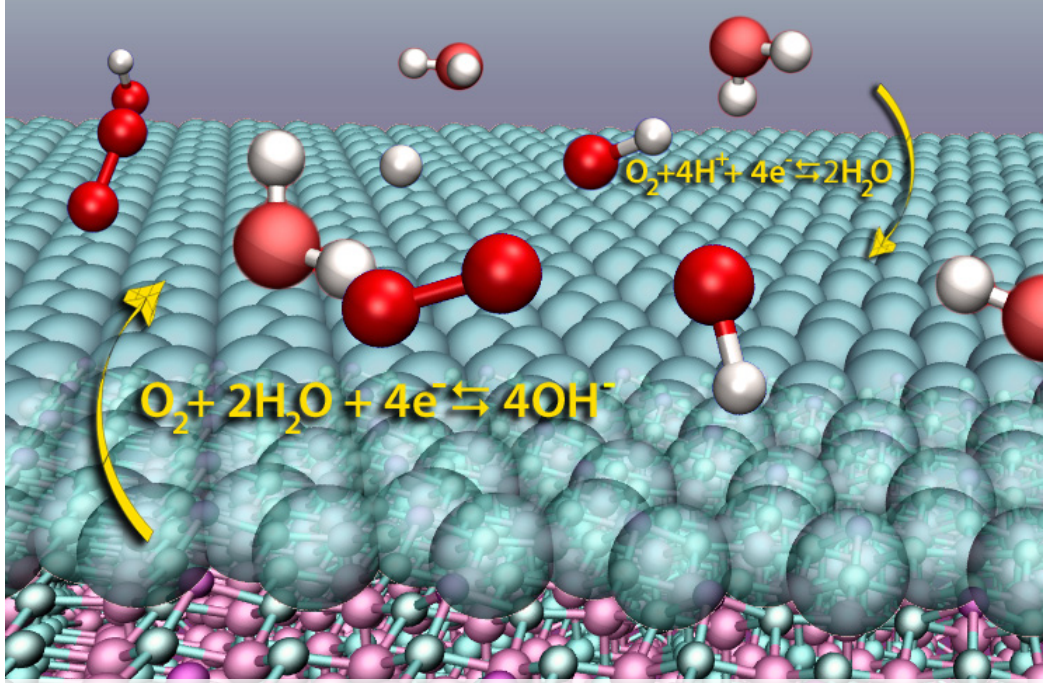
Theory of the electronic and transport properties of epitaxial graphene



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http://ermes.physics.ncsu.edu

Outline

- *Design and characterization of nanoscale materials for 21st century applications:*
- Notes on methodology
- Graphene systems for device applications
  - Electronic transport in mono- and bi-layer graphene
  - Epitaxial graphene on SiC, importance of interface geometry
  - Wetting graphene: charge transfer equilibria in ambient-exposed epitaxial graphene

Notes on methodology

The Theory of Everything

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi$$

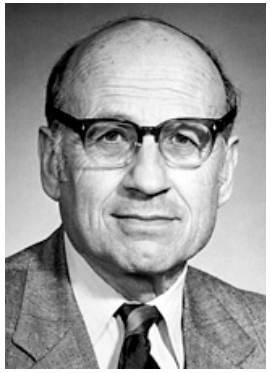
$$\mathcal{H} = -\sum_{j}^{N} \frac{\hbar^2}{2m}\nabla_j^2 - \sum_{\alpha}^{M} \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{j}^{N}\sum_{\alpha}^{M} \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \sum_{j<k}^{N} \frac{e^2}{|r_j - r_k|} + \sum_{\alpha<\beta}^{M} \frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

* Air	* Steel	* Paper	* Vitamins
* Water	* Plastic	* Dynamite	* Ham Sandwiches
* Fire	* Glass	* Antifreeze	* Ebola Virus
* Rocks	* Wood	* Glue	* Economists
* Cement	* Asphalt	* Dyes	* ...

From R.B. Laughlin Nobel lecture, 1998, http://large.stanford.edu/prizes/nobel/lecture/

Notes on methodology

Density Functional Theory


Walter Kohn

- 1998 Nobel Prize in Chemistry to Walter Kohn and John Pople
- **Key point** - the ground state energy for the hard many-body problem can in principle be found by solving non-interacting electron equations in an effective potential determined only by electron density

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\psi_i = \varepsilon_i \psi_i$$

- The effective potential contains all the information on the external potential and the many-body electron interactions - needs to be approximated! Accurate approximations for the functionals of the density exist: LDA, LSDA, GGA.
- Norm-conserving ab initio pseudopotentials to describe the ions
- Plane-wave-based techniques (www.quantum-ESPRESSO.org)
- Electronic polarization and transport (www.wannier-transport.org)

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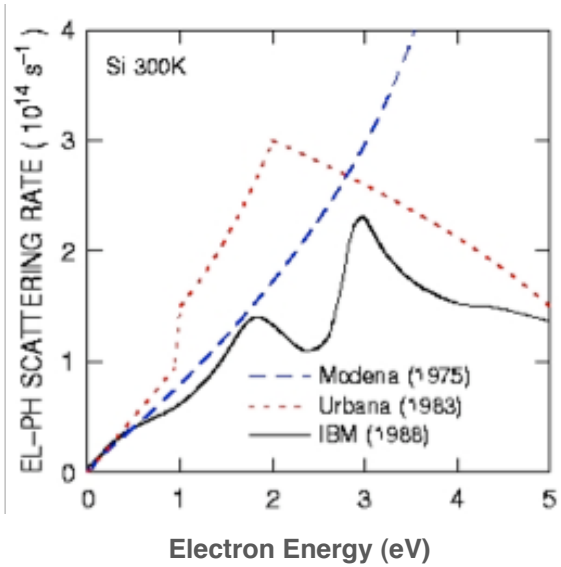
Electronic transport in mono- and bi-layer graphene

- In the design of novel materials for nanoelectronic applications properties of foremost importance are the charge and heat transport characteristics
- The evaluation of such critical parameters has not been obtained quantitatively from first principles even for the most common electronic material: Si
- A quantitative understanding of the charge scattering rate and mechanism still relies heavily on the use of simplified models and approximations fitted to experimental data
- Charge transport in the steady-state regime (Boltzmann):
  - electron-phonon coupling and scattering rates from Density Functional Perturbation Theory
  - Full band Monte Carlo simulation of charge mobility



Electron-phonon scattering

- The rate at which an electron or hole emits (-) or absorbs (+) a phonon is computed using the Fermi Golden rule (adiabatic, harmonic and weak-coupling approximation:

Sum over all bands

Electron-Phonon Matrix Element

Energy Conservation Law

Number of Phonons

$$\Gamma_{k\nu j} = \frac{2\pi}{h} \sum_{\nu'} \int |g^{qj}_{(k+q)\nu',k\nu}|^2 \delta(\epsilon_{(k+q)\nu'} - \epsilon_{k\nu} \pm h\omega_{qj})(N_{qj} + \frac{1}{2} \pm \frac{1}{2})$$

j – phonon branch index
v, v' – electron band index
k – electron wave vector [the initial state of electron is determined by quantum numbers (*v,k*)]
q – phonon wave vector

Electron-phonon scattering

- Critical parameter is the electron-phonon matrix element

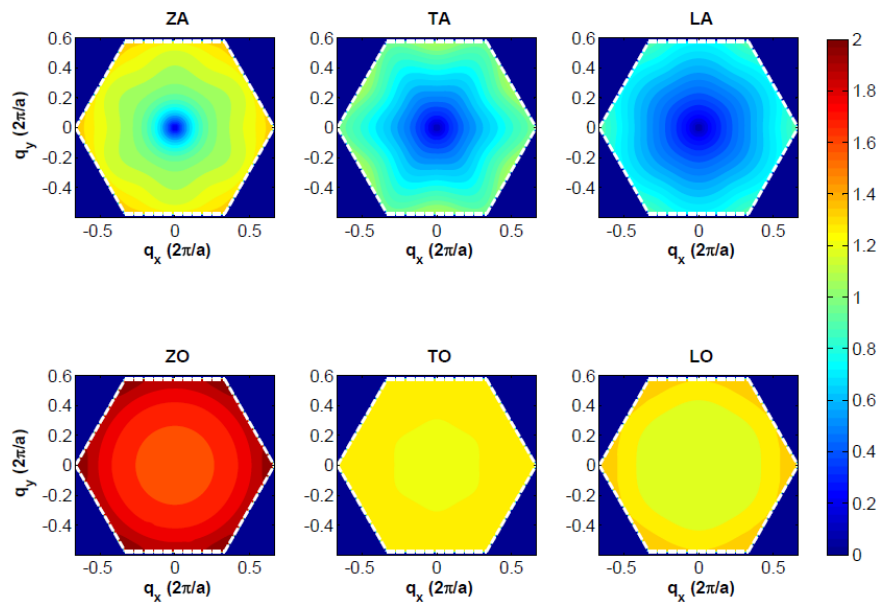
Electron eigenfunction

$$g^{(i,j)\nu}_{\mathbf{k}+\mathbf{q},\mathbf{k}} = \sqrt{\frac{\hbar}{2M\omega_{\nu,\mathbf{q}}}}\ \langle j, \mathbf{k}+\mathbf{q}|\Delta V^{\nu}_{\mathbf{q},SCF}|i,\mathbf{k}\rangle$$

The change of the self-consistent crystal potential due to perturbation – the phonon (j, **q**)

Typically, matrix elements are approximated with Deformation Potentials (continuum approximation with a displacement field)

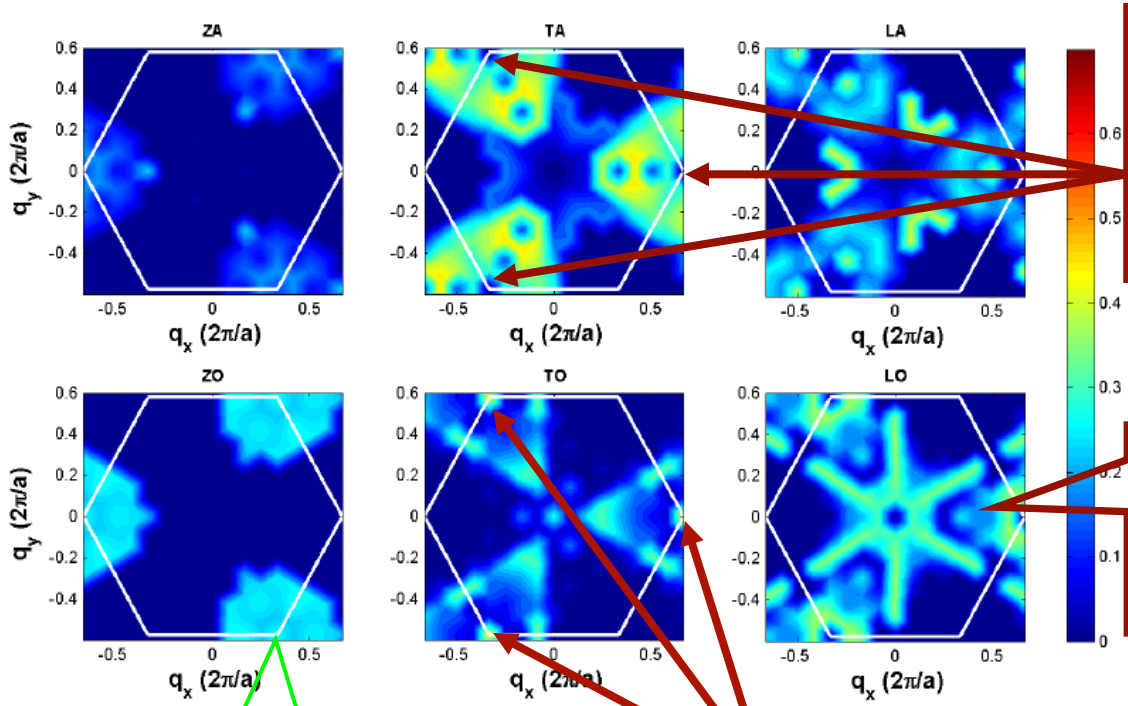
Matrix elements in DPA are isotropic and in graphene the DP parameter is assumed to be the same for all branches



(Akturk and Goldsman, JAP, 2008)

Electron-phonon scattering

- Electron-phonon matrix element as a function of phonon wave vector **q**
- DFT/DFPT calculation for electron in Dirac point: **k=K**



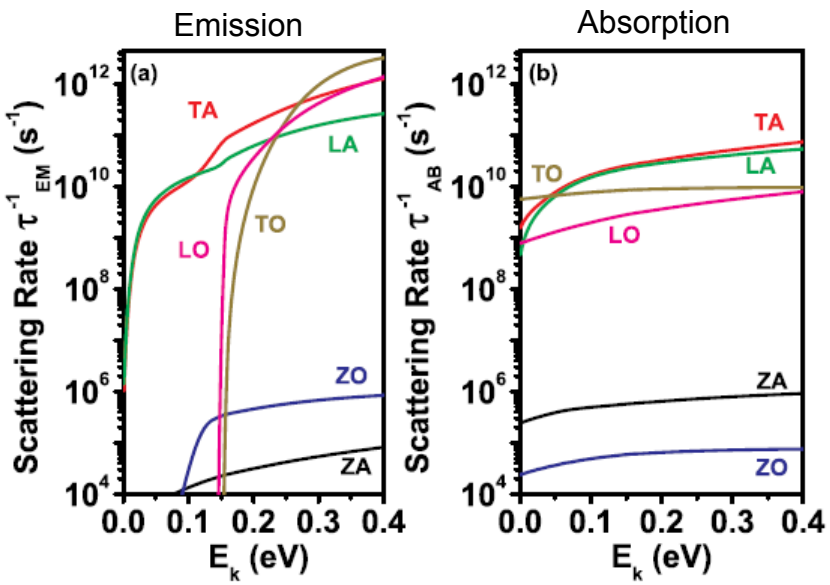
These transitions (q=K) <u>for all branches except TO</u> are forbidden by symmetry *(J. L. Manes, PRB 76 (2007))*

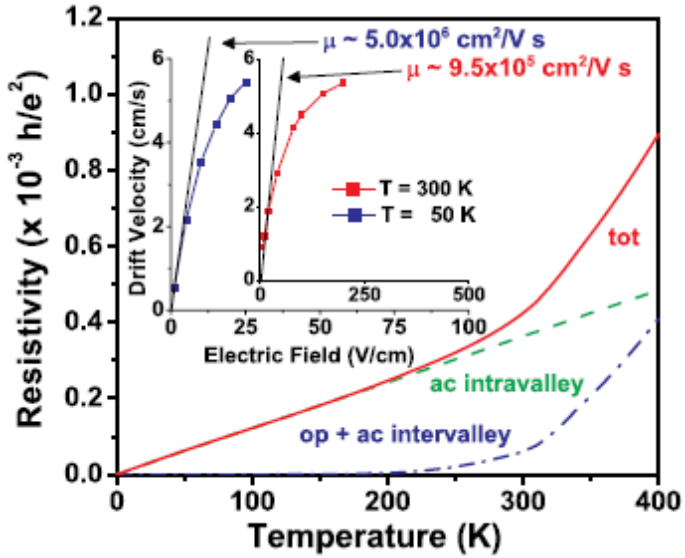
PRONOUNCED ANISOTROPY! (Compare with DPA)

White line is the border of the First Brillouin Zone of Graphene

These maxima in the TO branch are the result of the Kohn anomaly

First principles scattering rates





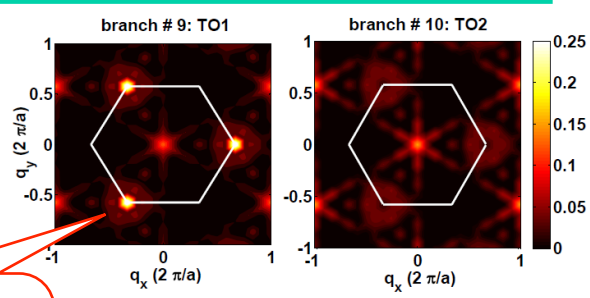
- The total scattering rate of ≈10^{10} s^{-1} in monolayer graphene is much smaller than previously believed
- Intrinsic mobility of monolayer graphene may be as large as 10^6 cm^2/Vs at 300 K under ideal conditions

*Physical Review B, Rapid Communications, **81**, 121412 (2010)*

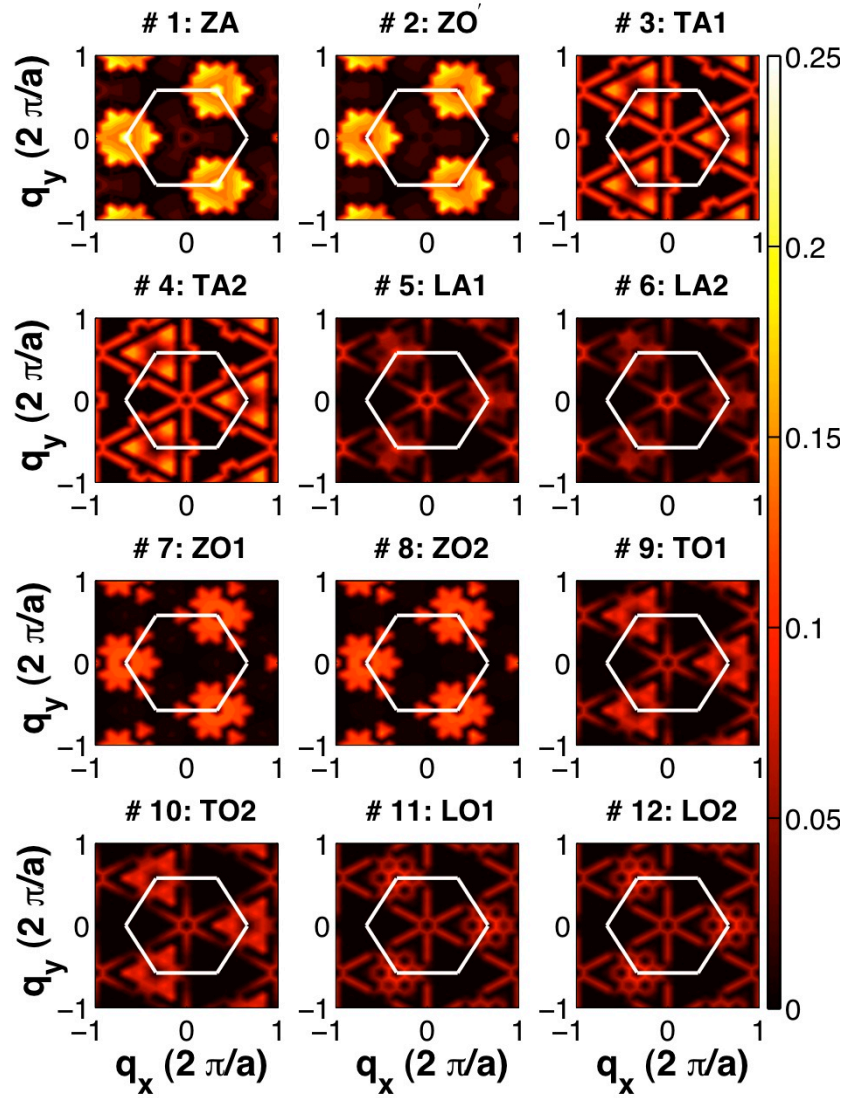
Bilayer Graphene: Electron-Phonon Interaction

DFPT electron-phonon scattering matrix element

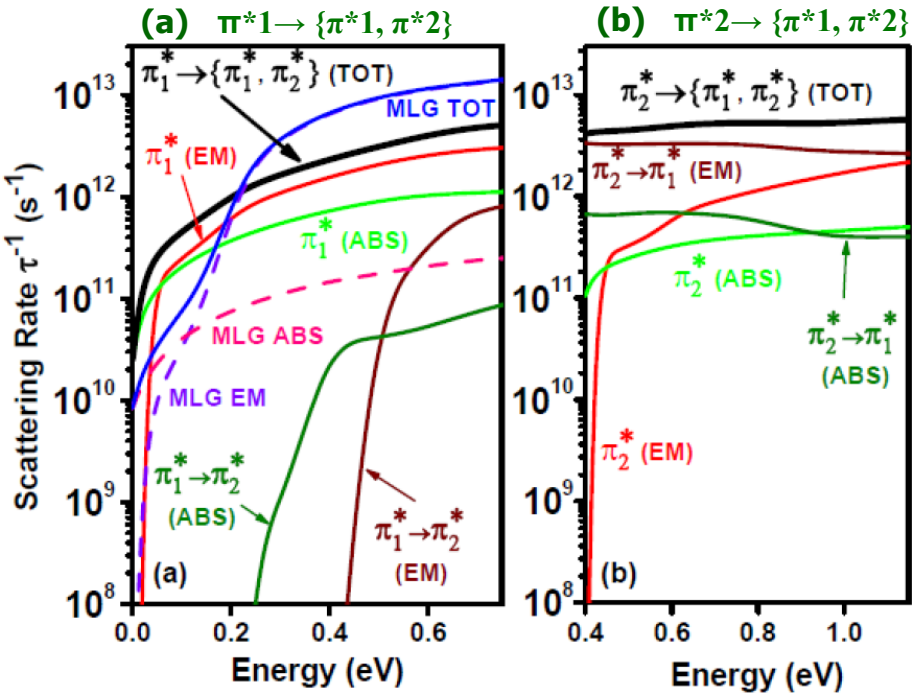
- Phonons in mono and bi–layer graphene are almost identical ➔ six pairs of almost identical matrices.
- Calculated results are shown for the electron in the band π*1, at the K point (Dirac point marked by a white dot inside the FBZ).
- The Kohn anomalies are observed in the interband matrix elements (π*1→π*2). The overall picture agrees with the symmetry analysis (L. M. Malard *et al.*, PRB **79** 125426 (2009))

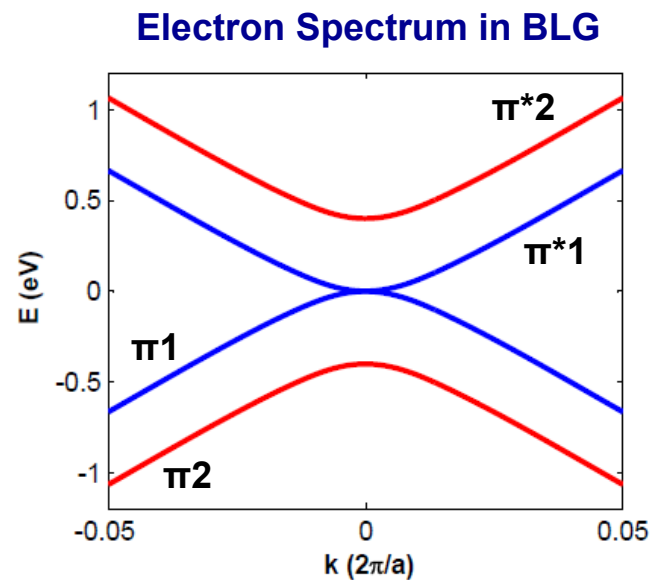


Kohn anomalies in BLG, observed in the interband scattering matrix elements (π*1→π*2)



Transport in bi-layer Graphene: Electron-Phonon Scattering Rate



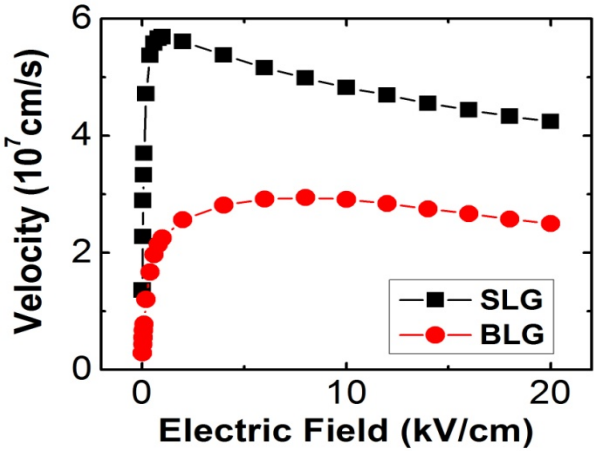


- The total scattering rate in bilayer graphene (BLG) is substantially higher than in monolayer graphene (MLG) at low energies ($E < 0.2$ eV) but lower at high energies.
- The largest contribution at low energies in BLG comes from the absorption of (TA-like) acoustic phonons.
- The role of TO/LO phonon emission appears to be much weaker than that in MLG.
- The Kohn anomalies observed in the interband scattering matrix elements do not play important role, due to energy and momentum conservation.

Electron Transport in SLG and BLG

Monte Carlo Simulation

- ❖ Electronic band structure for SLG and BLG calculated in TB approximation
- ❖ Realistic phonon spectra and accurate electron-phonon interaction calculated from DFT/DFPT in the entire FBZ



- ❑ Mobility of BLG (**1.0×10^5cm^2/v·s**) is much smaller than that of SLG (**5.2×10^5cm^2/v·s**), because
  - Acoustic phonon scattering rate in BLG is larger.
  - Speed of electrons in lower energy region is smaller than vF in BLG. (in parabolic approximation, velocity->0, when energy->0)
- ❑ High field velocity in BLG is degraded due to the lack of effective energy relaxation, in other words, optical phonon scattering.
- ❑ Preliminary results indicate that surface polar phonon may substantially enhance the saturation velocity in BLG by efficiently cooling the electron gas; the impact of remote ionized impurity scattering appears to be less significant.

Bilayer graphene more similar to graphite than to graphene!

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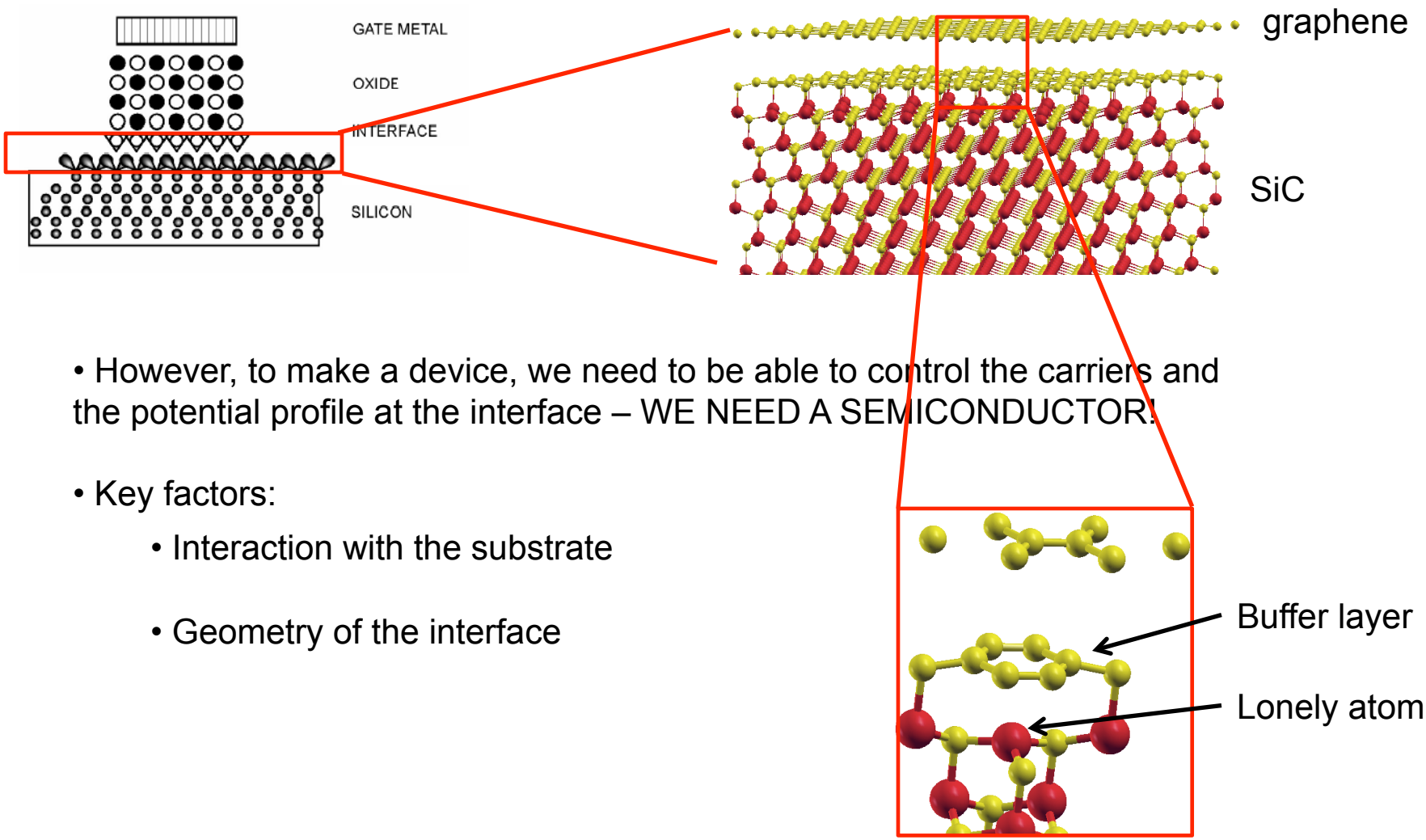
Graphene device geometry

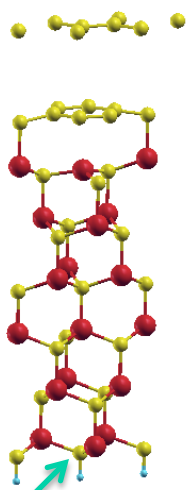


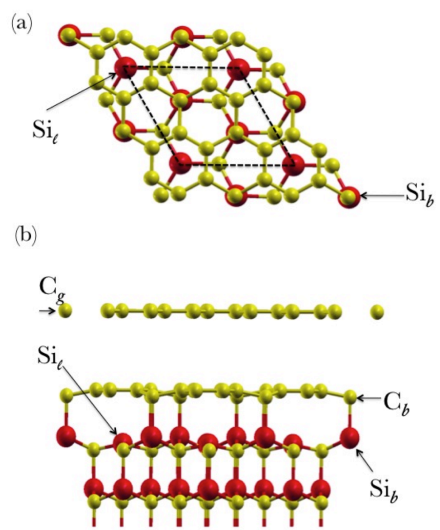
- However, to make a device, we need to be able to control the carriers and the potential profile at the interface – WE NEED A SEMICONDUCTOR!

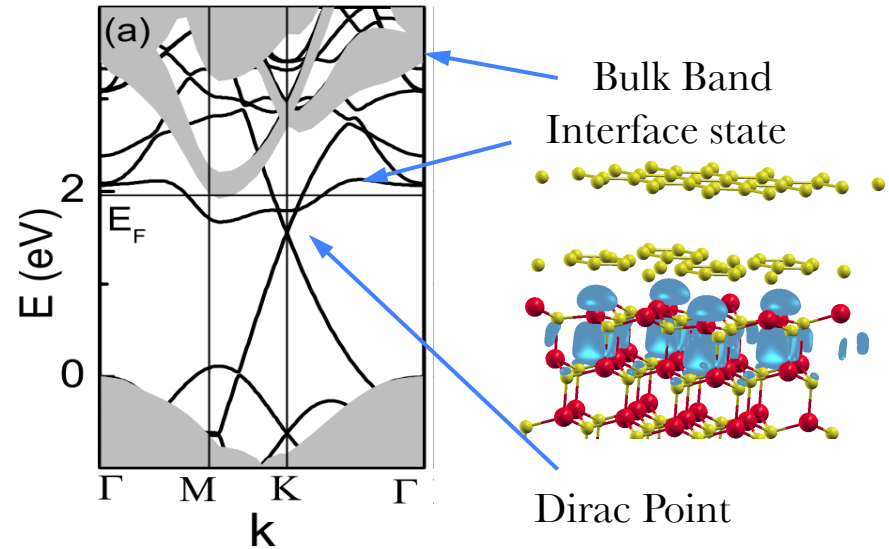
- Key factors:
  - Interaction with the substrate
  - Geometry of the interface

Epitaxial Graphene on Si-face SiC (0001)

2x2 Graphene on √3 x √3 R Cos 30^0 (R3) cell on (0001) surface of SiC



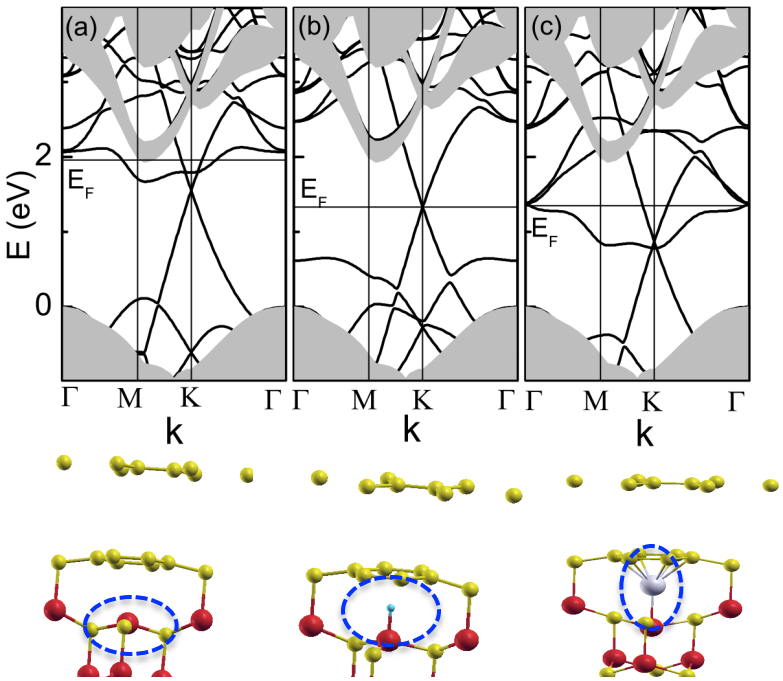




- charge transfer to the graphene layer → system behaves n-type
- The first C layer on SiC is bound to the substrate → buffer layer
- Interface state close to the Fermi level from the unbound Si atoms at the interface.

Presence of 'Lonely Atom' suggests a path for interface modifications

Tuning Electronic Properties by Surface Modifications



Interface with dangling bond | H-Passivated Interface | Li-Passivated Interface

Charge Transfer:

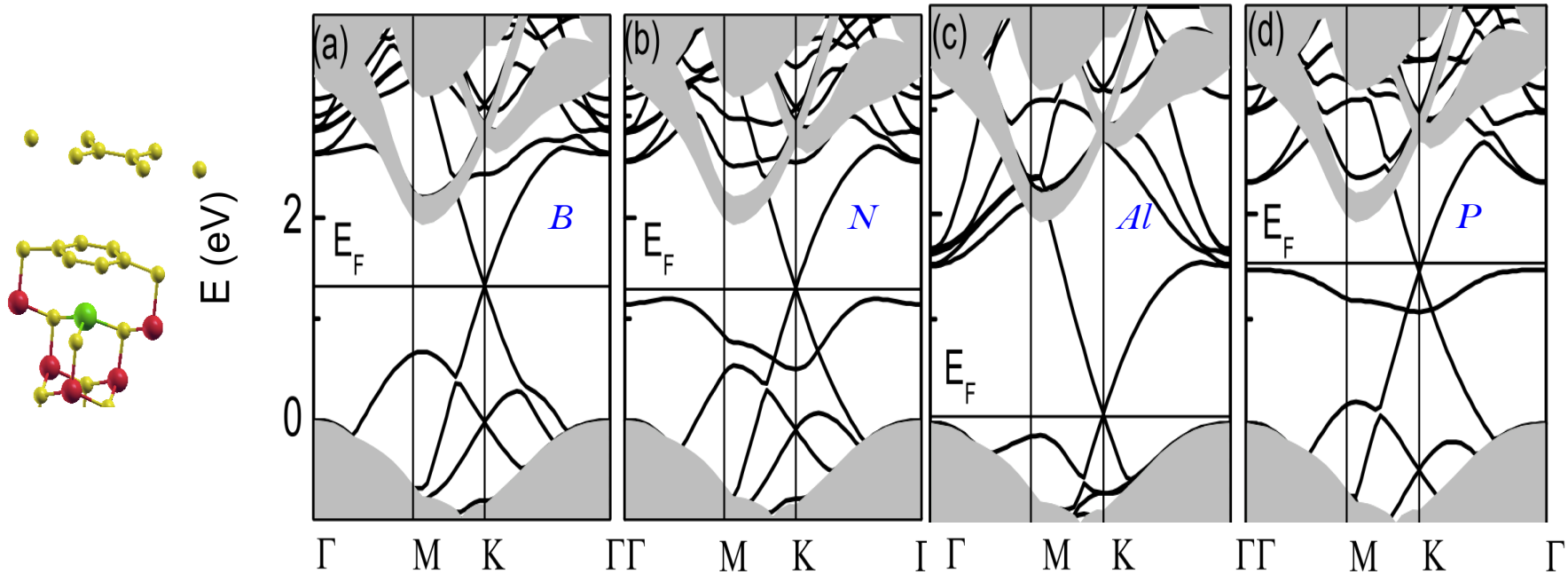
$1.9\times10^{13}cm^{-2}$ – $1.3\times10^{13}cm^{-2}$

Shift in Dirac Point:

$0.40eV$ – $0.47eV$

- Interface morphology can control the charge transfer between the substrate and the Graphene Layer
- Negligible effect on the electronic behaviors near the Dirac Point
- The properties (relative to the substrate) such as valance band offset, charge transfer are also tuned by changing the interface

Tuning Electronic Properties by Surface Modifications



Valence Band Offset: 1.32 eV 1.30 eV 0.06 eV 1.44 eV

Surface dipoles control the electrostatic potential at the interface, and thus a variation of the valance band offset.

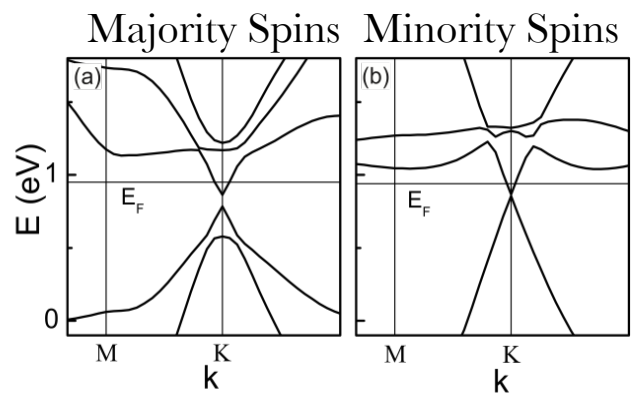
Slight Changes in the Charge Transfer:

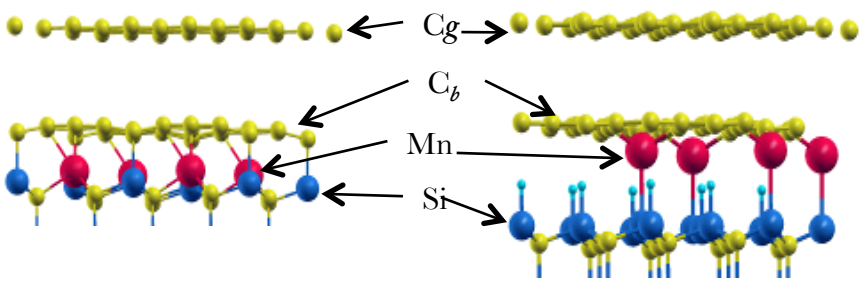
$-0.598\times10^{12}cm^{-2}$ $-1.98\times10^{12}cm^{-2}$ $-3.03\times10^{12}cm^{-2}$ $6.29\times10^{12}cm^{-2}$

Tuning Spintronic Properties by Magnetic Doping

- Due to the unbound electron on the lonely Si atom, epitaxial graphene on SiC (0001) has a nonzero intrinsic magnetic moment. However only the buffer layer is spin polarized and not the graphene layer.
- Two possible configurations:
  - Magnetic impurities replacing the 'Lonely Atom'
  - Magnetic impurities replacing C atoms in the buffer layer.

Magnetic impurities in the buffer layer





Magnetic impurities in the position of 'Lonely Atom'

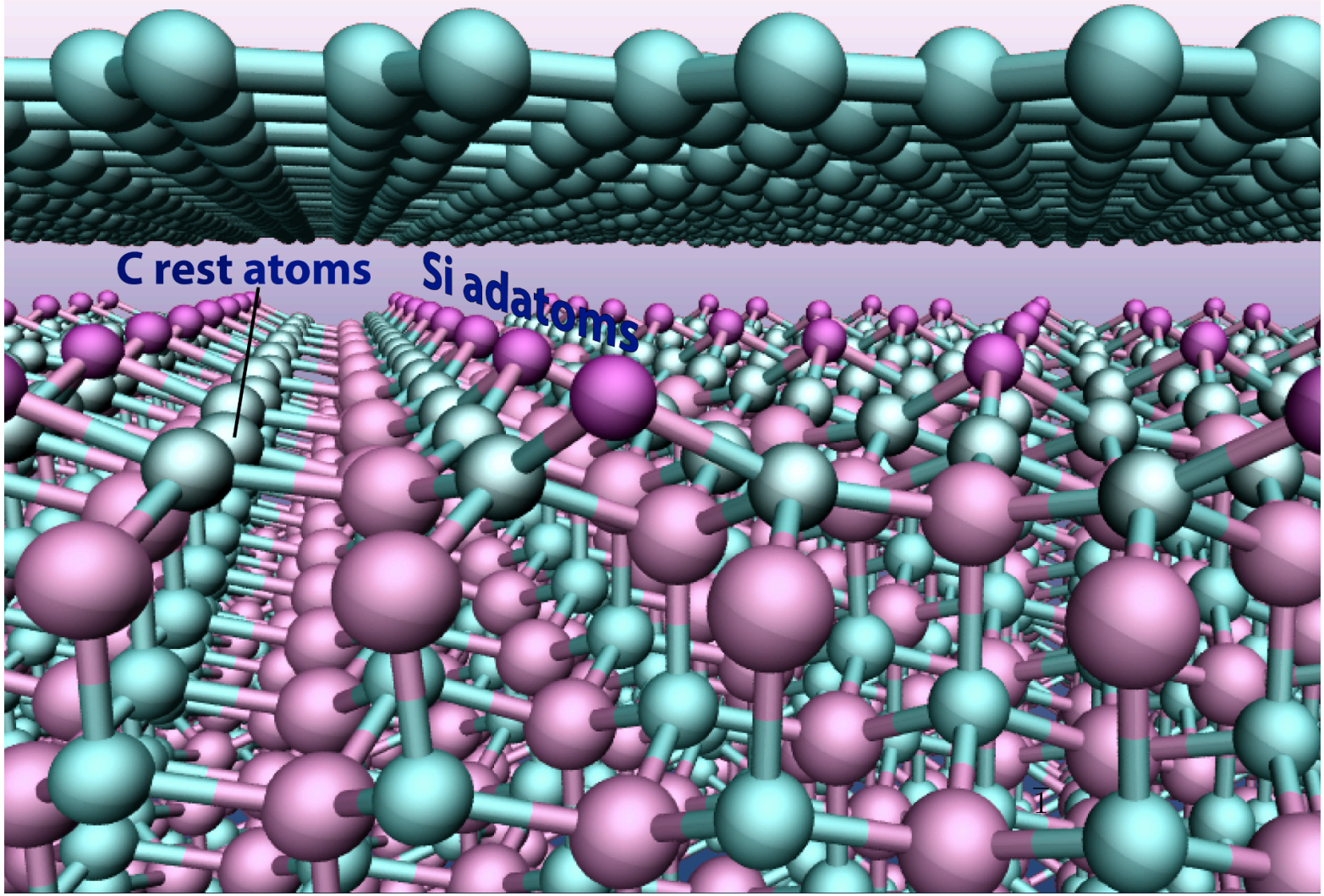
Magnetic impurities in the buffer layer

- Magnetic impurities in the surface of the substrate will spin polarize the buffer layer, but not the graphene layer, because of the strong screening by the buffer layer.
- Magnetic impurities in the buffer layer opens up a band gap of 81 meV for majority spins and stay half metallic for the minority spins.

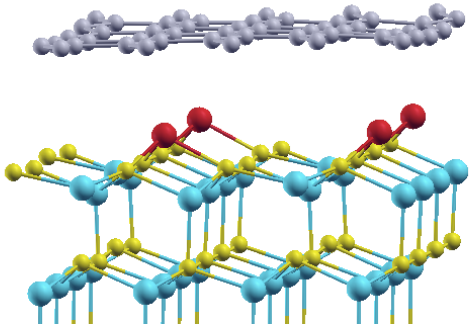
Physical Review Letters ***104****, 146801 (2010)*

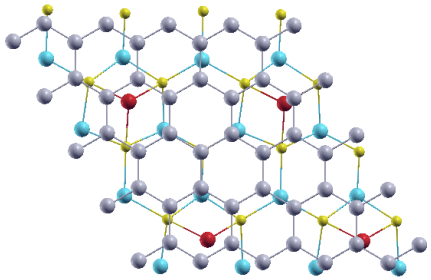
Epitaxial Graphene on C-face SiC $(000\bar{1})$

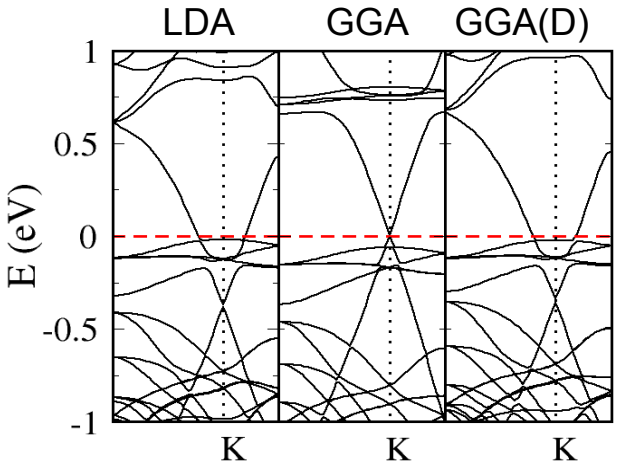
Reconstructed Structure - Si ad-atom model



Epitaxial Graphene on C-face SiC (000$\bar{1}$)







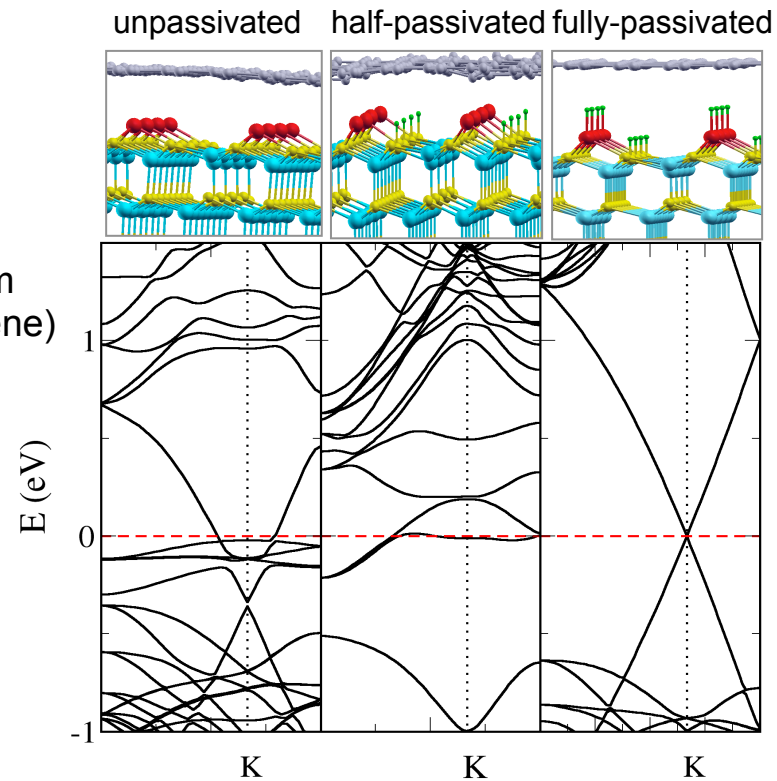
Note the shift in Dirac Point

- LDA (Si adatom – Graphene distance = 2.6 Å)
- GGA (Si adatom – Graphene distance = 3.2 Å)
- GGA with van der Waals (DFT-D) - an empirical potential is added to the regular density functional energy to take care of the long range interactions (Si adatom – Graphene distance = 2.6 Å)

Long-range interactions are responsible for shifting the graphene layer 0.6 Å towards the substrate
The shorter distance between graphene and substrate results in an electron transfer to the graphene layer.
→ n-doped graphene with E_F-E_D = 375 meV (good agreement with experiments)

Epitaxial Graphene on C-face SiC (000$\bar{1}$)

- C (bulk)
- Si (bulk)
- Si ad atom
- C (graphene)
- H



	unpassivated	half-passivated	fully-passivated
Si adatom – graphene distance	2.53 Å	2.0 Å	3.80 Å
Ripple width distance (shortest)	0.2 Å	0.49 Å	0.07 Å

- Unpassivated system results in an electron doped graphene layer
- Half passivated system does not support a graphene layer
- Graphene on fully passivated interface decouples from the substrate

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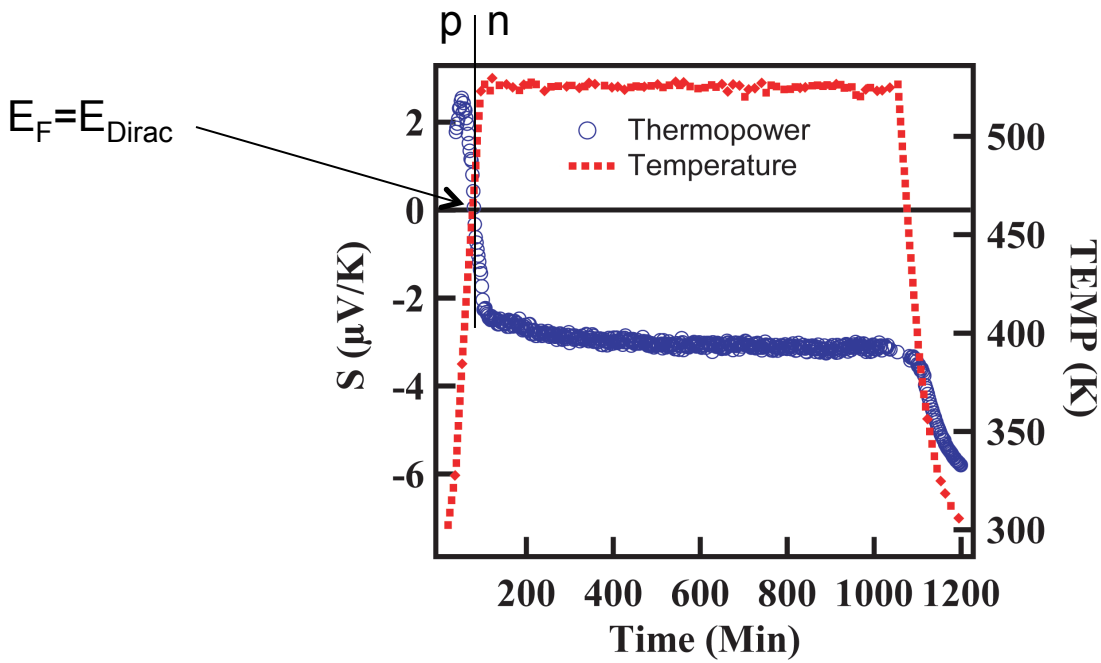
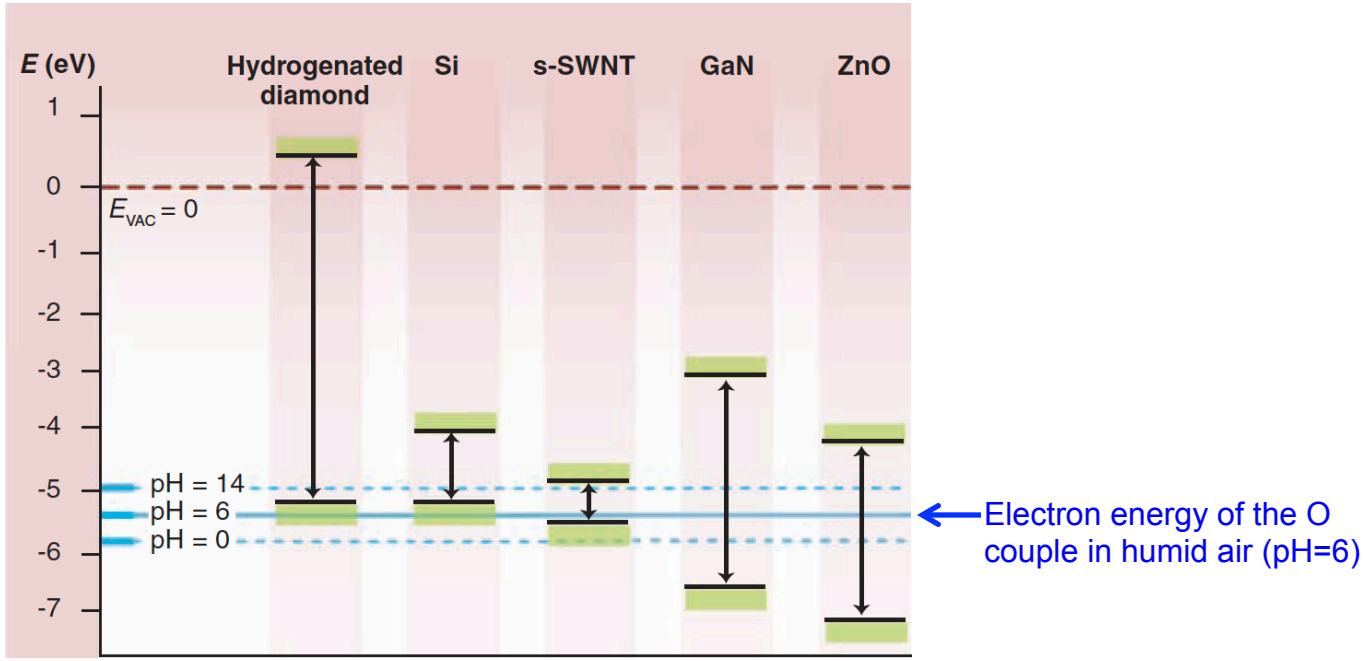
Wetting graphene



- Thermo-Electric Power (TEP) measurements on mono-layer graphene
- The sign of the TEP gives information about changes in the doping type of the graphene film
- The TEP is zero when the Dirac point and the Fermi energy coincide and upon annealing the sample goes from p-type to n-type

Experiments by the groups of A. Sidorov (GaTech), K. Gaskill (NRL) and G. Sumanasekera (U. Luiville)

Electrochemical charge transfer



- Presence of a wetting layer (aqueous phase) is unambiguous in samples exposed to ambient conditions
- electron exchange can systematically occur between the surface of the material and the aqueous redox couple $O_2+4H^++4e^- \rightleftharpoons 2H_2O$, which results in the consumption or formation of O_2
- General phenomenon that can influence a wide range of materials and processes, first studied in the context of the conductivity of hydrogenated diamond surfaces

*Chakrapani et al. Science **318** (5855), 1424 (2007)*

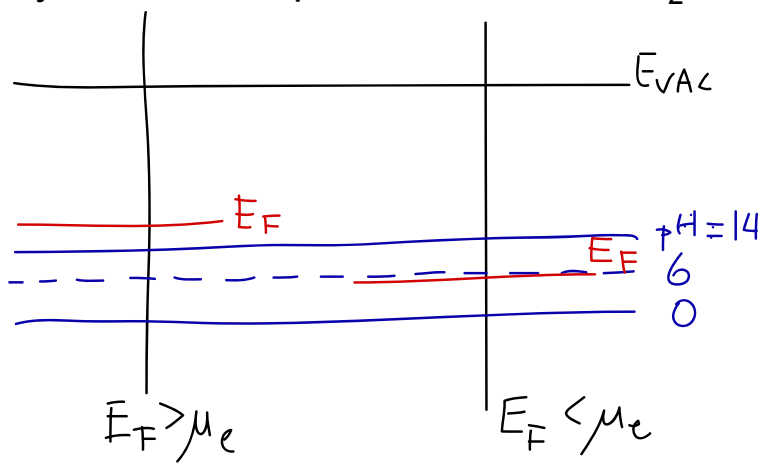
Electrochemical charge transfer

A water layer in contact with a surface is characterized by electrochemical redox couples involving dissolved oxygen in equilibrium with air

$$O_2+4H^++4e^- \rightleftharpoons 2H_2O \quad \text{(acidic conditions)}$$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad \text{(basic conditions)}$$

All this constrained by the water equilibrium reaction $H_2O \rightleftharpoons H^++OH^-$



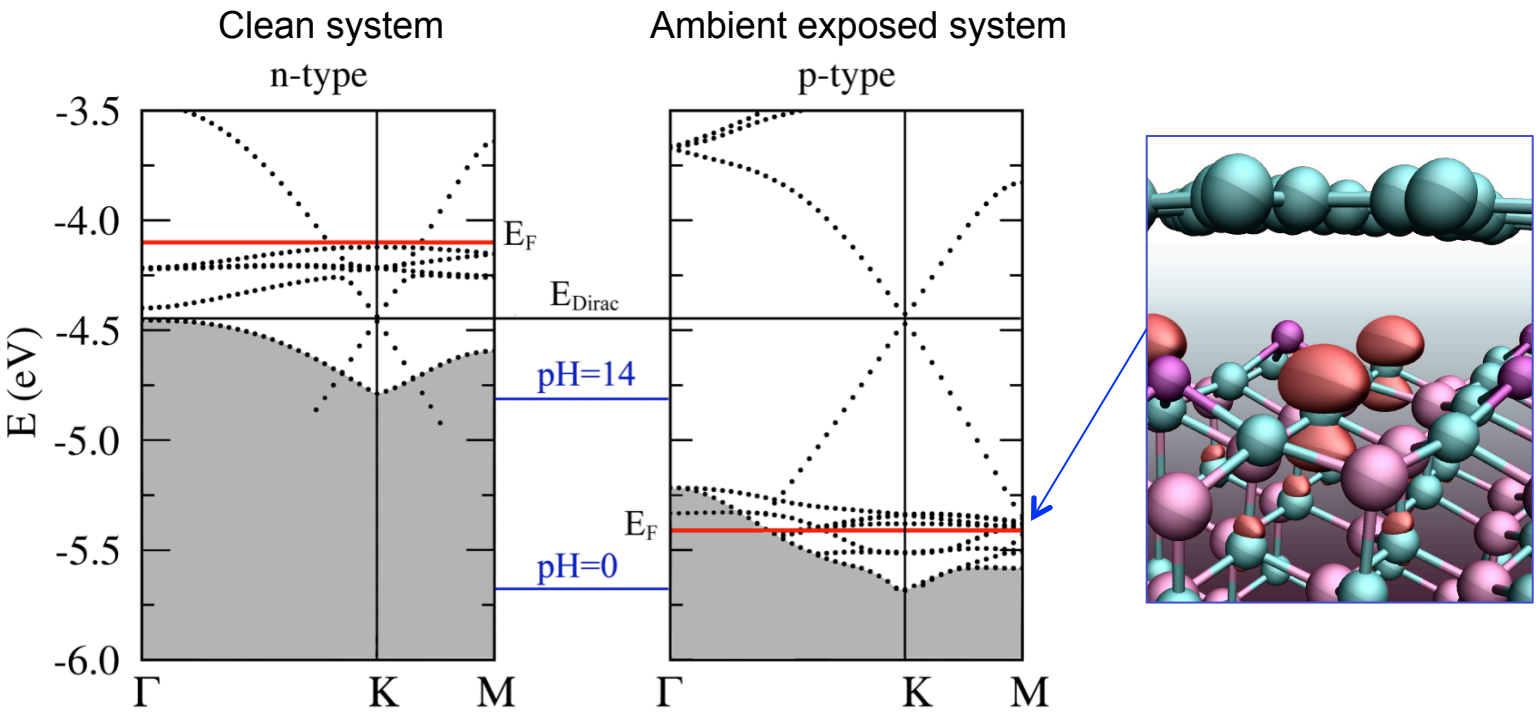
- Water in equilibrium with air has a pH ≈ 6 from the naturally occurring CO_2 in the air, which corresponds to an electrochemical potential of $\mu_e \approx -5.3$ eV
- When $E_F > \mu_e$, one has electron transfer from the system to the solution – **p-type**

  $$O_2+4H^++4e^- \rightarrow 2H_2O \text{ (proton consumption)}$$
- When $E_F < \mu_e$, electrons transfer from the solution into the system – **n-type**

  $$O_2 + 2H_2O + 4e^- \leftarrow 4OH^- \text{ (hydroxyl ions consumption)}$$

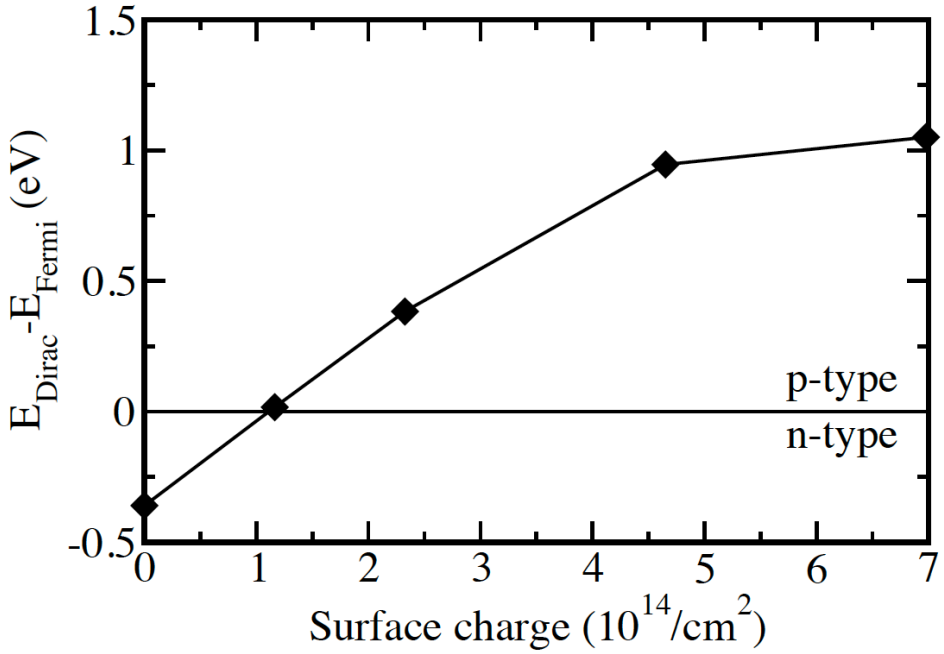
<u>The pH of the solution determines the electronic properties of the system!</u>

Wetting graphene



- Energy level diagram of the water/oxygen redox couple (blue lines) compared to the theoretical band diagrams of epitaxial graphene/SiC
- Water-free surface: the E_F is pinned by an interface state located in the conduction band just above the Dirac point causing electron doping of graphene. These states are due to dangling bonds of the C rest atom on the SiC *(0001)* $(2x2)_C$ surface reconstruction
- p-type doping of graphene when the Fermi energy, E_F, is pinned at the chemical potential μ_e determined by the redox potential of oxygen dissolved in the mildly acidic water adsorbed on the SiC surface.

Wetting graphene

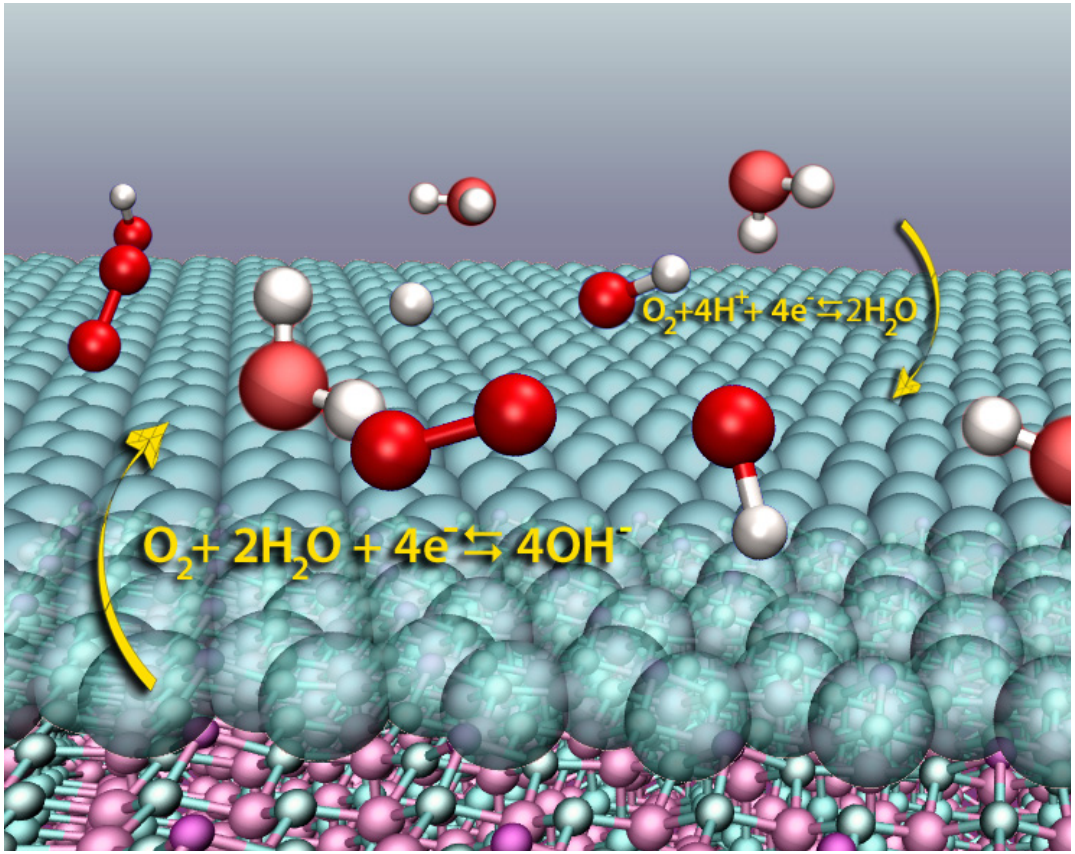


Difference between the Fermi and Dirac energy as a function of surface charge. The neutrality point (E_{Dirac}=E_{Fermi}) coincides with a charge of ~1x10^{14} electrons/cm^2

electronic transport properties of the surface cannot be treated independently from the underlying bulk (interfaces) and the surroundings

Wetting graphene

The redox couples in the ambient provide the mechanism for electron exchange

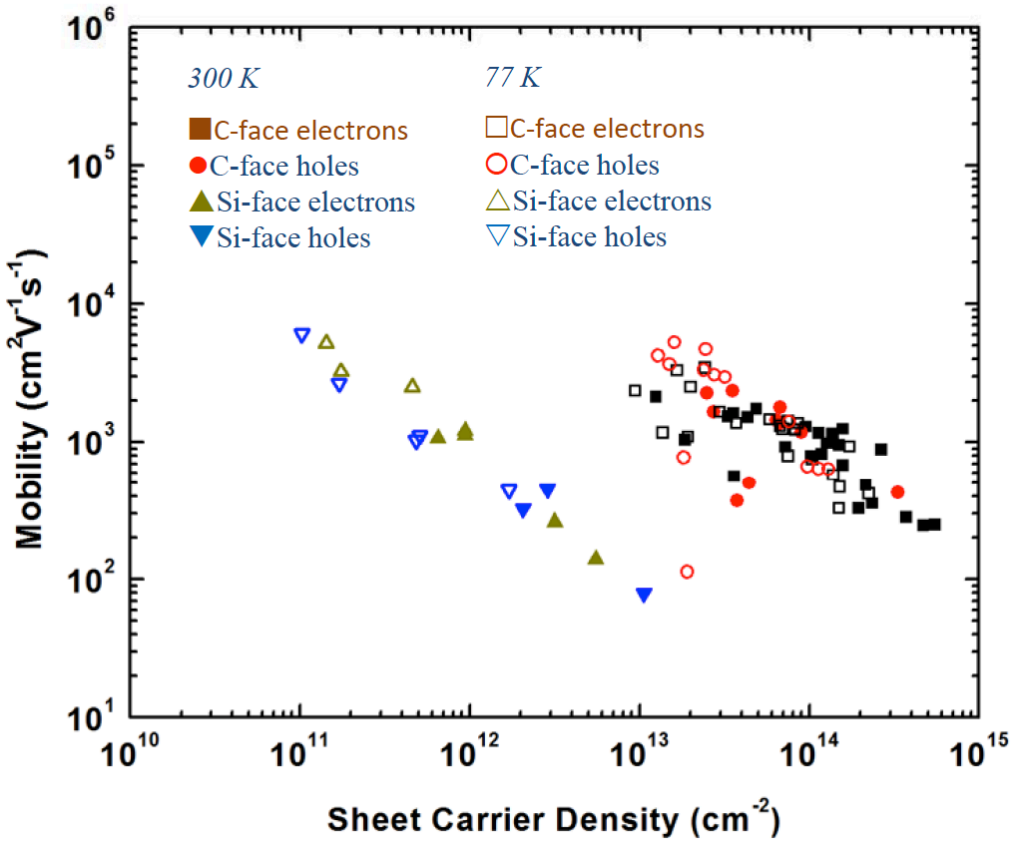


Graphene provides a medium for electron exchange

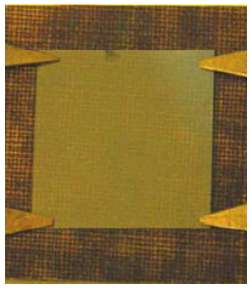
The SiC/graphene interface provides the electronic boundary conditions through the formation of the interface states that pin E_F

Future graphene devices will be constrained by surroundings engineered to affect desirable properties

More experimental evidence



van der Pauw Hall measurements on 16 x 16 mm^2 wafers
Various growth times, pressures and temperatures



Data from K. Gaskill *et al*.

Both n & p-type observed for each face
Wetting plays a similar role on both SiC terminations

Universal phenomenon!

Summary

- *First principles theory of the electronic and transport properties of epitaxial graphene on SiC*
- Notes on methodology
- Graphene systems for device applications
  - Electronic transport in mono- and bi-layer graphene
  - Epitaxial graphene on SiC, importance of interface geometry
  - Wetting graphene: charge transfer equilibria in ambient-exposed epitaxial graphene

http://ermes.physics.ncsu.edu

Credits: T. Jayasekera, J. Mullen, Y. Chen, S. Xu, K.W. Kim, K. Borysenko, K. Gaskill, A. Sidorov, G. Sumankasekera, A. Calzolari.

$$$: NCCS-ORNL, NSF, DOE, DARPA

Codes: quantum-ESPRESSO, WanT