Interface effects on the structural, electronic and transport properties of graphene grown on SiO_2

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Why Graphene?

- First 2D atomic crystal
- High electron mobility: $2.5 \cdot 10^5 cm^2 V^{-1} s^{-1}$ (Silicon $< 1400 cm^2 V^{-1} s^{-1}$)
- High thermal conductivity: above 3000 W mK^{-1}
- Impermeability to any gases
- Young's modulus $\sim 1 TPa$
- optical absorption $\sim 2.3\%$
- readily chemically functionalized

Applications

- Electronics
  - Touch screen; e-paper
  - Logic Transistors
- Photonics
- Energy storage
- Paints and coating
- Bioapplications

Production and processing

Mass production: scalable processes

- Micromechanical cleavage
- Liquid phase exfoliation
- Thermal exfoliation
- Chemical Vapour Deposition (CVD)
- Synthesis on SiC

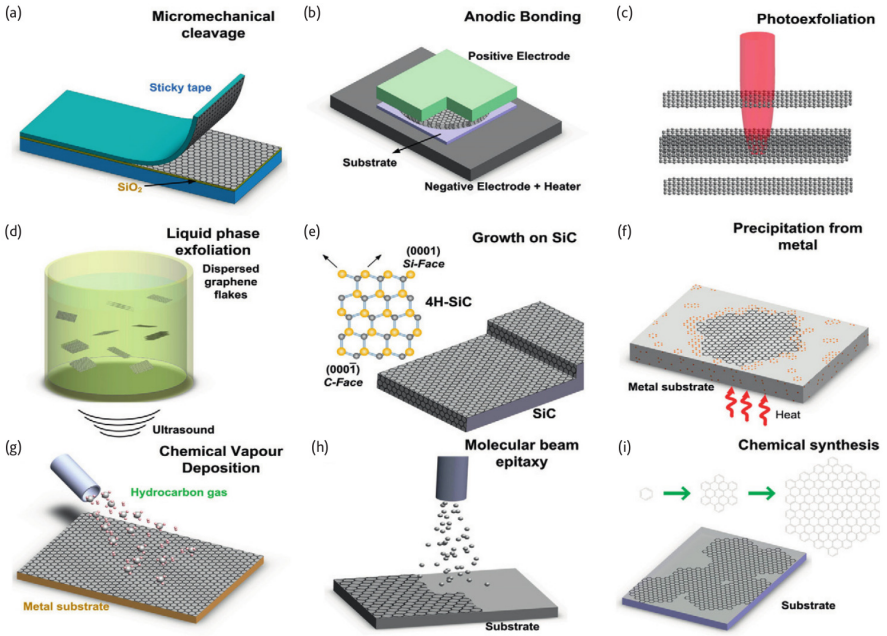


Figure : F. Bonaccorso et. al.,Materials Today **15**, 564 (2012) "Production and processing of graphene and 2d crystals"

Graphene/SiO_2

Why Graphene/SiO_2 interface?

- Different attempts to synthesize Graphene call for accurate theoretical investigation.
- It is essential to understand and control at the nanoscale its interaction with the supporting substrates.
- SiO_2 is one of the most important and common substrate for application in electronic.

Theoretical base (I)

- Electrons and nuclei Hamiltonian

$$H_{tot} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_I \frac{\mathbf{P}_I^2}{2M_I} + \sum_i V_{nucl}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J} \frac{z_I z_J e^2}{|\mathbf{R}_J - \mathbf{R}_J|}$$

$$V_{nucl}(\mathbf{r}) = -\sum_I \frac{z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}$$

Density Functional Theory (DFT)

- Hohemberg-Kohn Theorem: bijective relation charge density$\leftrightarrow$Potential
- Kohn-Sham equations
  - $\left[-\frac{\hbar^2\nabla^2}{2m} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$
  - $V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$.

Theoretical base (II)

Exchange-Correlation functionals

- Local-Density-Approximation (LDA)
  $E_{xc}^{LDA}[n] = \int \epsilon_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$
- Generalized Gradient Approximation (GGA)
  $E_{xc}[n(\mathbf{r})] = \int \epsilon_{xc}(n(\mathbf{r}))F_{xc}\Big(n(\mathbf{r}), |\nabla n(\mathbf{r})|\Big)n(\mathbf{r})d\mathbf{r}$

Hybrid functional: with HF exchange

- HSE*sol*: Screened-Coulomb PBEsol (GGA) functional combined with PBEsol correlation

SiO_2 E_{GAP}:

- BLYP(GGA):$\sim 6eV$
- HSEsol:$\sim 8.3eV$
- Experimental:$\sim 8.9eV$

Theoretical base (III)

Hellmann-Feynman's Theorem and the geometrical optimization problem

- $H(\lambda) \rightarrow H_e(\mathbf{r};\mathbf{R})$
- $H_e(\lambda)\psi_n(\mathbf{r};\mathbf{R}) = E_n(\lambda)\psi_n(\mathbf{r};\mathbf{R})$
- $\langle\psi_m(\mathbf{r};\lambda)| \frac{\partial H(\lambda)}{\partial\lambda_i} |\psi_m(\mathbf{r};\lambda)\rangle = \frac{\partial E_m}{\partial\lambda_i}$

Maximally-Localized Wannier Functions

- $w_{n\mathbf{R}}(\mathbf{r}) = \frac{V}{(2\pi)^3)} \int_{BZ} \left[\sum_m U^{(\mathbf{k})}_{mn}\psi_{m\mathbf{k}}(\mathbf{r})\right] e^{-i\mathbf{k}\cdot\mathbf{R}} d^3k$
- $\Omega = \sum_n \left[\langle w_{n\mathbf{0}}|\mathbf{r}^2|w_{n\mathbf{0}}\rangle - \langle w_{n\mathbf{0}}|\mathbf{r}|w_{n\mathbf{0}}\rangle^2\right]$

KS-DFT codes

Quantum ESPRESSO (QE)

- Basis set: Plane-waves

CRYSTAL14

- Linear Combination of Atomic Orbitals (LCAO) approximation $\rightarrow$ Basis Set: Gaussian

WAN-T

- WANnier-Transport
  - Basis Set: Localized (Wannier) Functions
  - Landauer's approach: $T(E) = Tr(\Gamma_L G^r \Gamma_R G^a)$
  - $I(V,T) = \frac{2e}{h} \int T(E)[f(E-\mu_L) - f(E-\mu_R)]dE$

Graphene/SiO_2

- α-quartz SiO_2: 3D $\rightarrow$2D
  - Electronic band structure, projected band structure, geometry optimization
- Graphene mono-layer: Electronic band structure
- Graphene mono-layer on top SiO_2: geometry optimization, electronic band structure
- Electronic transport

SiO_2

α-quartz SiO_2 Bulk Crystal

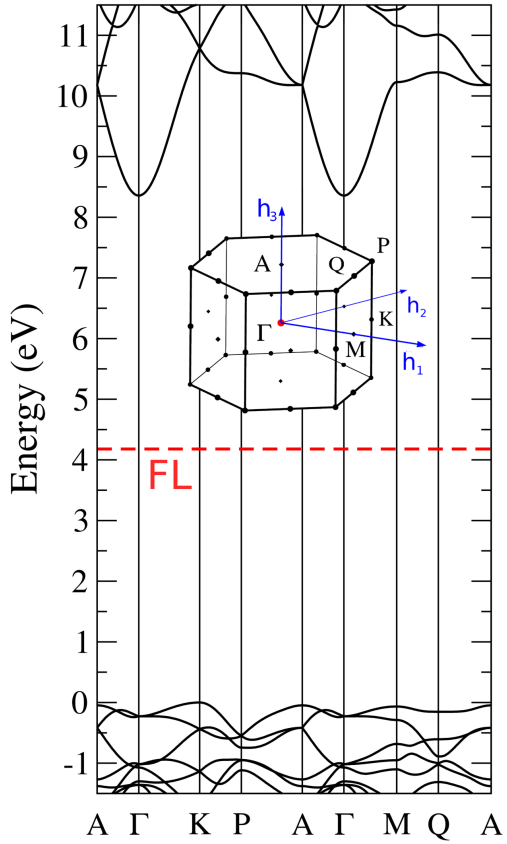
Primitive vectors:

$$\mathbf{t}_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right)$$
$$\mathbf{t}_2 = a\,(0, 1, 0)$$
$$\mathbf{t}_3 = c\,(0, 0, 1)$$

Reciprocal vectors

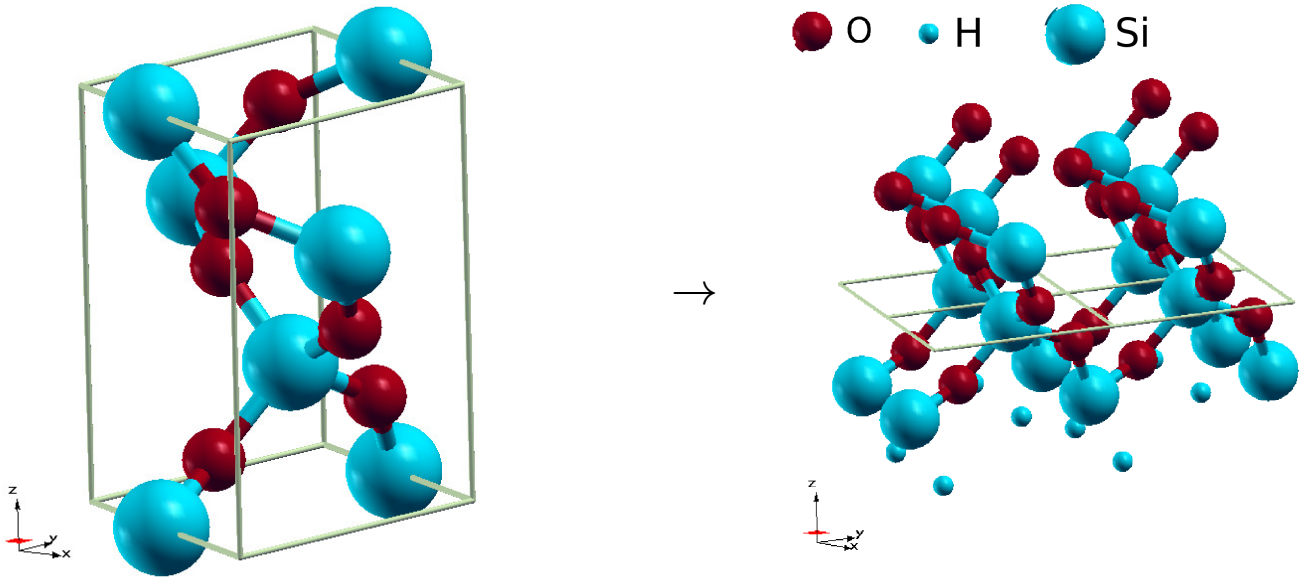
$$\mathbf{h}_1 = \frac{2\pi}{a}\left(\frac{2}{\sqrt{3}}, 0, 0\right)$$
$$\mathbf{h}_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 1, 0\right)$$
$$\mathbf{h}_3 = \frac{2\pi}{c}\,(0, 0, 1)$$

- a=4.913 Å, c=5.405 Å



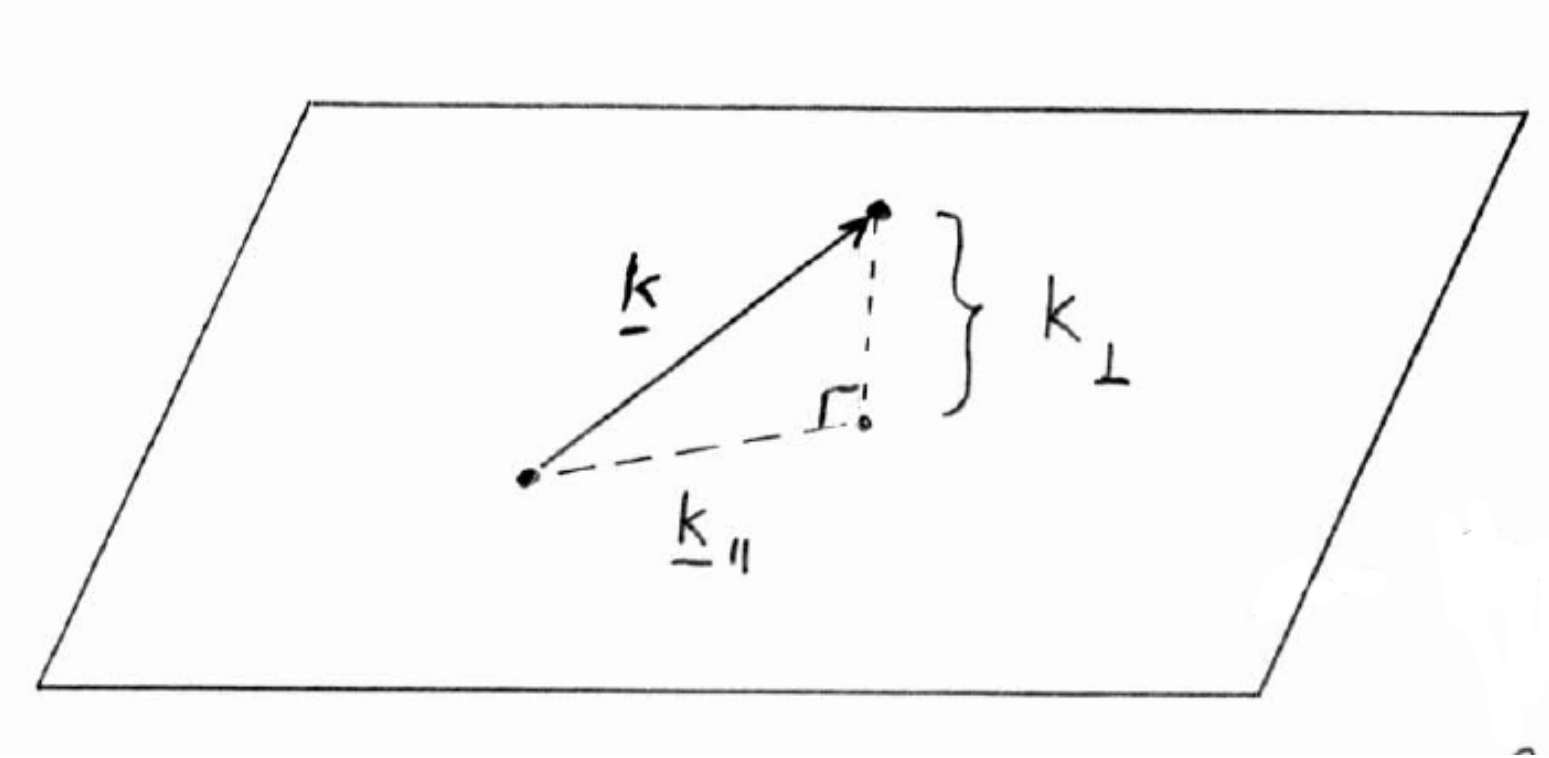
SiO_2: 3D→2D

Slabcut (0001) O-terminated Surface



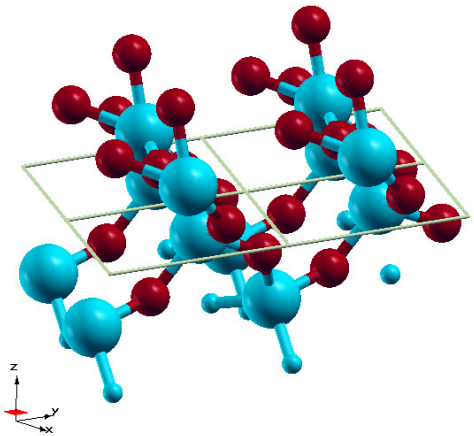
Projected Band Structure

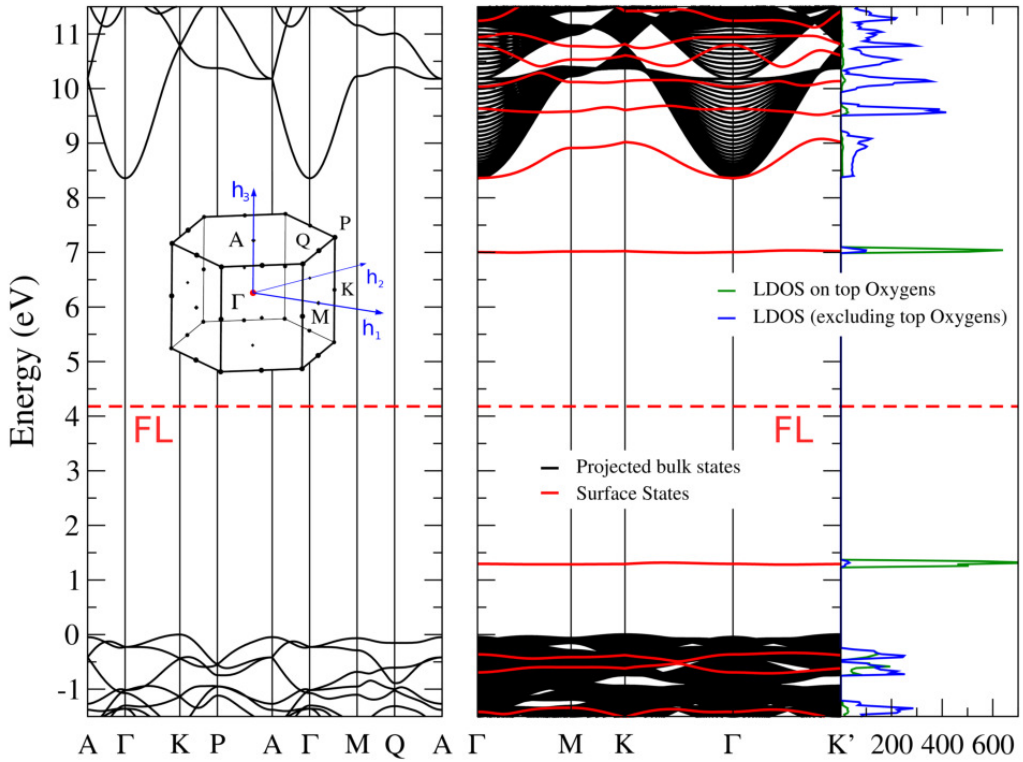
- $\mathbf{k}_{\parallel}$: component of $\mathbf{k}$ parallel to the surface
- $k_{\perp}$: component of $\mathbf{k}$ orthogonal to the surface



Geometrical relaxation with fixed cell parameters

The Total Energy minimization checks:
$\Delta E < 10^{-7}$ u.a., RMS of the gradient < 0.0003 a.u, RMS of the displacement < 0.0012 a.u.





Graphene

Primitive vectors 1x1 cell:

$\mathbf{t'}_1 = a' \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right)$

$\mathbf{t'}_2 = a' (0, 1, 0)$

Reciprocal vectors 1x1 cell:

$\mathbf{h'}_1 = \frac{2\pi}{a'} \left(\frac{2}{\sqrt{3}}, 0, 0\right)$

$\mathbf{h'}_2 = \frac{2\pi}{a'} \left(\frac{1}{\sqrt{3}}, 1, 0\right)$

Primitive vectors 2x2 cell:

$\mathbf{t}_1 = 2a' \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\right)$

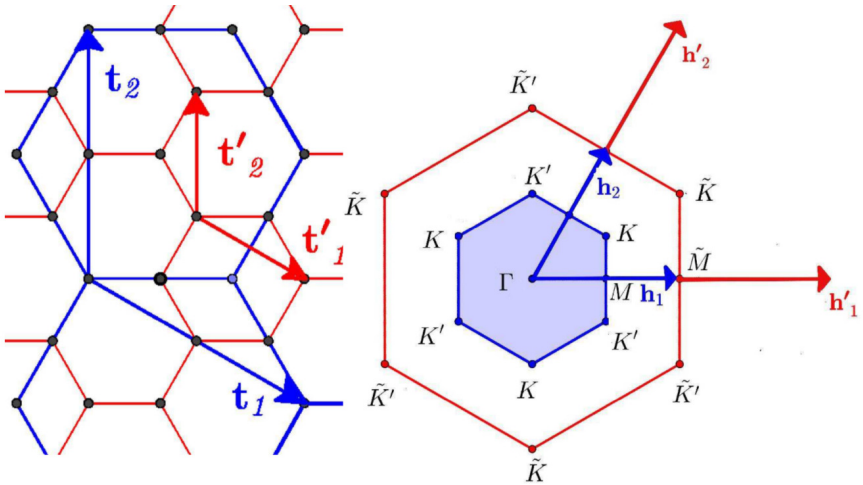
$\mathbf{t}_2 = 2a' (0, 1, 0)$

Reciprocal vectors 2x2 cell:

$\mathbf{h}_1 = \frac{2\pi}{2a'} \left(\frac{2}{\sqrt{3}}, 0, 0\right)$

$\mathbf{h}_2 = \frac{2\pi}{2a'} \left(\frac{1}{\sqrt{3}}, 1, 0\right)$

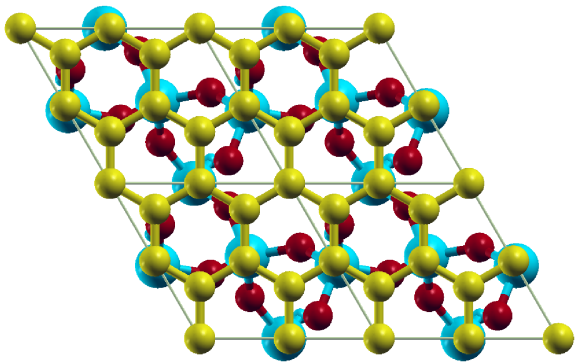
a=4.913Å, a'=2.464Å ($\frac{2a'-a}{a} \simeq 0.3\% \rightarrow$ for the calculations a=4.92Å,a'=2.46Å

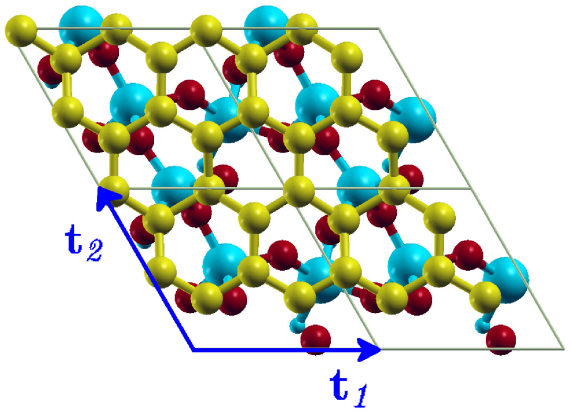


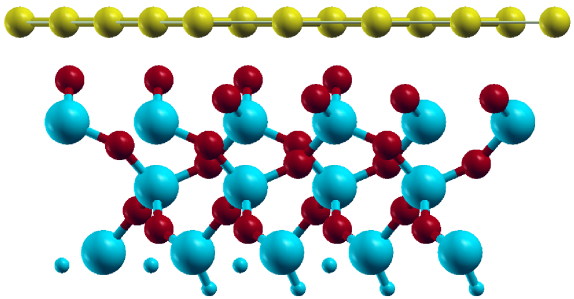
Graphene/SiO_2: Geometrical Relaxation (fixed cell parameter)

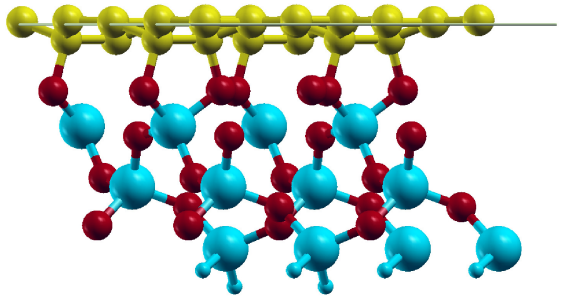
BEFORE

AFTER



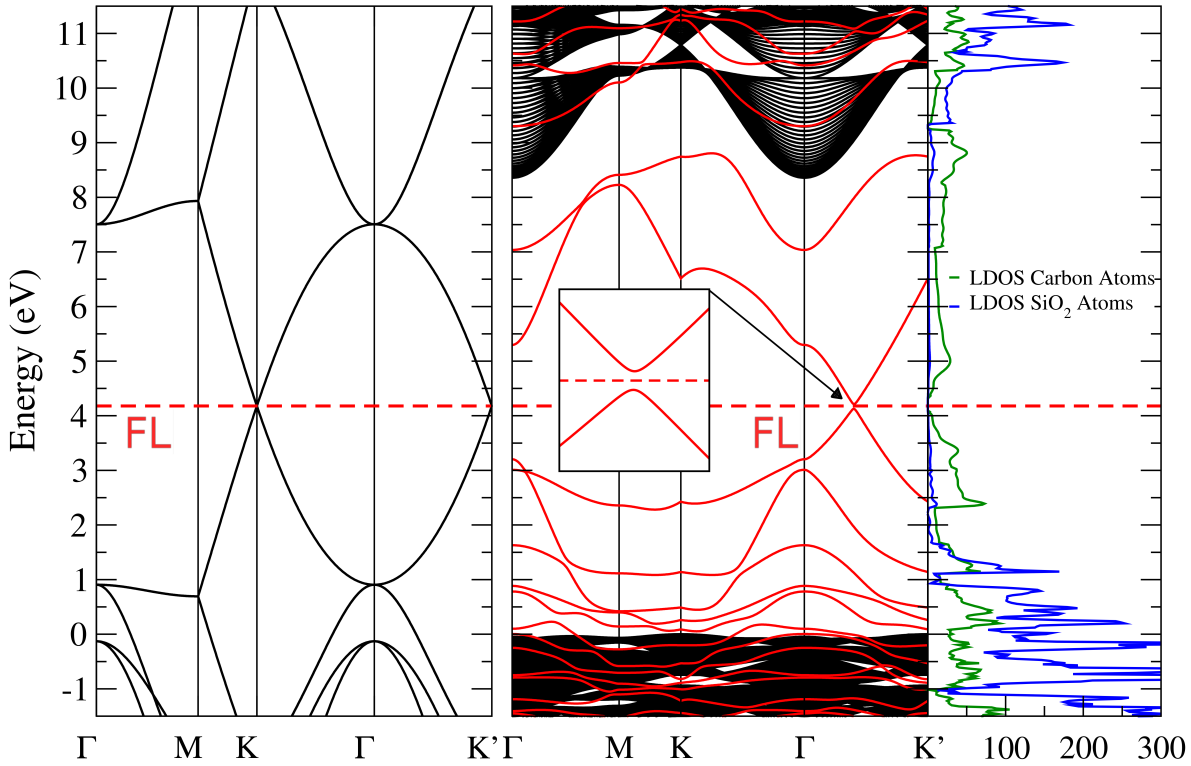






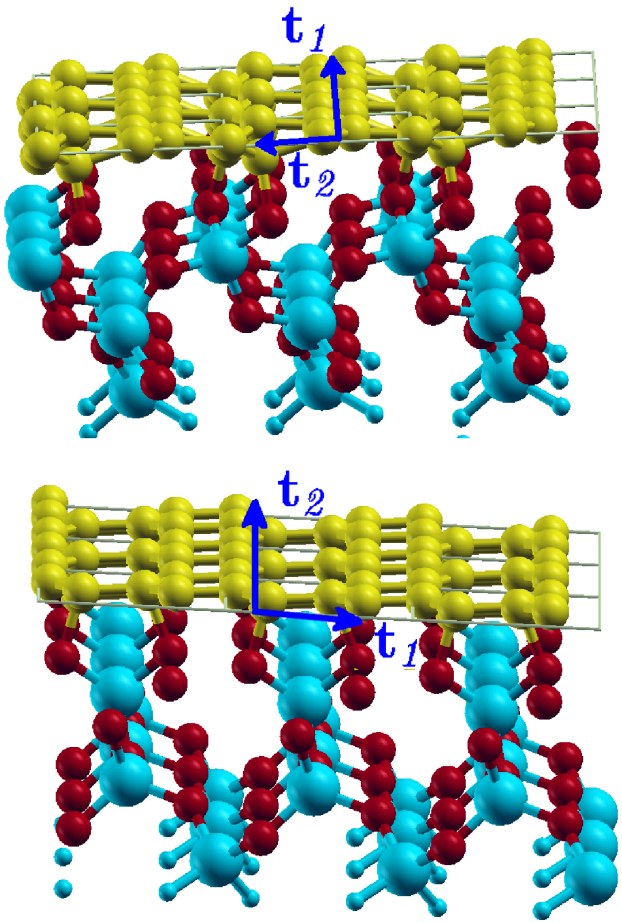
Graphene/SiO_2 bands structure

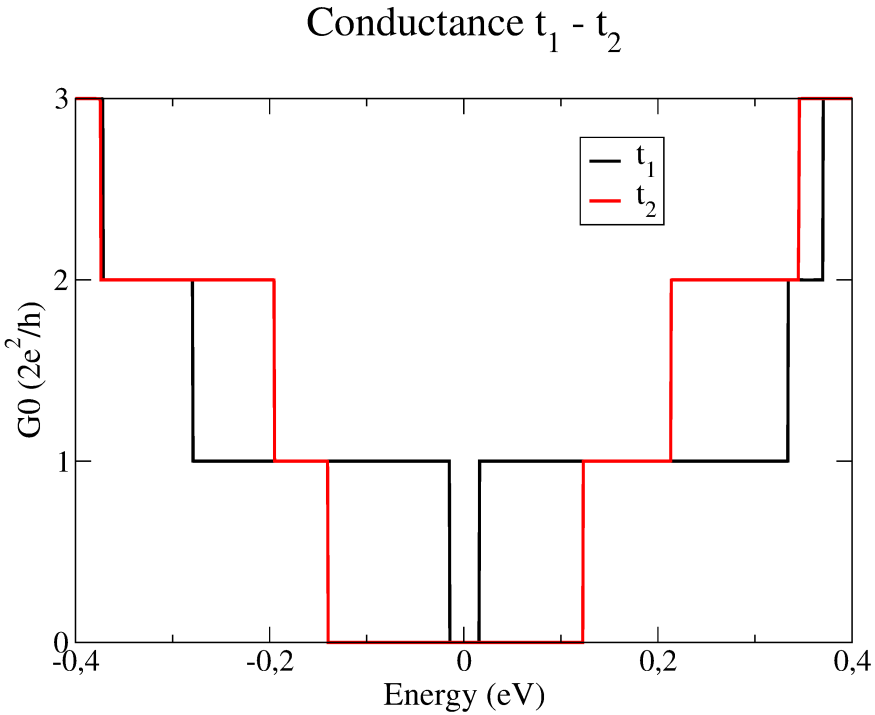
- Left: Graphene 2x2 cell
- Right: Graphene/SiO_2 relaxed with projected DOS Graphene/SiO_2



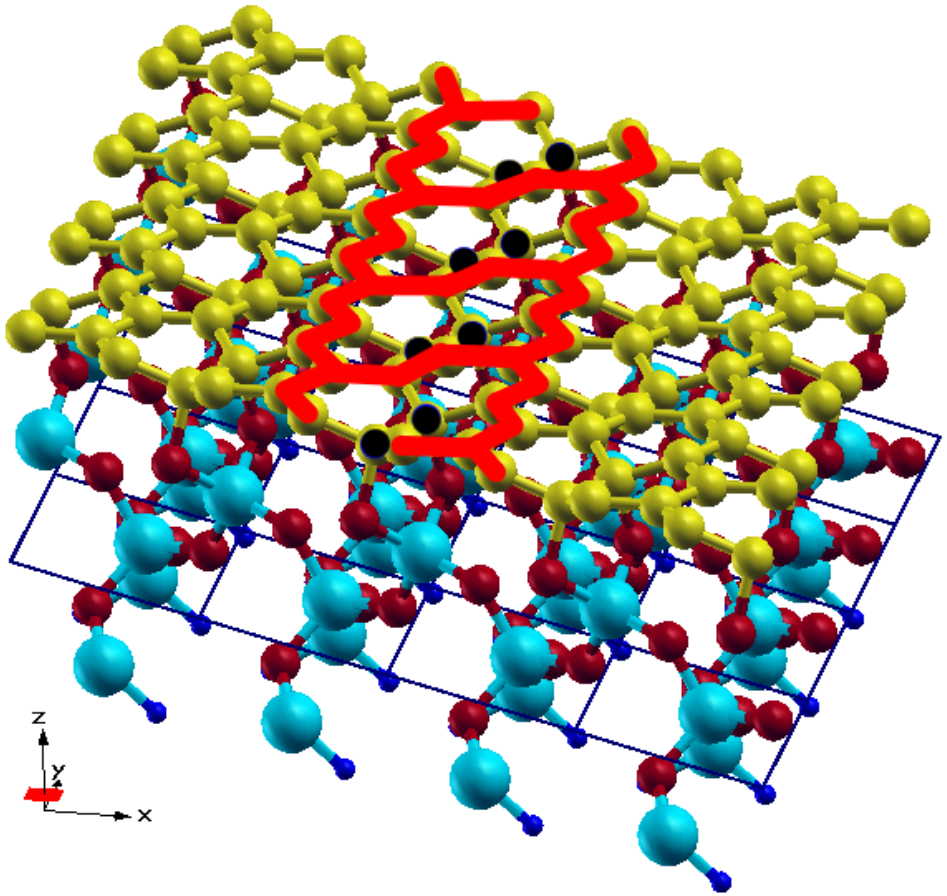
Asymmetry & Conductance

Landauer's approach: $T(E) = Tr(\Gamma_L G^r \Gamma_R G^a)$



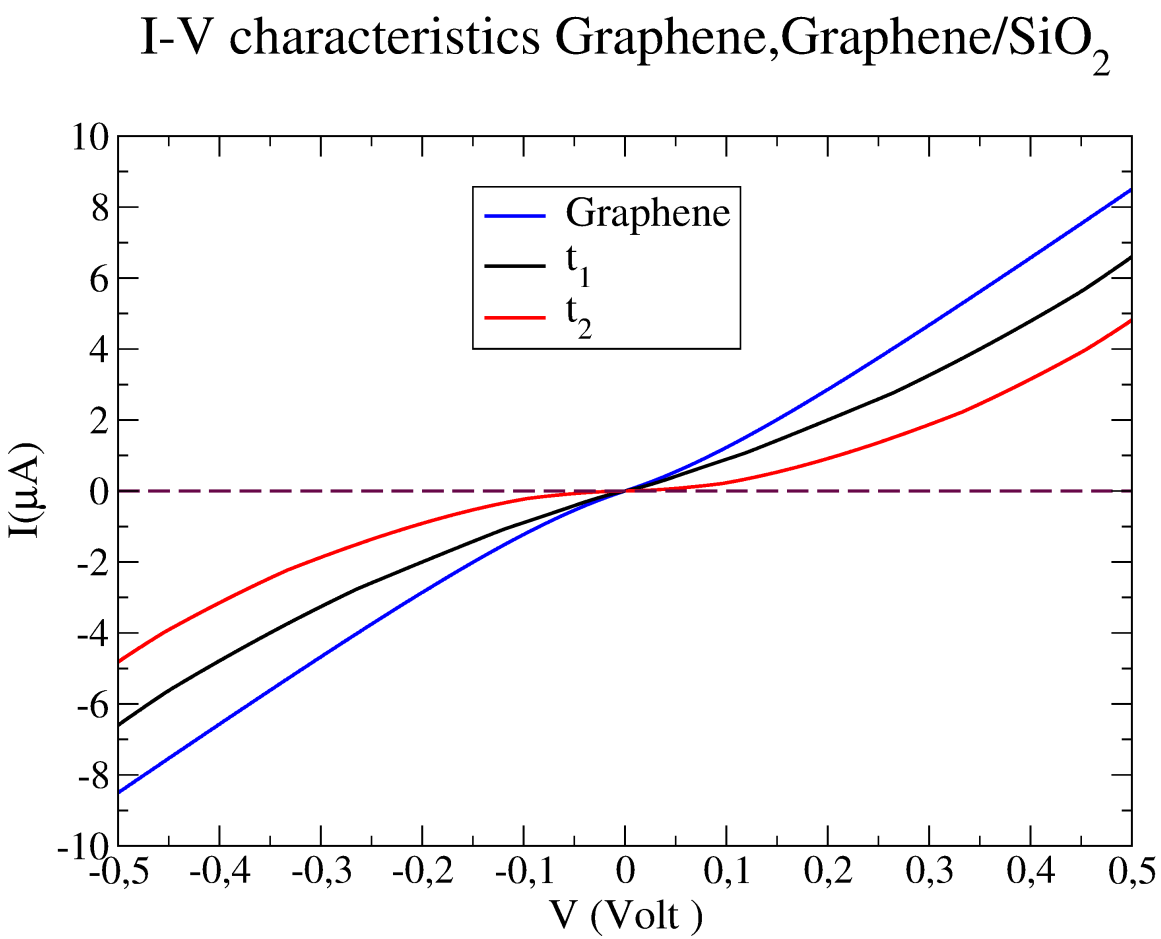


Conduction channels



I-V characteristics

$$I(V,T) = \frac{2e}{h} \int T(E)[f(E-\mu_L) - f(E-\mu_R)]dE$$



Conclusions

- Graphene/SiO_2 $\rightarrow$ corrugation: C-O covalent bonds
- Band gap opening, Band Profile modulation
- Modification of $\pi - \pi$ carbon conjugation: preferred directions for conduction

Parallel works

- OFET: PDIF-CN_2/Si(SiO_2)
- Electronic properties with H_{eff}
- Graphene/BN