Hydrogen Vacancies in Quasi-Free-Standing Monolayer Graphene

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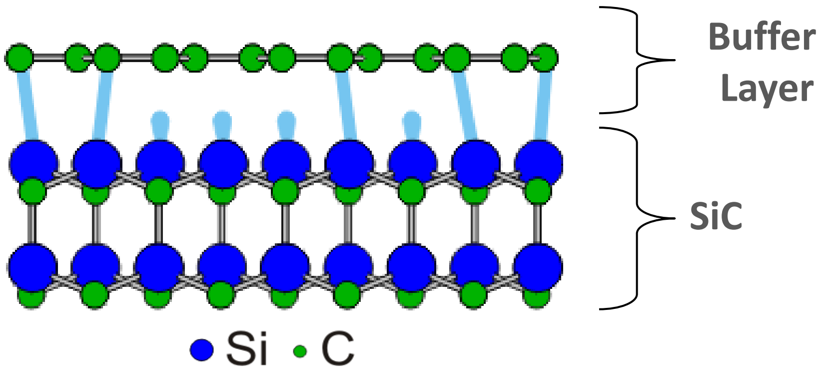
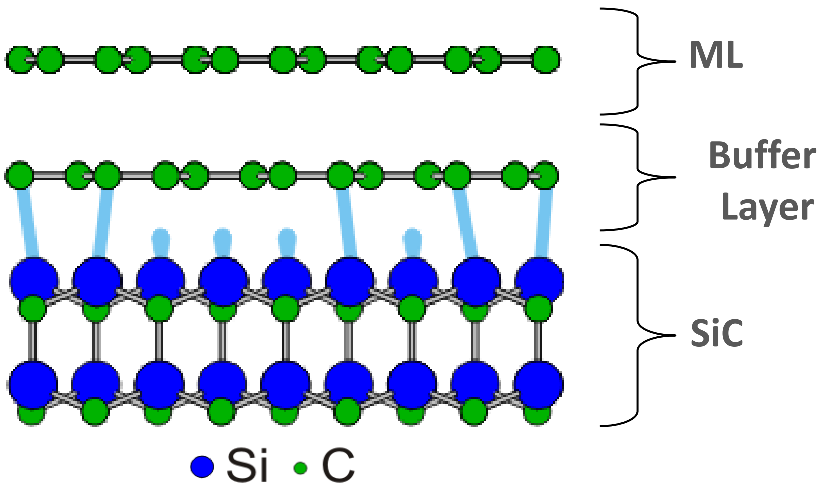
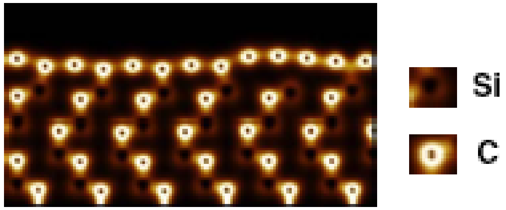
NEST

Graphene growth on SiC(0001)



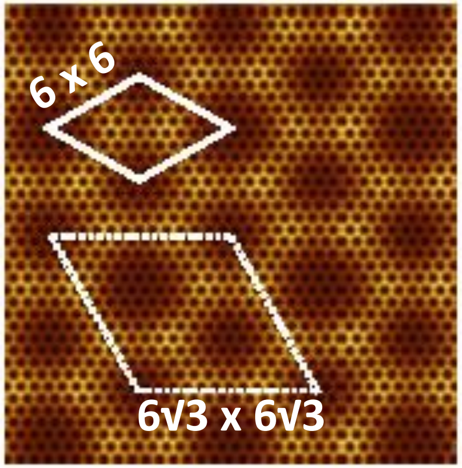


Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp^3 C-Si bonds.



F. Varchon, et al., PRB 77, 235412 (2008).

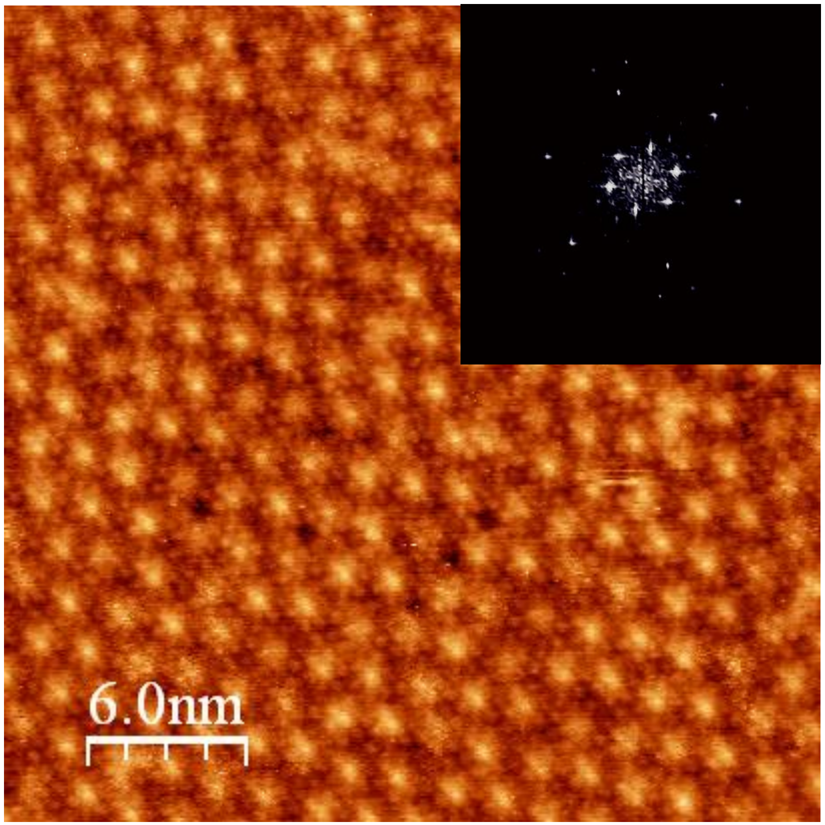
Theoretical Calculations



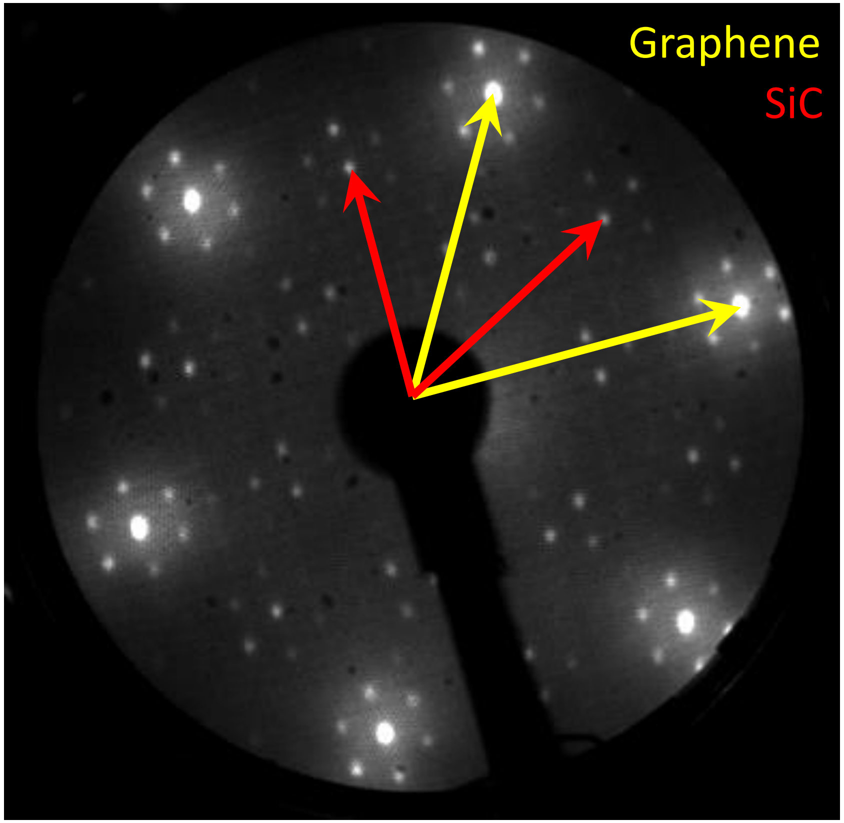
F. Varchon, et al., PRB 77, 235412 (2008).

Superstructure of both the buffer layer and monolayer graphene on the Si face from the periodic interaction with the substrate.

Superstructure



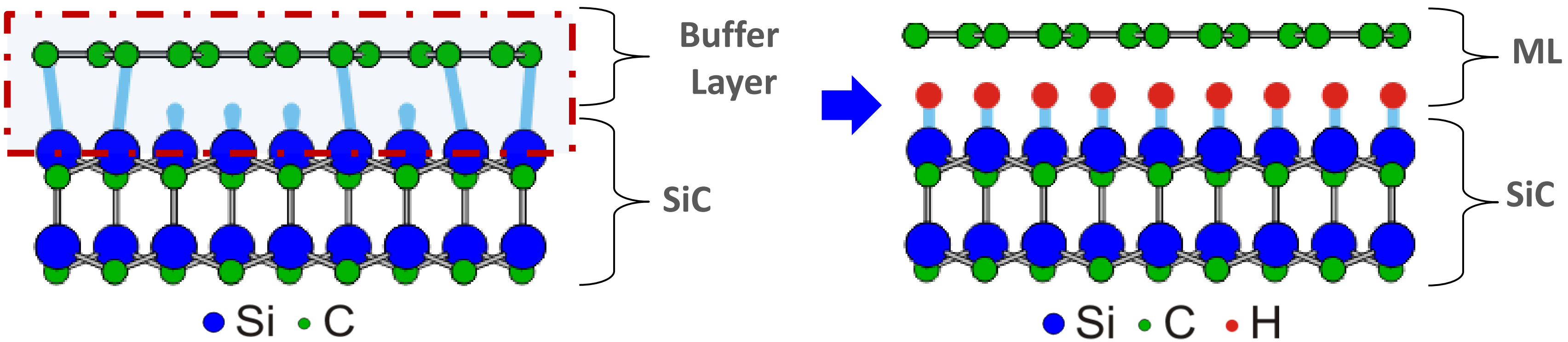
30 nm, 1V, 100 pA



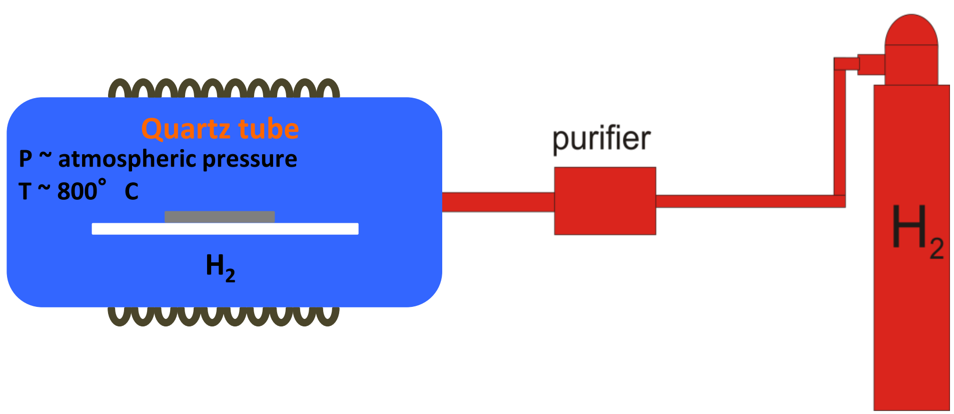
E= 75 eV

T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013).

Hydrogen Intercalation



Buffer Layer (BL) **Quasi-free standing monolayer graphene**



C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009)

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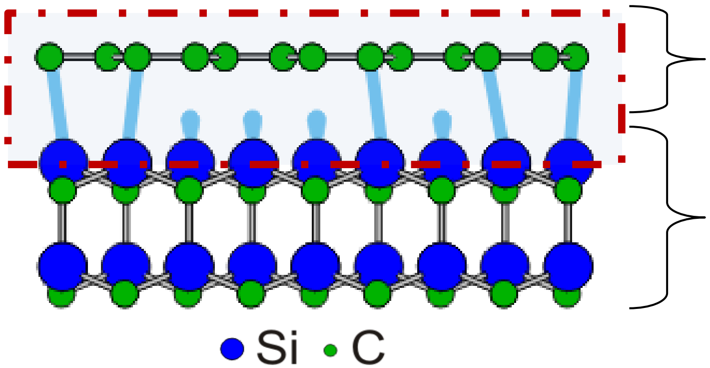
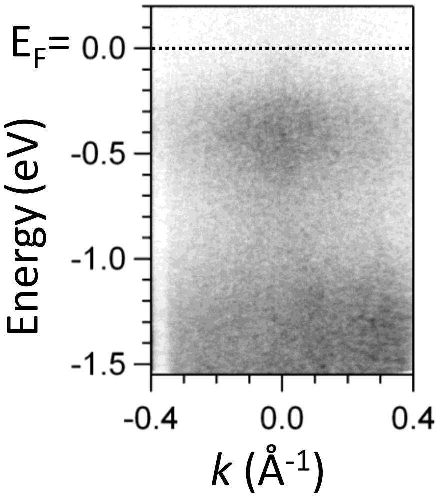
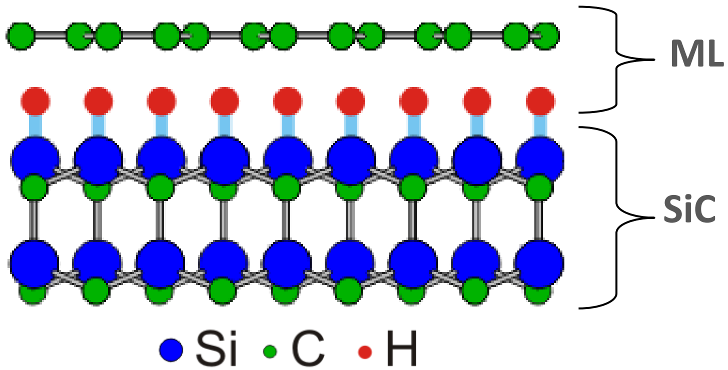
Hydrogen Intercalation

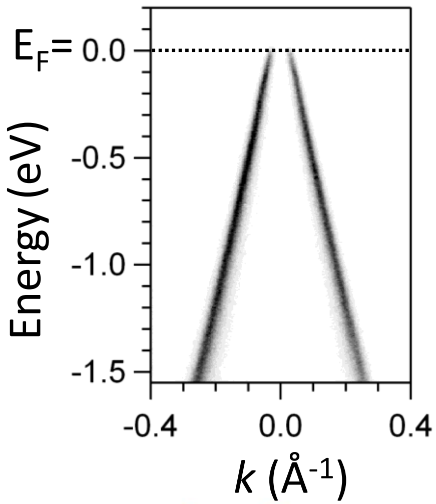


Buffer Layer (BL)





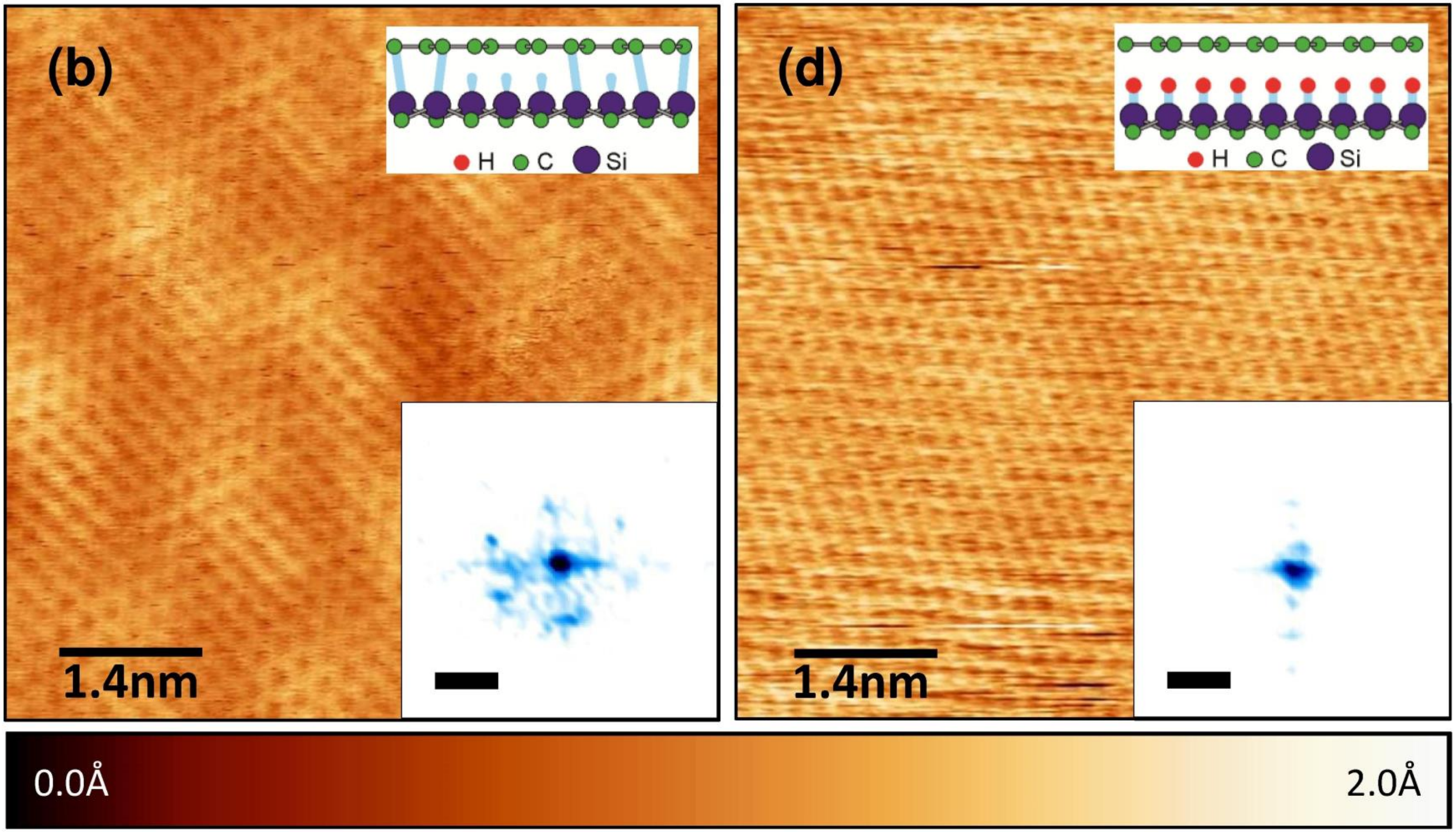
Quasi-free standing monolayer graphene



$p=2.6\cdot10^{12}$ cm^{-2}

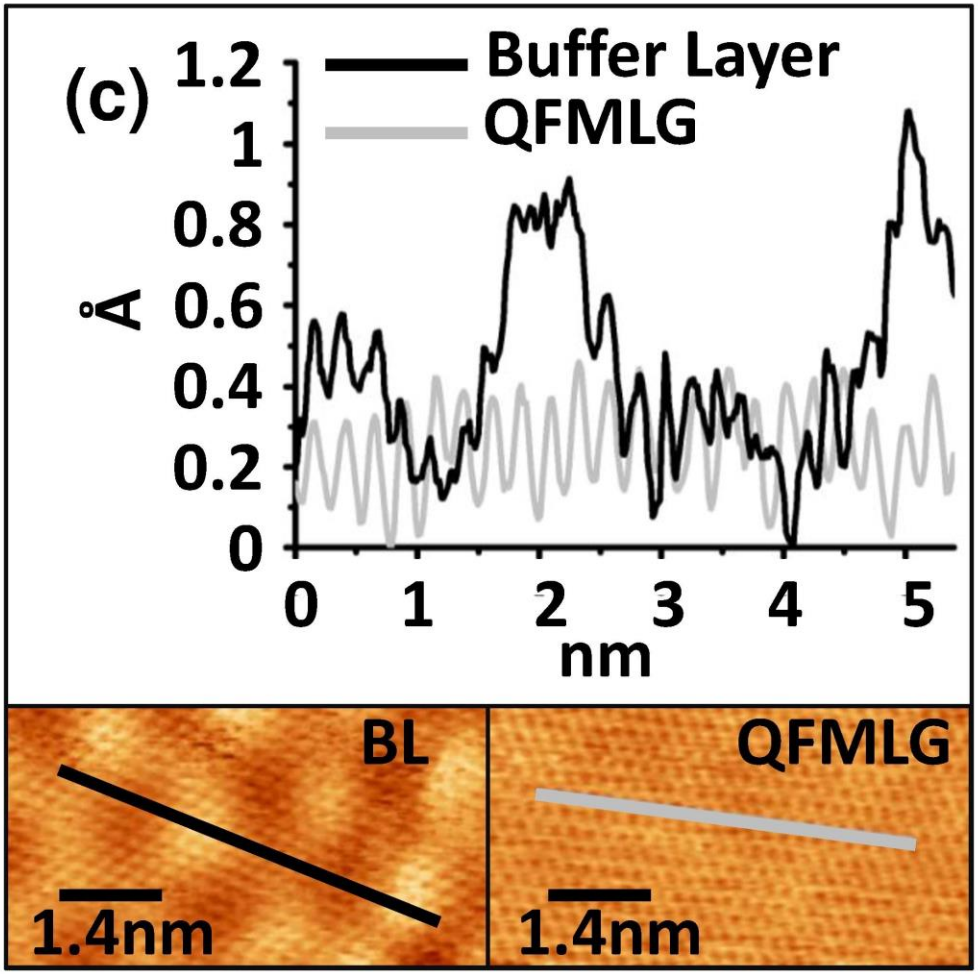
C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009)

BL vs. QFMLG



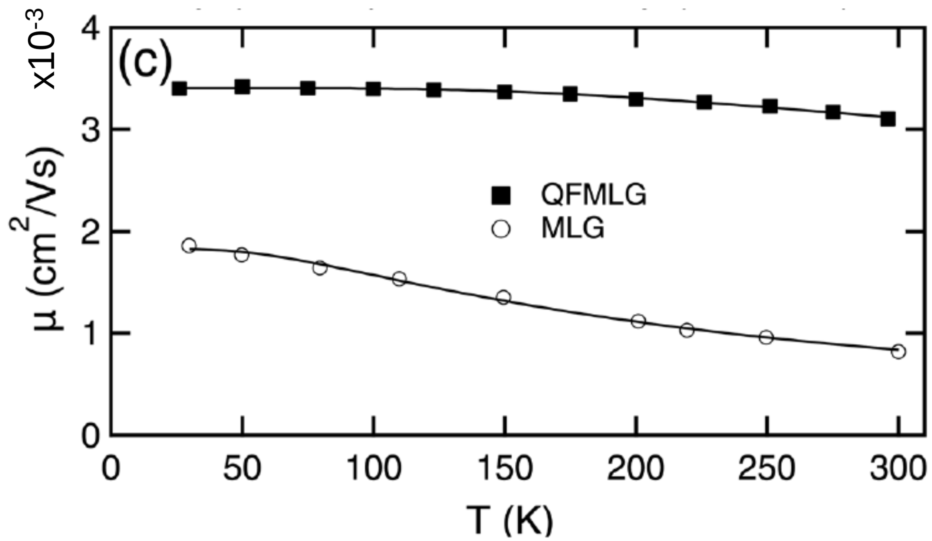
S. Goler *et al.*: Carbon **51**, 249 (2013).

BL vs. QFMLG



S. Goler *et al.*: Carbon **51**, 249 (2013).

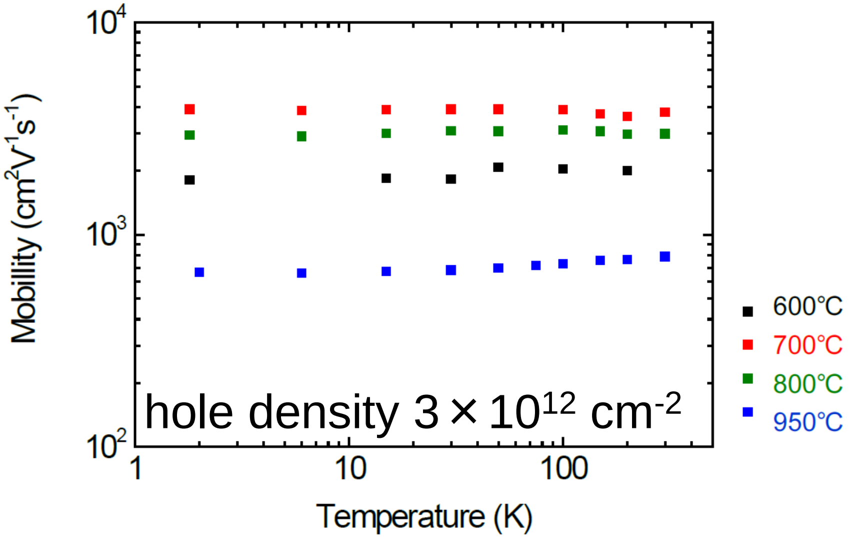
Carrier Mobility

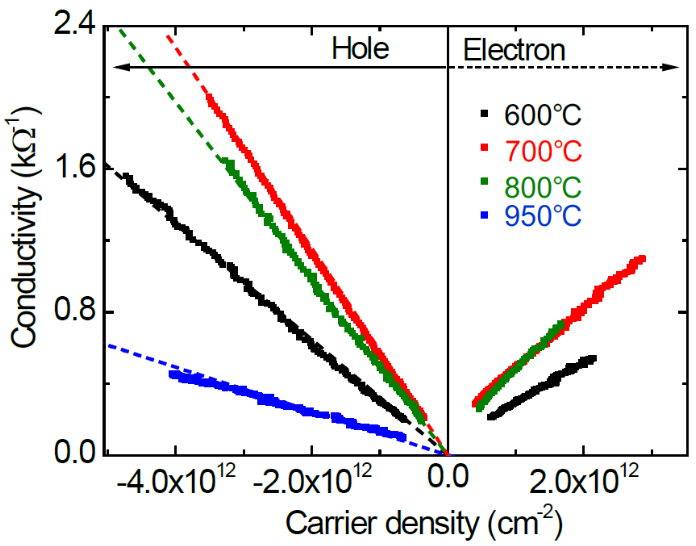


F. Speck, J.Jobst, F. Fromm, M. Ostler, D. Waldmann, M. Hundhausen, H. B. Weber, and Th. Seyller, Appl. Phys. Lett. **99**, 122106 (2011).

The carrier mobility of QFMLG shows less temperature dependence than MLG, indicating less interaction between QFMLG and the SiC substrate.

However, the mobility of QFMLG is still lower than that of exfoliated graphene on SiO_2 or free standing graphene.





S. Tanabe, M. Takamura, Y. Harada, H. Kageshima, and H. Hibino, Jpn. J. Appl. Phys. **53**, 04EN01 (2014).

The QFMLG mobility depends on T_H,
the substrate temperature during H intercalation

Highest mobility at T_H = 700ºC

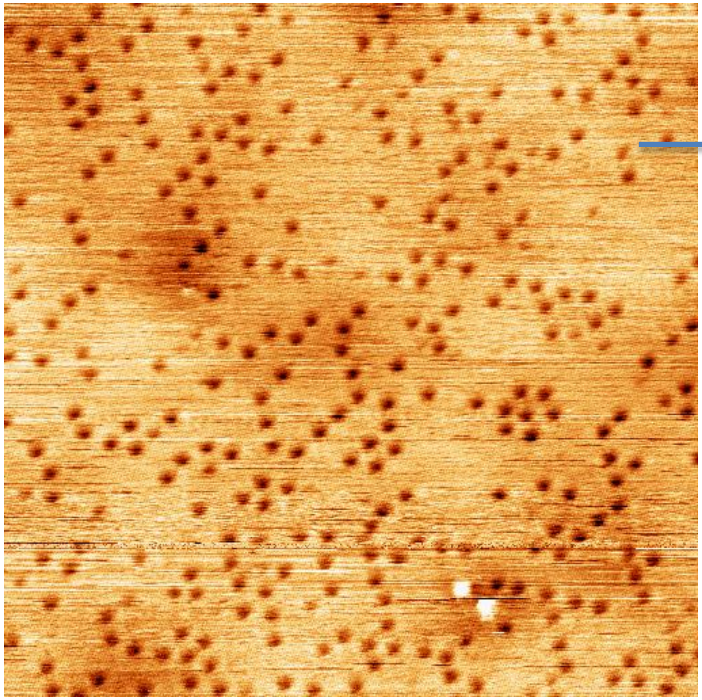
conductivity vs. carrier density:

- linear for T_H = 600-800ºC
  - charged impurities
- sublinear for T_H = 950ºC
  - additional scattering by defects

Our Purpose :
to observe the morphology of QFMLG formed at different T_H and investigate the relationship with transport property

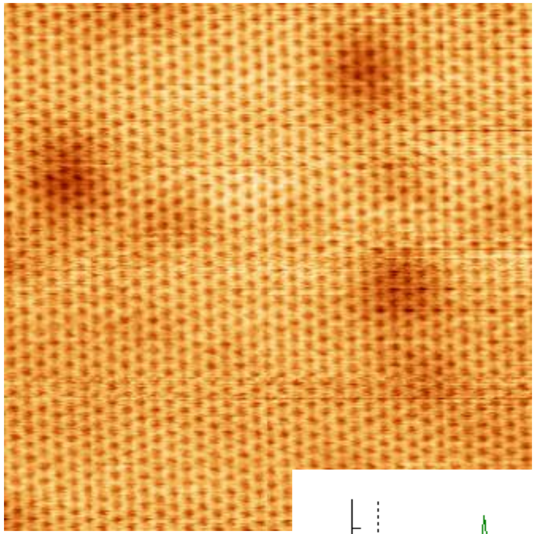
Intercalation at 600-800ºC

T_H = 800ºC sample

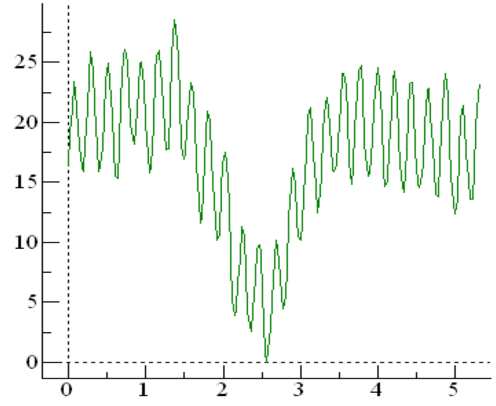


50 nm
0.6 V, 0.4 nA

- dark spot width: 1.5 nm



8 nm

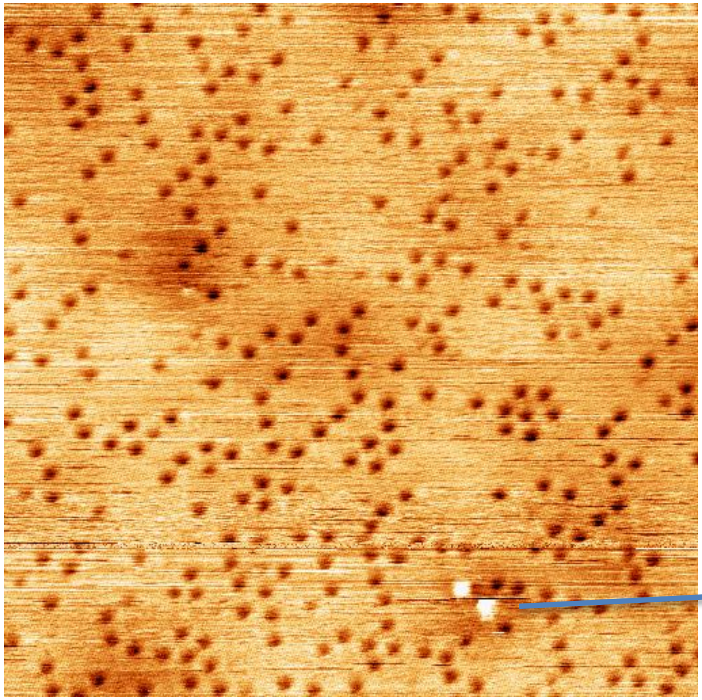


- width: 1.5 nm
- depth: 15-25 pm
- honeycomb inside
- no defect

Y. Murata *et al.*: Appl. Phys. Lett. **105**, 221604 (2014).

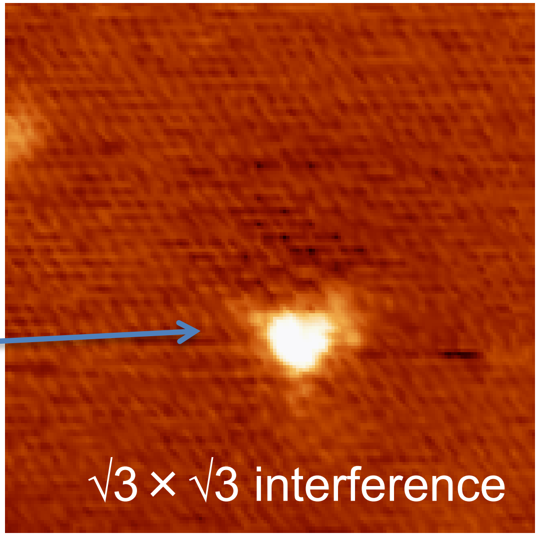
Intercalation at 600-800ºC

T_H = 800ºC sample



50 nm
0.6 V, 0.4 nA

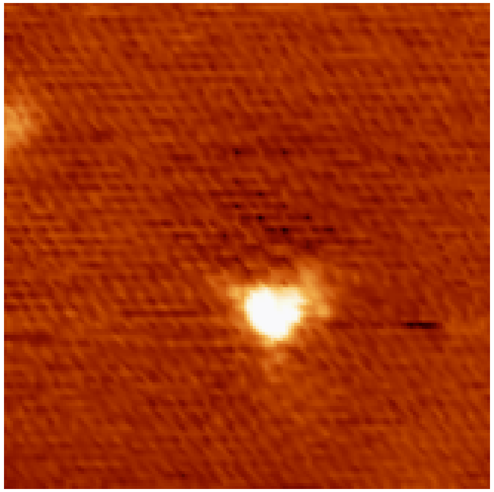
- graphene defect



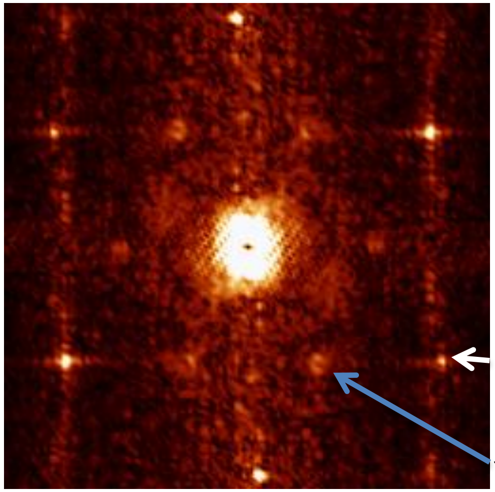
8 nm
0.8 V, 0.4 nA

Y. Murata *et al.*: Appl. Phys. Lett. **105**, 221604 (2014).

Graphene defect

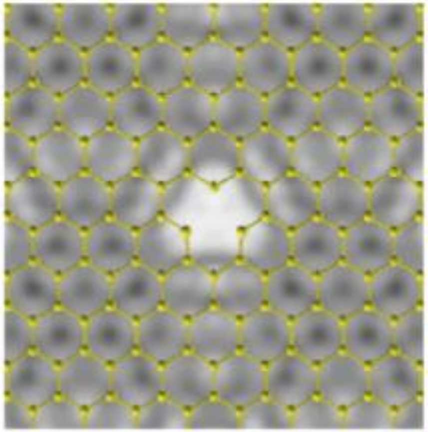


8 nm
0.8 V, 0.4 nA



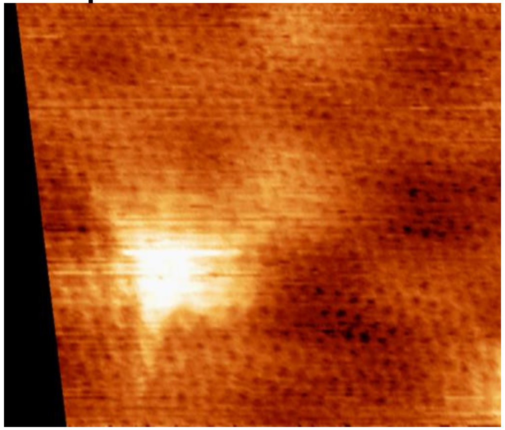
electron interference at defect

STM simulation



S. H. Rhim, Appl. Phys. Lett. **100**, 233119 (2012).

N-sputtered EMLG

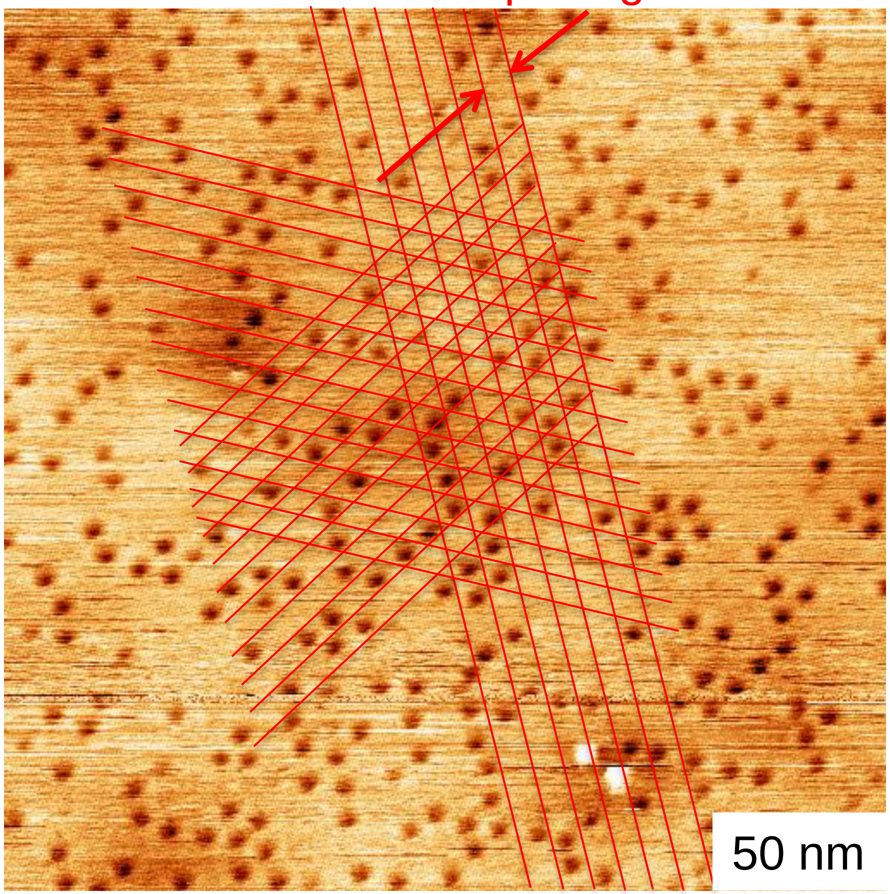


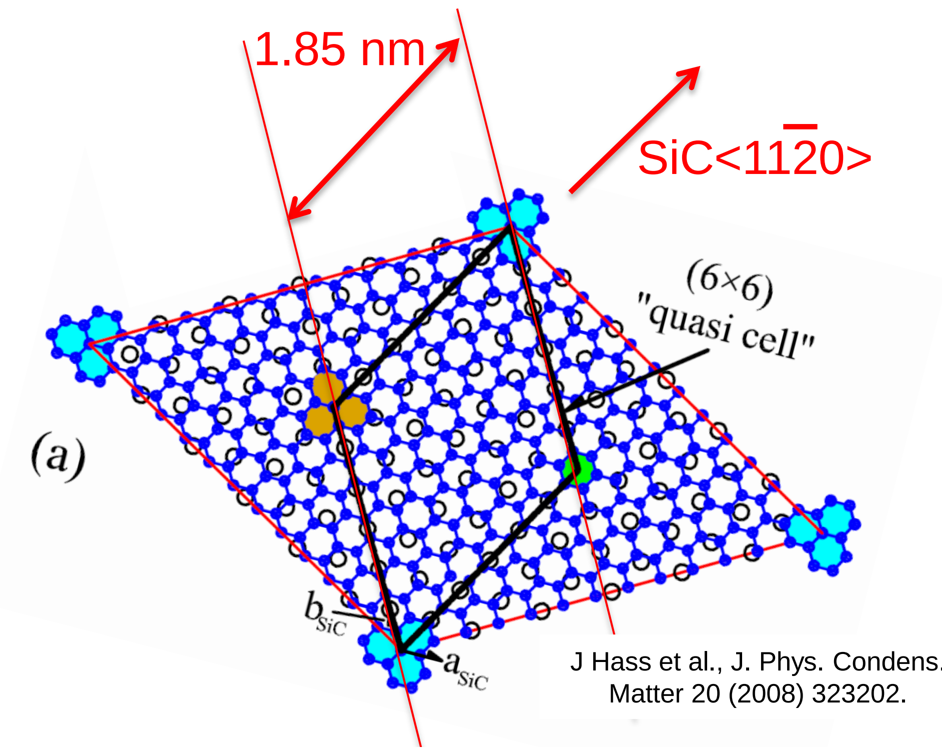
T. Mashoff et al., Appl. Phys. Lett. 106, 083901 (2015).

Intercalation at 600-800ºC

SiC$\langle 11\bar{2}0\rangle$ directions
1.8 nm spacing

~ SiC 6 × 6 cell
~ quasi cell of Moiré pattern produced by graphene and SiC(0001) lattices





J Hass et al., J. Phys. Condens. Matter 20 (2008) 323202.

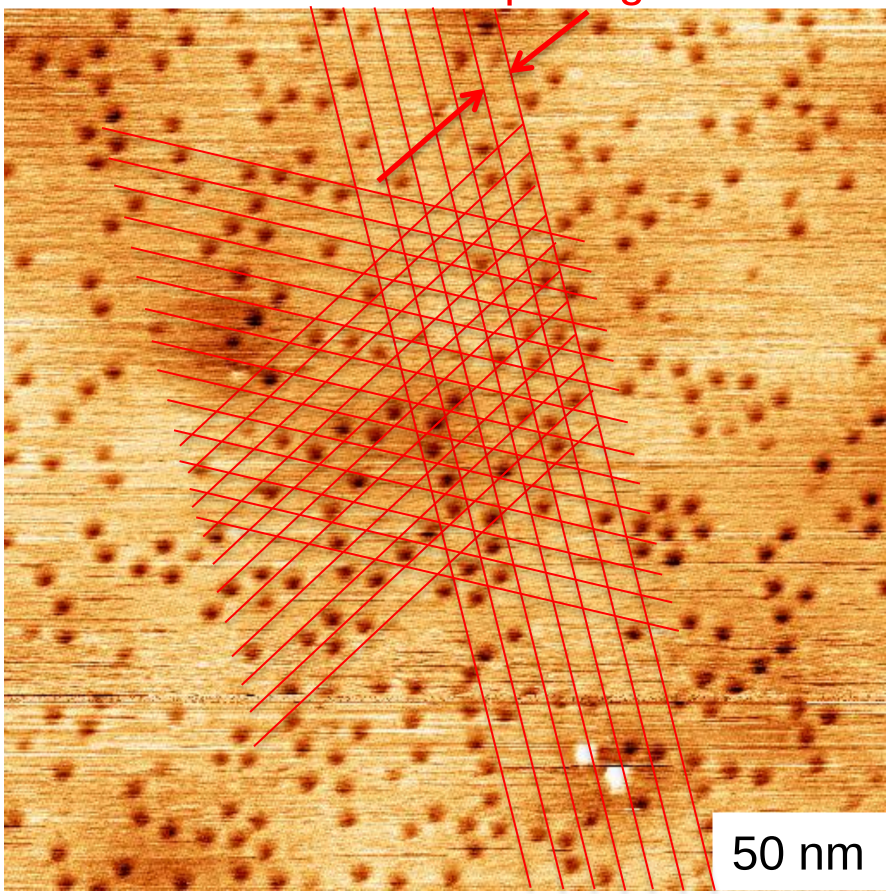
blue: graphene a = 0.24589 nm
white: a = Si 0.30805 nm

Y. Murata *et al.*: Appl. Phys. Lett. **105**, 221604 (2014).

Hydrogen Vacancies

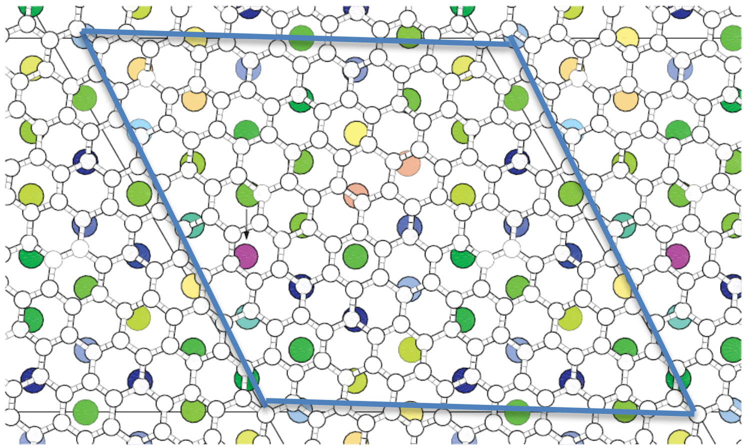
SiC<11$\bar{2}$0> directions
1.8 nm spacing

~ SiC 6 × 6 cell
~ quasi cell of Moiré pattern produced by graphene and SiC(0001) lattices



Y. Murata *et al.*: Appl. Phys. Lett. **105**, 221604 (2014).

spatial distribution of hydrogenation energy on Si sites in $4\sqrt{3} \times 4\sqrt{3}$ buffer layer

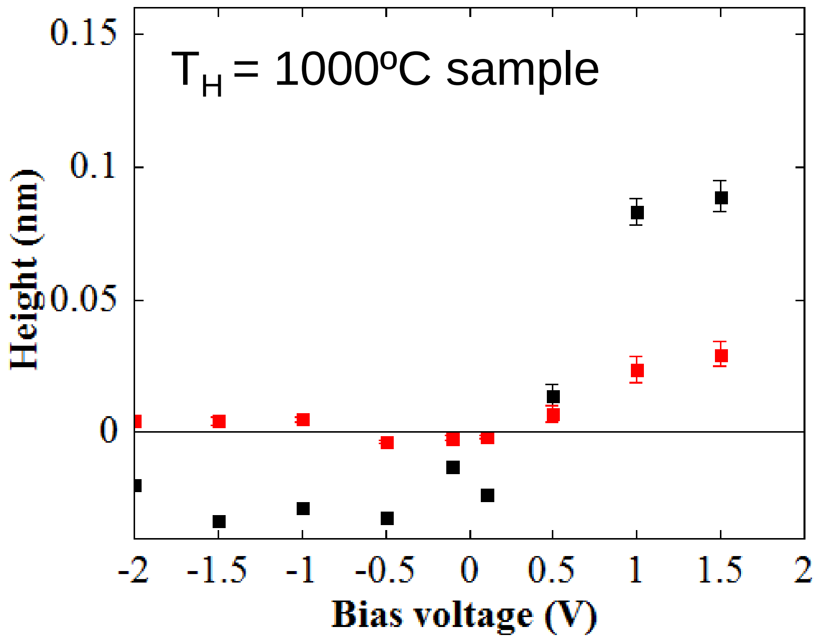


dark blue: the least favored H adsorption site

G. Sclauzero, A. Pasquarelo, Appl. Surf. Sci. 291, 64 (2014).

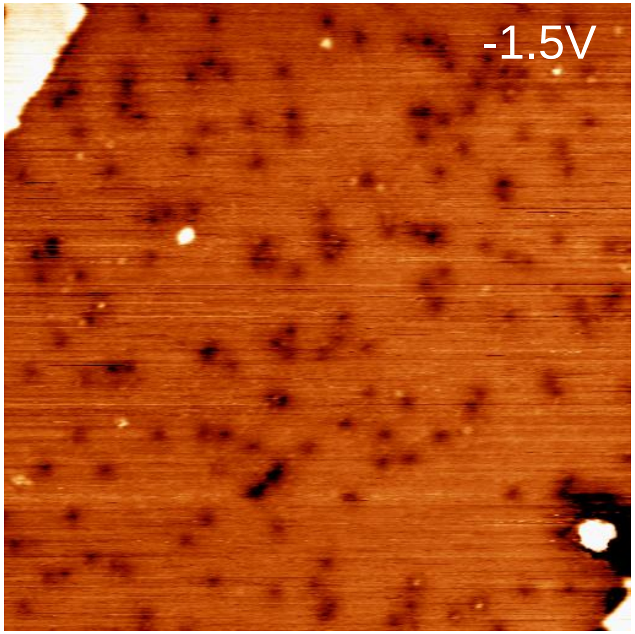
Si dangling bonds distribute along the periodicity of the Moiré pattern

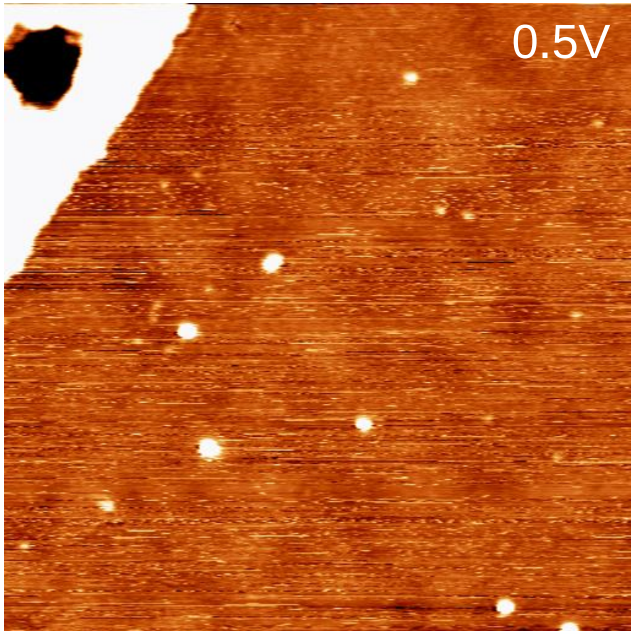
spots' apparent height vs V_b

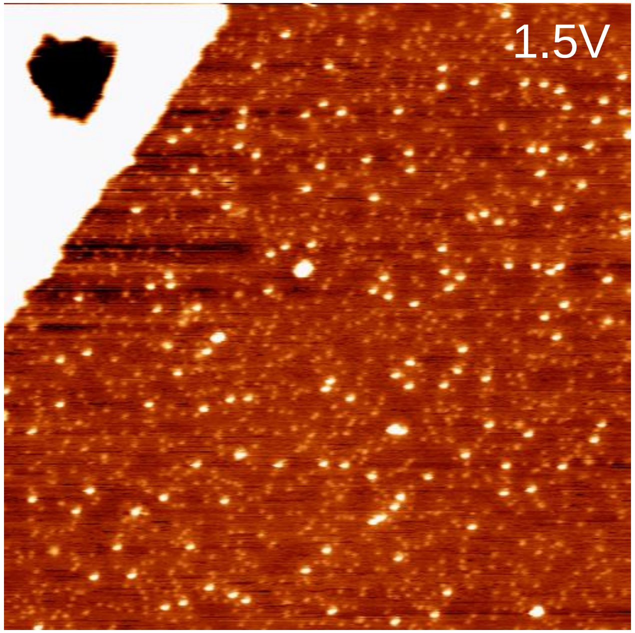


- spots' apparent height varies with V_b
- electronic effect rather morphology
- two types of spots

0.1nA 100nm

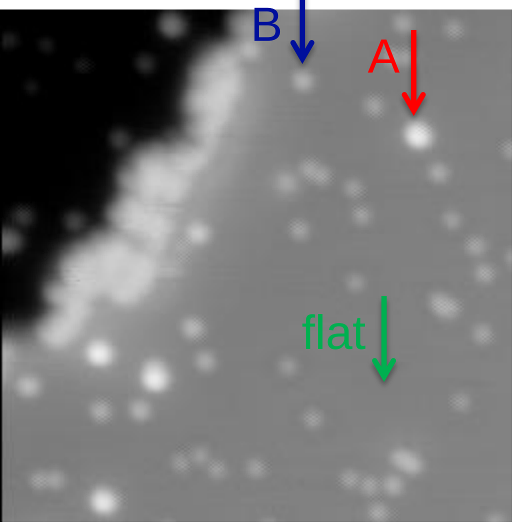




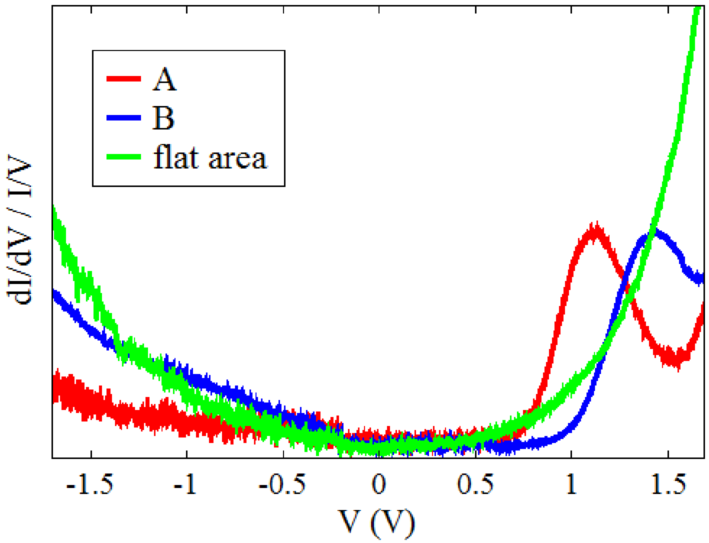


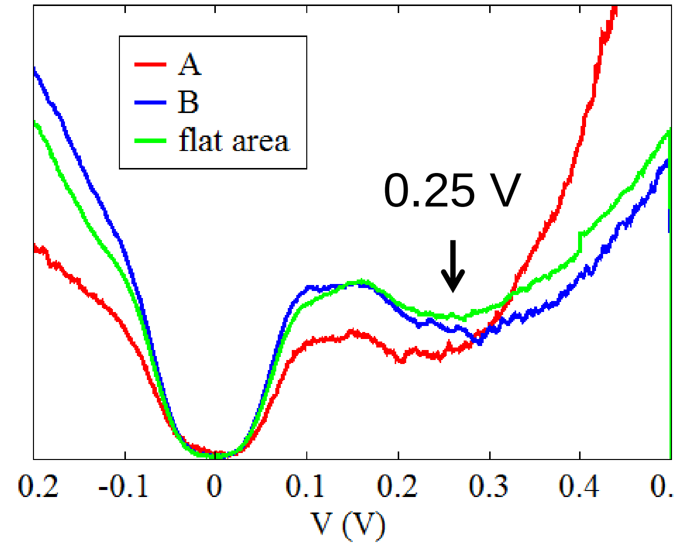
Si dangling bonds

STM and STS at 6K IBM



1.8V, 0.01nA, 20 nm



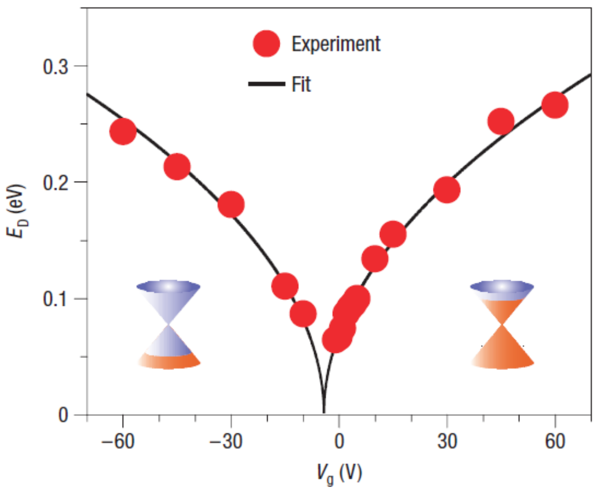


gap like feature at 0 V
dip at 0.25 V

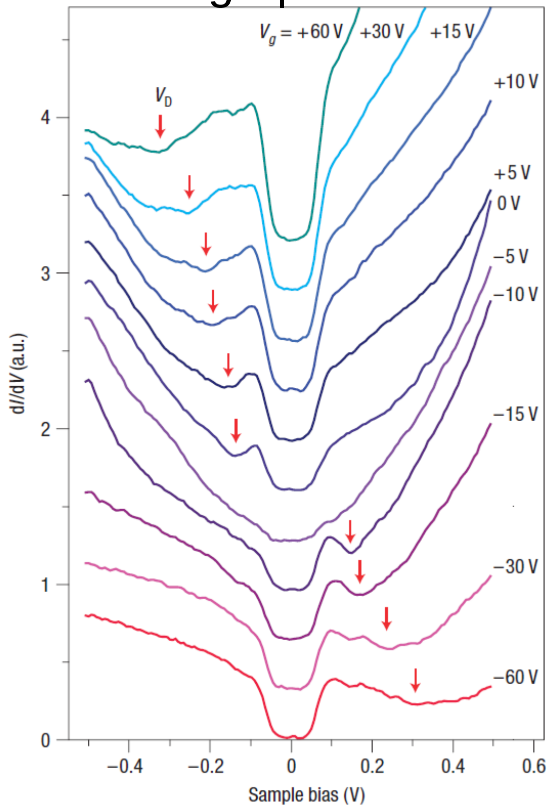
Si dangling bonds

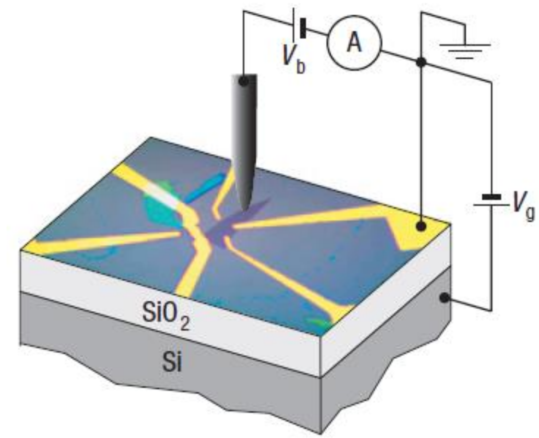
STS on graphene on SiO_2 with Vg

Energy position of Dirac point vs Vg



$$E_{\mathrm{D}} = \hbar v_{\mathrm{F}} \sqrt{\pi\alpha |V_{\mathrm{g}} - V_0|}$$



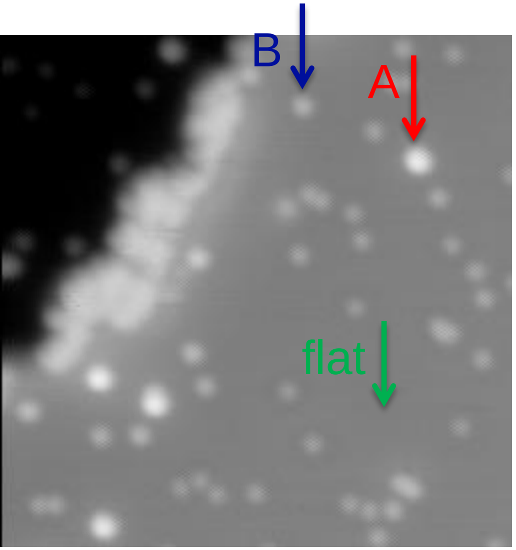


Zhang, et.al,
Nature Phys. 4, 627 (2008).

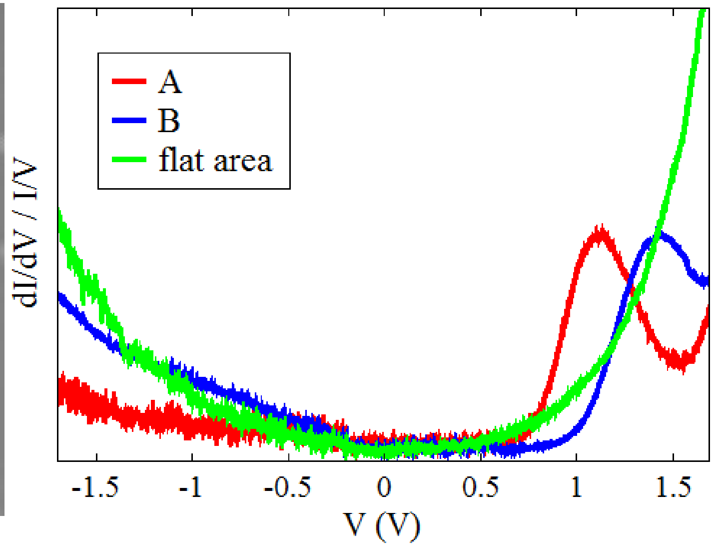
- The dip moves with Vg, corresponds to energy position of Dirac point
- Gap like feature at 0V due to suppression of tunneling to states with large momentum and tunneling enhancement at higher energy due to a phonon-mediated inelastic channel (±63meV)

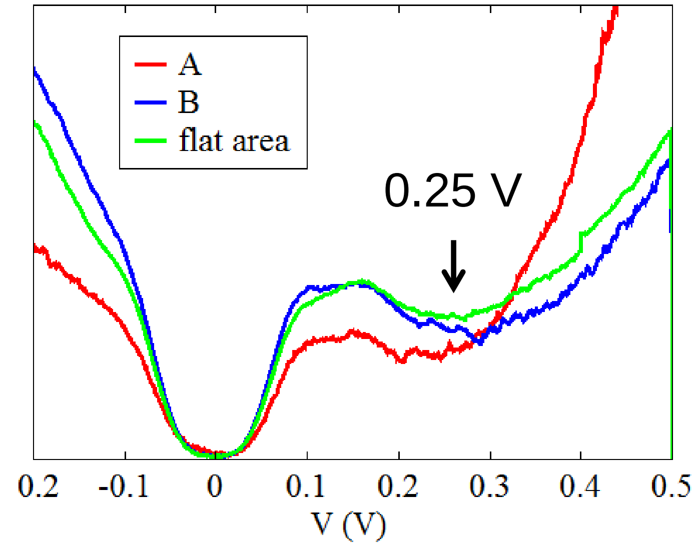
Si dangling bonds

STM and STS at 6K IBM



1.8V, 0.01nA, 20 nm





- p-type doping of QFMLG

- consistent with other experimental (ARPES) and theoretical reports

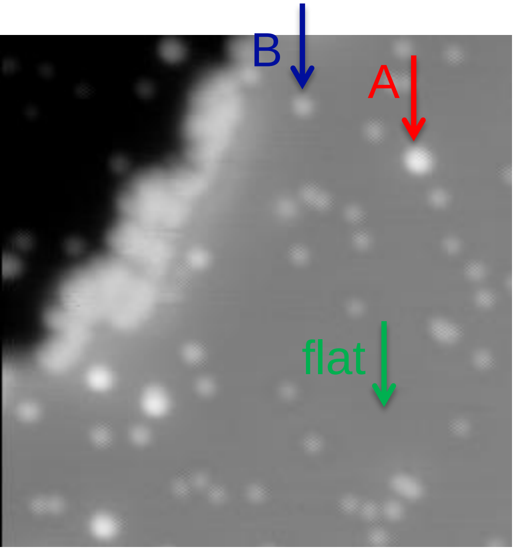
  C. Riedl et al., Phys. Rev. Lett. **103**, 246804 (2009). J. Sławińska et al., Carbon 93, 88 (2015).

- spontaneous polarization of polar surface on SiC substrate

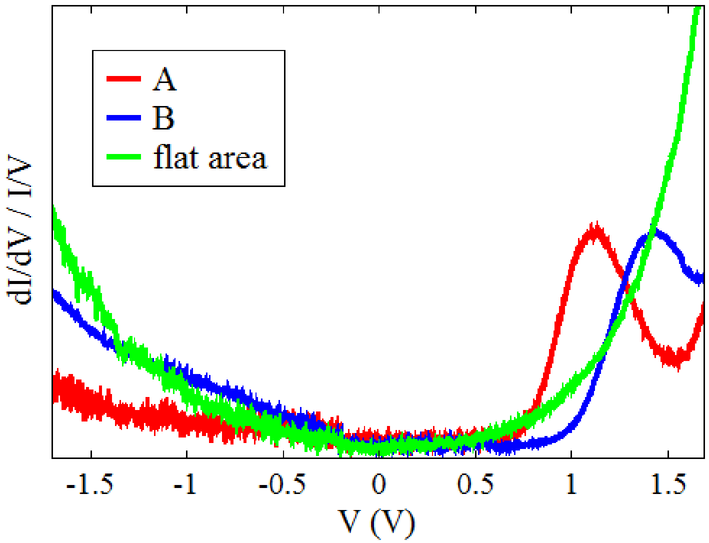
  J. Ristein et al., PRL 108, 246104 (2012).

Si dangling bonds

STM and STS at 6K IBM

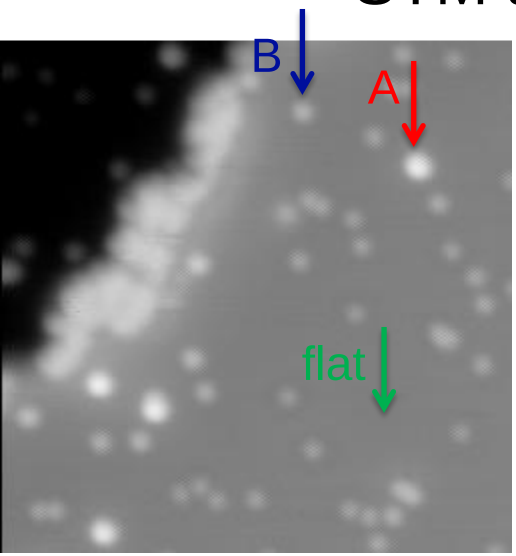


1.8V, 0.01nA, 20 nm



Si dangling bonds

STM and STS at 6K IBM



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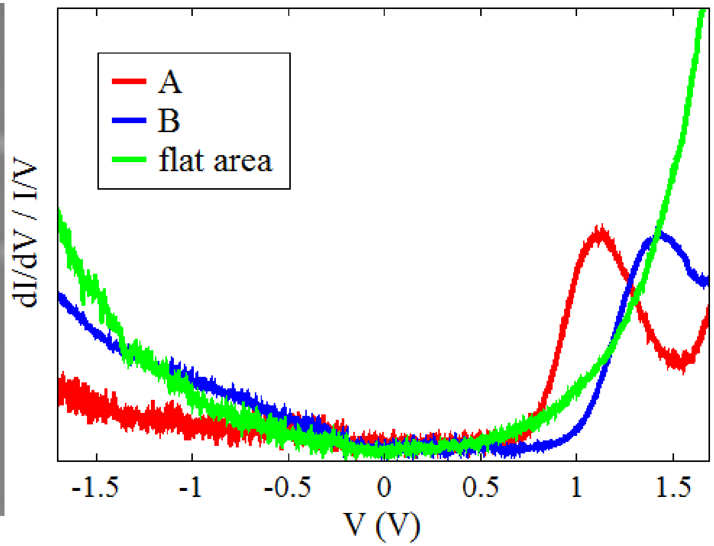
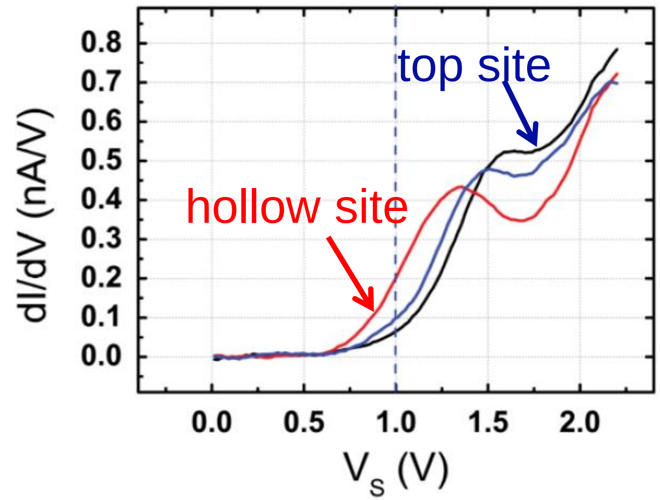
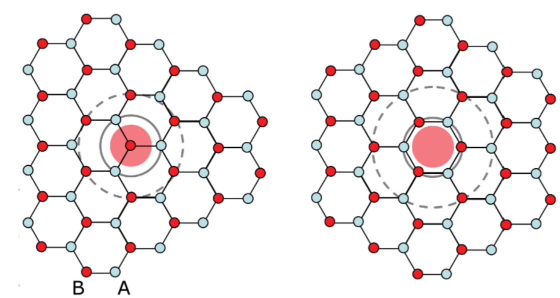
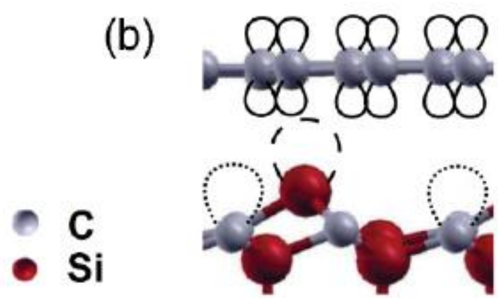


STS on G/SiC(000$\bar{1}$)



top site hollow site





2 types of Si dangling bonds at different graphene / Si stacking configurations

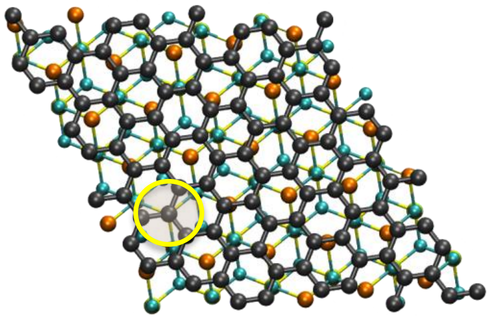
F. Hiebel, P. Mallet, J.-Y. Veuillen, and L. Magaud, Phys. Rev. B 86, 205421 (2012).

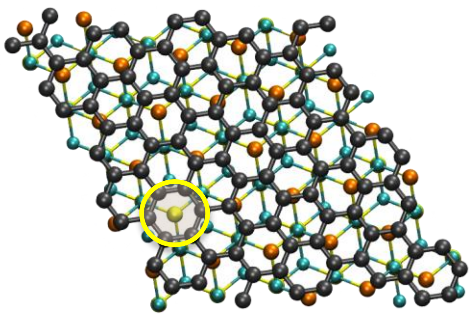
DFT: Single H vacancy

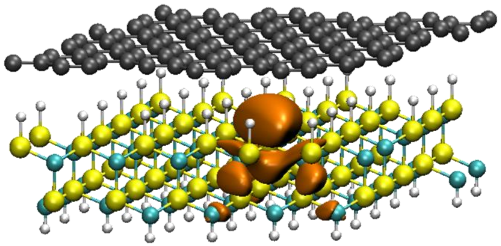
Single H vacancy

C atom on top of the vacancy

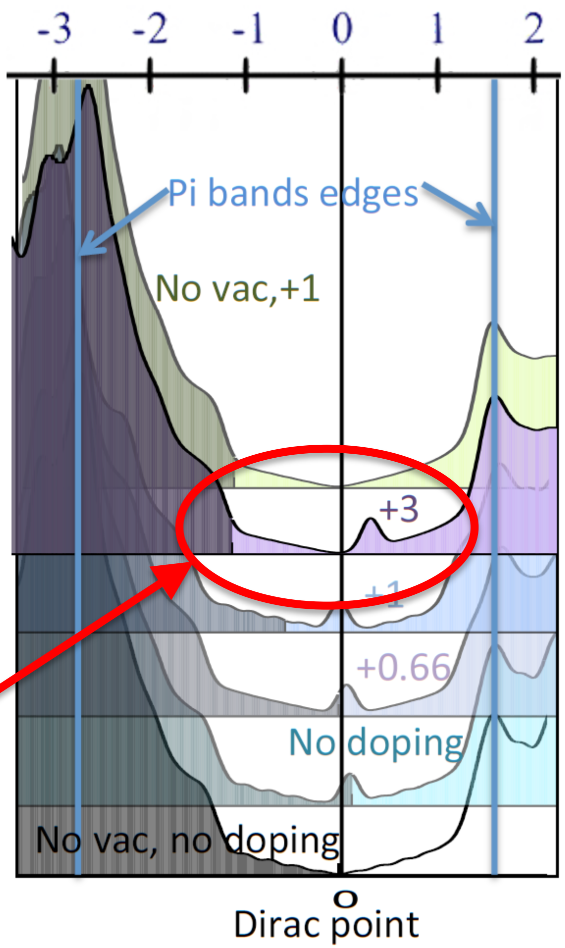
Hollow site







Doping of 1.1 eV shifts localized state by 0.3 eV.



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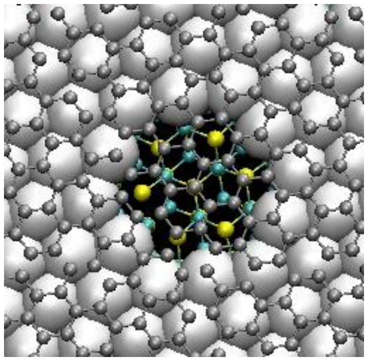
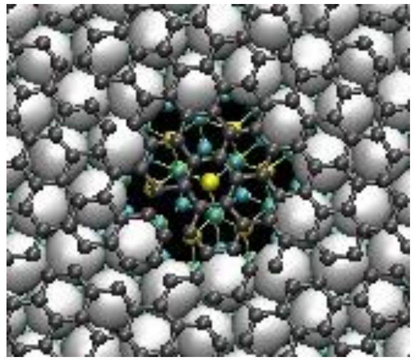
DFT: 7-H vacancy

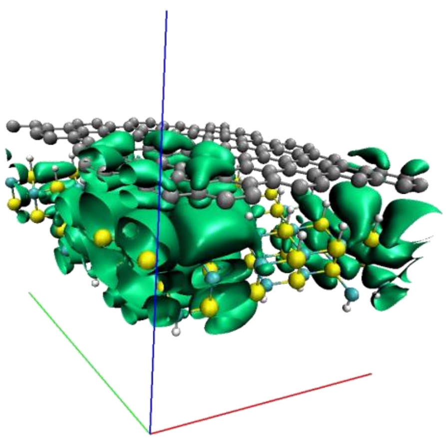
7-H vacancy

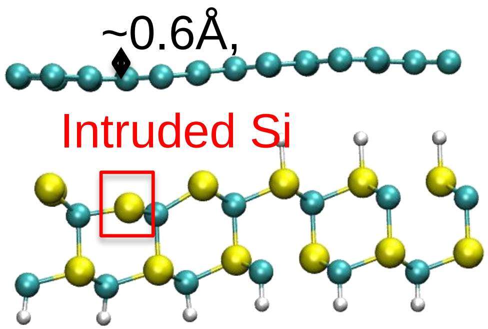
top

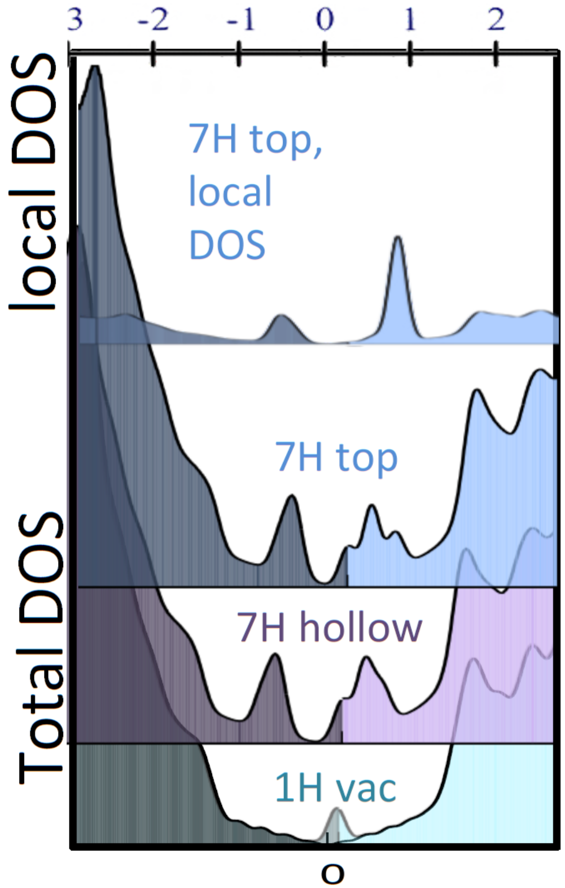


hollow









Work in progress !

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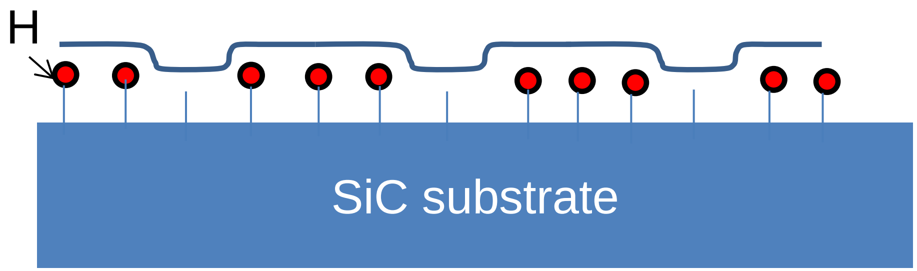
Summary

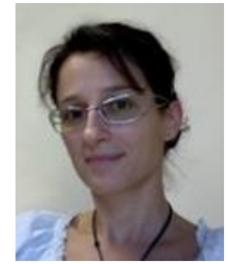


- Small dark spots (T_H = 600-800ºC)
- Incomplete H intercalation
- Hydrogen vacancies / Si dangling bonds
- Carrier scattering as charged impurities
- Mobility-limiting mechanism


Y. Murata


T. Mashoff


T. Cavallucci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