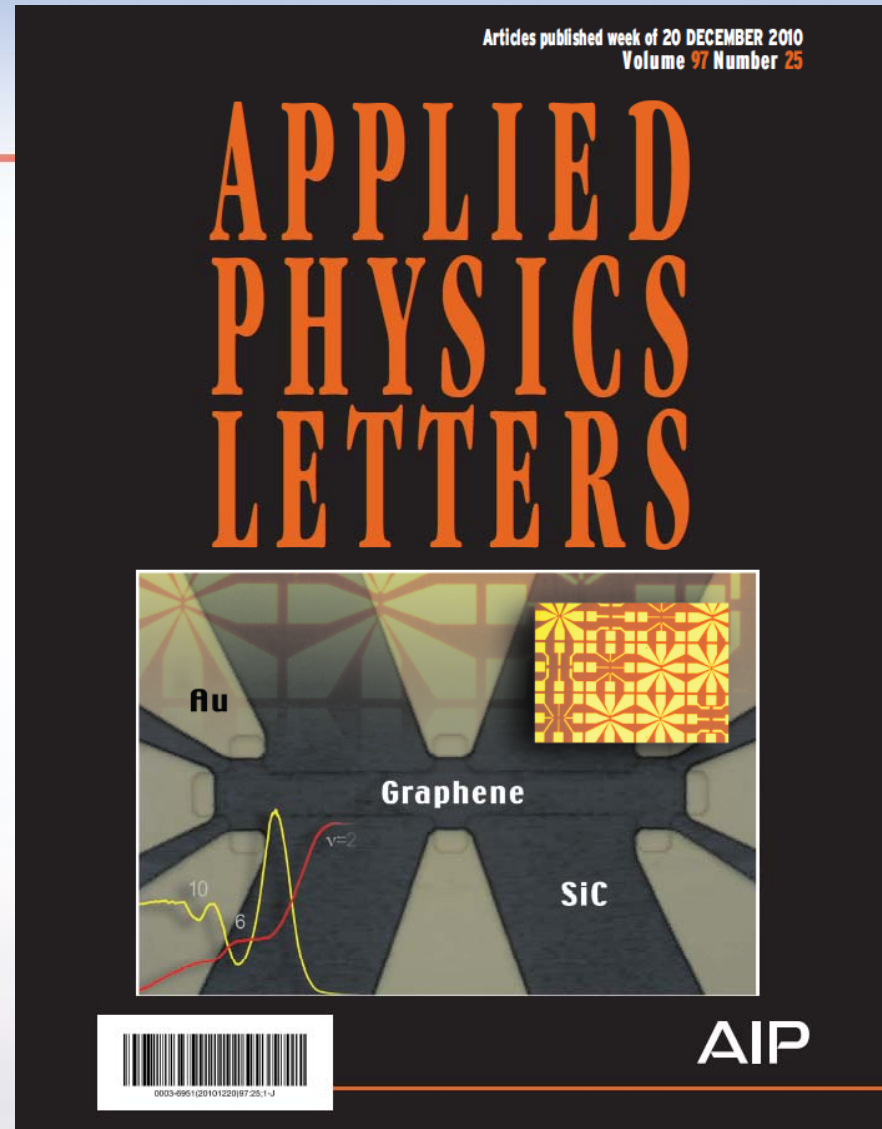
Buildings Complete	January 2006
Begin Operations	April 2006
Core Dedication	August 23, 2006
Construction Complete	June 2007



Partnerships and Collaboration Accelerate Innovation




Back to Graphene and Graphene Nanoelectronics...

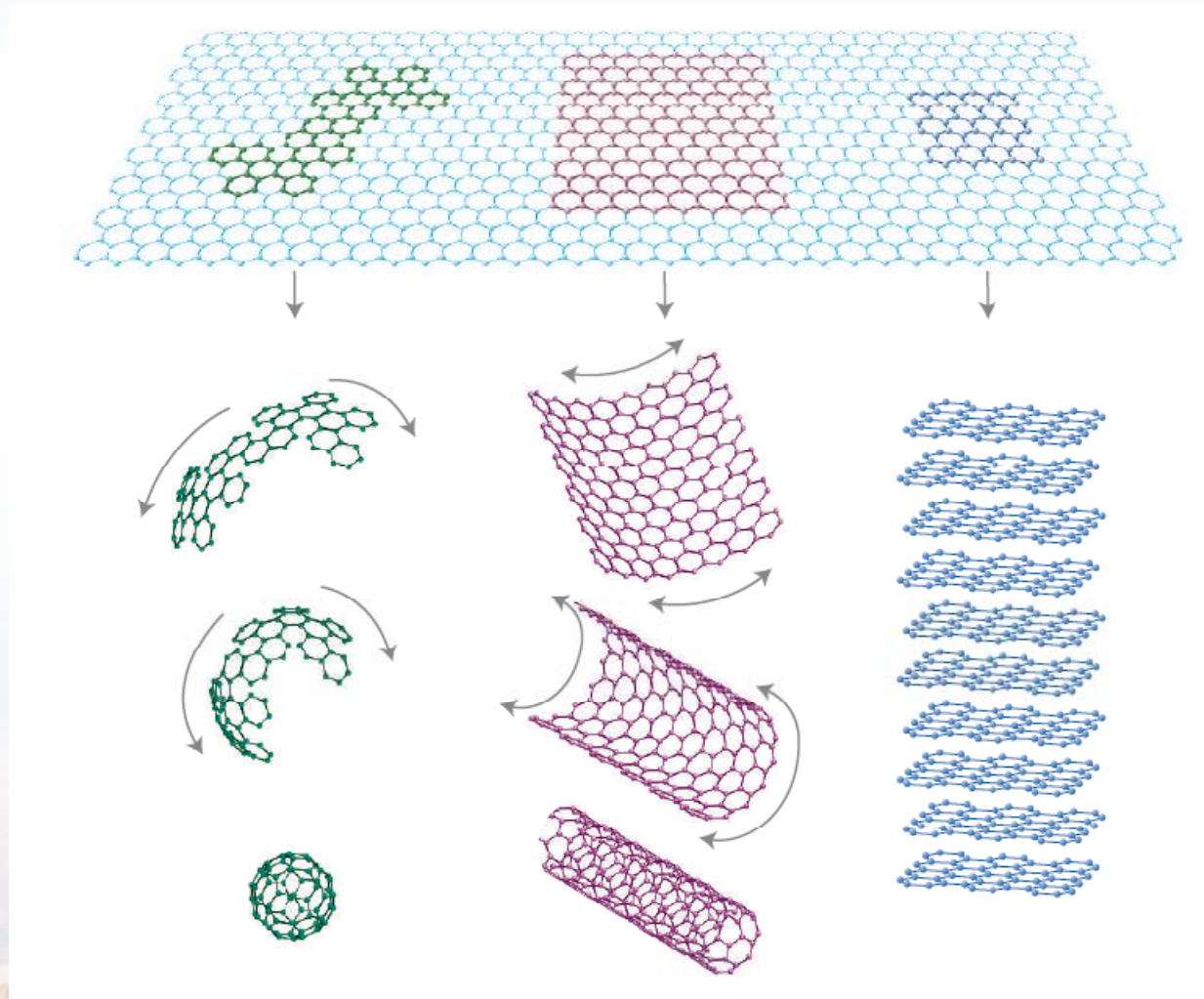


Pan, Howell, Ross, Ohta and Friedmann
Appl. Phys. Lett. 97, 252101 (2010)



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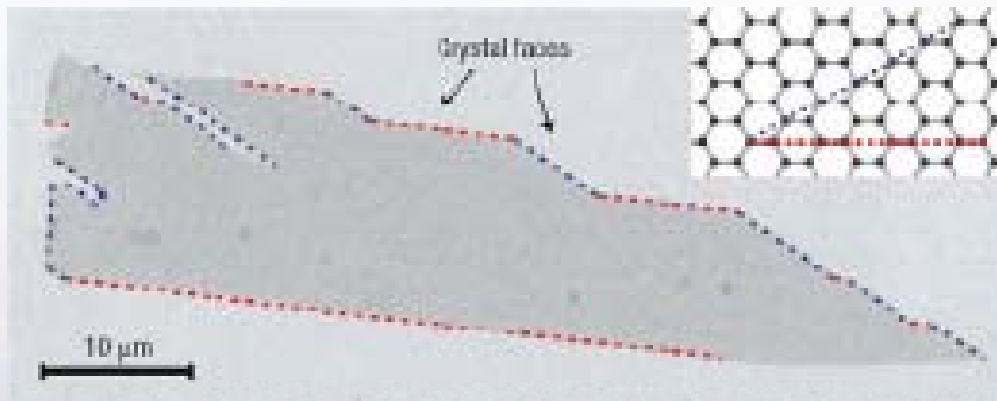
The 2D Graphene Sheet: The “Mother of All Graphitic Forms”



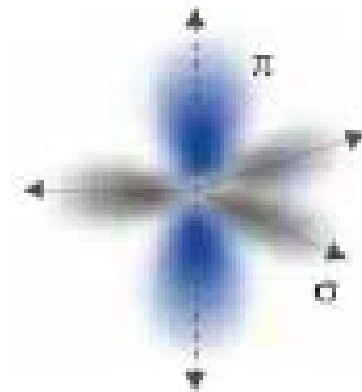
A. K. GEIM AND K. S. NOVOSELOV, Nature Materials, March 2007

Graphene: Brief Facts & History

- Graphene (like CNT) is held together by strong in-plane sp^2 bonding (diamond has sp^3 bonding), and weak intralayer π bonding.
- 2D Monolayer graphene was first isolated in 2004 (Geim et al, U Manchester)
- Major fabrication approaches:
 - exfoliation of pyrolytic graphite (“scotch tape”)
 - CVD of hydrocarbons on metal substrates
 - Thermal decomposition of SiC



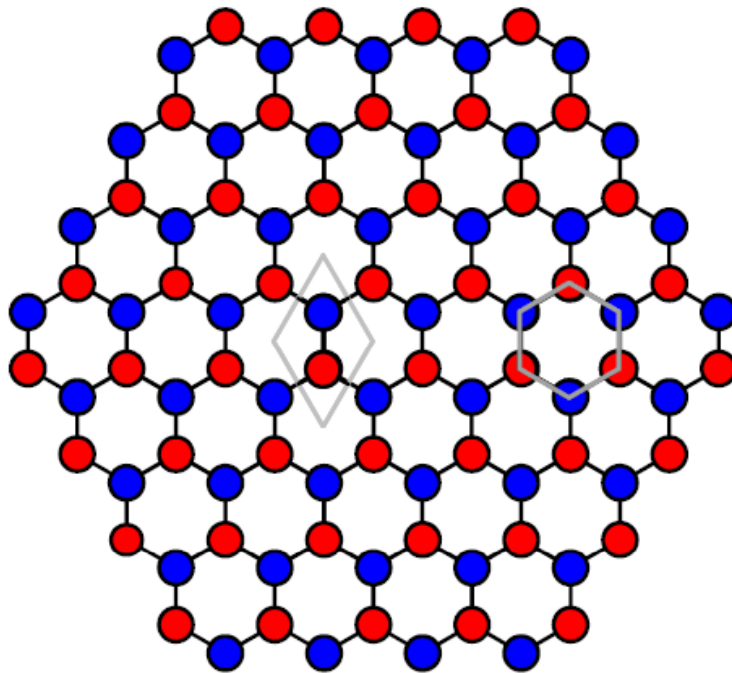
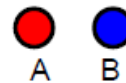
A.K. Geim and K.S. Novoselov,
Nature Mat. 6, 183 (2007).



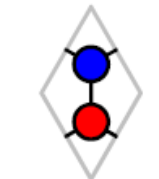
Graphene's Basic Structure and Electronic Description

- Typical semiconductor materials electronic properties can be described by the non-relativistic Schrödinger equation, BUT graphene's honeycomb periodic potential results in charge carrier interactions that are better described by the relativistic Dirac equation with massless relativistic quasiparticles.

Two identical atoms in unit cell:



Two representations of unit cell:



Two atoms



$1/3$ each of 6 atoms = 2 atoms



Michael S. Fuhrer

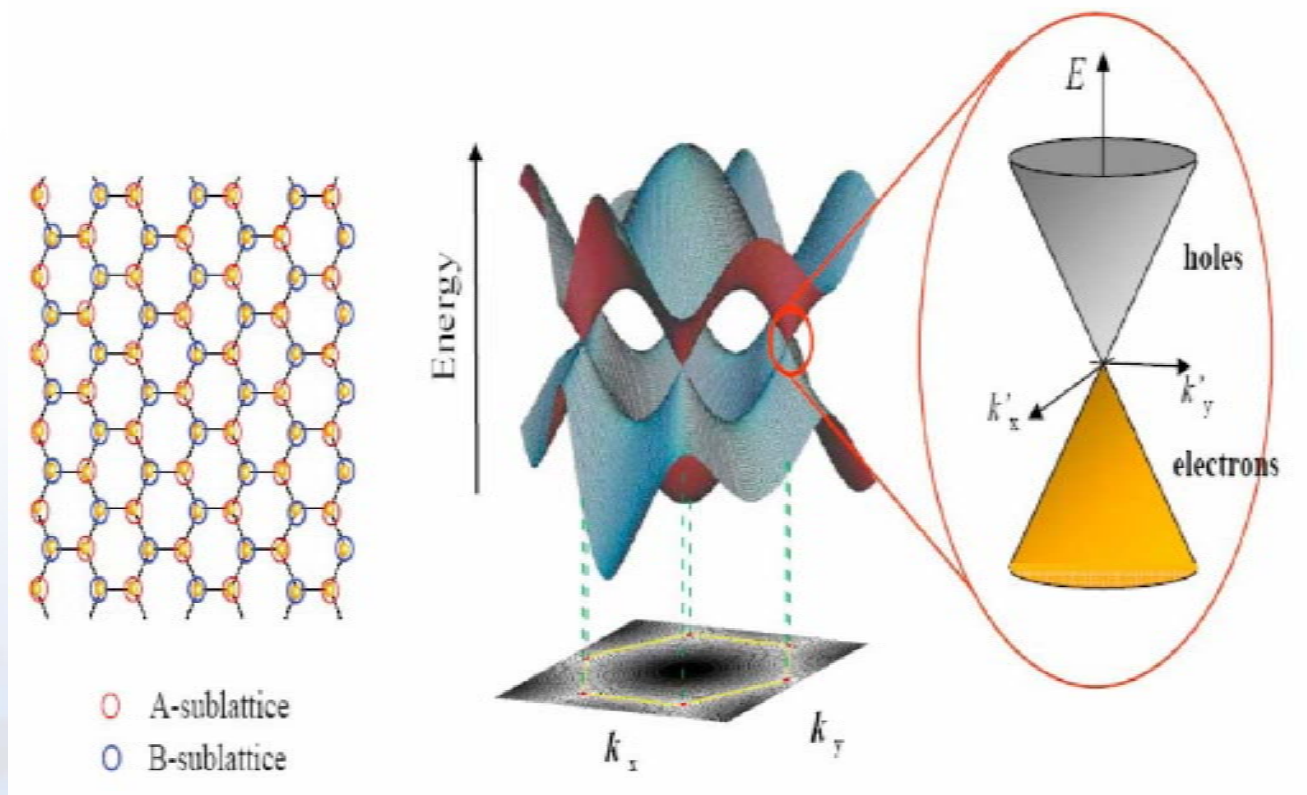
University of Maryland



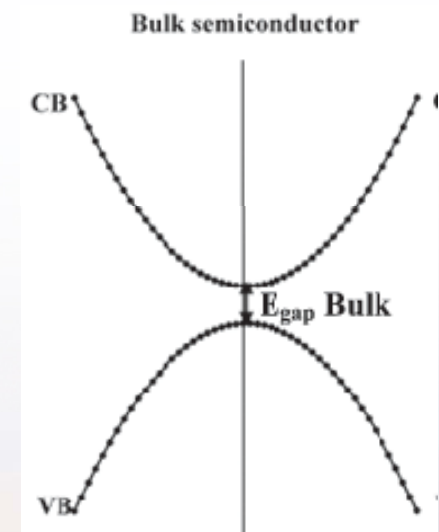
Sandia National Laboratories

Graphene's Band Structure

Graphene's low-energy band structure consists of cones at the corners of the Brillouin zone, rather than paraboloids at the center. The density of states vanishes at the conduction/valence band cone "Dirac points".



VS

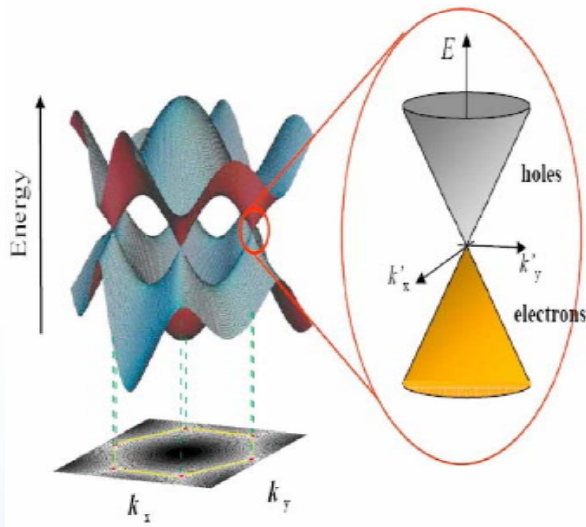


Simple Parabolic
Semiconductor Model



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Graphene's Interesting Properties



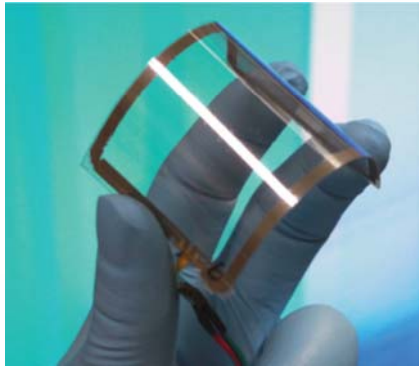
- Semi-Metal Band Structure (zero-bandgap)

Properties	Applications
High Mobility (250,000 cm ² /Vs)	RF and other high speed electronics (up to 300 GHz Demonstrated)
Ambipolar	Low Noise Freq Mixing
Spin Coherence Length (> 1 μm)	Quantum Information/ Spintronics
Voltage control of carriers	FETs and Metamaterials
High Mechanical Strength (Elastic modulus ~ 1 TPa)	MEMS and NEMS
Relaxation of cryogenic temperature dependence due resulting from Dirac Quantum Mechanics.	Potential for 2D quantum-dependent non-cryo temperature performance not seen in standard semiconductors (i.e., RT quantum interference effects, FET-based IR detection)



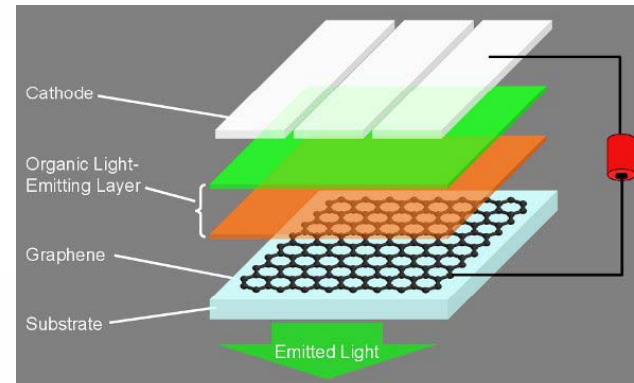
Some Proposed Graphene Device Ideas

Transparent electrodes

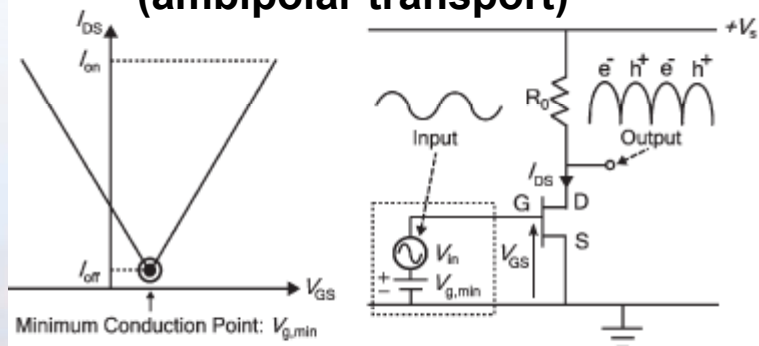


S. Bae *et al*, *Nature Nano.*,
5, 574-578 (2010)

Graphene OLED - Junbo Wu/Stanford U

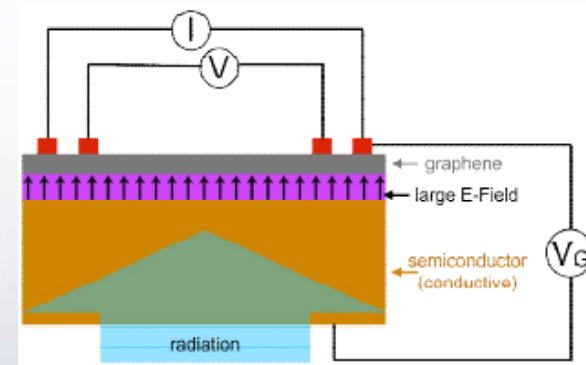


RF Frequency multiplier (ambipolar transport)



H. Wang *et al*, *IEEE Elec. Dev. Lett.*,
30, 547-549 (2009).

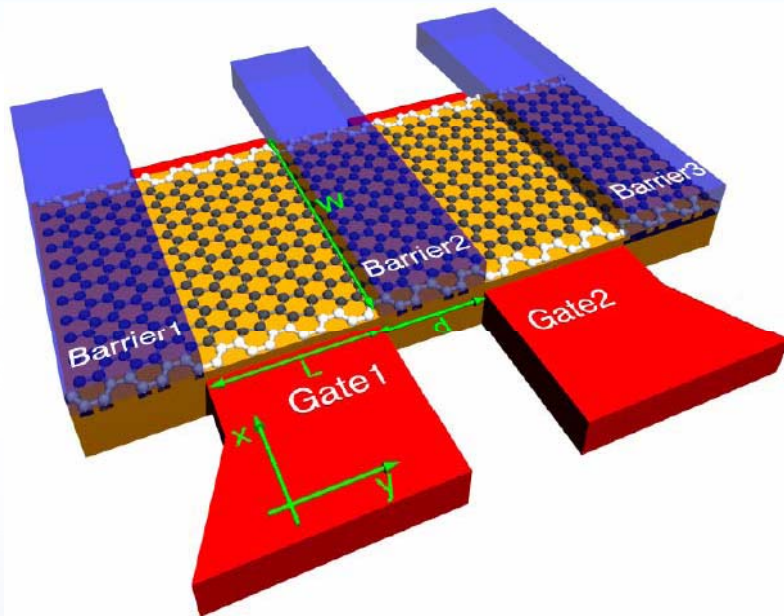
Read-out for radiation detection



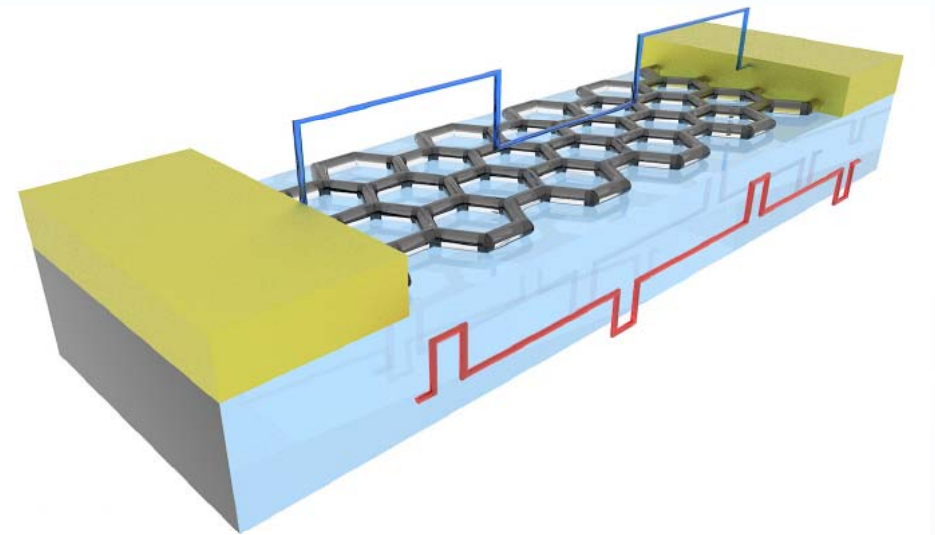
M. Foxe *et al.*, *IEEE Trans. Nuclear Sci.*, submitted (2010).



Additional Graphene Device Ideas



Graphene double quantum dot structure proposed by the Trautzel Group (Nature Physics 2007)

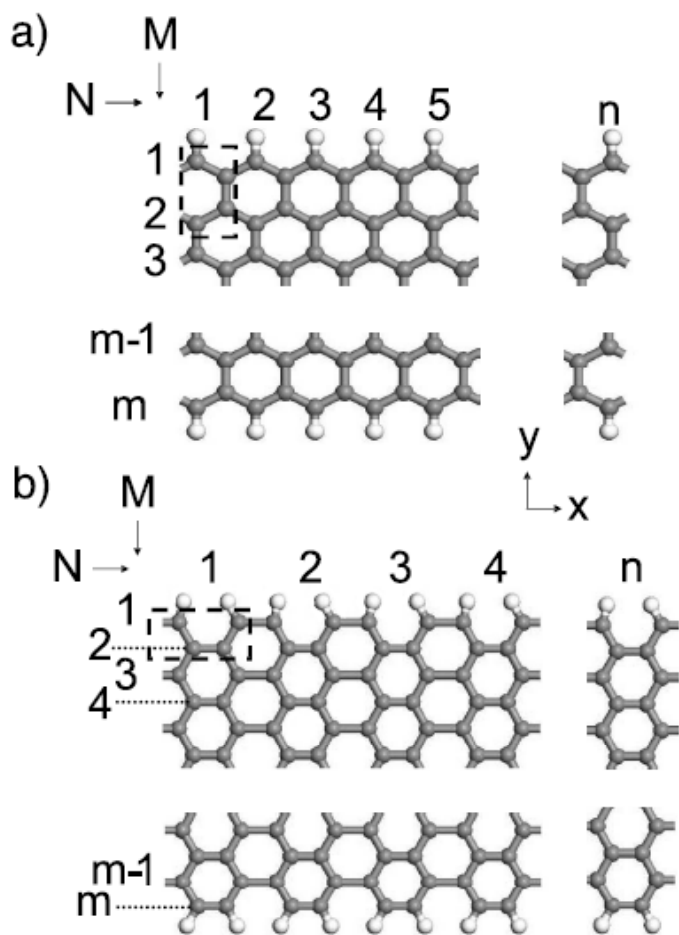


Graphene NR-based memory, Sordan group, SMALL 2010, 6, No. 24, pp 2822–2825



Graphene Nanoribbons (GNR): A Way to Introduce a Band Gap

GNR electronic states largely depend on the edge structures (armchair or zigzag). Zigzag edges provide the edge localized state with non-bonding molecular orbitals near the Fermi energy causing large changes in optical and electronic properties. To first order, their bandgap should scale inversely with the width of the ribbon and also depend on the rotation of the hexagonal lattice with respect to the long edge of the ribbon.



Scheme of H-terminated (a) zigzag and (b) armchair nanoribbons. Periodic boundary conditions are assumed in the x direction. N and M are the numbers of columns and rows of atoms used to label the MN ribbon.



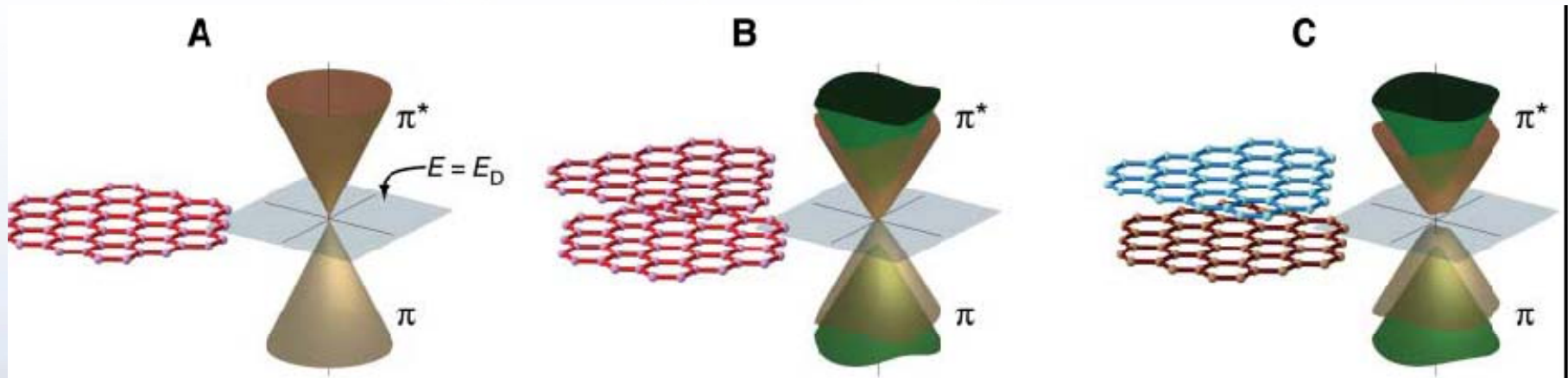
PRB77, 165427 (2008)



Sandia National Laboratories

Graphene Band Gap via Layer Asymmetry or Applied Electric Fields

- Undoped graphene is a semimetal because at $E_D = E_F$, the density of states is zero and conduction is possible only with thermally excited electrons at finite temperature. However, a gap can be formed via layer asymmetries formed by SiC substrate depletion layers, dipole effects caused by doping (i.e., K), and internal/external electric fields.



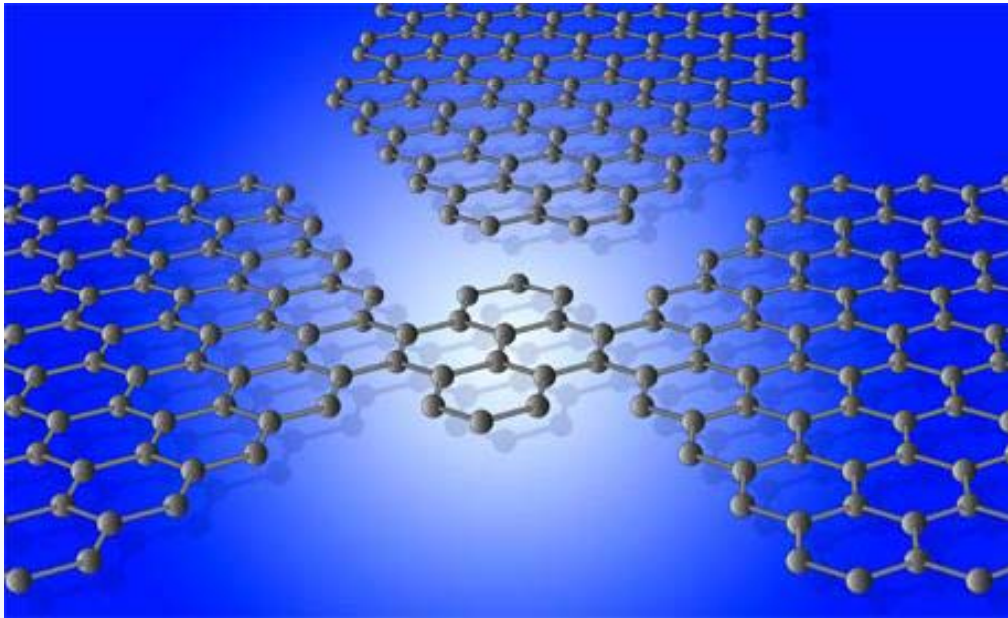
T. Ohta, et al, *Science* **313**, 951-954 (2006)



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A Proposed Quantum Dot Single Electron Graphene Transistor Switch

Geim et al, Manchester University Mesoscopic Physics Group



Science 320 (2008)

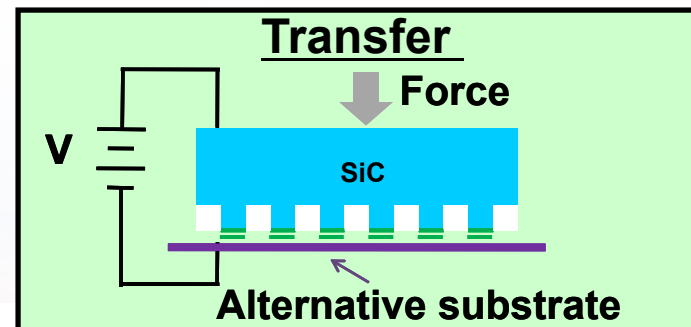
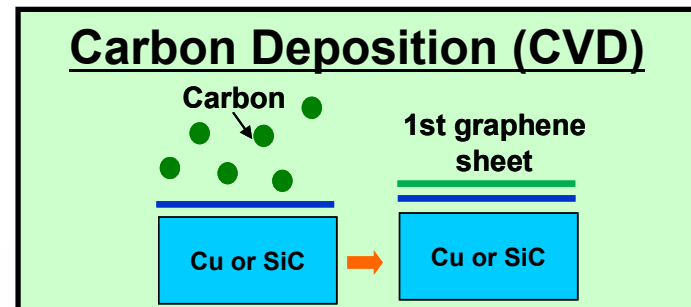
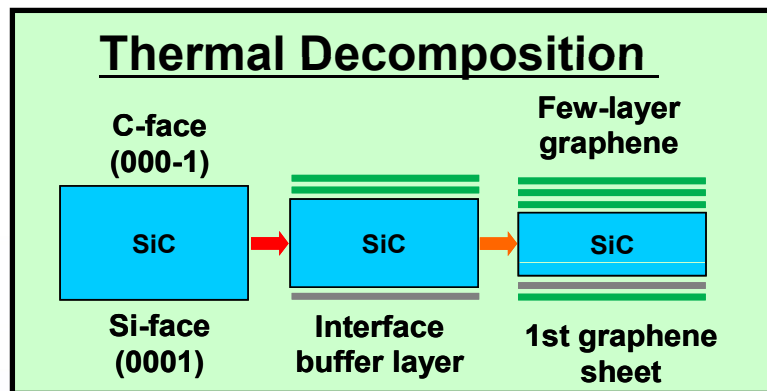
- Transistor devices have been made one atom thick & ten atoms wide
- Novoselov and colleagues found that cutting small "quantum dots" of graphene can give it needed switching properties unavailable in semi-metal graphene.



Sandia Graphene Project Goals

■ Technical

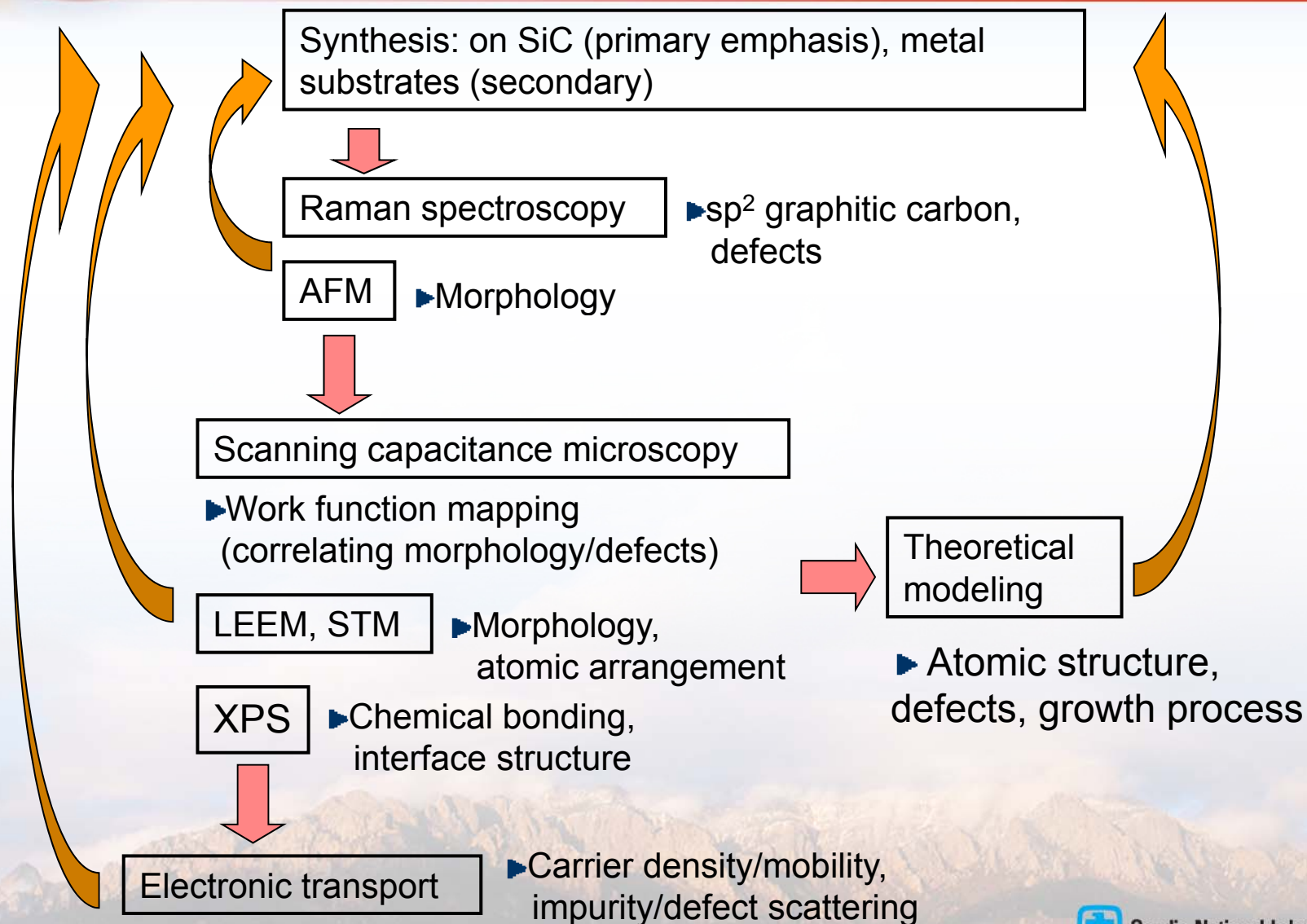
- Develop several graphene synthesis/transfer approaches, developing the science-based understanding necessary for large area synthesis on substrates



■ Strategic

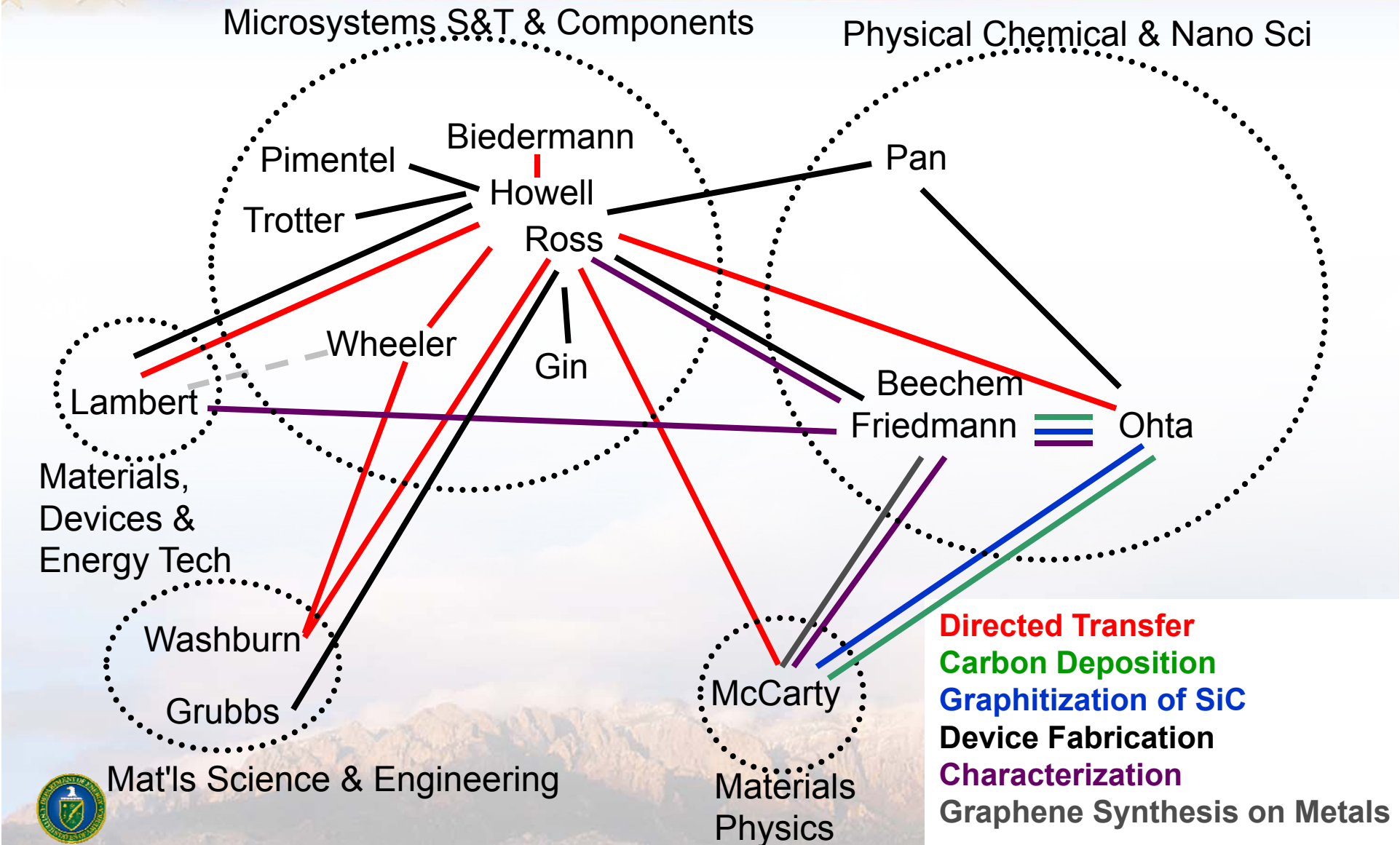
- To build a strong collaborative relationship between Sandia Scientists focused towards Graphene Materials and Devices
- To position MESA as a leader in this VERY competitive R&D field
- To initiate the first steps towards a larger nanoelectronics program within MESA (going beyond Moore's Law)

Activity Coordination Flowchart





Internal Team Networking/Acknowledgement

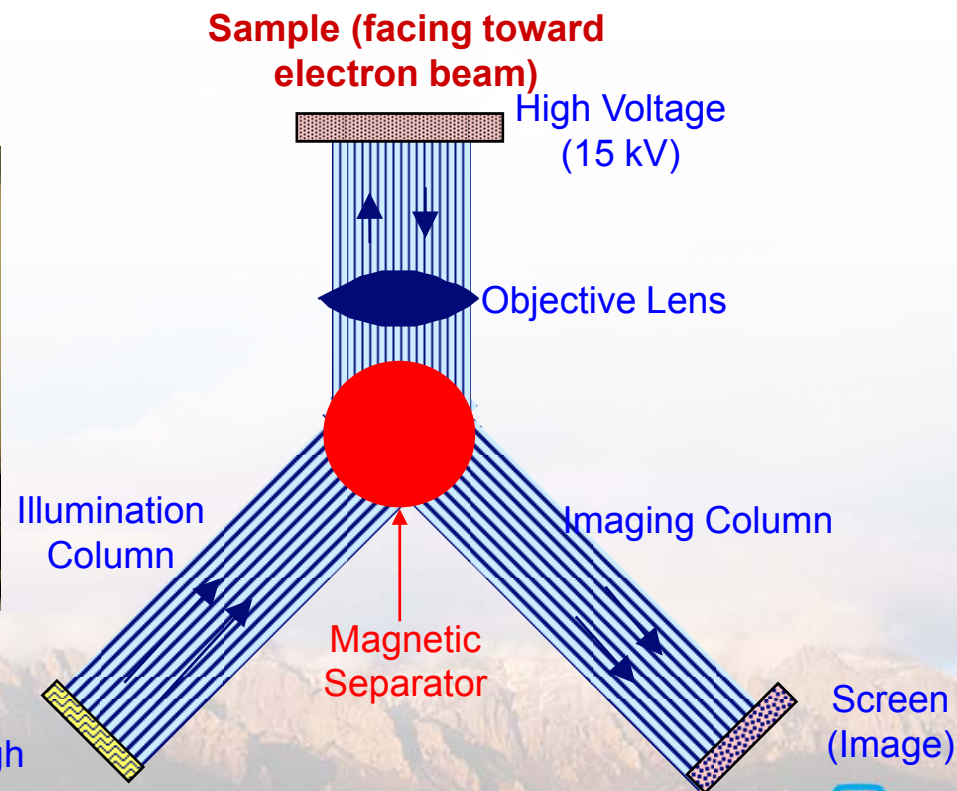
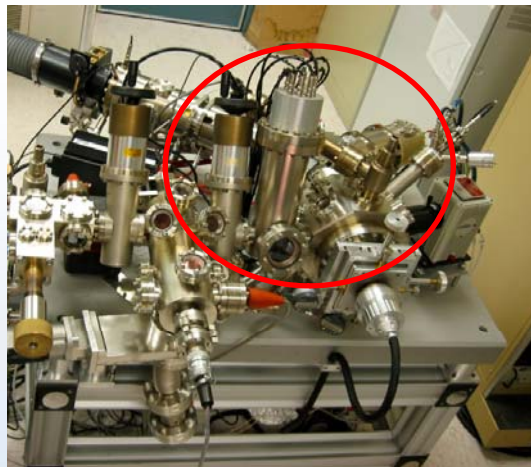


Sandia has Unique LEEM Resources, but... What is LEEM (and PEEM)?

- LEEM: Low Energy Electron Microscopy
- PEEM: Photo-Emission Electron Microscopy

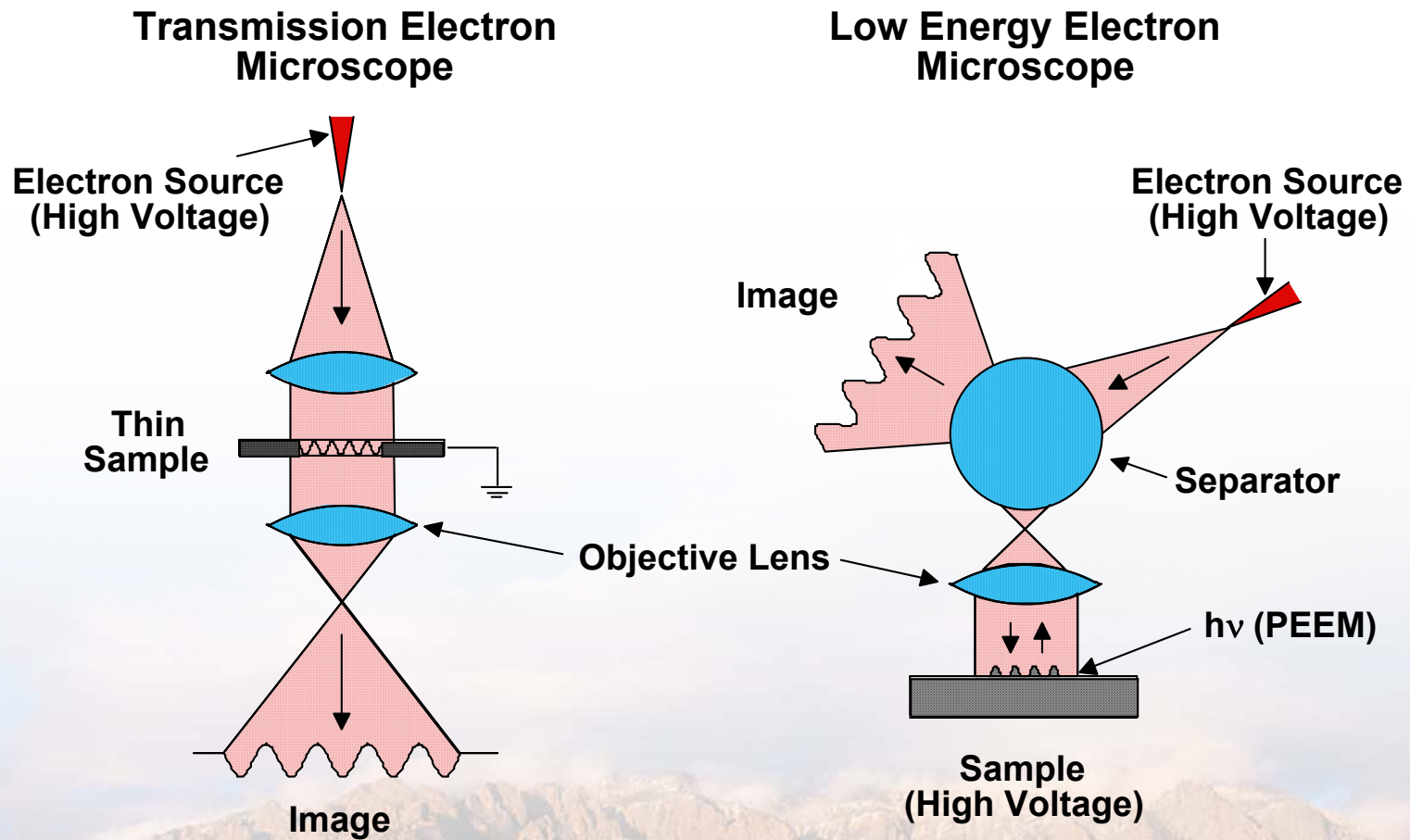
Reflection electron microscopy

Information of surfaces (low energy electrons)



Sandia National Laboratories

Schematic of TEM versus LEEM





What can we learn?

■ Electronic structure

- Work function (i.e. surface potential)
- Valence band and its density-of-states (DOS)
- Fermi-surface, i.e., carrier concentration

Band alignment

■ Chemical compositions

- Alloys
- Structured surface, i.e., devices
- Nano-materials

■ Resolution

- 7-10 nm lateral resolution
- 100-200 meV energy resolution (PEEM), 0.8eV (LEEM)
- 0.5-5nm depth sensitivity (electron escape depth)

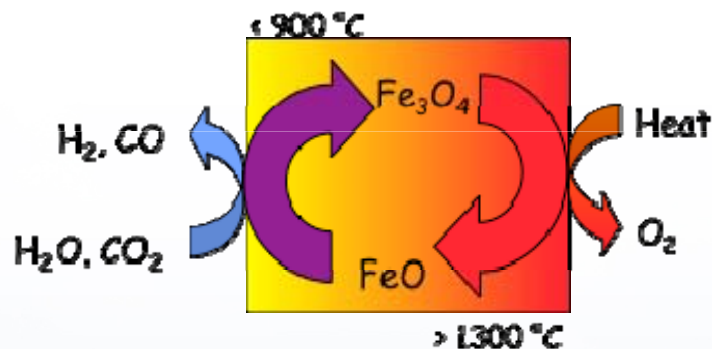
Probing properties (electric, chemical, structural, etc.) at nano-scale, and of single nano-material



Example: Structure identification

■ Polymorphs of iron-oxide films on YSZ(001)

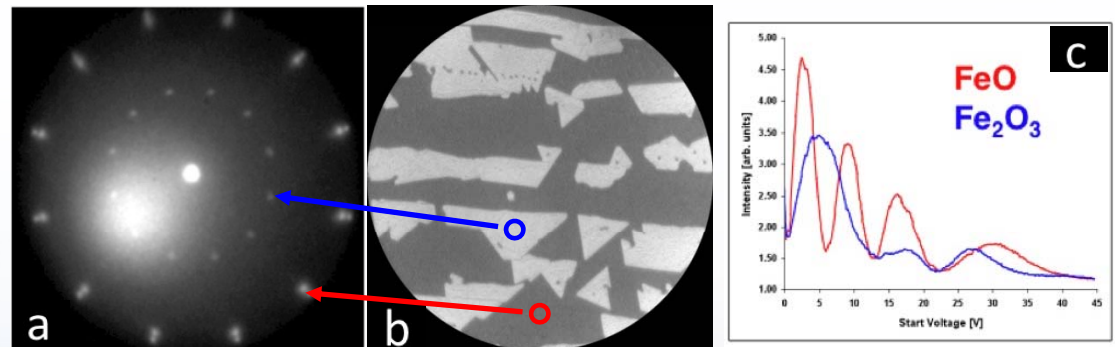
- Diffraction pattern from a $\sim 0.5\mu\text{m}$ region



Thermochemical
reaction of Iron-oxide

Note: Yttria-stabilized zirconia (YSZ) is a zirconium-oxide (ZrO_2) based ceramic, in which the particular crystal structure of zirconium oxide is made stable at room temperature by an addition of yttrium oxide (Y_2O_3).

Second-layer growth on YSZ(001) is Fe_2O_3

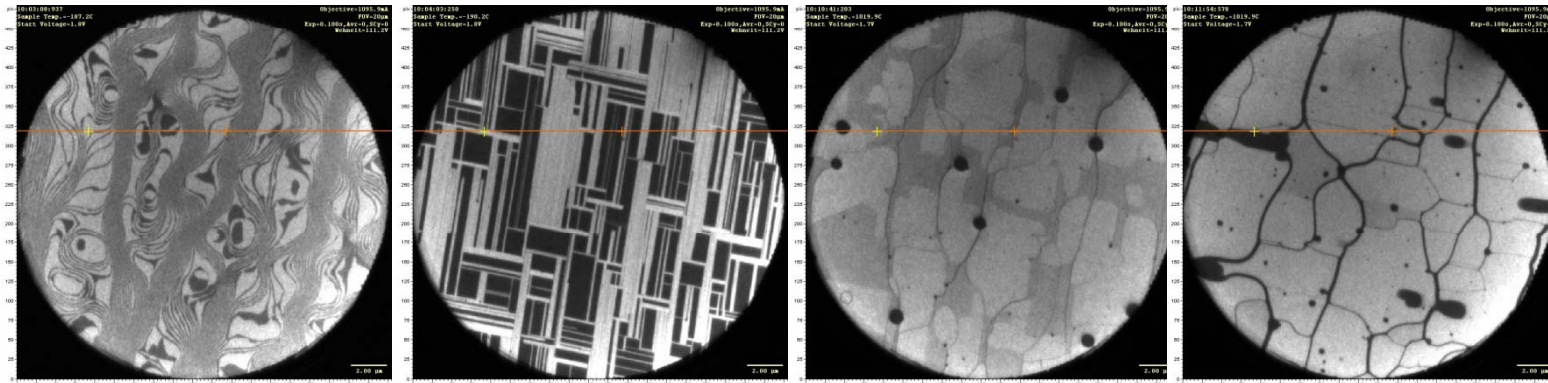


(a) LEED pattern showing new 12-fold pattern with a lattice constant corresponding to $\text{Fe}_2\text{O}_3(0001)$
(b) LEEM image (6.0 eV) showing regions of first- (red) and second-layer (blue) growth. (FOV = $20\mu\text{m}$)
(c) LEEM-IV spectra from first- and second-layer regions are markedly different and can be used as fingerprints of the oxide phase.

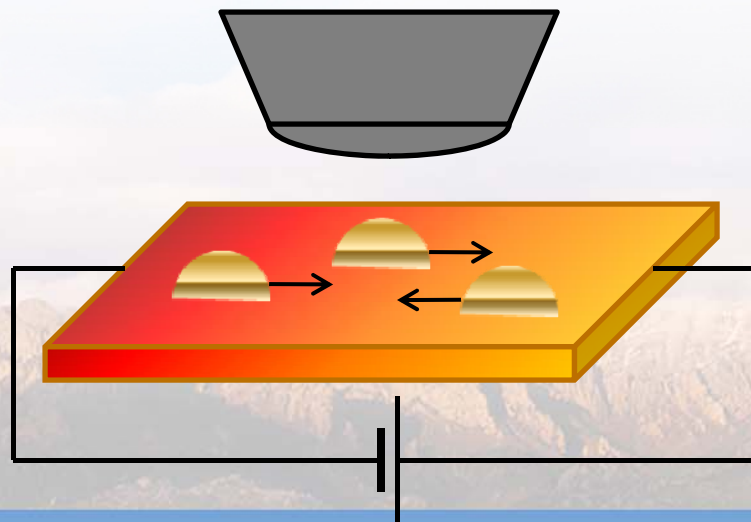


Example: Biased structure

■ Electro-migration of Au droplet on Si(001)



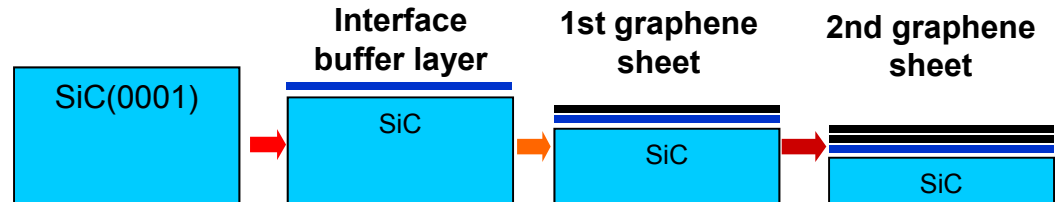
(a) Clean Si(001) surface (20 μm fov). (b) Deposition at 900° C produces highly anisotropic growth of the Au wetting layer. (c) Three-dimensional droplets appear and (d) move across the surface parallel to the dc current.



Understanding Graphene Growth on SiC(0001)

■ Graphitization of SiC:

- Sublimation of Si at high temperature ($>1200\text{ }^{\circ}\text{C}$) leaves graphene layer at SiC surface



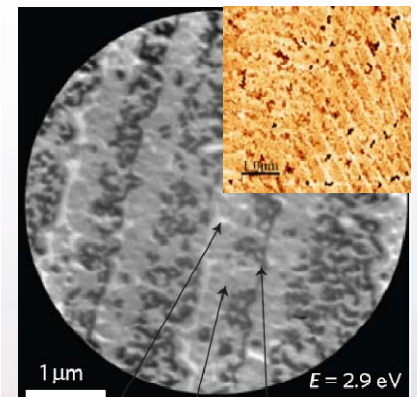
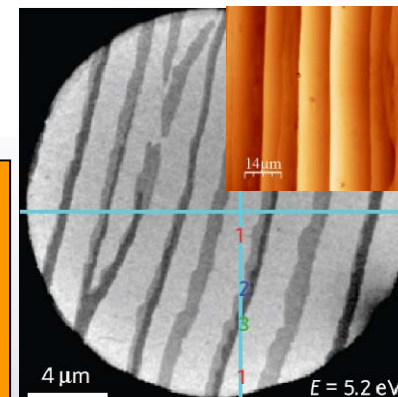
■ Argon-assisted graphene synthesis

- Samples prepared using Ar at atmospheric pressure and high temp
- This method yields:
 - Domain sizes $> 100\text{ }\mu\text{m}^2$ and high uniformity
 - Exquisite control of mono/bilayers coverage

Atmospheric pressure Ar high temp. processing



Ultrahigh vacuum mid temp. processing



K. V. Emtsev et al., Nature Mater. 8, 203 (2009).
C. Virojanadara et al., Phys. Rev. B 78, 245403 (2008)

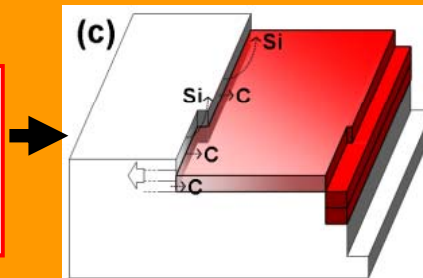
T. Ohta, N. C. Bartelt, S. Nie, K. Thürmer, G. L. Kellogg, PRB 81, 121411(R)(2010)

■ Understanding the growth mechanism of graphene on SiC

- Growth morphology strongly depends on the step structure

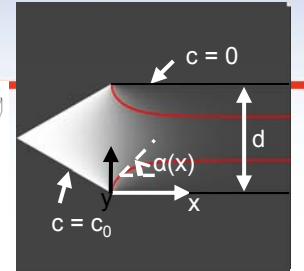
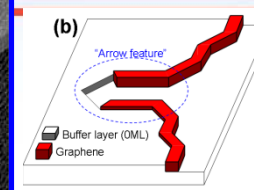
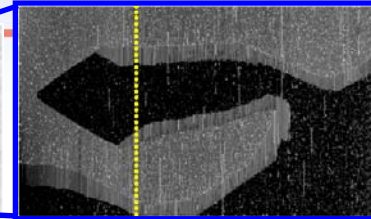
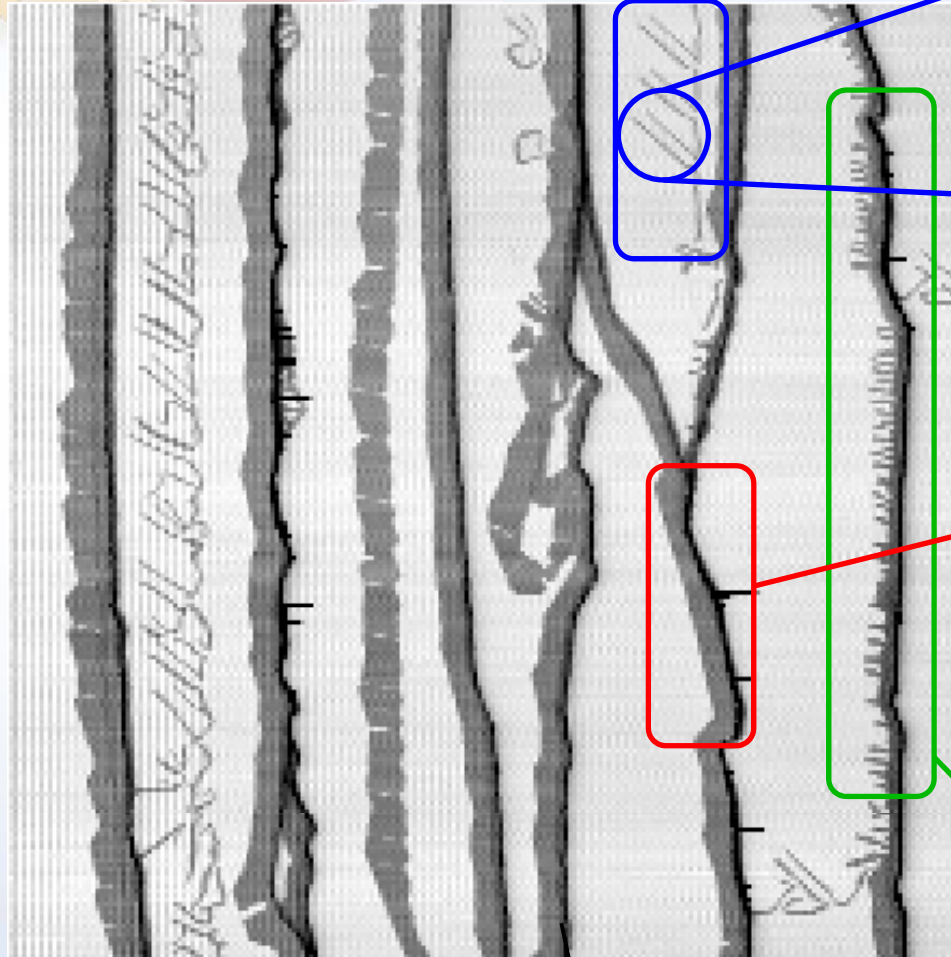
Step-flow growth

- Key for high large-area growth
- Real-time growth observations using LEEM



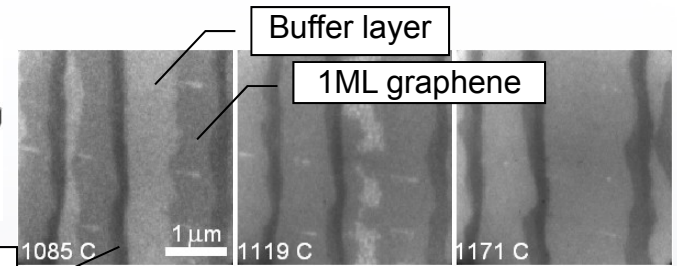
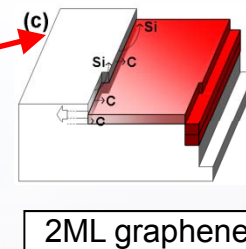
Understanding the Growth Mechanism of Graphene on SiC

AFM phase contrast image 26x26 μm^2



Arrow-shape feature

- Grown via cooperative processes of Si sublimation and carbon diffusion
- Shape predicted by simple diffusion model



Step-flow growth

- Key for high large-area growth
- Real-time growth observations using LEEM



Finger-shape growth

Single SiC step
Bunched step (~few nm high)

2ML graphene
1ML graphene

- Growth morphology strongly depends on the step structure

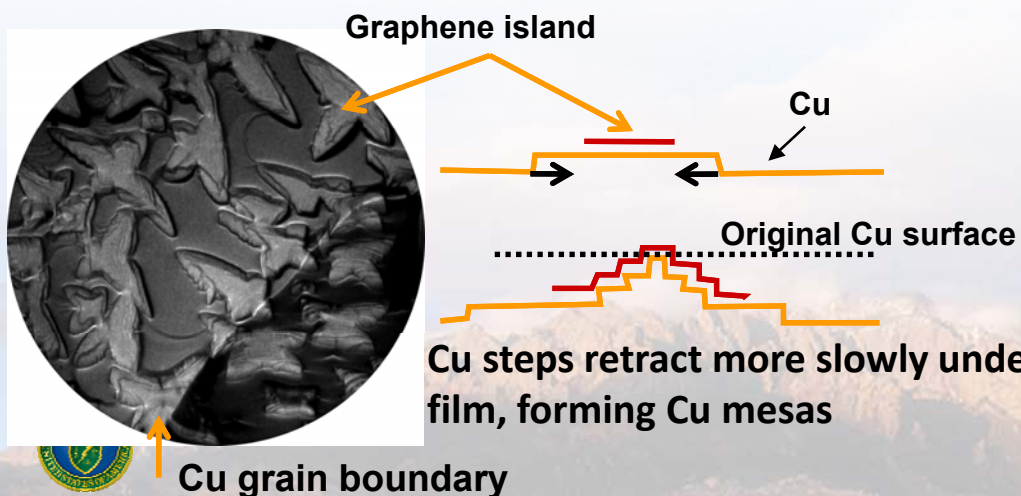


Understanding and Improving Graphene Growth on Copper Foils

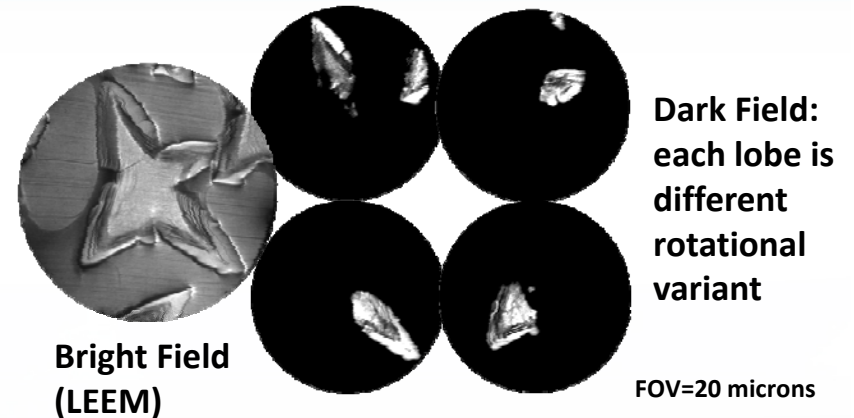
- CVD on Cu foil offers another scalable approach to large-area films
 - Chemically dissolve the cheap foil
 - Ruoff and coworkers, Science 2009
- What are the film defects and how can they be minimized?
- Answer by watching growth and in-situ characterization

Findings

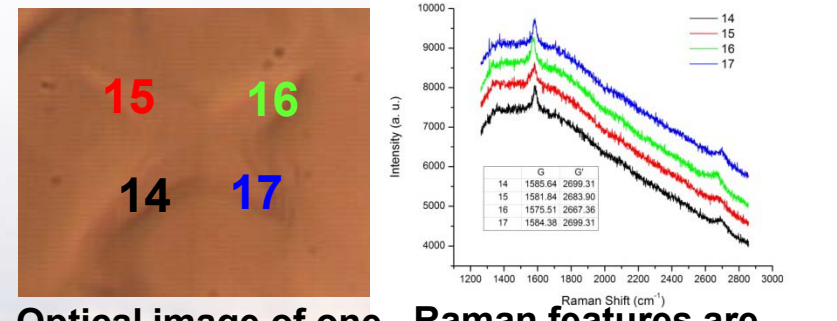
- Cu foils have (100) texture
- Slower Cu evaporation under growing graphene islands greatly roughens surface



- Each island has 4 rotational domains



- Raman spectroscopy shows extremely weak film/substrate coupling



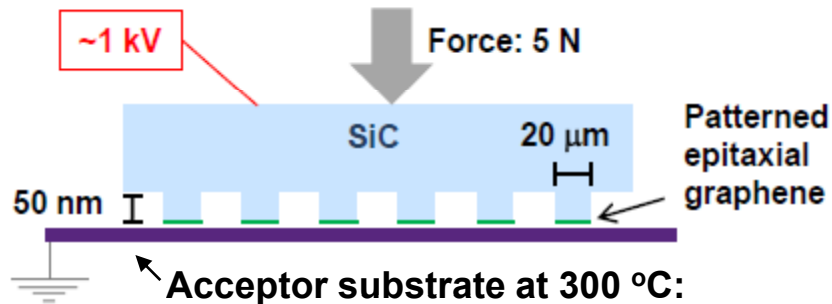
Optical image of one 4-lobed island

Raman features are identical to uncoupled graphene

With Shu Nie, Joe Wofford (UC Berkeley) & Oscar Dubon (UC Berkeley)

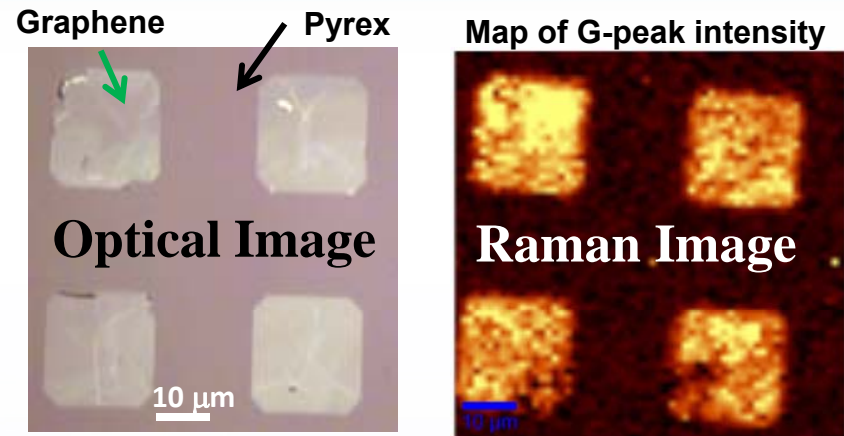
First demonstration of epitaxial graphene transfer to arbitrary substrates using electrostatics method

Electrostatic transfer method:

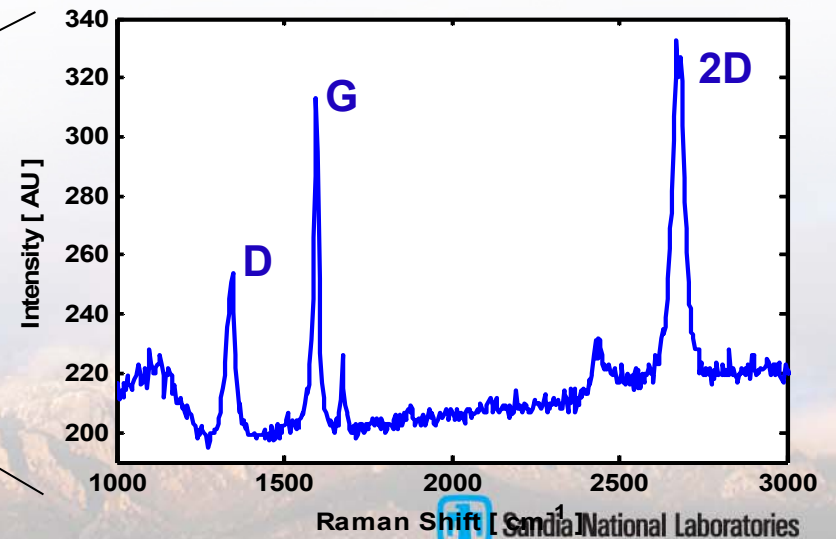
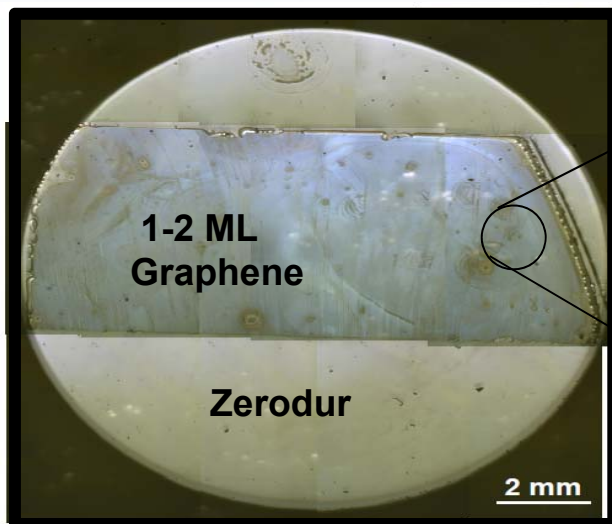


- Graphene transfer to Pyrex and Zerodur (a glass ceramic) has been demonstrated

Graphene transferred from SiC (000-1)

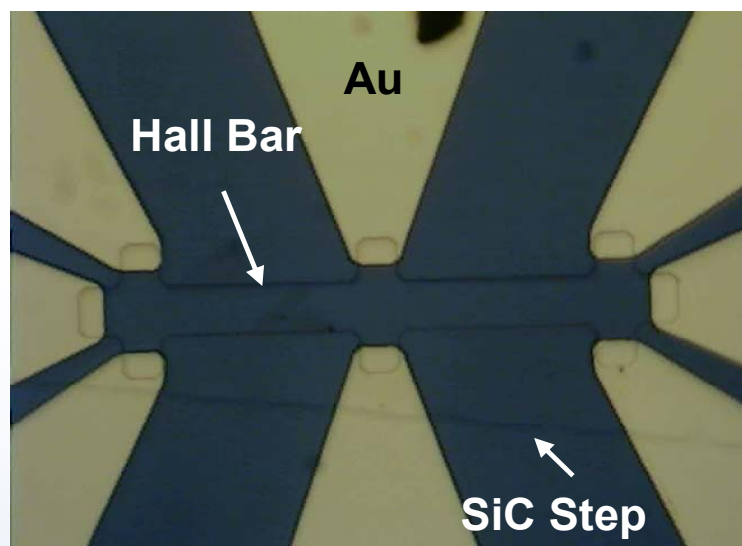


Large-area transfer graphene from SiC (0001) (Si-face) to Zerodur:

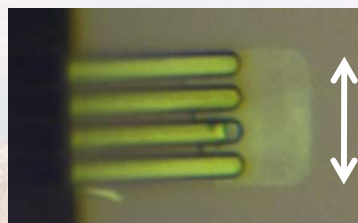
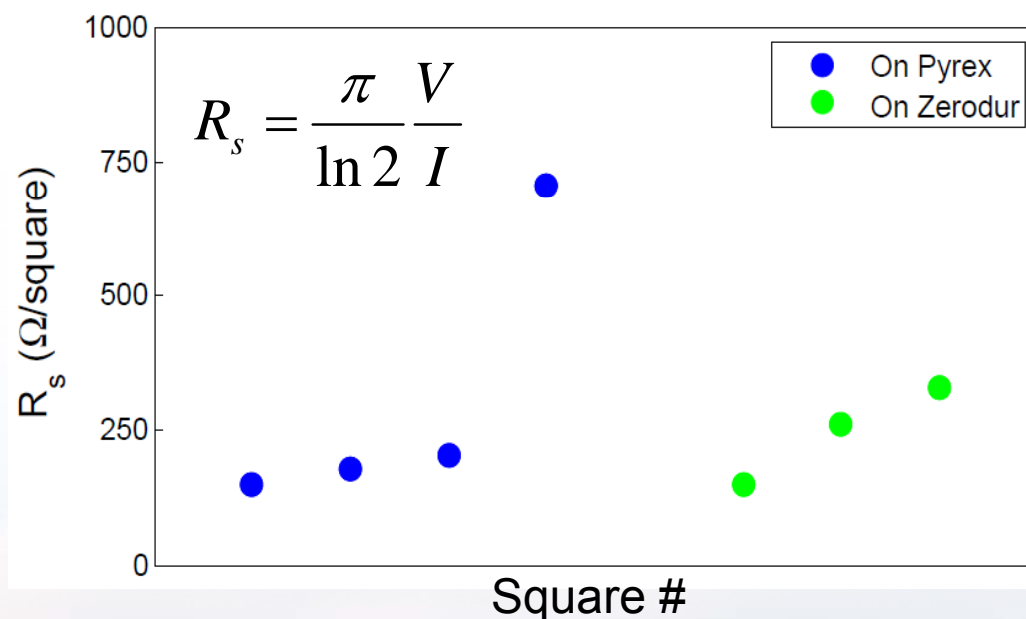


Electronic characterization of transferred C-face graphene

At ~10 K, $R_s = 180 \pm 70 \, \Omega/\text{sq}$ for epitaxial graphene on SiC(000-1)



At RT, R_s is as low as $150 \, \Omega/\text{sq}$ for transferred graphene



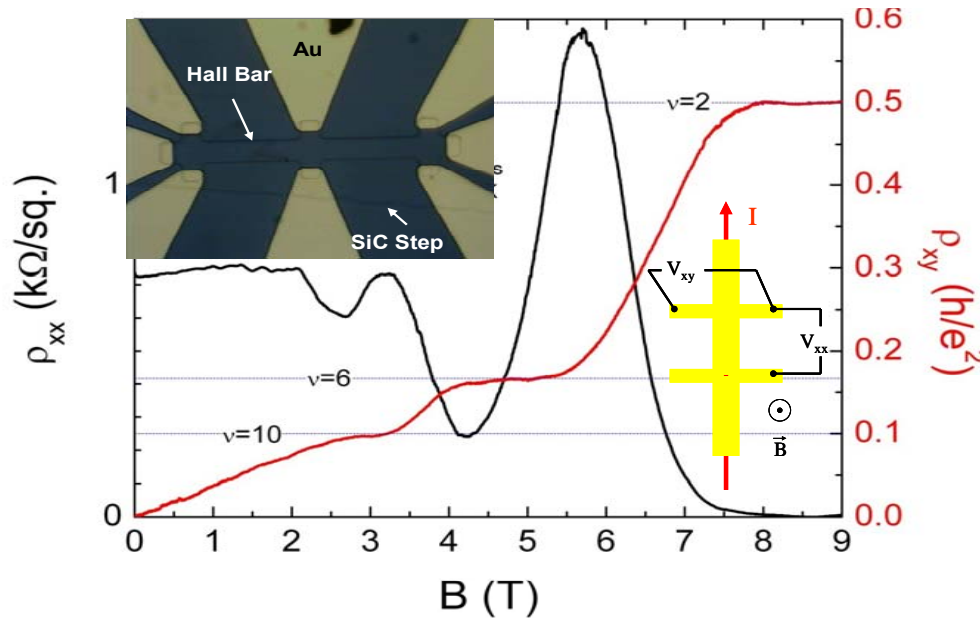
- Average R_{sheet} :
 - Pyrex: $320 \, \Omega/\text{sq}$
 - Zerodur: $250 \, \Omega/\text{sq}$



L. Biedermann, T. Beechem, A. Ross, T. Ohta, and S. Howell, *New J. of Physics* 12 (2010) 120516

Electronic characterization of EG grown on SiC (0001)

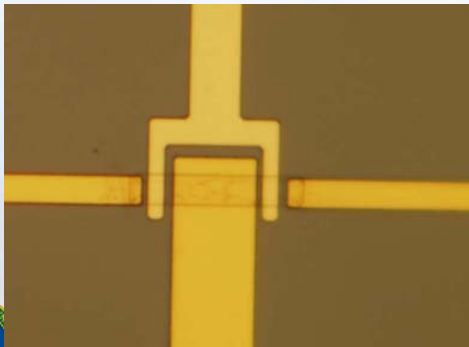
Low Temp Transport Measurements (4 K)



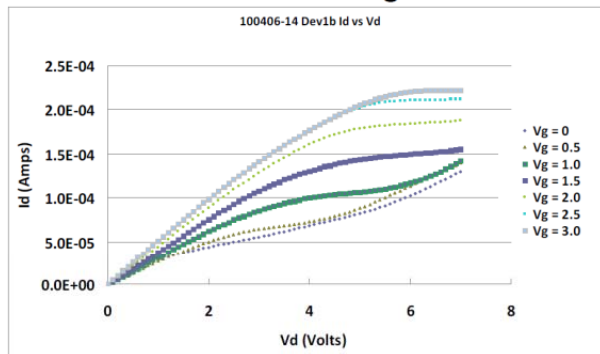
- EG electron mobility: 14,000 cm²/Vs
 - Record mobility (at time of measurement)
- Electron density: 6 x 10¹¹ cm⁻²
- Graphene sheet resistance:
 - ~1600 Ω /sq (average from 12 devices)
 - Indicates high uniformity
- Observed IQHE on 3 devices on the same chip

Pan, Howell, Ross, Ohta and Friedmann
Appl. Phys. Lett. 97, 252101 (2010)

GFET Development



GFET fabricated from graphene grown on semi-insulating SiC



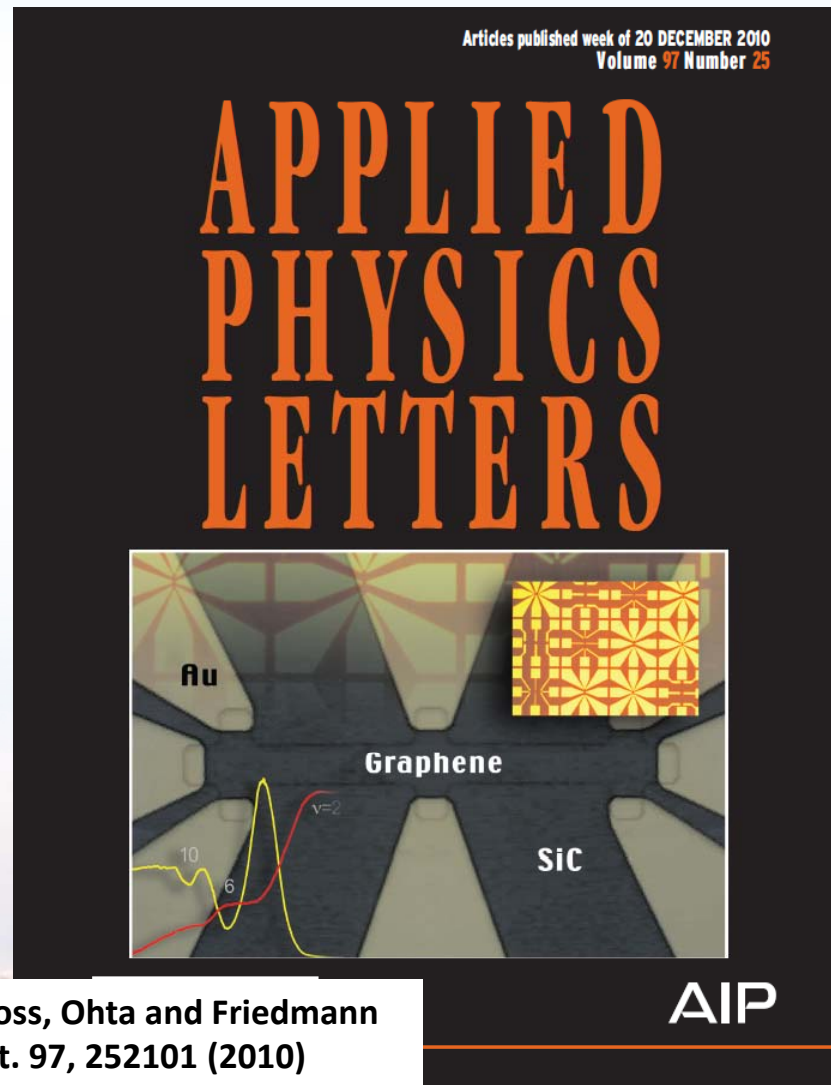
• Measurements made at room temperature



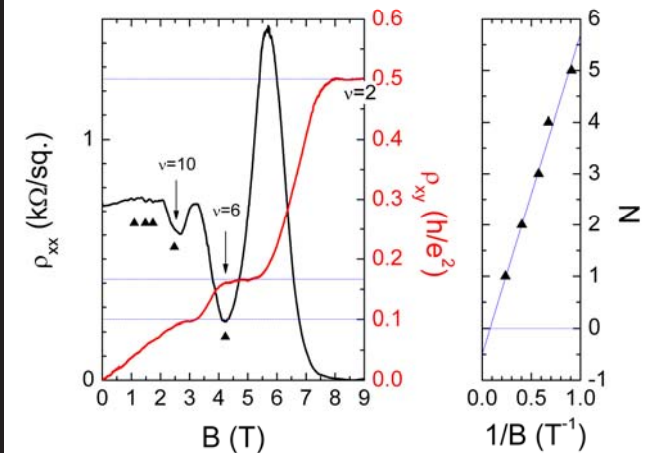
Hall Bar Devices for Confirming the Integer Hall Effect in Graphene/SiC

Hall Bar Device Structures range in size from:

$400 \times 50 \mu\text{m}^2$,
 $200 \times 25 \mu\text{m}^2$,
 $100 \times 12.5 \mu\text{m}^2$
& $50 \times 6.25 \mu\text{m}^2$.



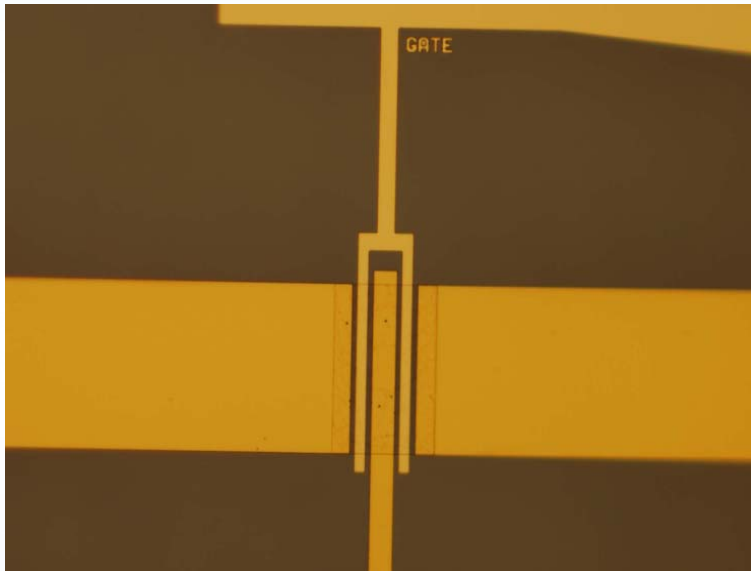
Pan, Howell, Ross, Ohta and Friedmann
Appl. Phys. Lett. 97, 252101 (2010)



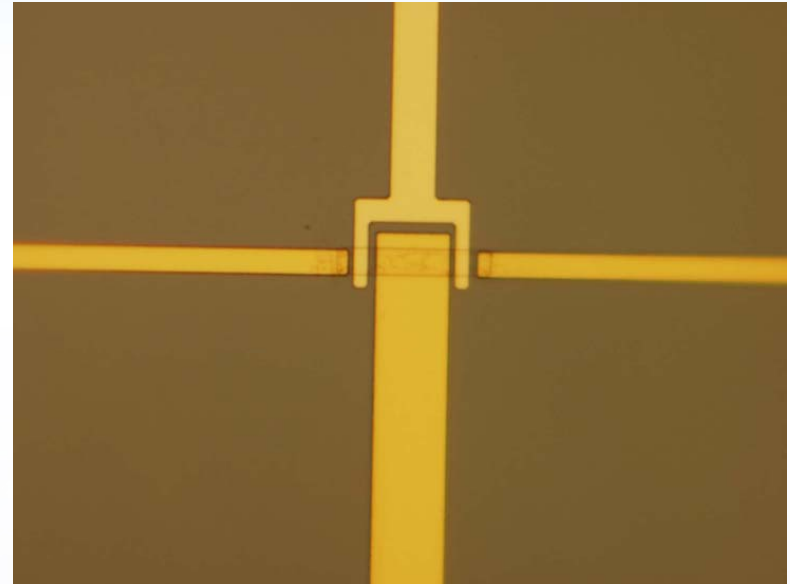
Left: ρ_{xx} and ρ_{xy} measured in a typical graphene Hall bar device. The sample temperature is 4 K.
Right: Landau fan diagram for Shubnikov-de Haas oscillations.

Initial GFET Devices

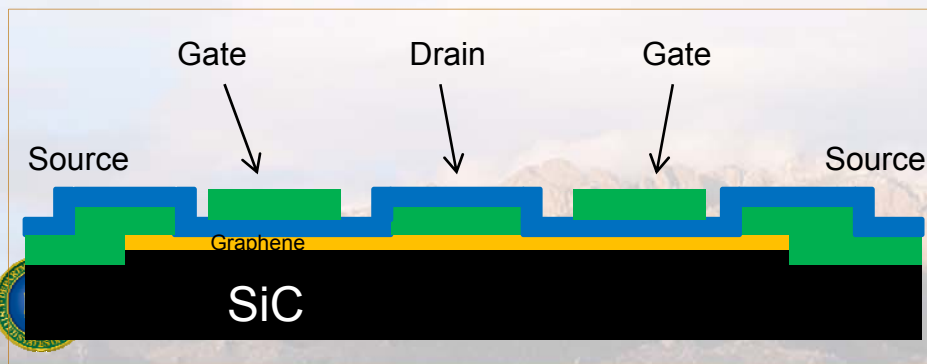
- 20 nm SiO₂ Gate Oxide PVD deposited



Gate Length 6 μm
Gate Width 100 μm
Source/Drain Width 12 μm



Gate Length 3 μm
Gate Width 6 μm
Source/Drain Width 6 μm



Graphene	< 1nm
Gate Oxide	2-20nm
Metal	Ti/Au 320nm
SiC	Substrate

Summary of Recent Major Results

This LDRD was the first of its kind funded by the Nano-to-Micro IAT (mini-grand challenge) and was considered a strategic investment.

- Starting to establish technical leadership in the graphene research community

- Produced several high impact publications and presentations

- **Achieved large area ($\sim 100 \mu\text{m}^2$) synthesis on SiC**

- Developed graphene synthesis using carbon deposition on SiC

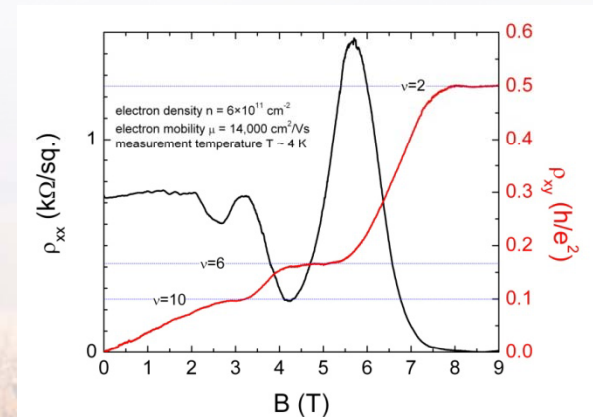
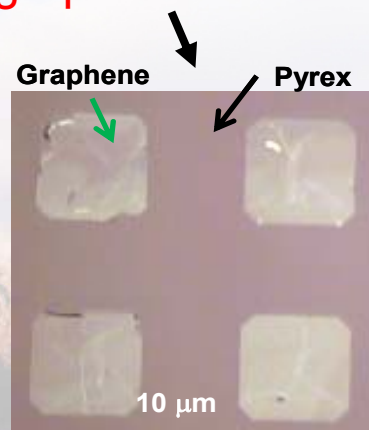
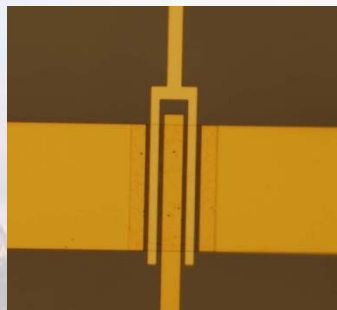
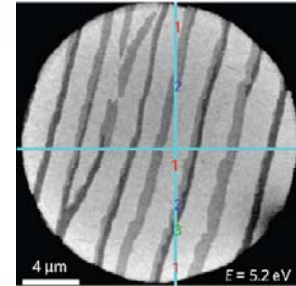
- Demonstrated CVD graphene synthesis on Cu Foils

- **Observed record mobility ($14,000 \text{ cm}^2/\text{Vs}$) for epitaxial graphene**

- Observed IQHE in several devices

- **Demonstrated controlled transfer of graphitic material**

- Fabricated 1st generation GFETS





Back up slides



Graphene's Potential

- *More consistent electronic properties than carbon nanotubes (CNT)*
- *Reported phenomenal electronic/material properties (possible beyond Si material)*
 - High electron mobility (reports of > 200,000 cm²/Vs for exfoliated graphene)
 - ♦ (~ 20 x > than GaAs, ~30 x > than Si)
 - High carrier velocity (300 times < speed of light)
 - Room temperature ballistic transport (minimum scatter)
 - Possible short source-drain transit times (0.1 ps for 100 nm long channel)
 - ♦ Competitive material for RF applications
 - A good material for spintronic applications (reported spin coherence lengths of 1 μm)
 - ♦ Possible quantum information processing (QIP) applications
 - **Standard semiconductor lithographic techniques** can be adapted to make graphene devices
 - Reported thermal conductivity as high as 5300 W/m•K near room temperature
 - ♦ (~ 1.5 x > than CNTs, ~2.5 x > than Diamond and ~ 37 x > than Si)

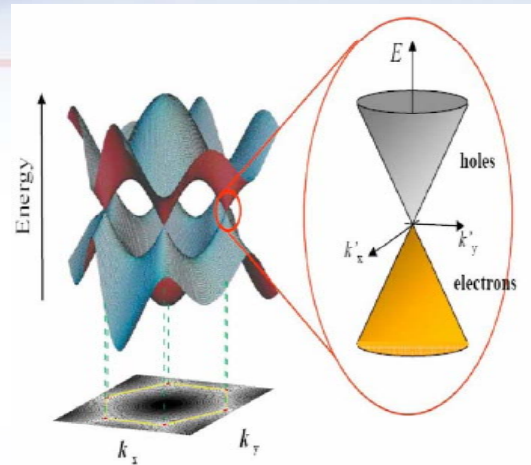
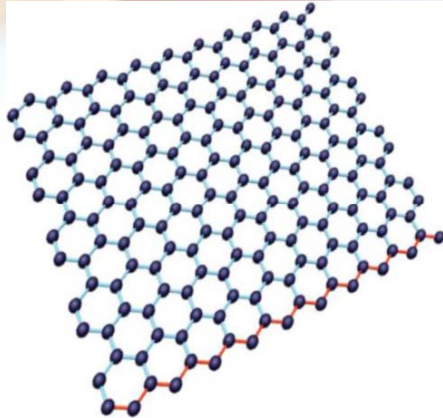


Nice review article: A. K. Geim et al., Science 324, 1530 (2009)



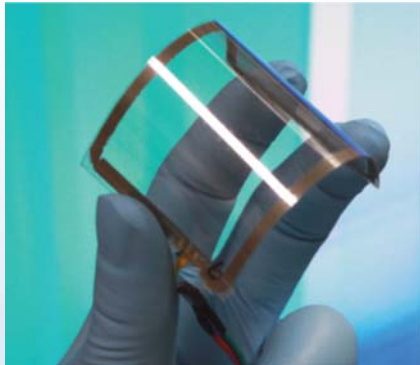
Sandia National Laboratories

Why graphene?



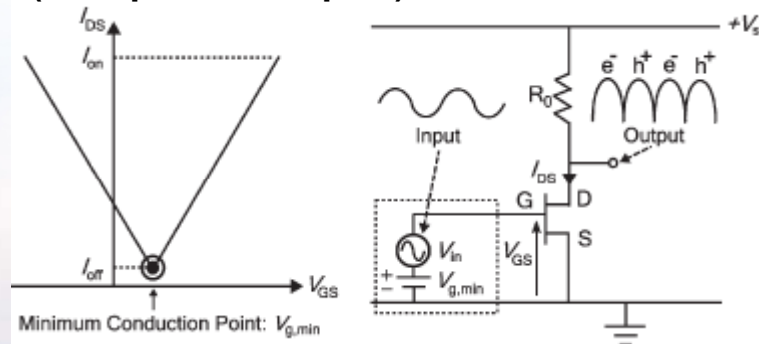
Mobility, μ , up to 250,000 cm²/Vs
(suspended exfoliated graphene)
Ambipolar, zero-bandgap
Current densities up to 5×10^8 A/cm²
Elastic modulus ~ 1 TPa

Transparent electrodes



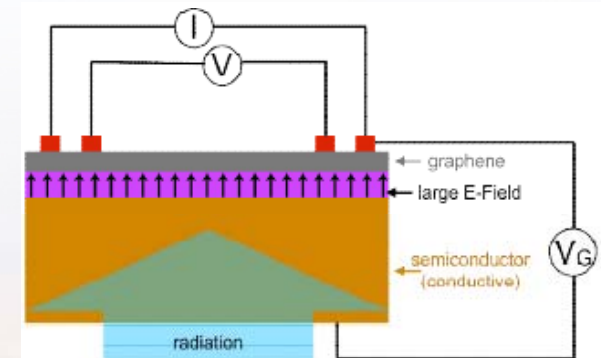
S. Bae et al, *Nature Nano.*,
5, 574-578 (2010)

RF Frequency multiplier (ambipolar transport)



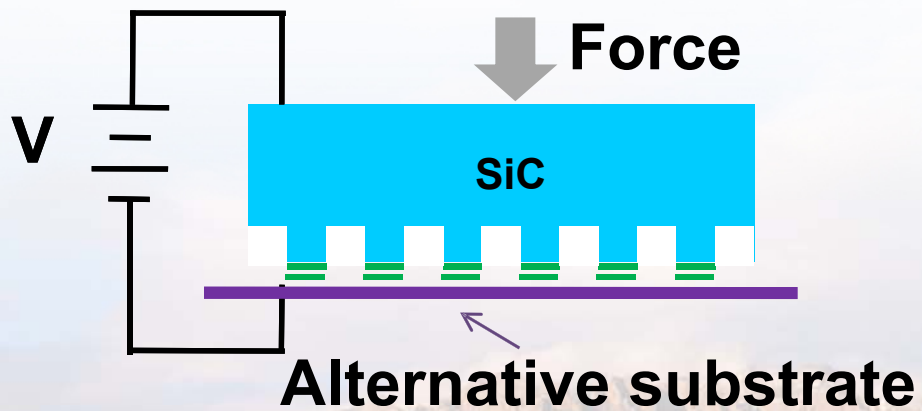
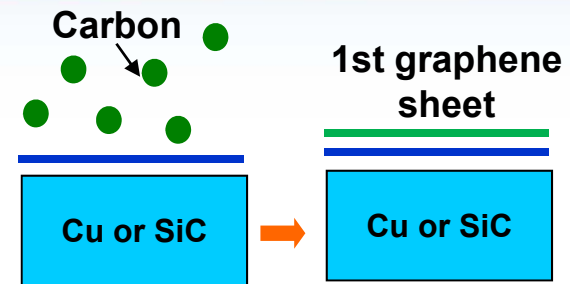
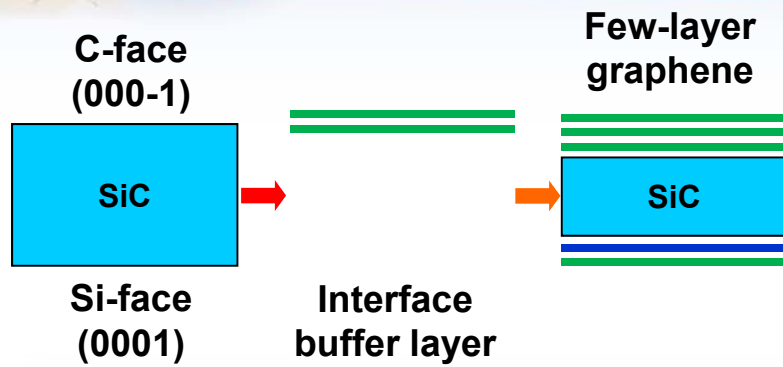
H. Wang et al., *IEEE Elec. Dev. Lett.*,
30, 547-549 (2009).

Read-out for radiation detection

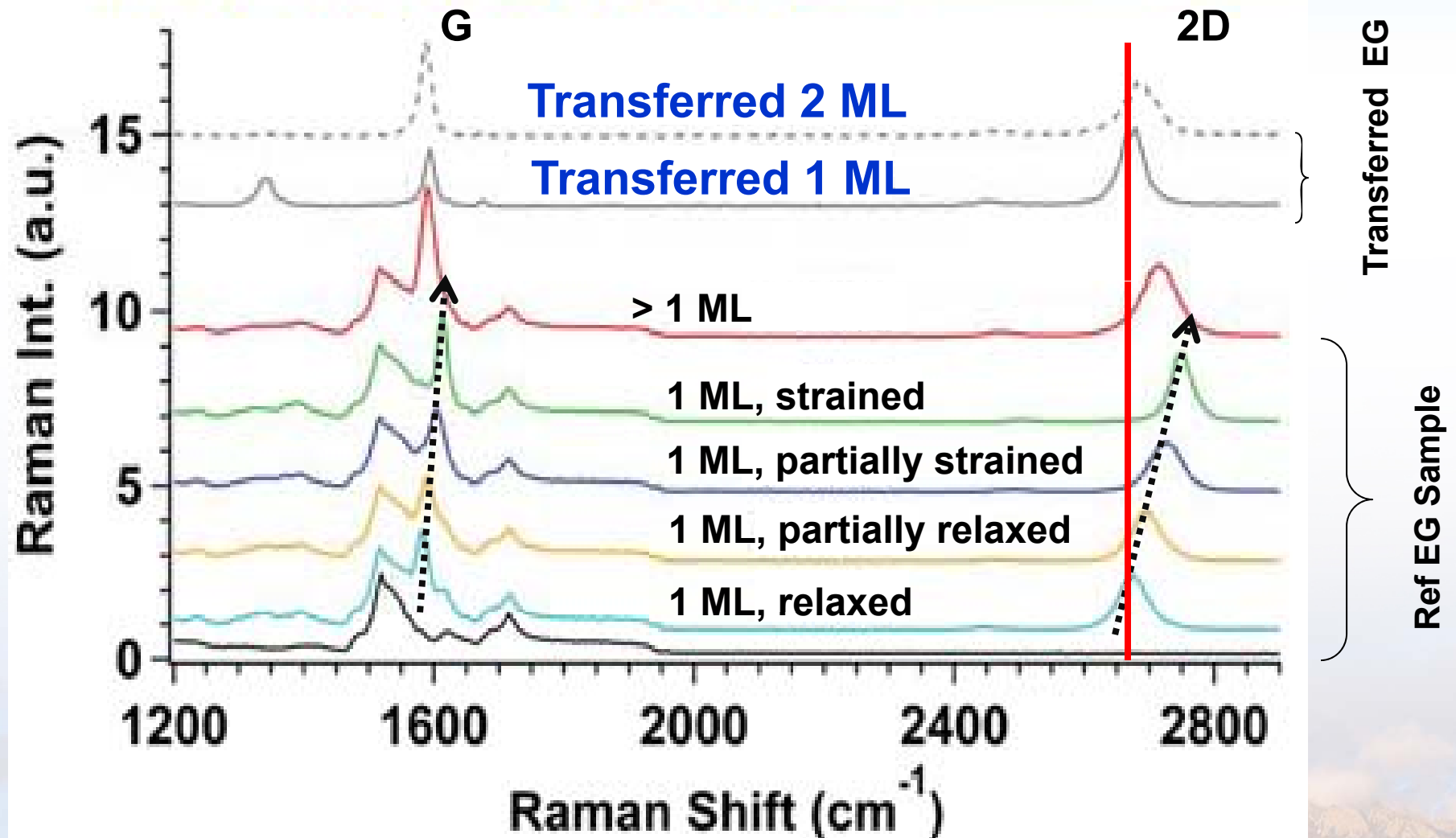


M. Foxe et al., *IEEE Trans. Nuclear Sci.*, submitted (2010).





Transfer relaxes strain inherent in epitaxial graphene



D. Schmidt *et al.*, submitted to *PRB* (2010).



Sandia National Laboratories

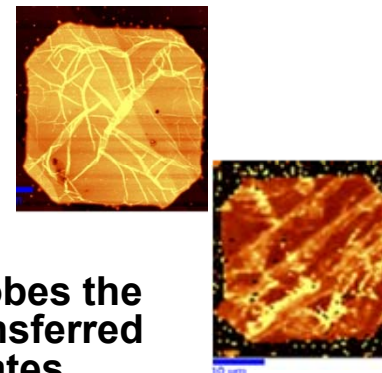
Supporting Graphene Development with Raman

Raman Capability

- Raman spectroscopy is a core tool in the characterization of graphene used to:
 - Identify the presence of the material
 - Identify mono and bilayer regions
 - Quantify doping and stress in the mat'l.
- Our Raman imaging capability builds pictures that show the evolution and distribution of these features.

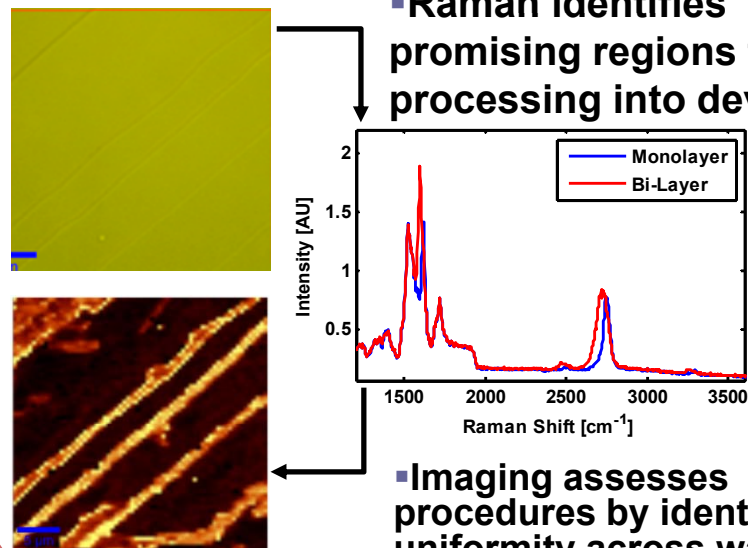
Electrostatic Transfer

- Combining AFM (top) and Raman images, surface and material specific information is acquired.
- These correlations probes the quality of graphene transferred onto alternative substrates.



Imaging Graphene Growth

- Raman identifies promising regions for processing into devices.



- Imaging assesses procedures by identifying uniformity across wafer.

Monitoring Graphene Processing

- Using fluorescence and Raman spectra, we have identified cleaning procedures to remove photoresist without damaging the graphene.

