Tailoring the electronic structure of epitaxial graphene on SiC(0001): transfer doping and hydrogen intercalation

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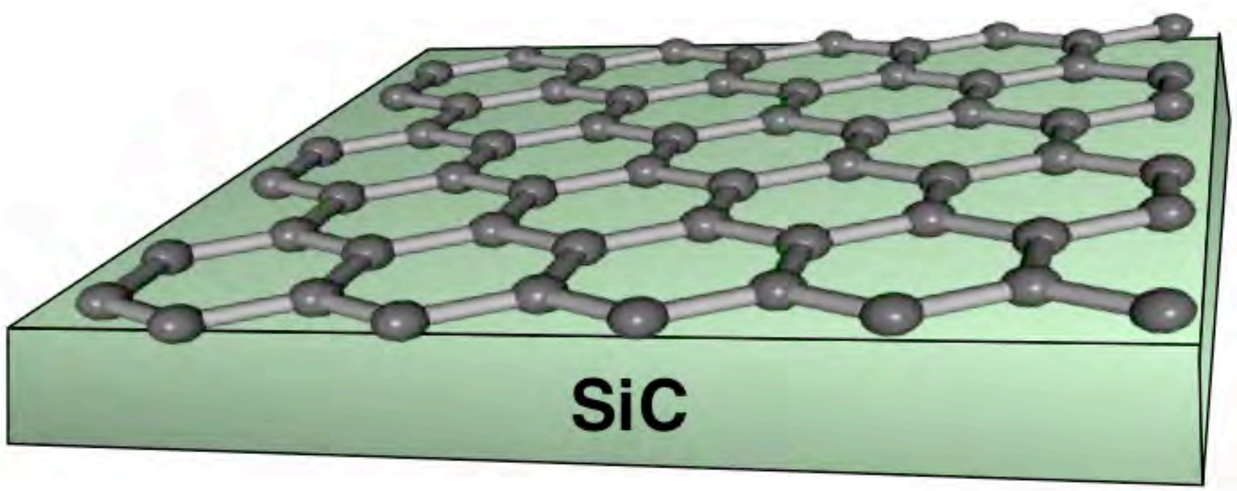
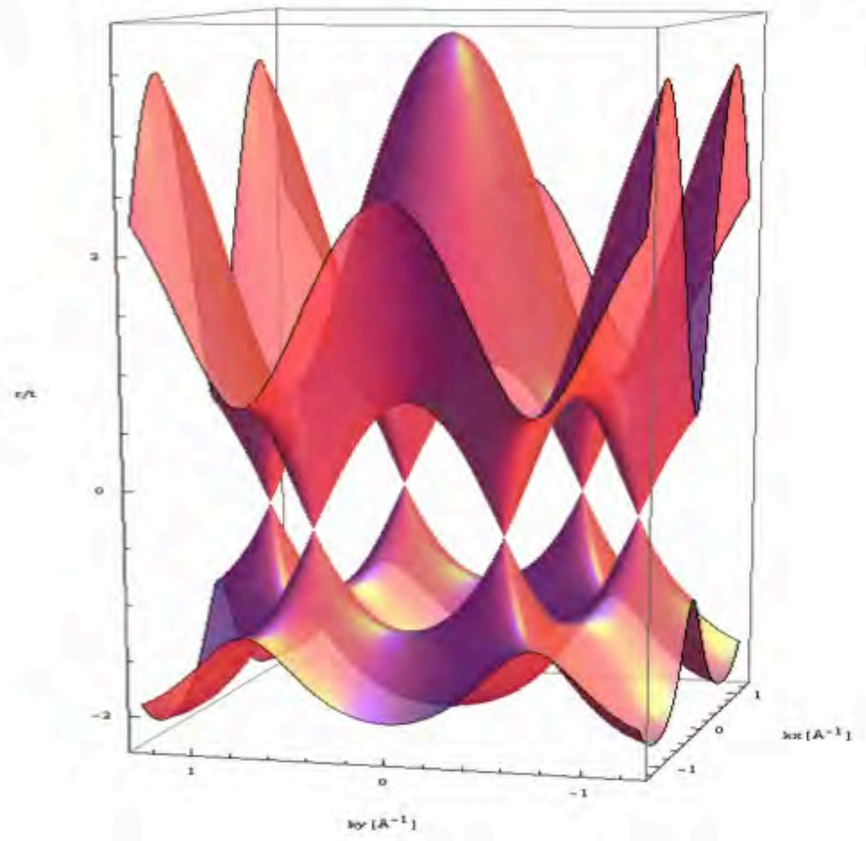
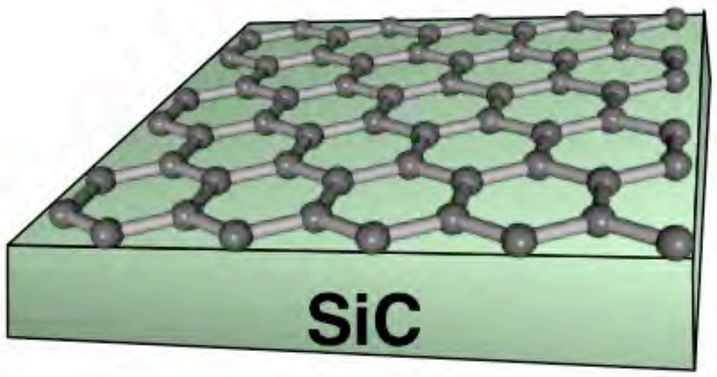




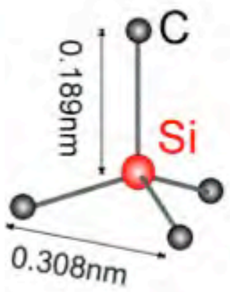
Epitaxial graphene on SiC

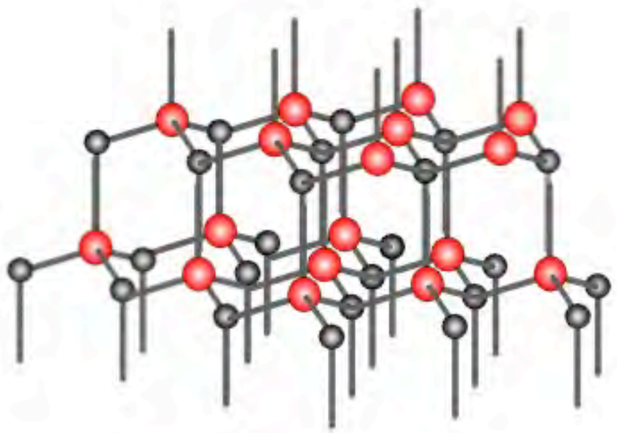


Graphene or thin graphite film forms on SiC surfaces upon annealing at high temperatures as a result of SiC decomposition

$$SiC \rightarrow Si_{(g)} + C_{(s)}$$

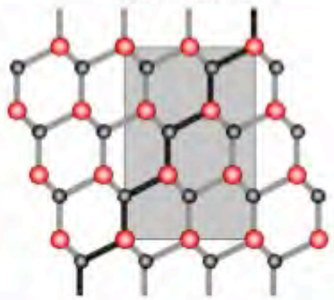
SiC Polytypes



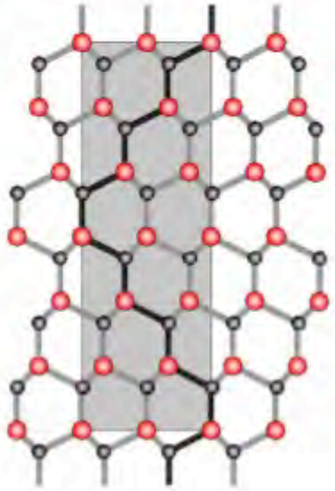


Bilayer of Si-C tetrahedra

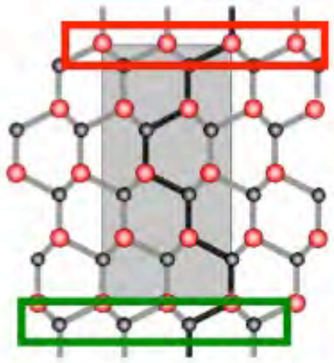
3C-SiC



6H-SiC



4H-SiC



Si-face SiC(0001) → **Graphene: Ordered stacking Good thickness control** ✓

C-face SiC(000$\bar{1}$) → **Graphene: Rotational disorder Poor thickness control**

A candidate for C-based electronics

Advantages:

- Insulating SiC substrate ➡ no transfer necessary
- Single crystal wafers up to 6” available
- Robustness and chemical inertness
- Uniform large area graphene with domains of hundreds of micrometers. **K.V. Emtsev et al., Nature Materials 8, 203 (2009)**

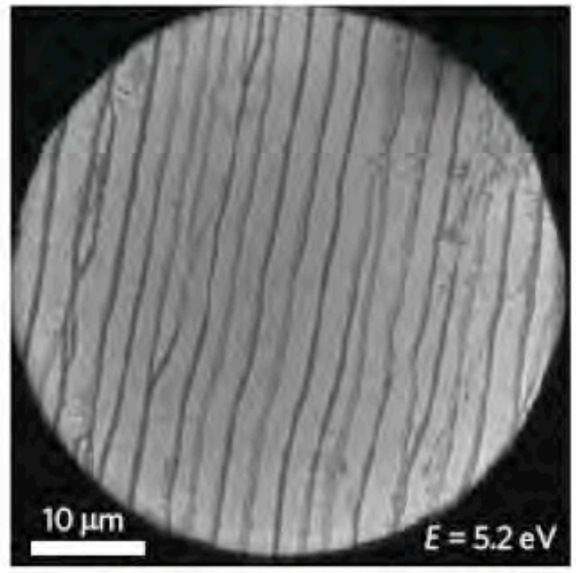


Image: K.V. Emtsev, Nat. Mater.

Applications of graphene on SiC:

- Field effect transistor
  J. Kedzierski, IEEE Trans. Electron Devices 55, 2078 (2008)
- High frequency transistors
  Y.-M Lin, et al., Science 327, 662 (2010)
- Metrology (quantum resistor standards)
  A. Tzalenchuk et al. Nature Nanotech. 5, 186 (2010)

2“ graphene-on-SiC wafer

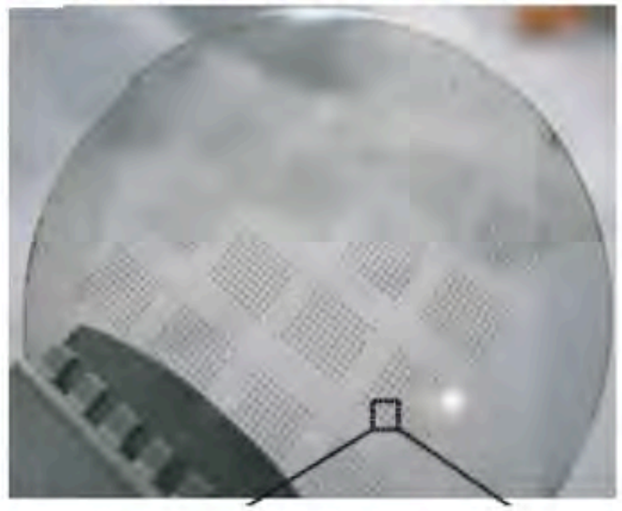
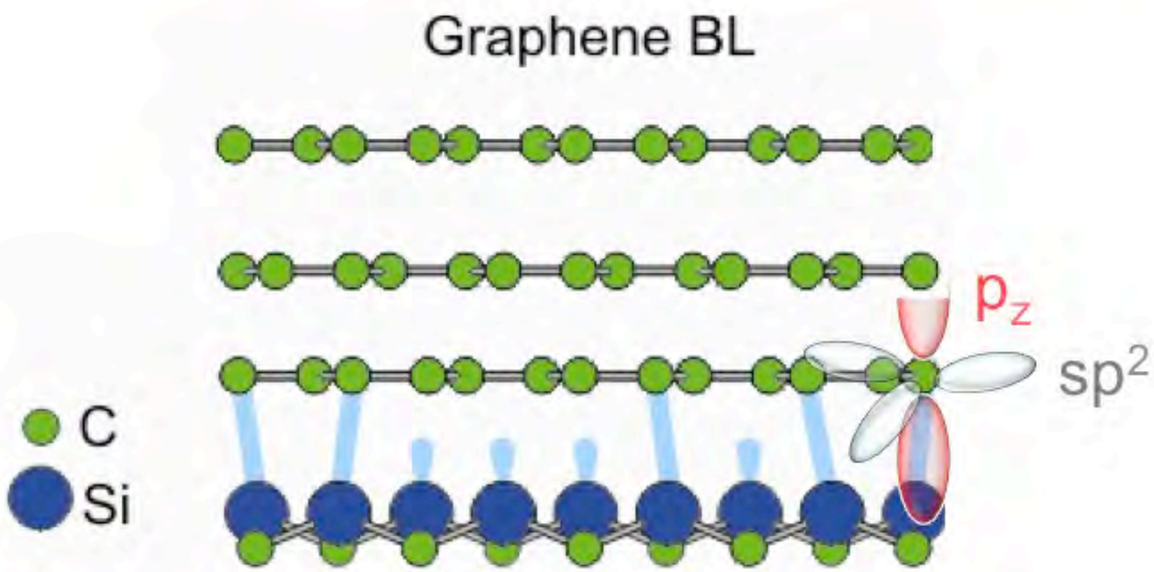


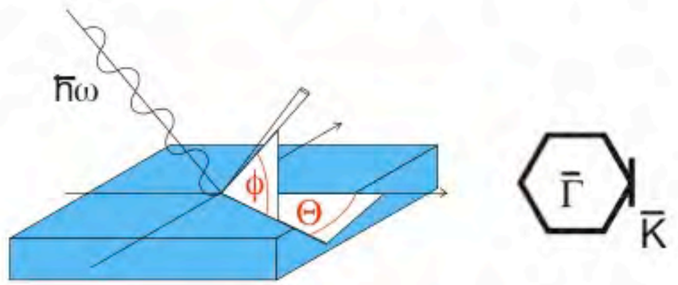
Image: Y.-M. Lin, Science

Understanding and controlling electronic properties

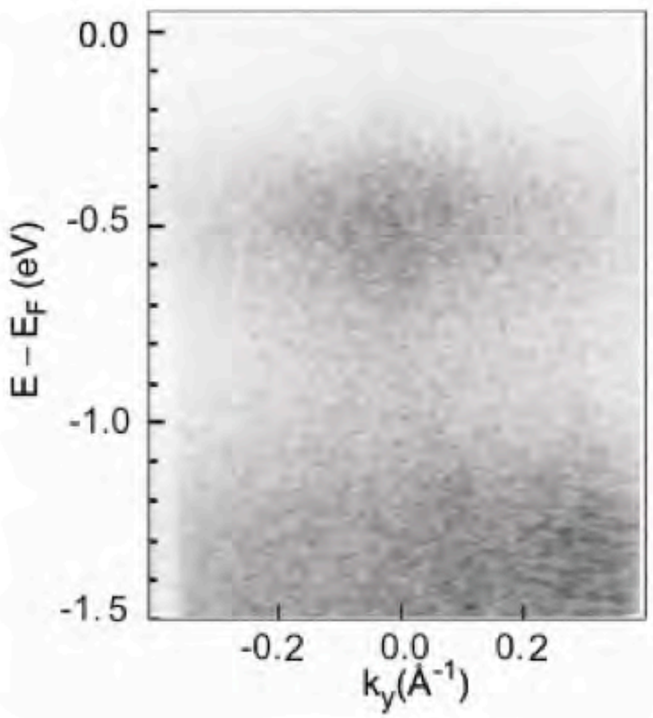
Graphene on SiC(0001): Band Structure

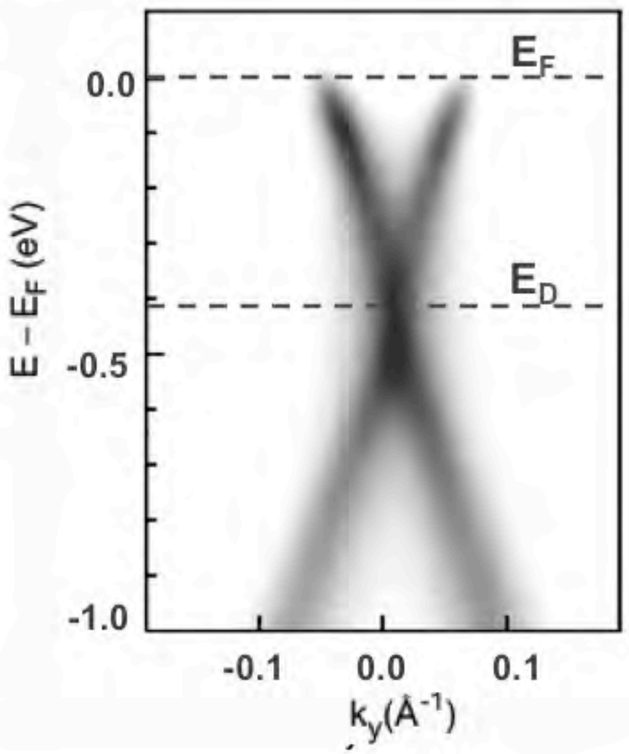


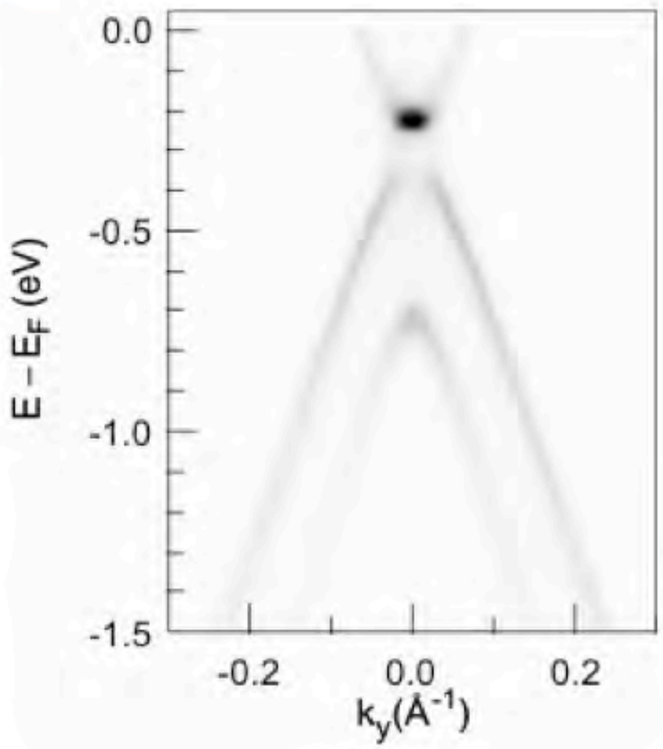
- **Zero-layer**: 30% of carbon atoms covalently bound to SiC: electronically dead
- **Monolayer**: Electron doped ~ 10^{13} cm^{-2}
- **Bilayer**: Electron doped , BG ~ 120 meV



ARPES



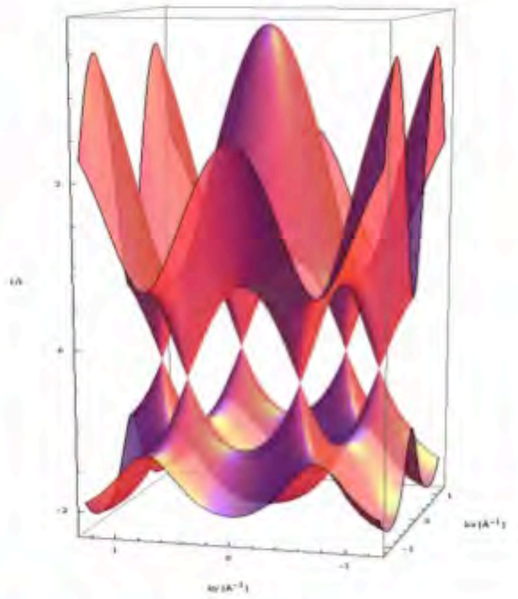




Graphene on SiC(0001): Drawbacks and Solutions

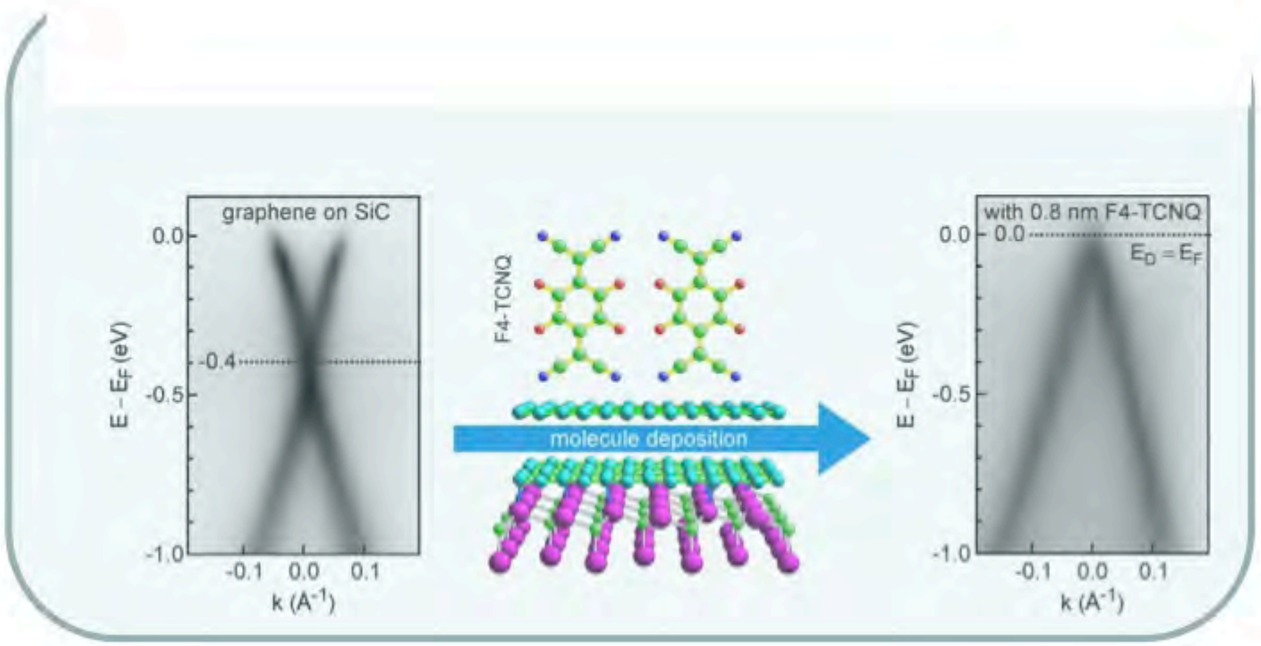
Limitations for electronic applications:

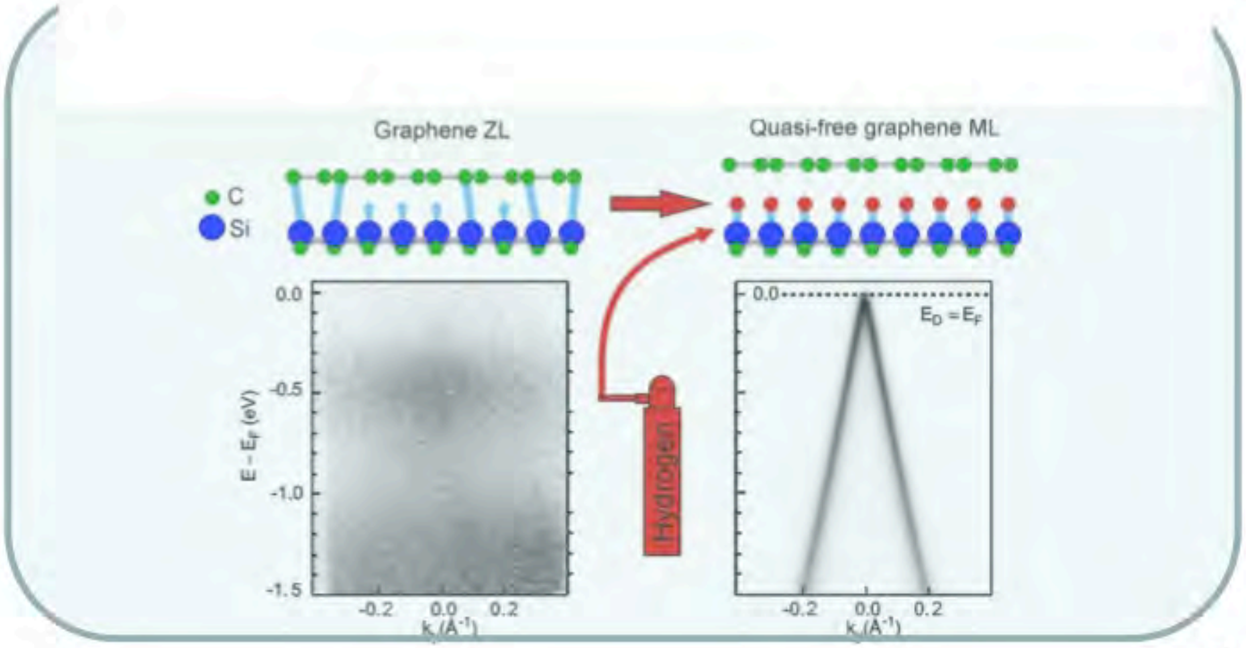
- High doping level ($n=1\cdot10^{13}$ cm^{-2})
- Small bandgap in BL
- Reduced charge carrier mobility (1000-3000 cm^2/Vs)



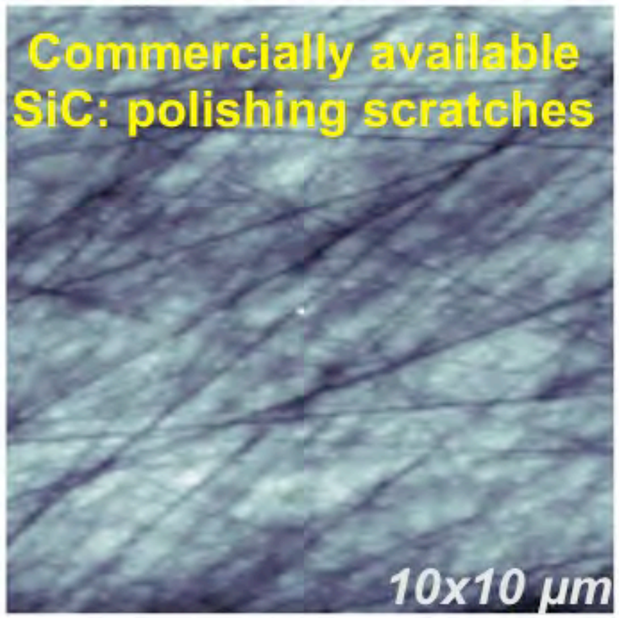
How to tune the electronic properties of graphene on SiC(0001)?

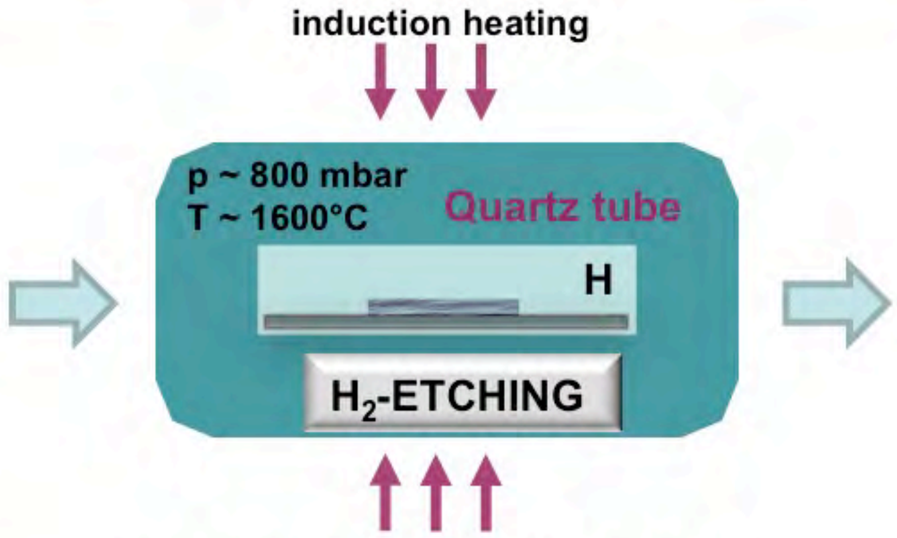
We present two solutions



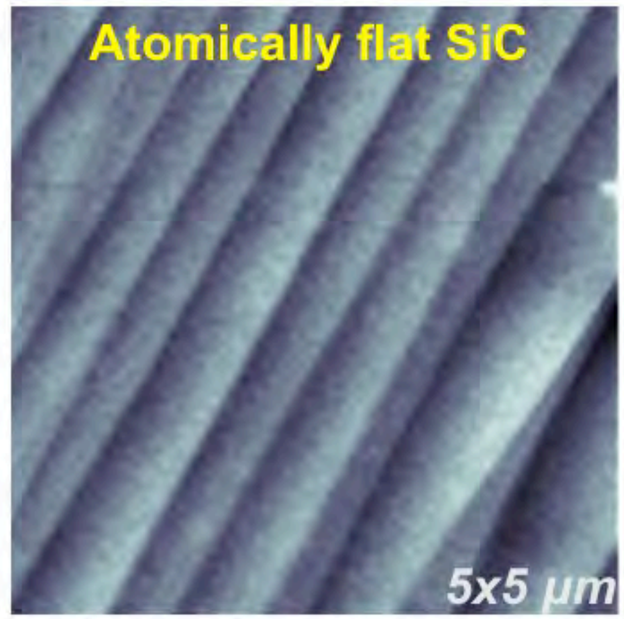


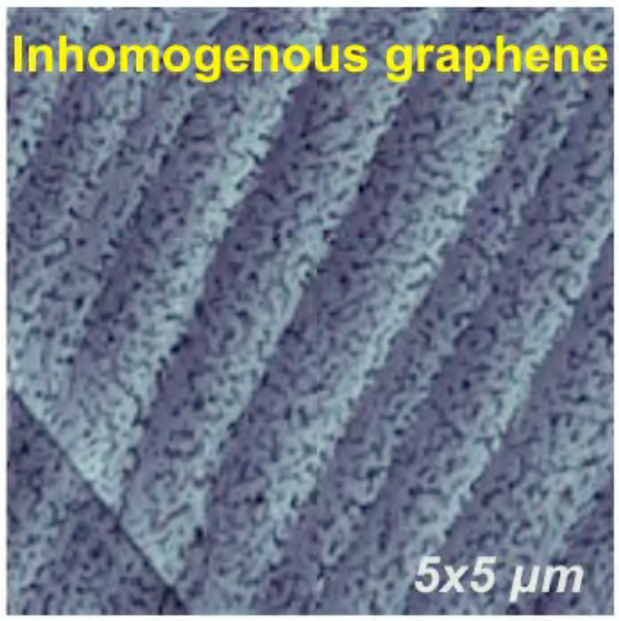
Grapene on SiC(0001): growth



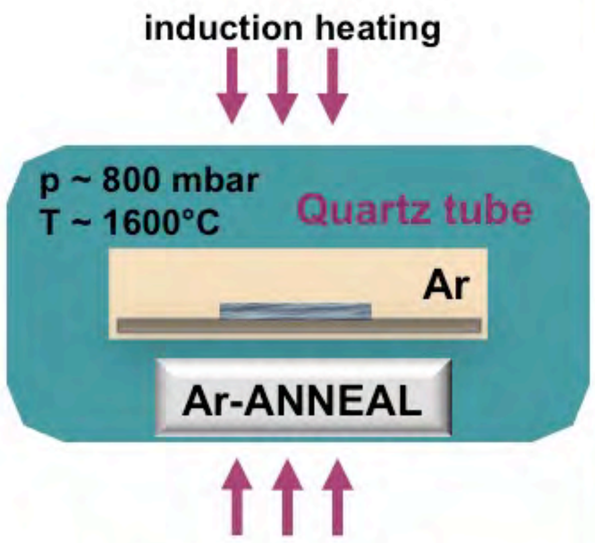


C. Coletti et al., *Appl. Phys. Lett.* 91, 061914 (2007)

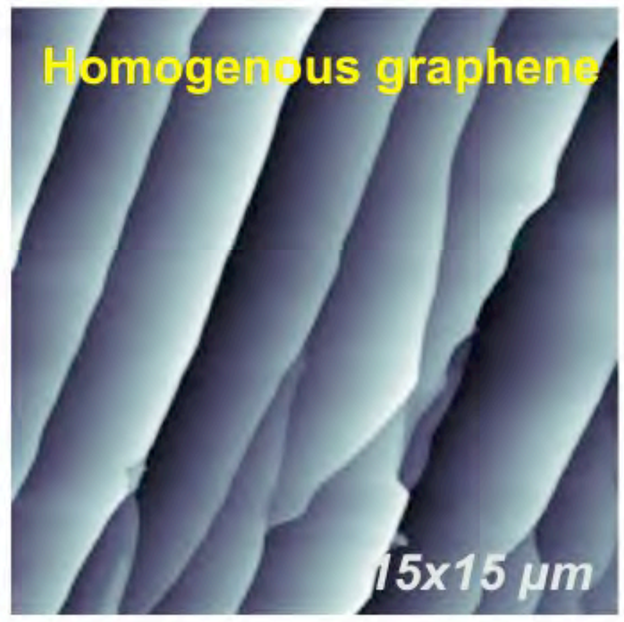




C. Riedl et al., PRB 76, 245406 (2007)



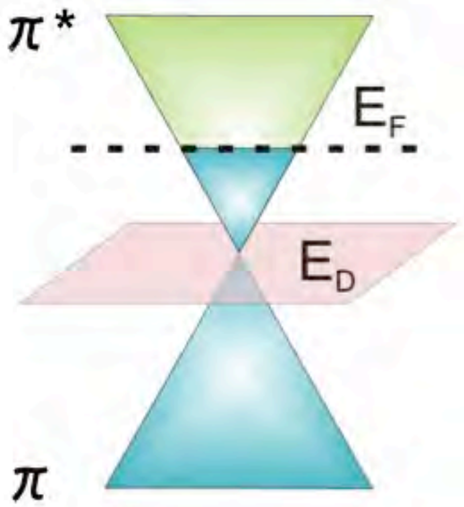
K.Emtsev et al., Nature Mater. 8, 203 (2009)

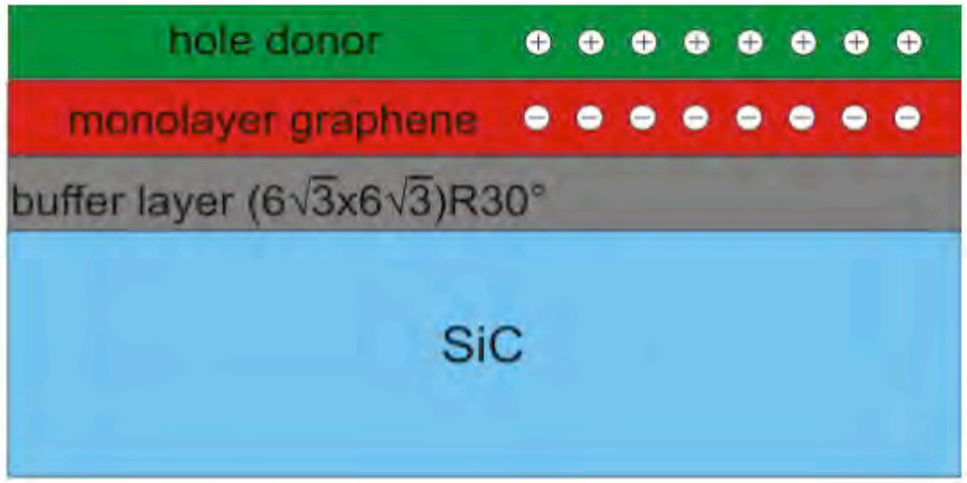


1° Solution: Molecular doping

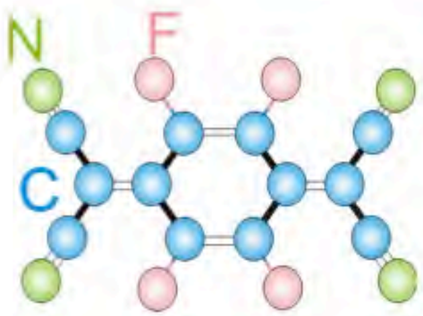
Molecular doping promising solution for excess charge compensation and band structure engineering

- Chemical functionalization of graphene surfaces with molecule presenting high electron affinity



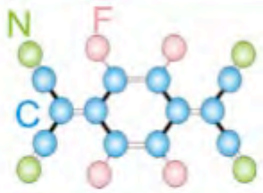


- **F4-TCNQ:** Tetrafluoro-tetracyanoquinodimethane

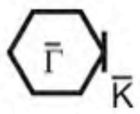


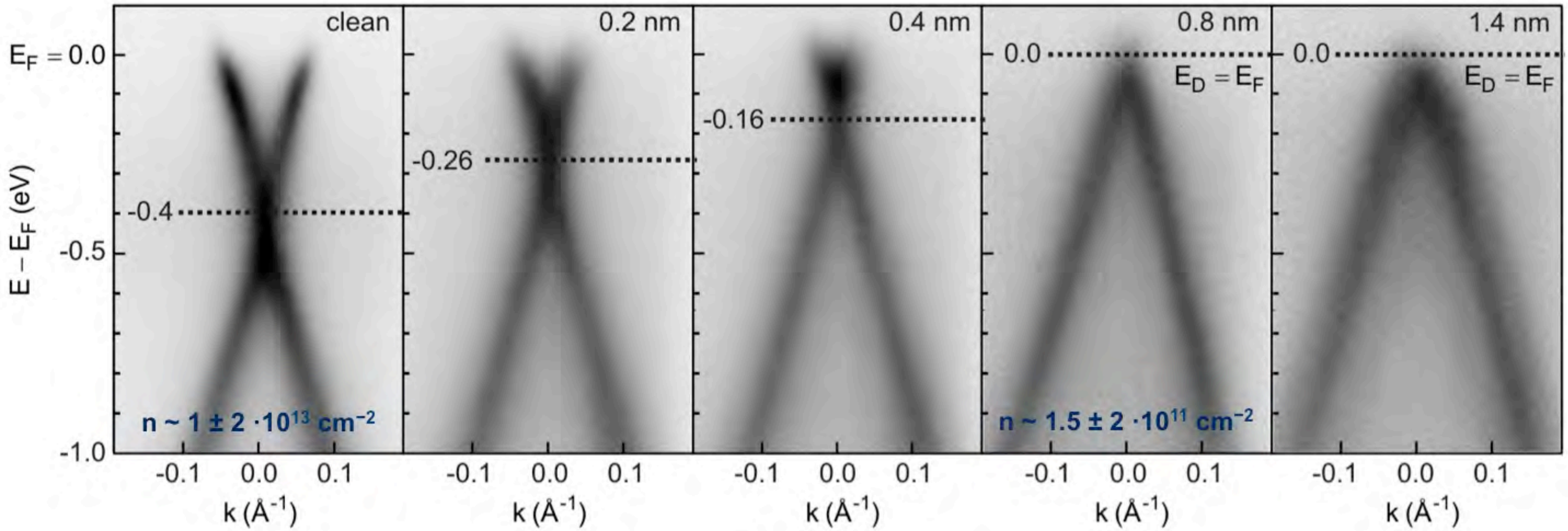
- electron affinity: 5.24 eV
- p-type dopant in OLEDs and carbon nanotubes

Back to charge neutrality with F4-TCNQ



increasing molecular coverage

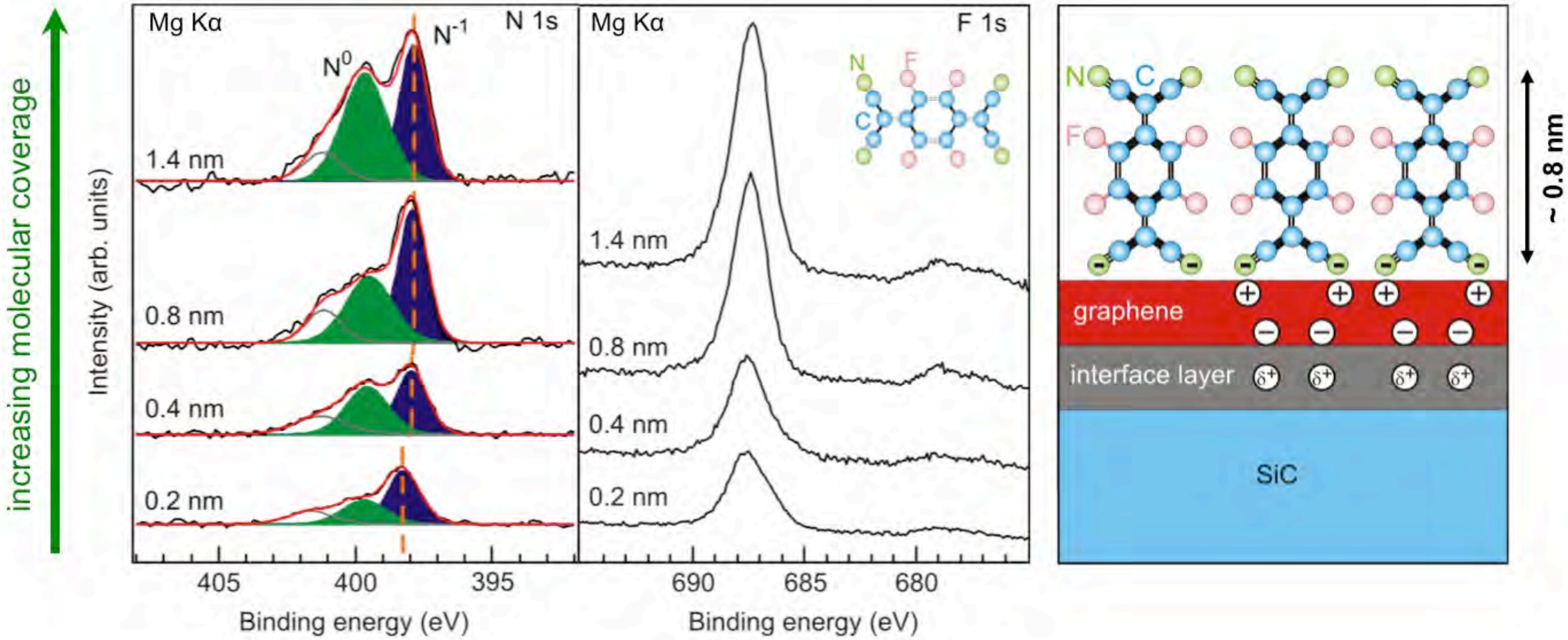




- Fermi level shifted back to Dirac energy for a molecular coverage of roughly 0.8 ML
- Band structure quality preserved
- Saturation of charge transfer for thicker films

C. Coletti, et al., PRB 81, 235401(2010)

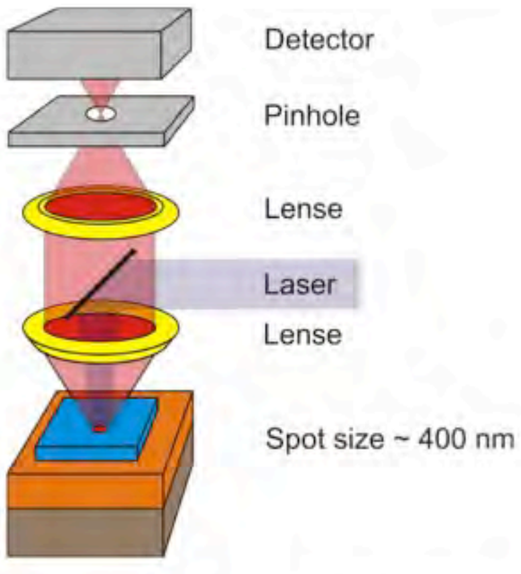
XPS core levels



- Anion species N^{-1} at 398.2 eV and neutral species N^0 at 399.6 eV
- F passive, charge transfers through cyano groups
- Core levels shifted by 0.4 eV

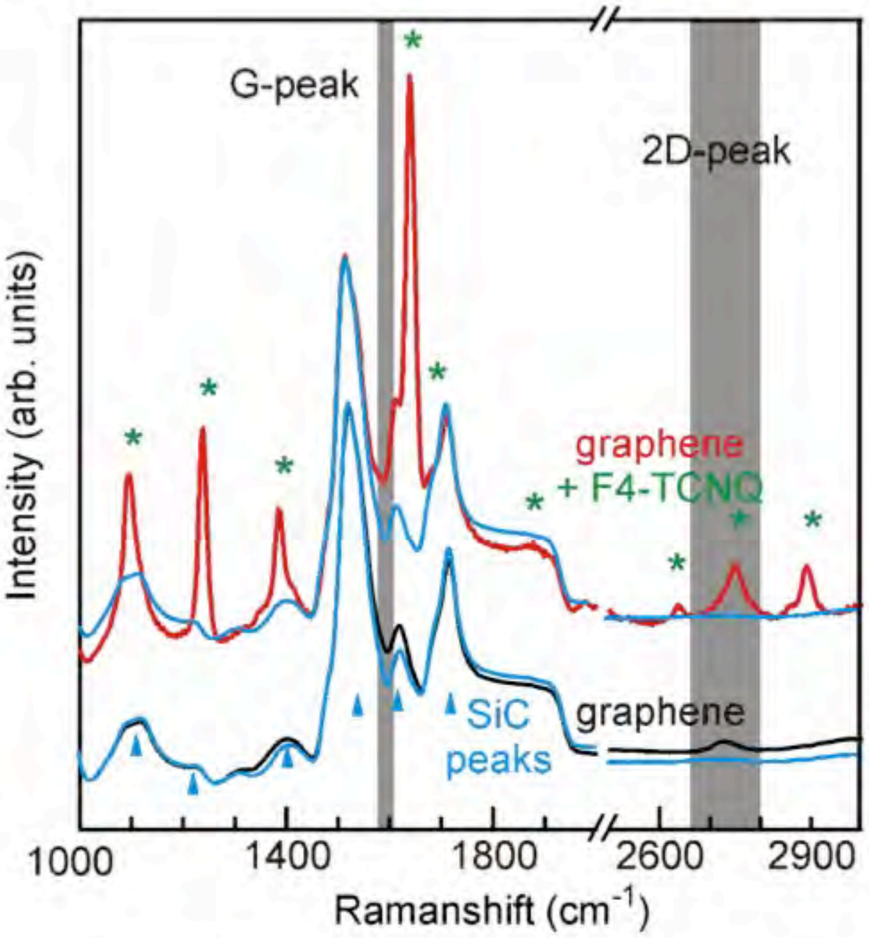
- 0.4 <t< 0.8 nm: ~45% of the cyano groups are uncharged (N^0)→ in the condense film most of the molecules are standing upright

Raman spectroscopy

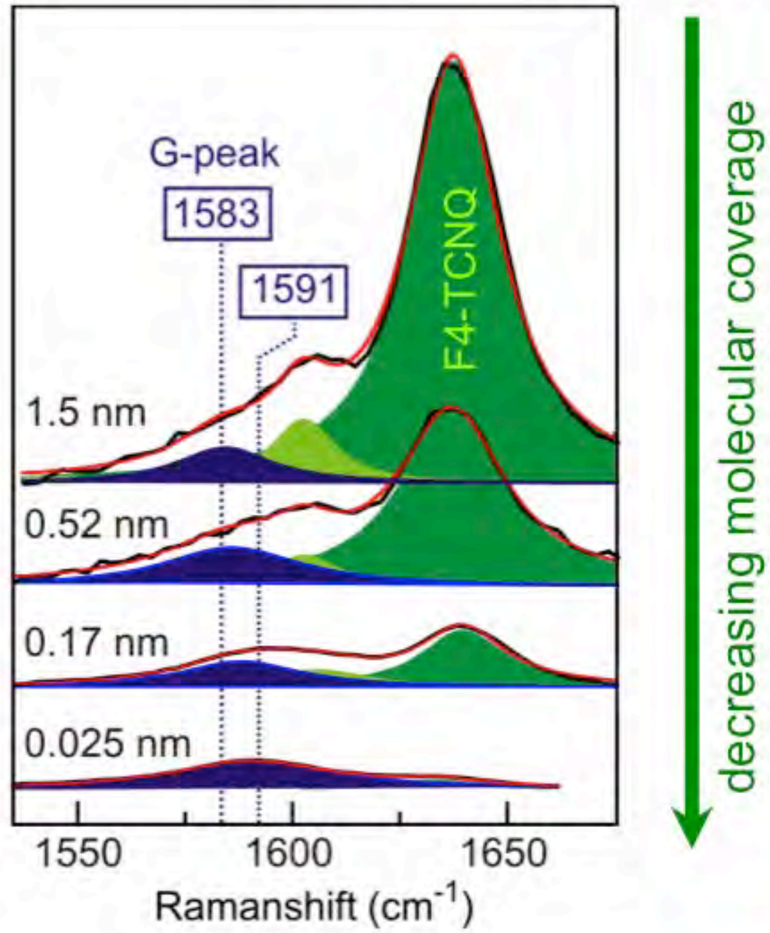


(488 nm Ar^+ laser)

Raman spectra

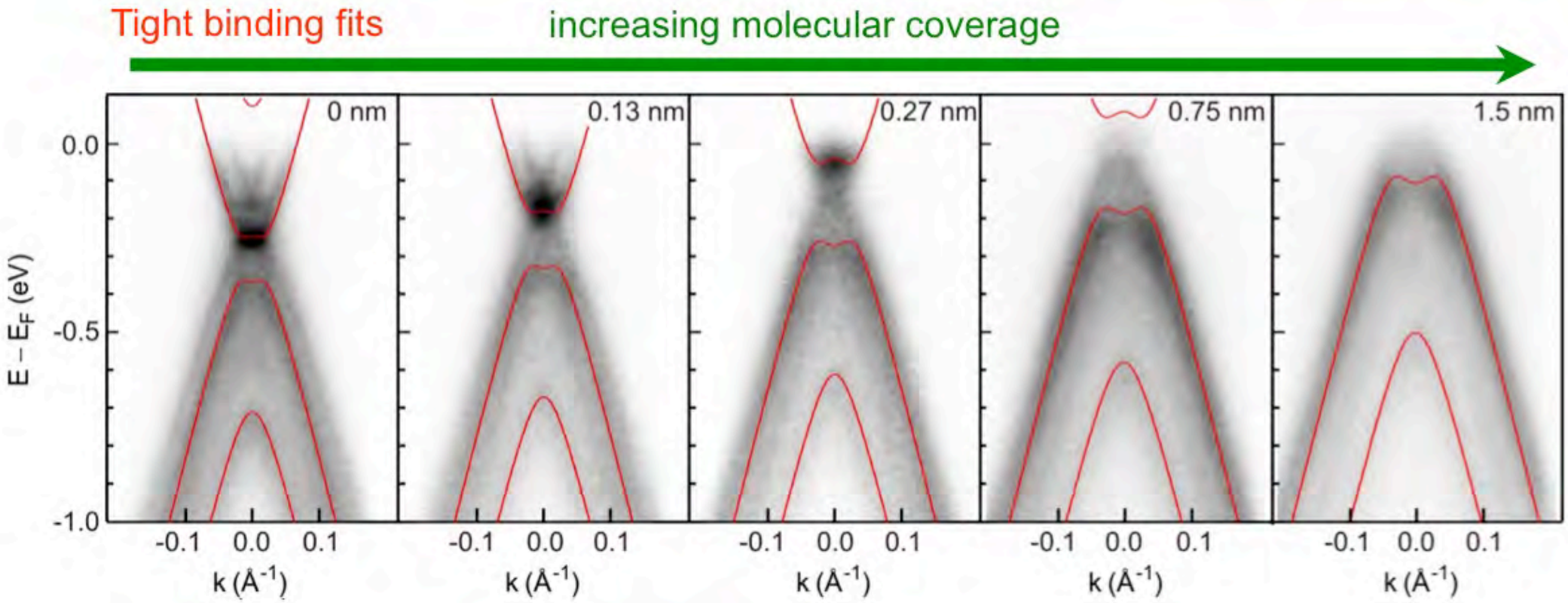


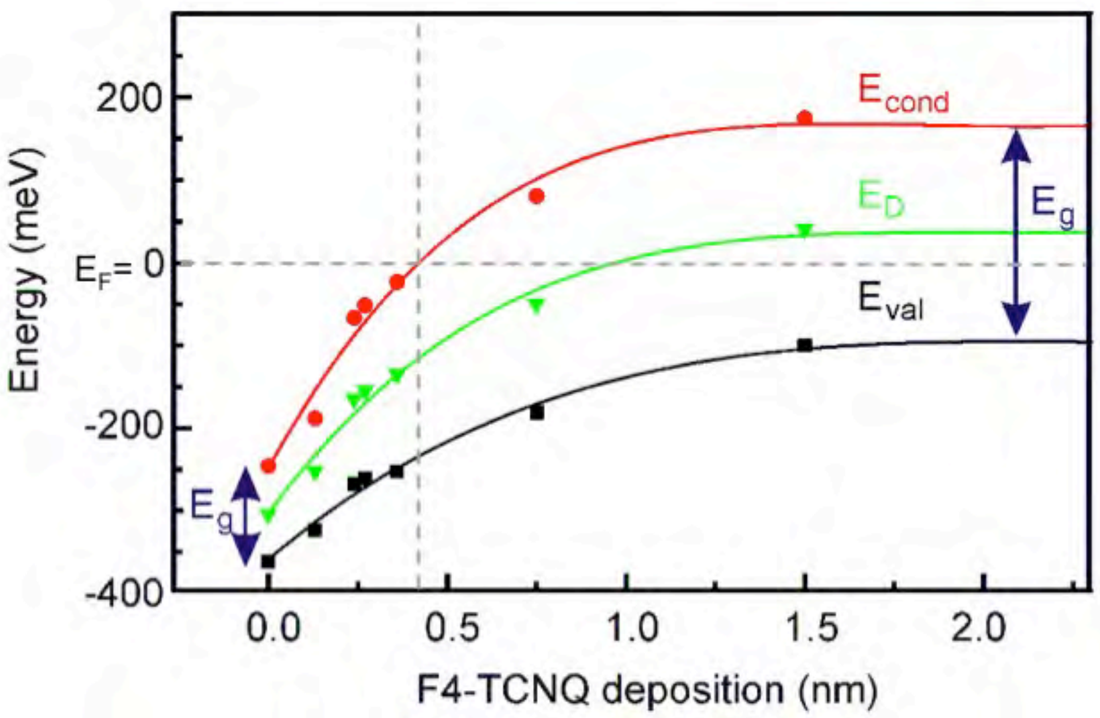
Differential G peak region



- Layers removed by laser exposure
- G-peak position indicates charge neutrality
- Blue-shift of G-peak upon molecule trimming: increasing n-type doping

F4-TCNQ on epitaxial bilayer graphene



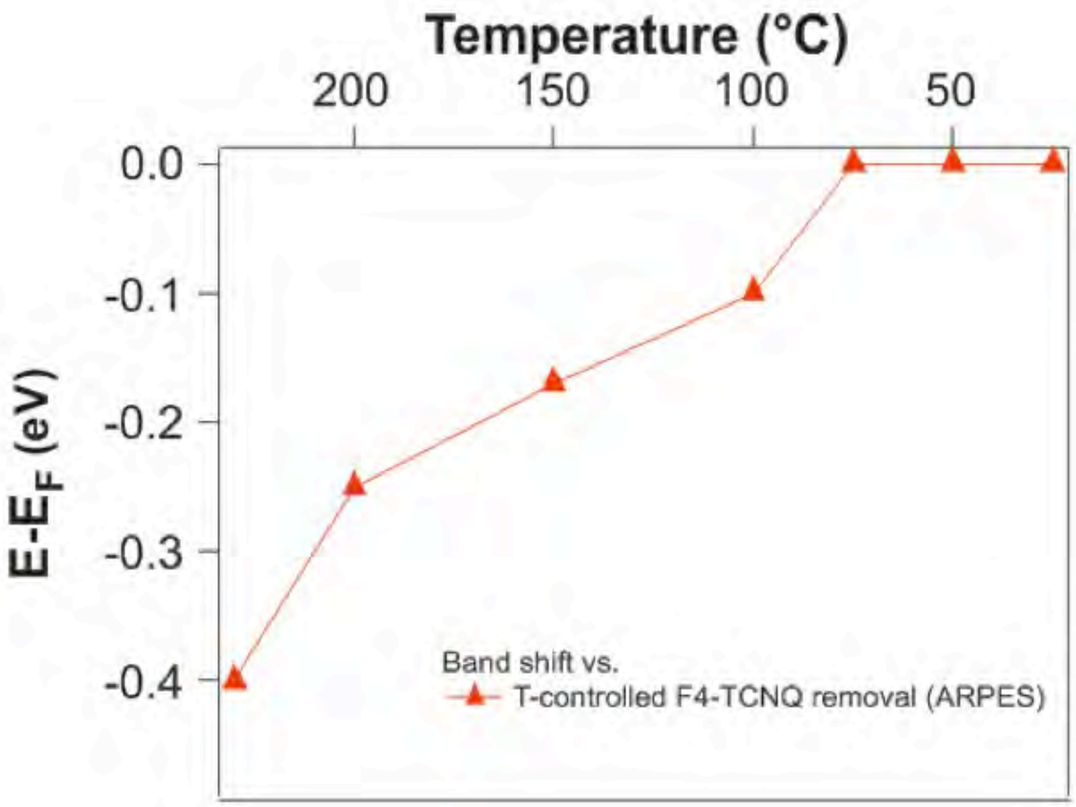


- Hole doping
- Charge transfer saturation
- Band gap increases: from 116 to 275 meV
- Semiconducting @ 0.4 nm

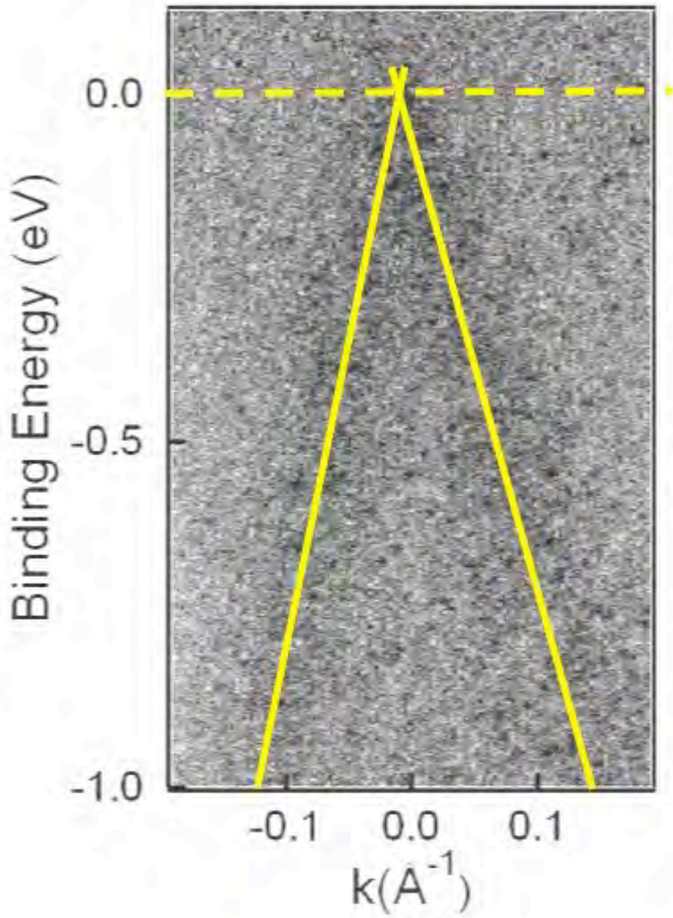
FET with acceptable on/off ratio possible

Robustness of F4-TCNQ on epitaxial graphene

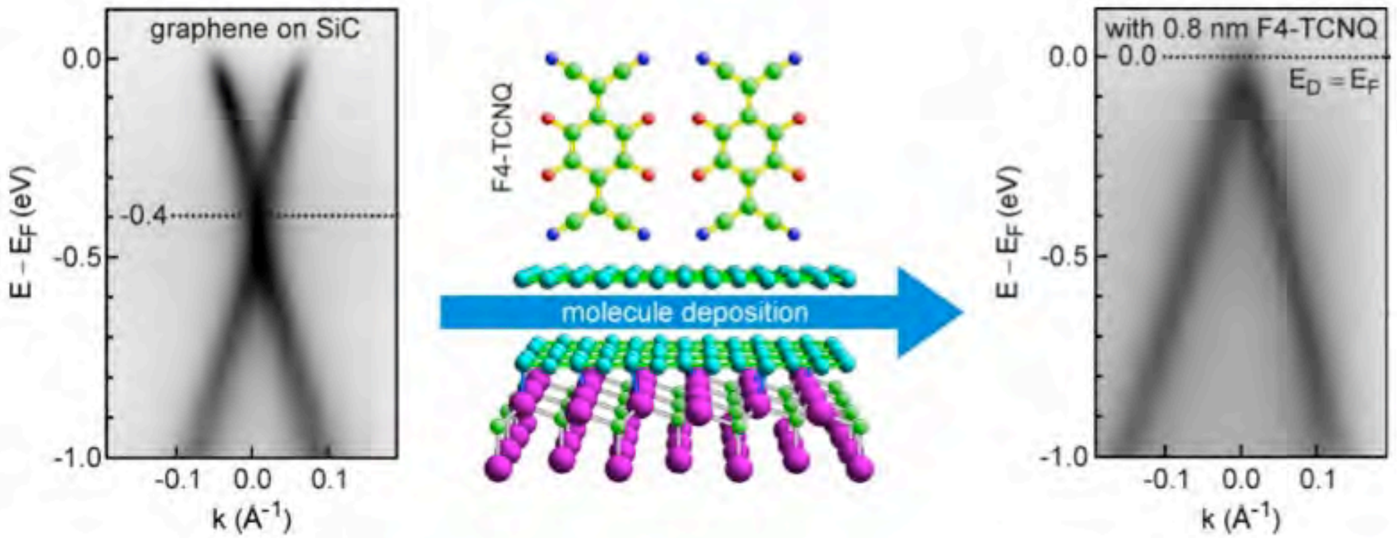
- Raman measurement: stable in air
- Dedicated annealing experiments: good temperature stability (likely higher in air)



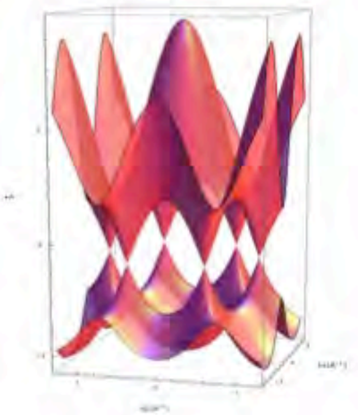
- F4-TCNQ applied via wet chemistry: sample immersed in F4-TCNQ-DMSO solution (12h)



Summary: F4-TCNQ functionalization



Limitations:



- High doping level
- Small bandgap in BL
- Reduced charge carrier mobility

Solutions?

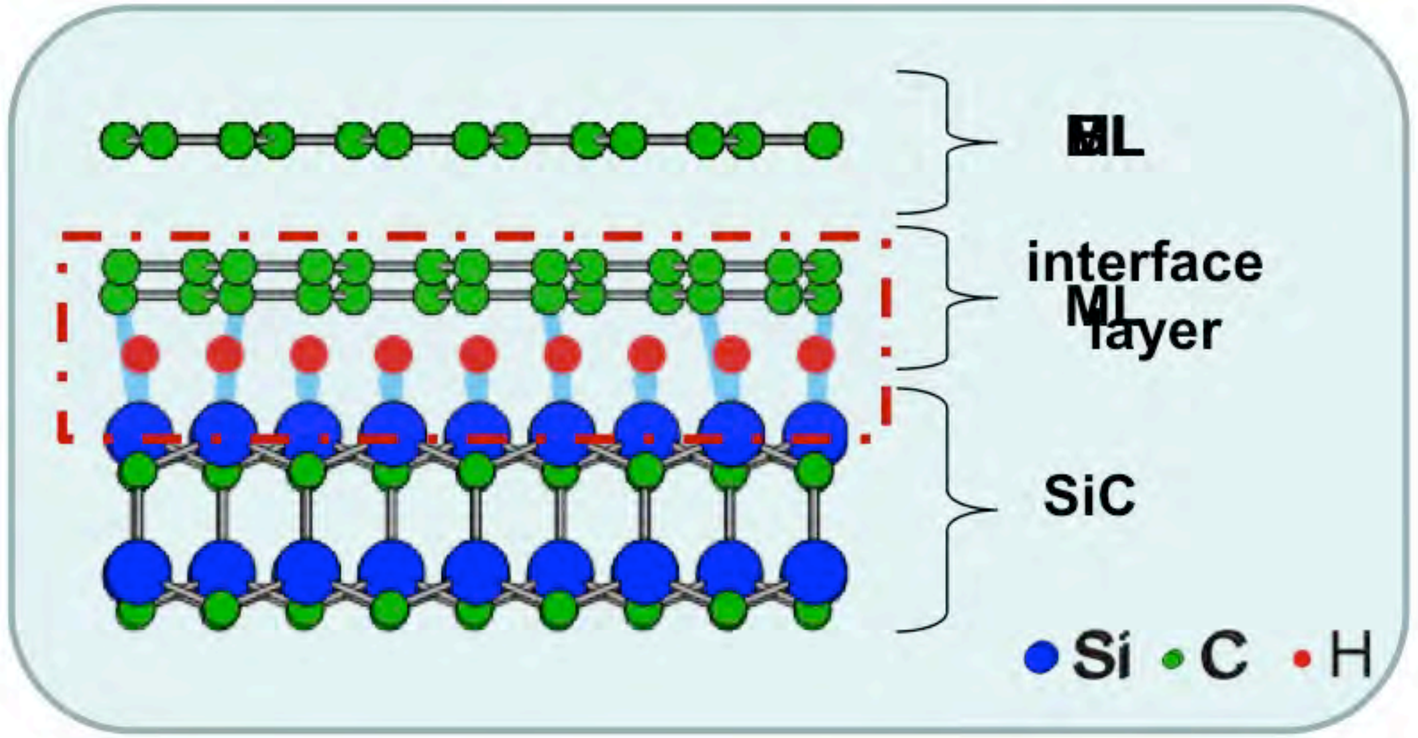
- ✓ Charge neutrality achieved for mono- and bilayer graphene ($n=1\cdot10^{11}$ cm^{-2})
- ✓ Bandgap of bilayer graphene can be more than doubled
- ✓ Observation of QHE and high mobilities (29000 cm^2/Vs @ T= 25K)

J. Jobst et al., Phys. Rev. B 81, 195434 (2010)

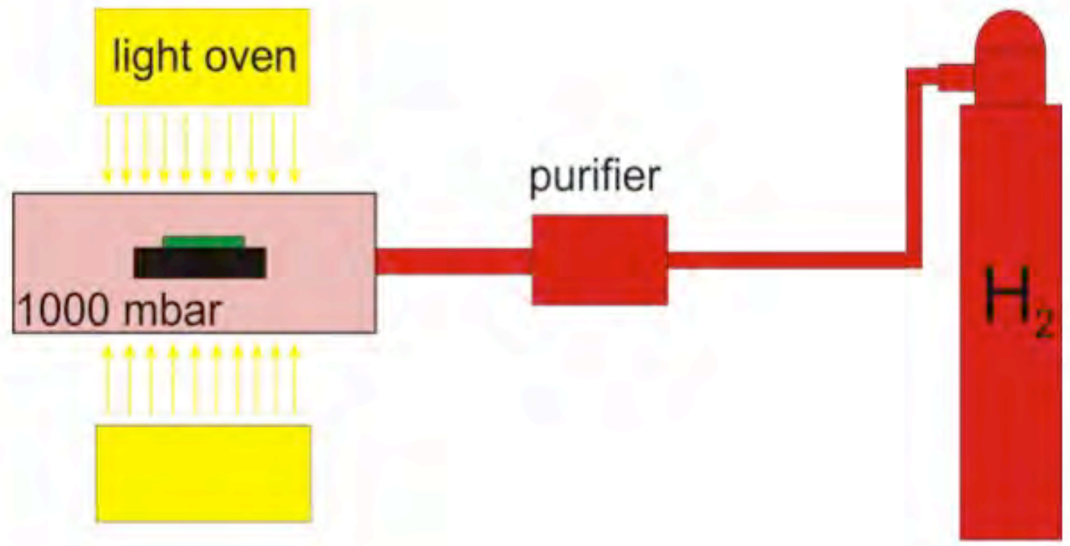
- ✓ Technologically robust

2nd Solution: Hydrogen intercalation

Drawbacks originate from the coupling bewteen graphene and SiC and are embodied by the existence of a covalently bound interface layer .



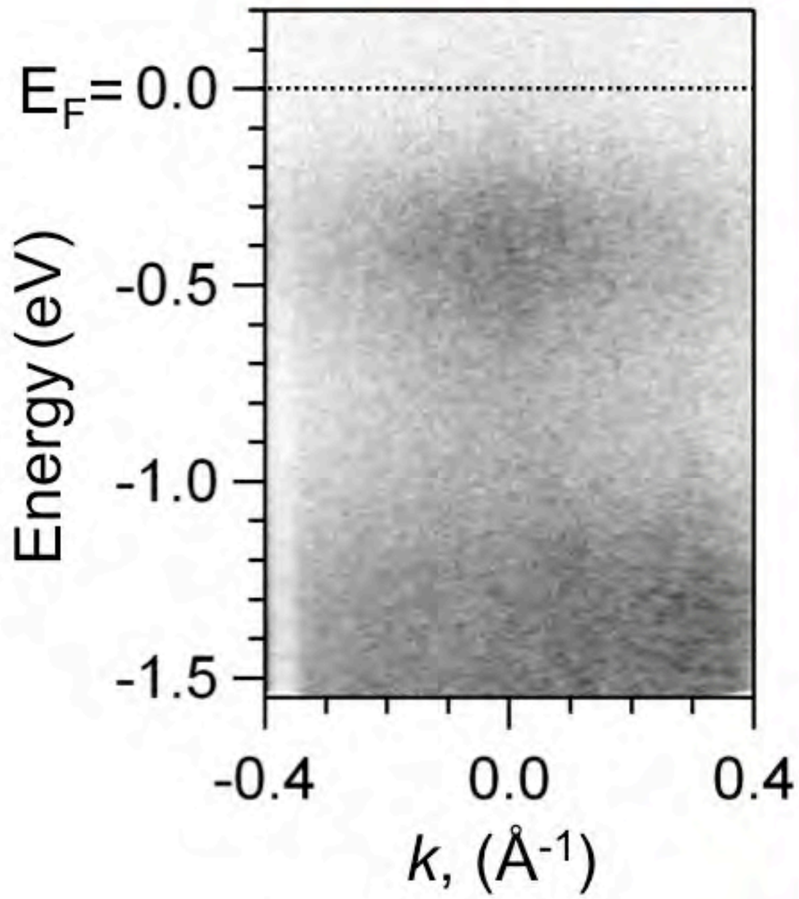
Method: annealing at 600°C - 1000°C in an atmosphere of ultra-pure H_2 gas

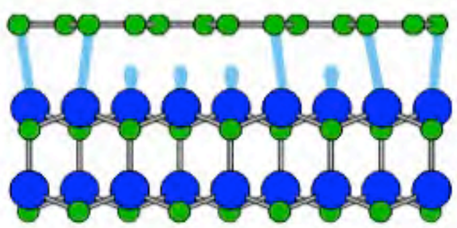


H. Tsuchida et al., J. Appl. Phys. 85, 3569 (1999).
T. Seyller, J. Phys. CM 16, S1755 (2004).
C. Coletti et al., Electrochem. Solid-State Lett. 11, H285 (2008).

ARPES: Quasi free-standing ML

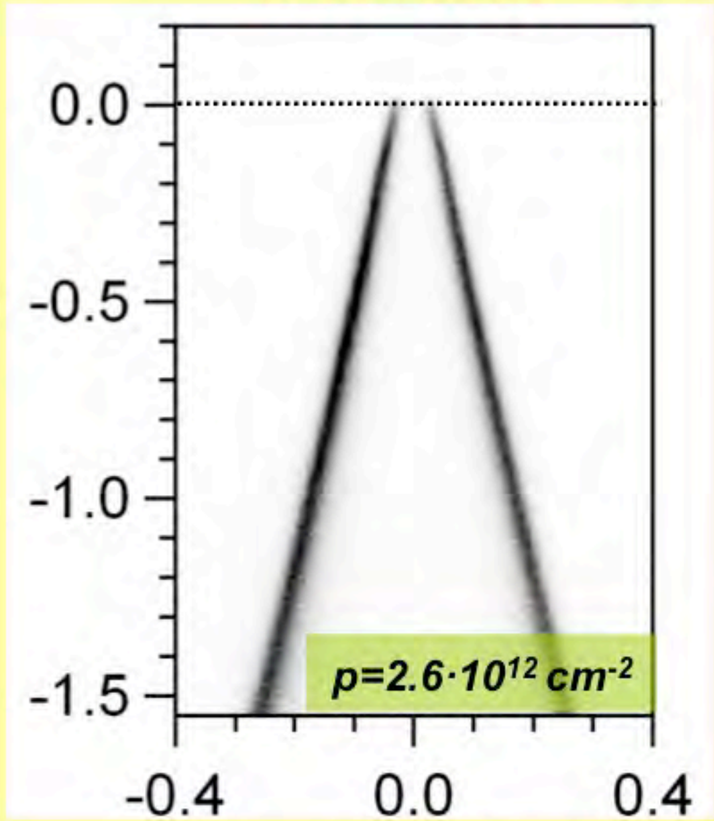
Zerolayer (ZL)

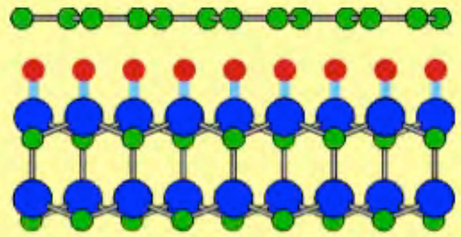




● Si ● C

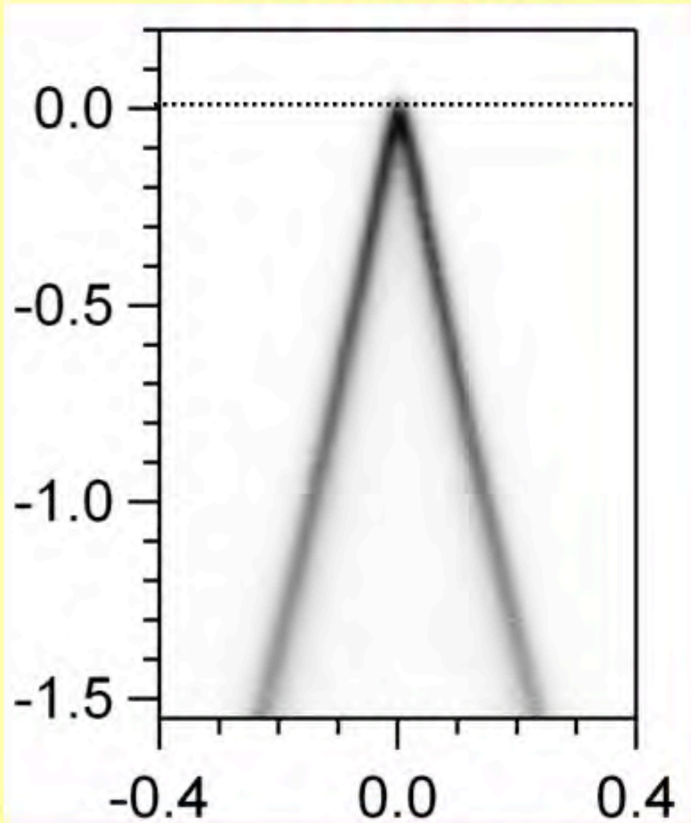
Hydrogen treatment





Quasi-freestanding monolayer graphene

Annealing in vacuum

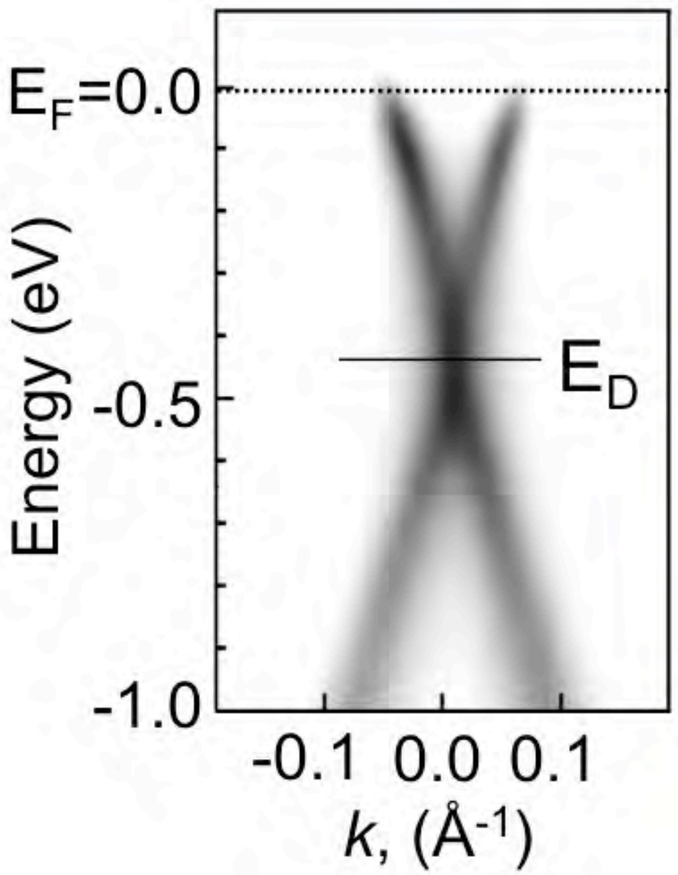


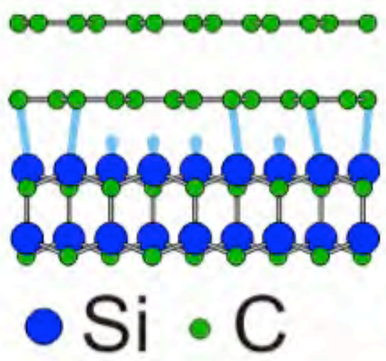
p < 10^{11} cm^{-2}

Stable up to 700°C in UHV

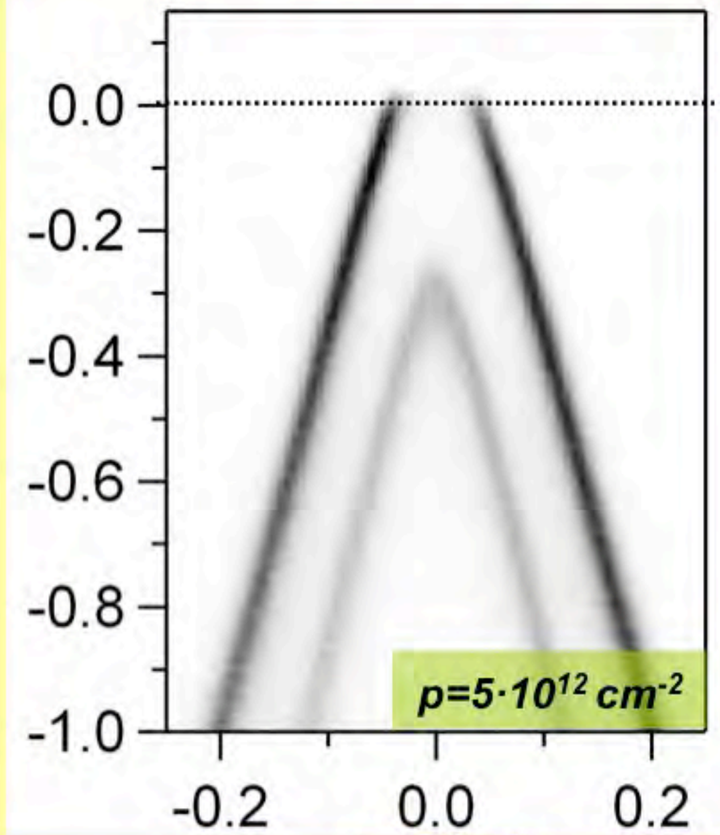
ARPES: Quasi free-standing BL

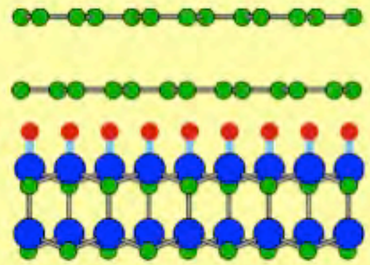
Monolayer (ML)





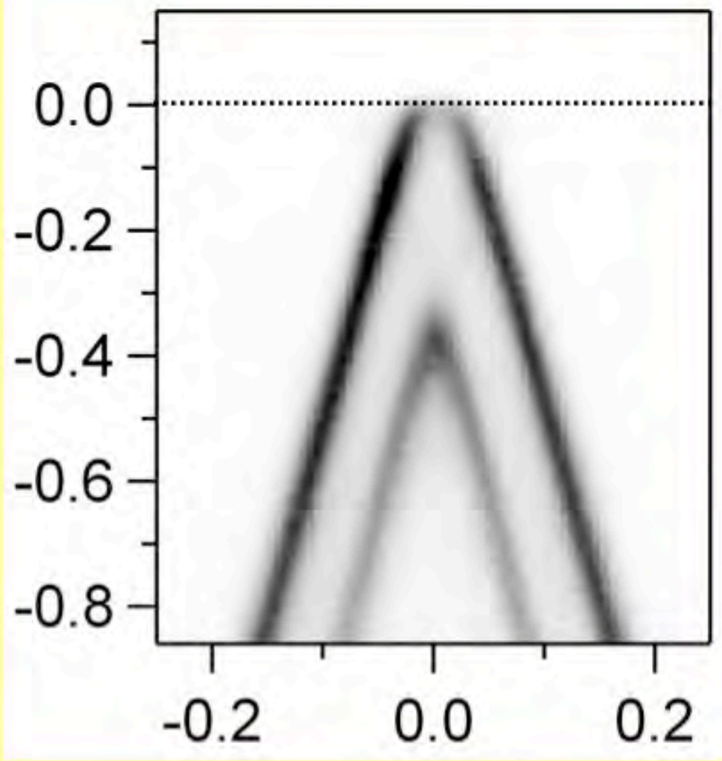
Hydrogen treatment





Quasi-freestanding bilayer graphene

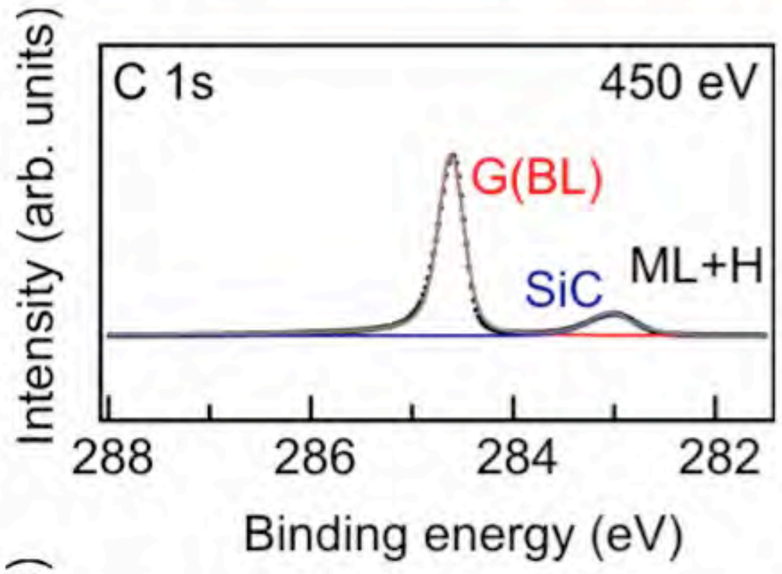
Annealing in vacuum

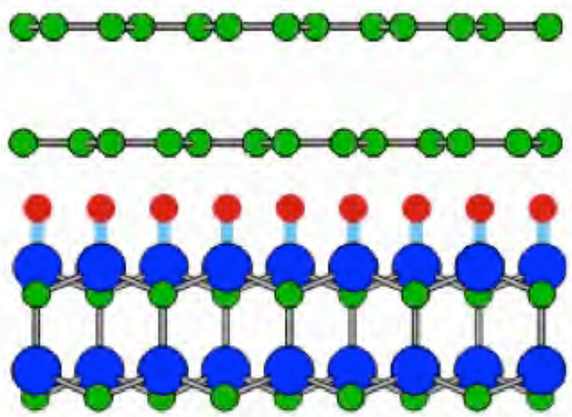


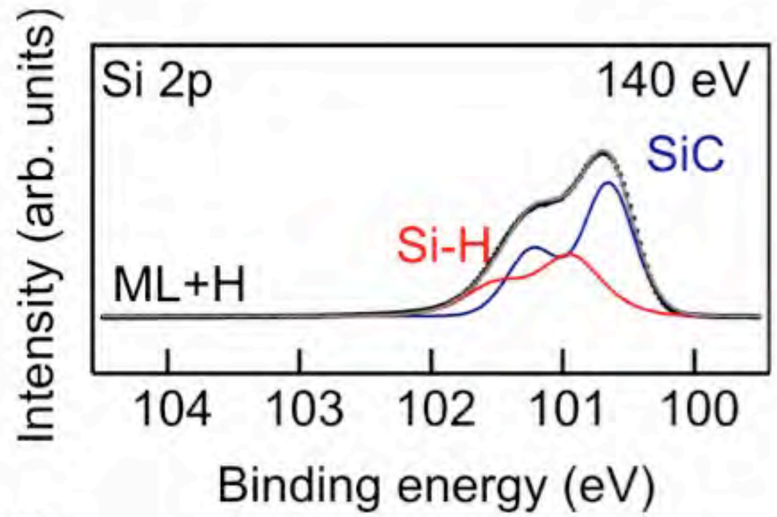
p ≈ 7·10^11 cm^-2

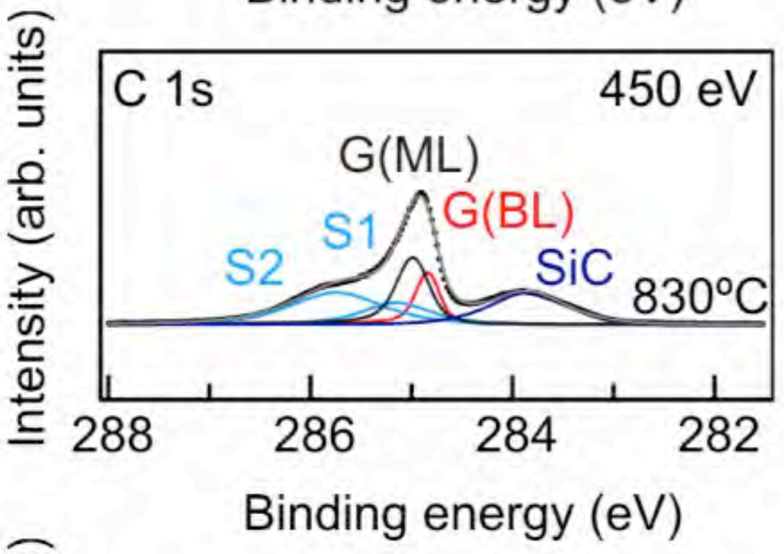
Stable up to 700°C in UHV

CLPES: Bond configuration

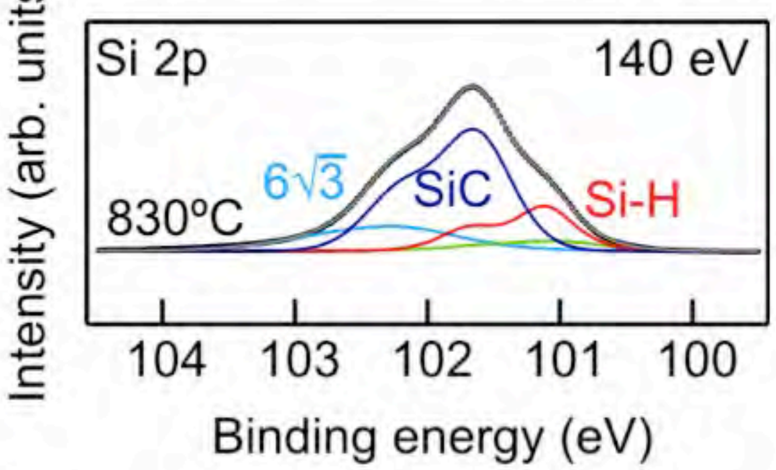


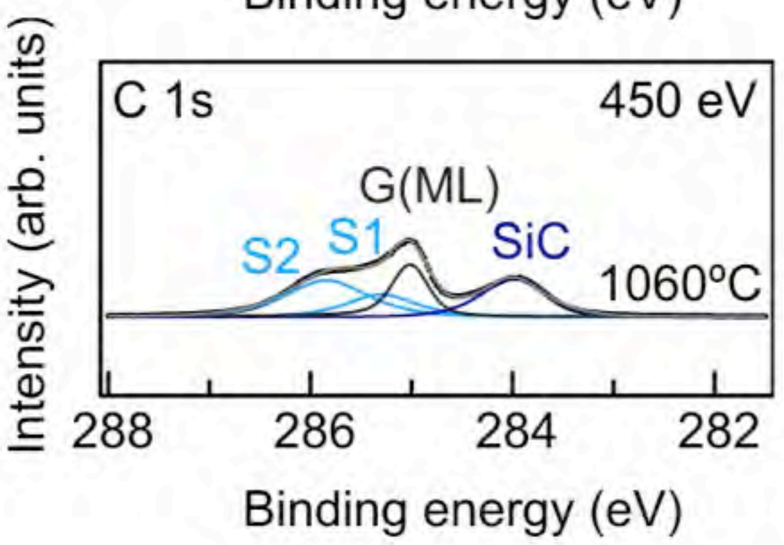


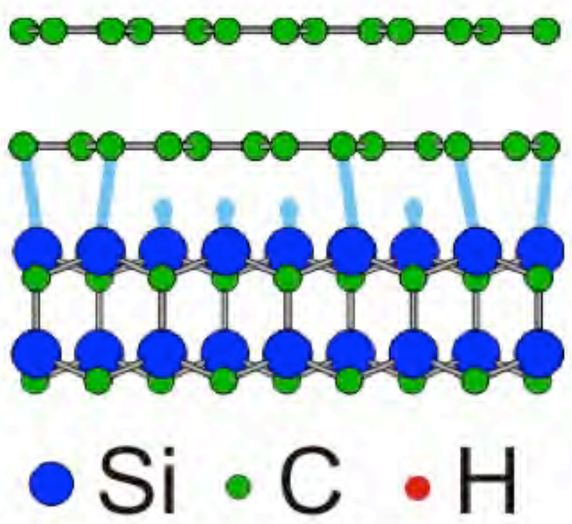


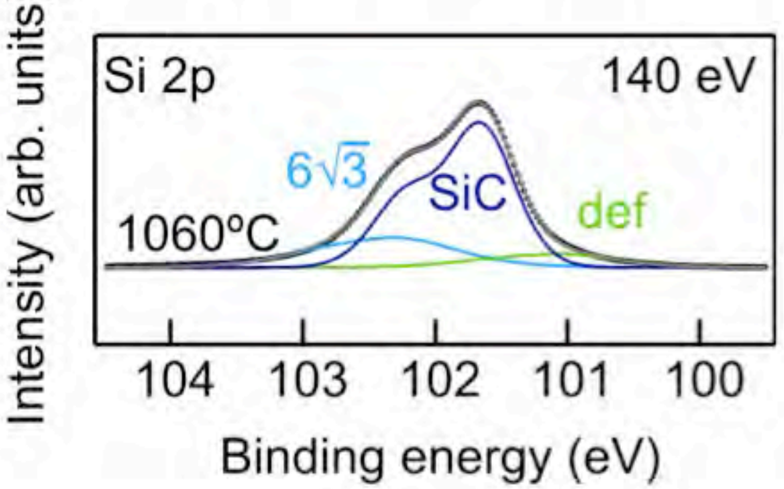


Hydrogen desorption



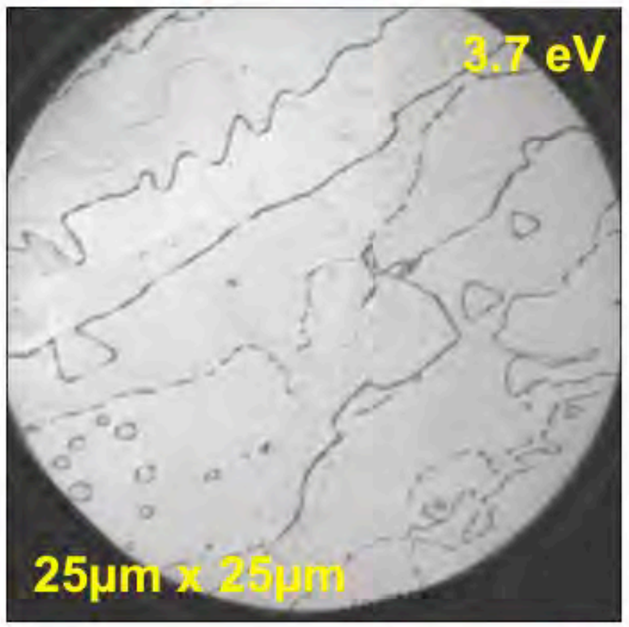




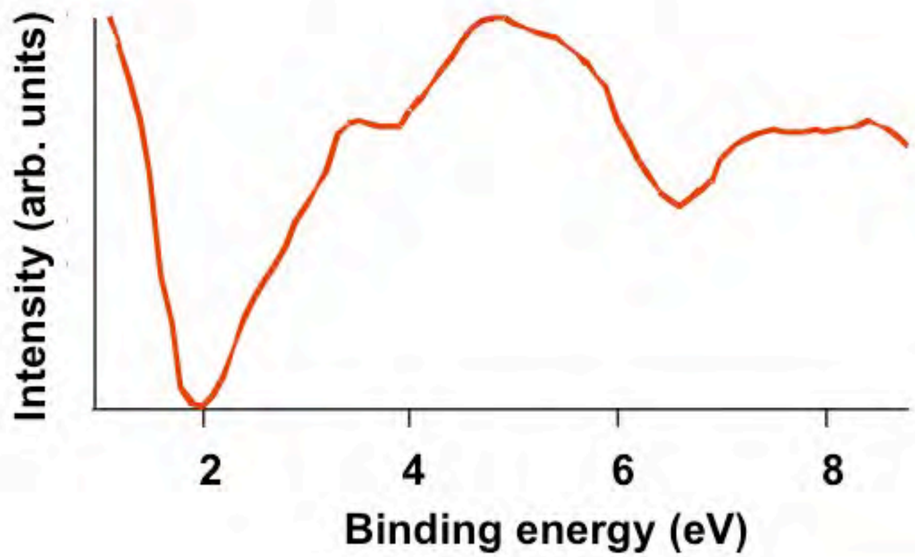


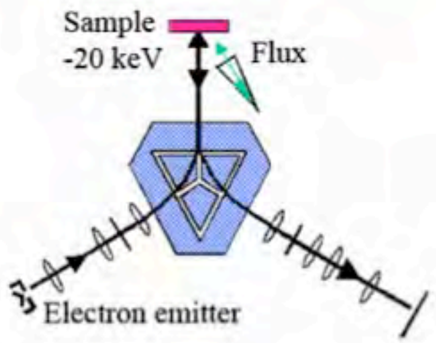
LEEM: Structural analysis

Graphene + H

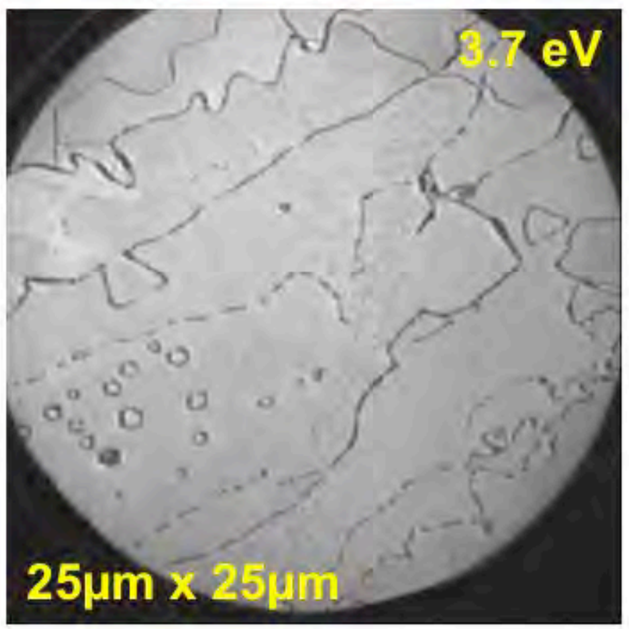


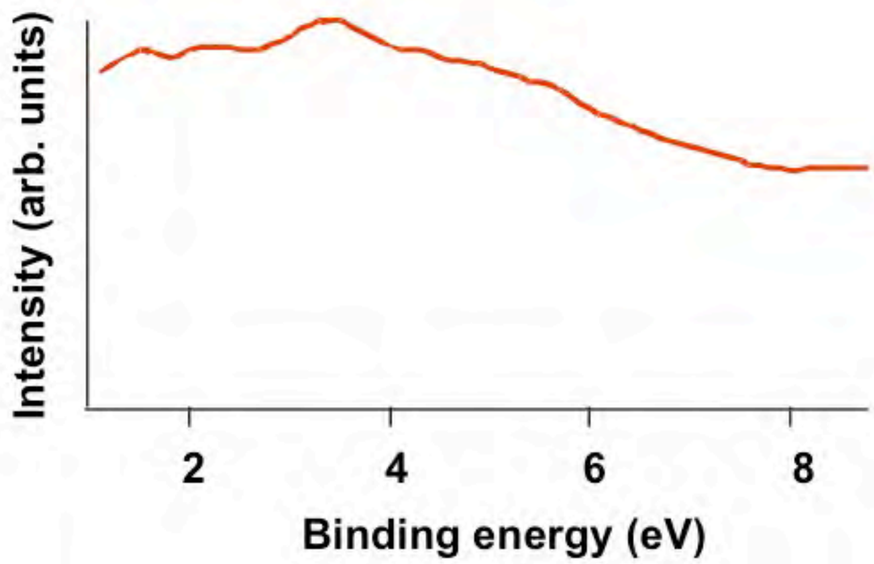
LEEM-reflectivity curve





Annealing 900 °C





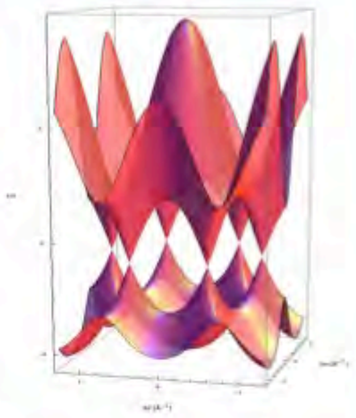
Successful intercalation of large area homogeneous domains (> 10µm²)

H. Hibino et al., Phys. Rev. B 77, 075413 (2008).

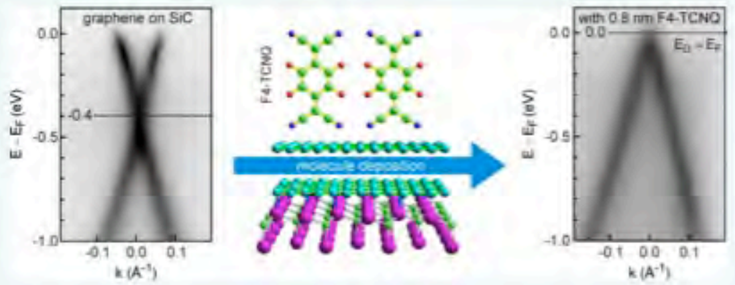
➔ *we can obtain quasi-free standing MONO and BILAYER graphene*

Summary

Limitations:



- High doping level
- Small bandgap in BL
- Reduced charge carrier mobility



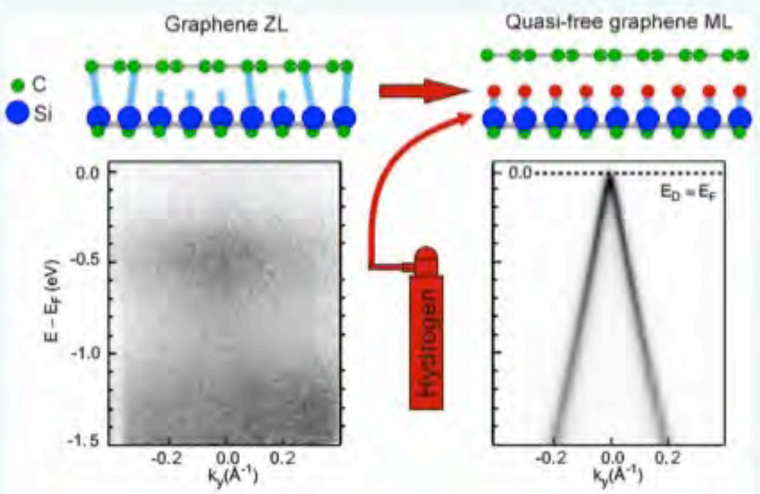
F4-TCNQ: Solutions?

- ✓ Charge neutrality achieved for mono- and bilayer graphene
- ✓ Bandgap of bilayer graphene can be more than doubled
- ✓ Observation of QHE and high mobilities
- ✓ Technologically robust

C. Coletti, et al., PRB 81, 235401(2010)

H-INTERCALATION: Solutions?

- ✓ Charge neutral large area quasi free-standing ML, BL, TL
- ✓ BL and TL with no BG but tunable with electric field (rhombohedral stacking in TL)
- ✓ Higher mobilities already measured (10000 cm^2/Vs , RT)
- ✓ Technological robust: relevance for future electronic applications!



C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov, U.Starke, PRL 103, 246804 (2009)

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Thank you for your attention!