Hydrogen interaction with graphene

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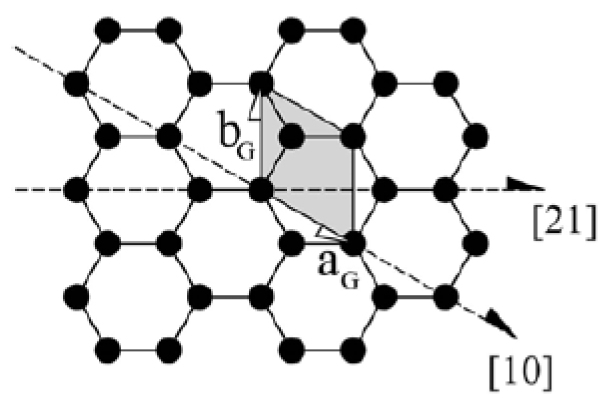
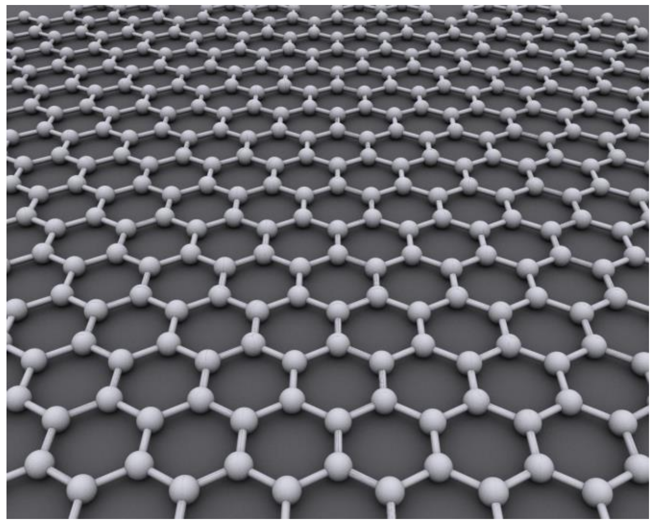
graphene

- one layer of graphite
- a sheet of carbon atoms arranged in a honeycomb lattice





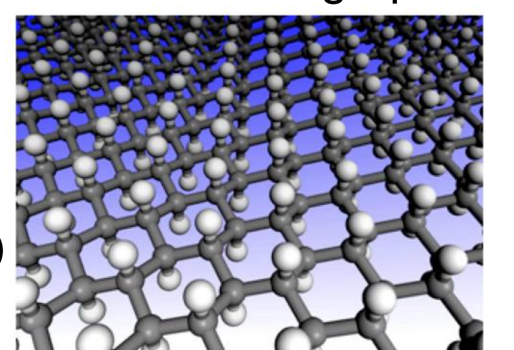
H interaction with graphene

1. H storage

high gravimetric density 8.3%

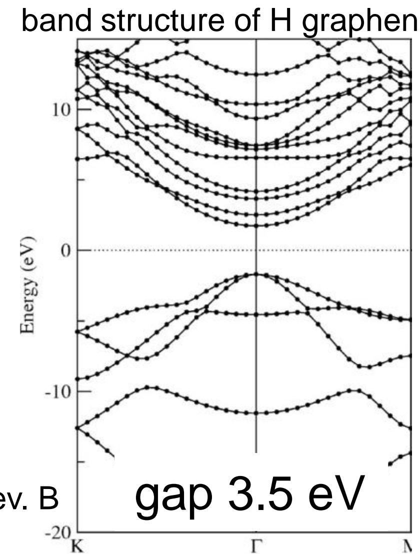
(compressed gas tank in FCV 5.7 %)

H-chemisorbed graphene



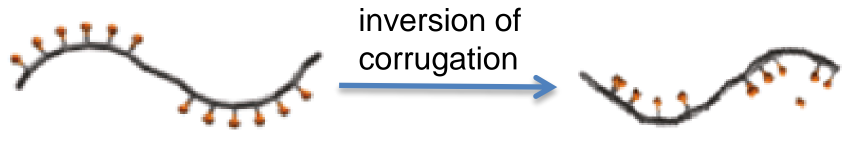
2. gap engineering

band structure of H graphene



Sofo, et.al., Phys. Rev. B 75, 153401 (2007).

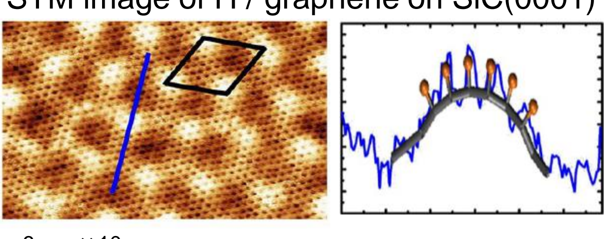
H adsorption / desorption at RT controlled by graphene local curvature



inversion of corrugation

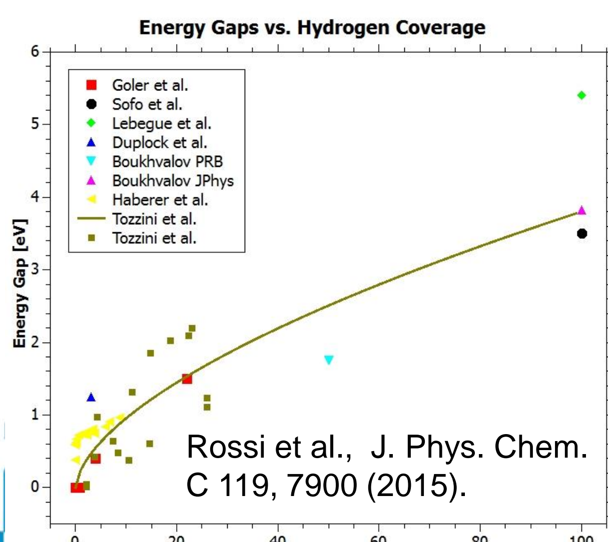
Tozzini, et.al., J. Phys. Chem. C 115, 25523 (2011)

STM image of H / graphene on SiC(0001)



6 nm × 10 nm

Goler, et.al., J. Phys. Chem. C 117, 11506 (2013)



Rossi et al., J. Phys. Chem. C 119, 7900 (2015).

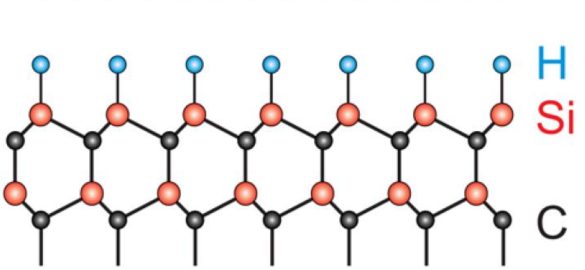
H interaction with graphene

3. modification of graphene-substrate interaction by H intercalation

- graphene receives influences from a supporting substrate in its morphology and electronic property
- H intercalation reduces the influences from substrate
- quasi-free-standing monolayer graphene (QFMLG)

graphene

side view



SiC substrate

Riedl, et.al., Phys. Rev. Lett. **103**, 246804 (2009)

mobility of graphene

- intrinsic limit of mobility of free standing graphene 2×10^5 $cm^2 \cdot V^{-1} \cdot s^{-1}$

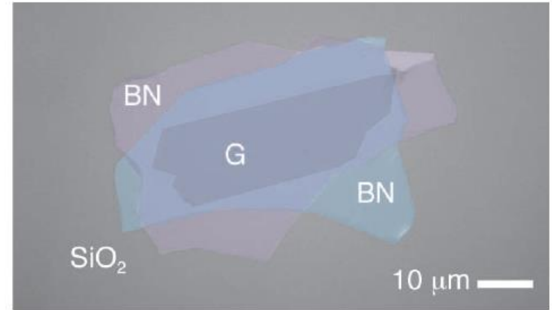
  Bolotin, et.al., solid state communications 146, 351 (2008).

  difficult to handle and make a contact

- graphene on hBN 1.4×10^5 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at R.T.

  Wang, et.al., Science 342, 614 (2013).

graphene flake on hBN



- graphene on SiO_2 4.6×10^4 $cm^2 \cdot V^{-1} \cdot s^{-1}$

  Chen, et.al., Nature Nanotech. 3, 206 (2008).

mobility decreases due to substrate’s phonon mode, charged impurity, defect

need to transfer graphene from graphite or growth substrate

quasi-free-standing monolayer graphene (QFMLG)

- graphene grown on SiC(0001) with H at interface

side view

graphene

H
Si
C

SiC substrate

Riedl, et.al., Phys. Rev. Lett. **103**, 246804 (2009)

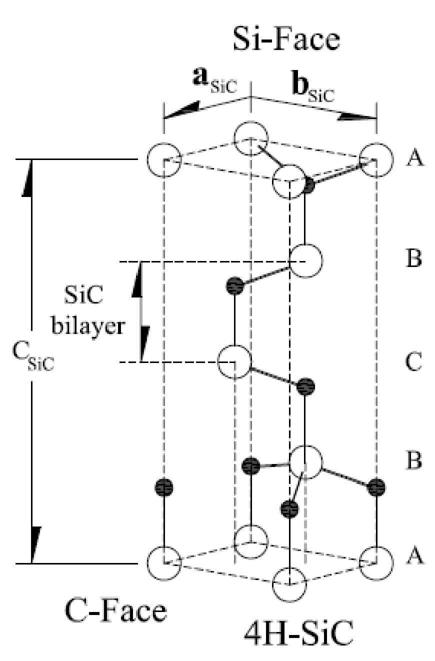
- graphene epitaxially grown on insulator, no need to transfer
- H atoms terminate dangling bonds of substrate

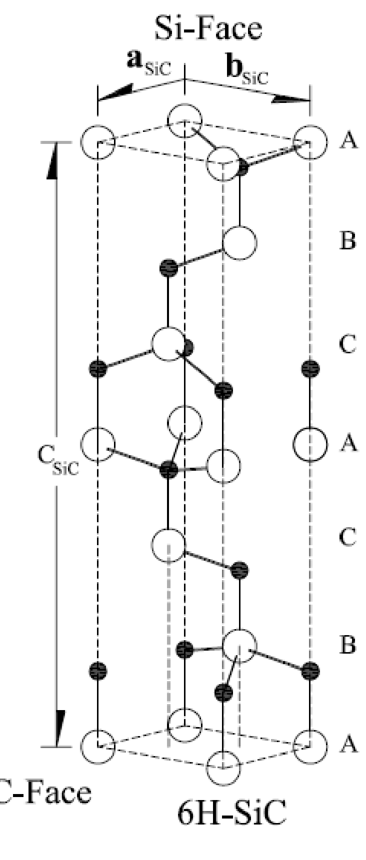
the reported highest mobility QFMLG 6000 $cm^2 \cdot V^{-1} \cdot s^{-1}$

Ciuk et al., Carbon 101, 431 (2016).

Why is the mobility still so low? What is carrier scatterer?

SiC





QFMLG grown on Si-rich SiC(0001)

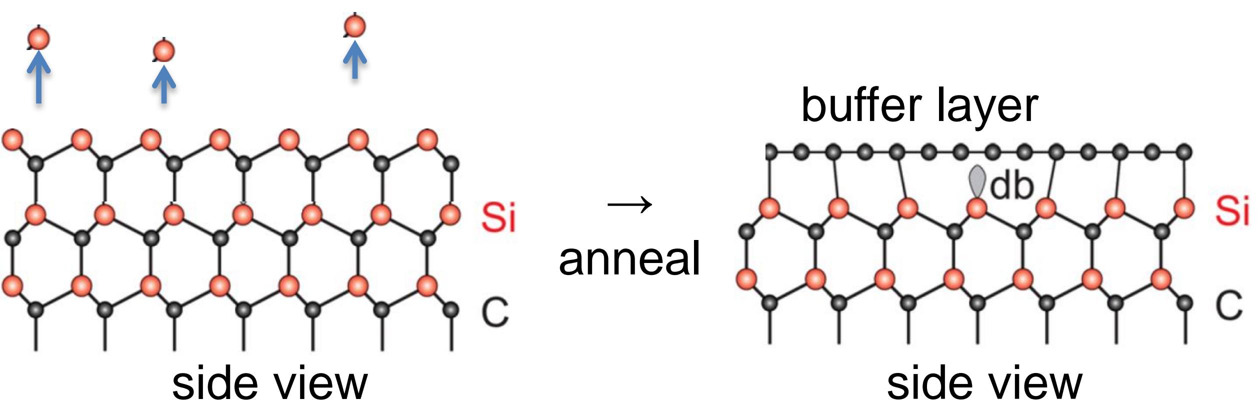
SiC polytype	a_{SiC} (Å)	c_{SiC} (Å)
4H	3.0805	10.0848
6H	3.0813	15.1198

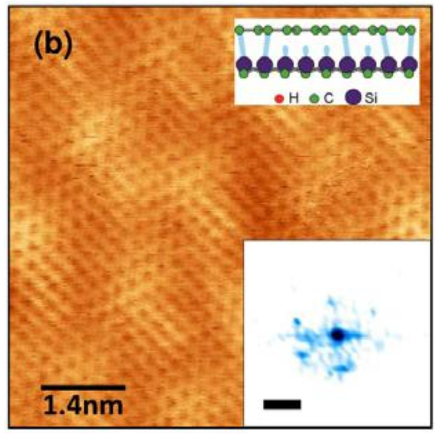
band gap 3 eV

SiC(000-1)

graphene on SiC(0001)

- anneal SiC(0001) surface in vacuum or inert gas
- Si atoms preferentially desorb and remaining C atoms form buffer layer



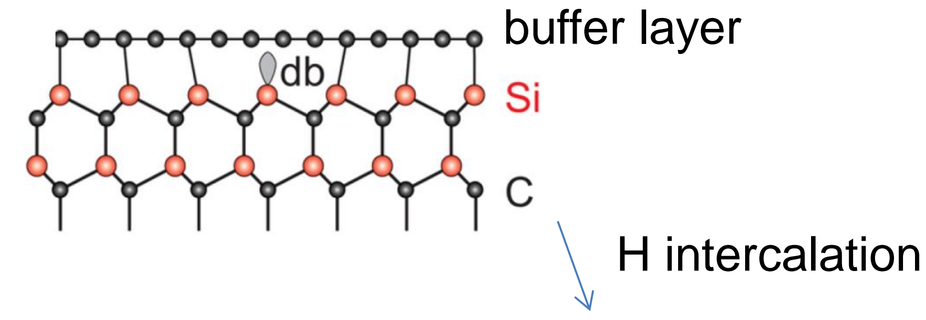


STM of buffer layer
Goler et al., Carbon 51, 249 (2013).

- graphenelike C sheet
- covalently bound to Si atoms of SiC substrate; insulator
- Si dangling bonds at interface
  Sclauzero, et.al., Phys. Rev. B 85, 161405 (2012)

graphene on SiC(0001)

side view

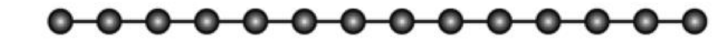


annealing in vacuum
or inert gas

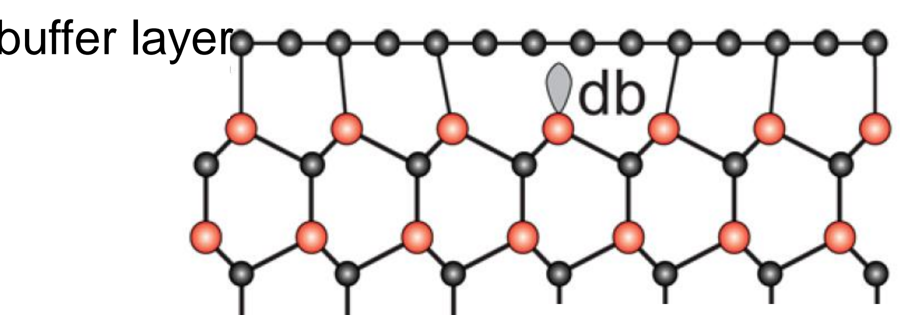
H intercalation

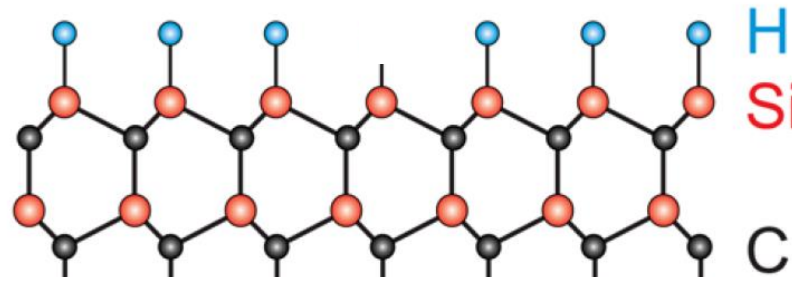
epitaxial monolayer graphene (EMLG)

quasi-free-standing monolayer
graphene (QFMLG)



buffer layer





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

mobility vs temperature

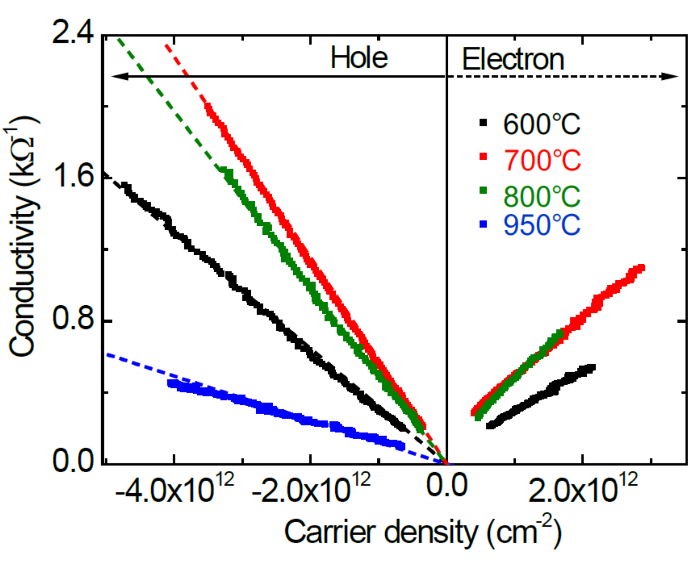
(c)
QFMLG
MLG
10^3 μ (cm^2/Vs)
T (K)

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 mobility of QFMLG is relatively constant with T, while EMLG decreases.

QFMLG has a less influence by phonon scatterings derived from substrate.
(quasi free standing graphene)

conductivity vs carrier density of QFMLG samples formed at different T_H



T_H: temperature of substrate during H intercalation

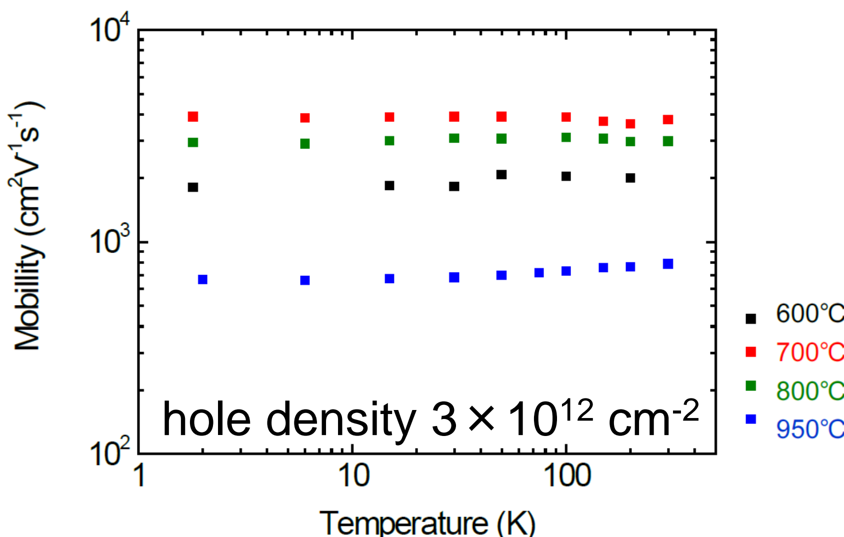
S. Tanabe, M. Takamura, Y. Harada, H. Kageshima, and H. Hibino, Jpn. J. Appl. Phys. **53**, 04EN01 (2014).

relationship between conductivity and carrier density

- charged impurity - linear $\sigma_C = C \frac{e^2}{h} \frac{n}{n_{imp}}$
- defect - independent

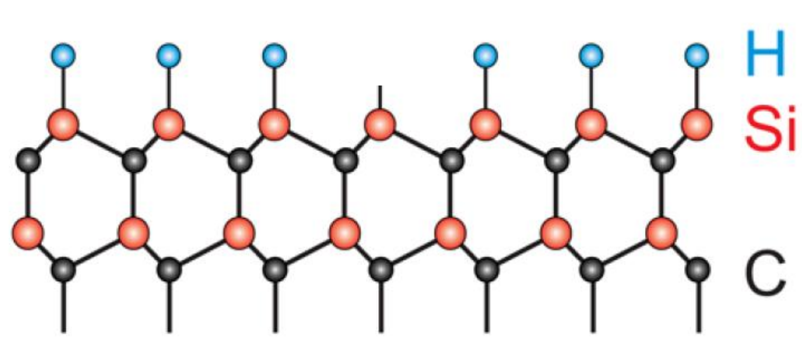
charged impurity is main scatterer in QFMLG

the 950ºC sample shows sublinear relationship ; relatively more defects exist



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

- QFMLG mobility depends on T_H
- highest mobility obtained by T_H = 700ºC



- Unsaturated Si dangling bonds exist and act as charged impurities.
- However, the detailed structure of Si dangling bond has not been fully understood.

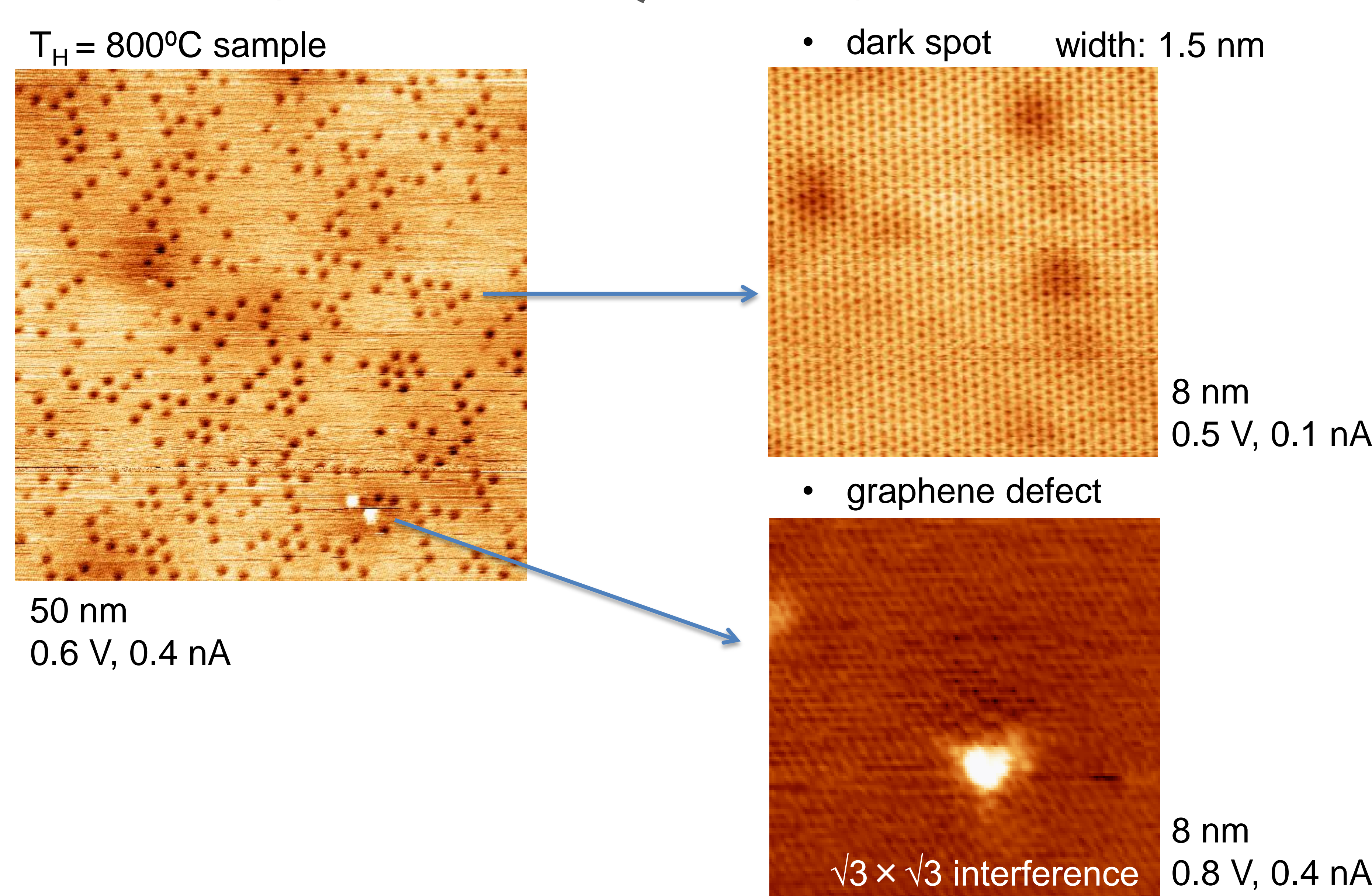
motivation

structure of carrier scatterer in QFMLG?
(Si dangling bond)

We studied

the atomic/electronic structure of QFMLG by scanning tunneling microscopy (STM) and spectroscopy (STS).

STM on QFMLG at RT

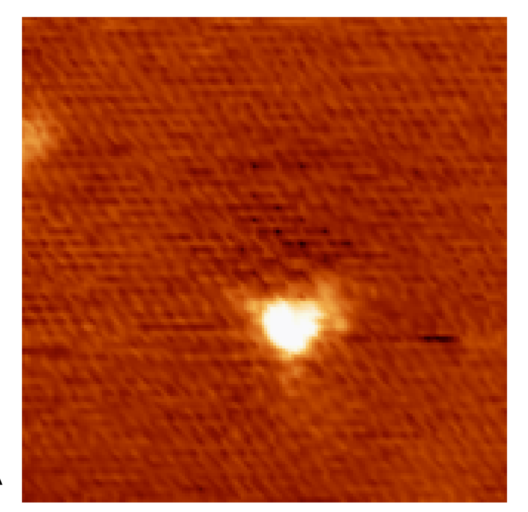


Murata, Appl. Phys. Lett. 105, 221604 (2014)

graphene defect

2D Fourier transform

8 nm
0.8 V, 0.4 nA

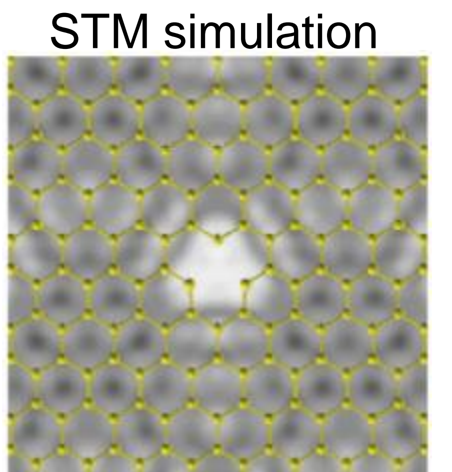


graphene-1 × 1

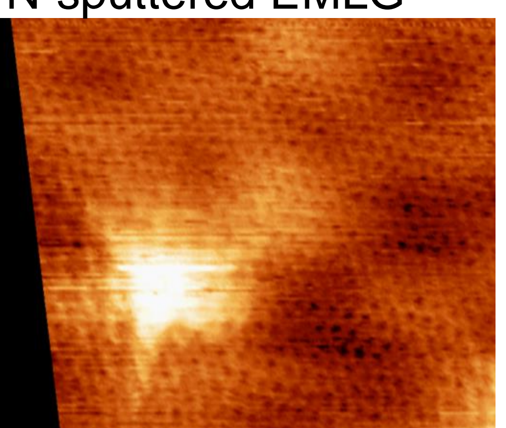
$\sqrt{3} \times \sqrt{3}$

electron interference at defect

STM simulation



N-sputtered EMLG

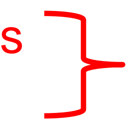


Rhim, Appl. Phys. Lett. **100**, 233119 (2012)

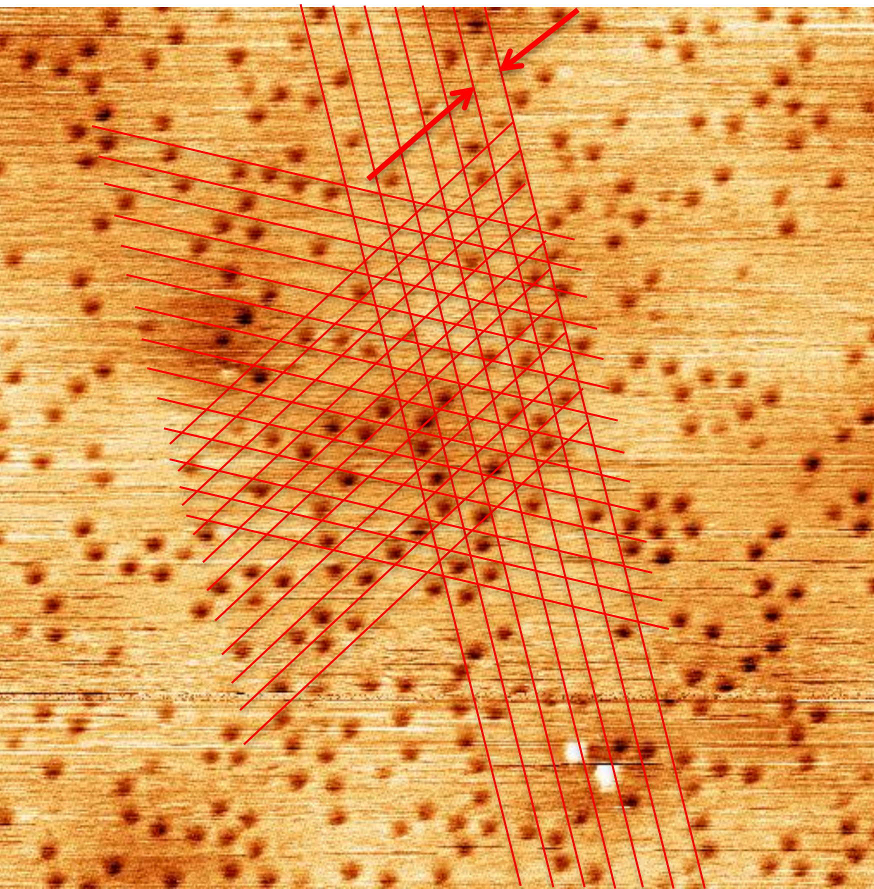
Mashoff, et.al., Appl. Phys. Lett. 103, 013903 (2013).

Si dangling bonds

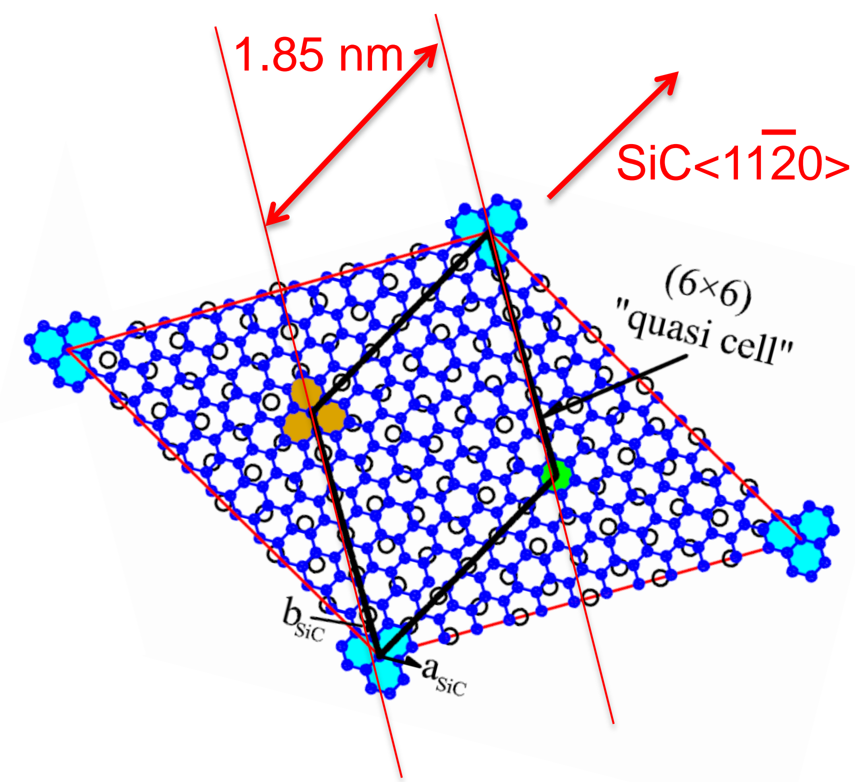
SiC<11$\bar{2}$0> directions
1.8 nm spacing



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



50 nm

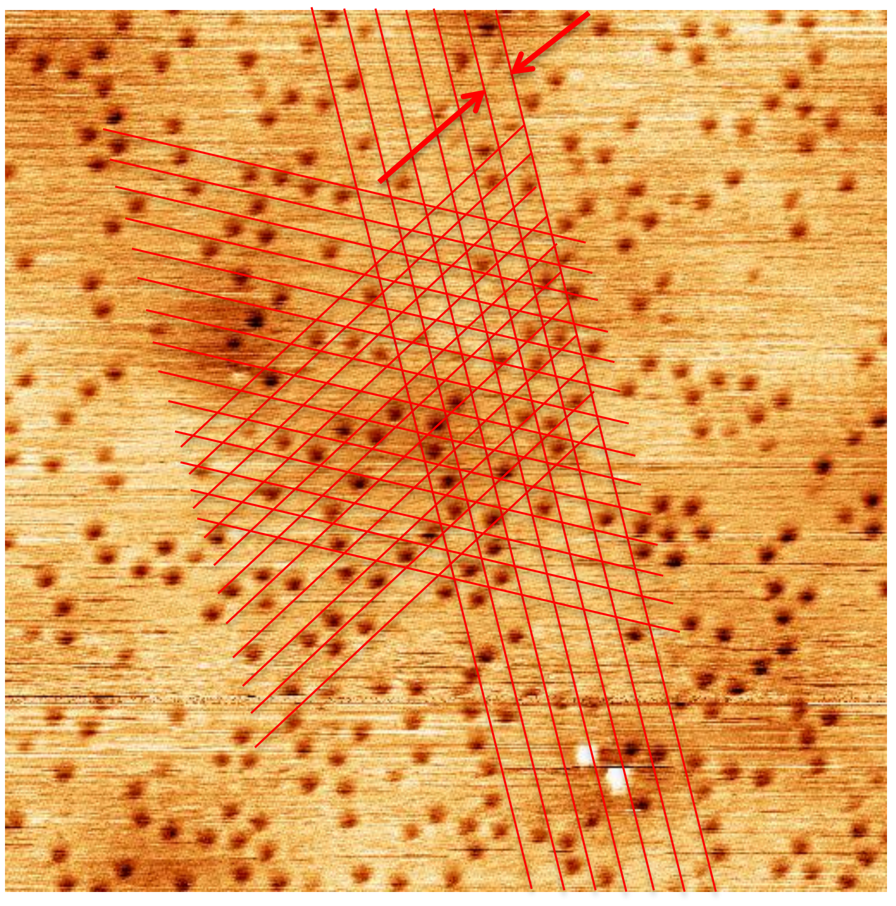


blue: graphene a = 0.24589 nm
white: a = Si 0.30805 nm

Murata, Appl. Phys. Lett. 105, 221604 (2014)

Si dangling bonds

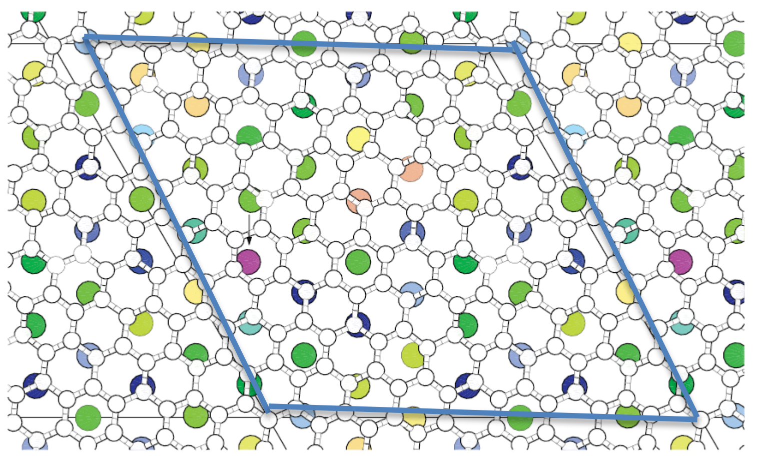
SiC$\langle 11\bar{2}0 \rangle$ directions
1.8 nm spacing



50 nm

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

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



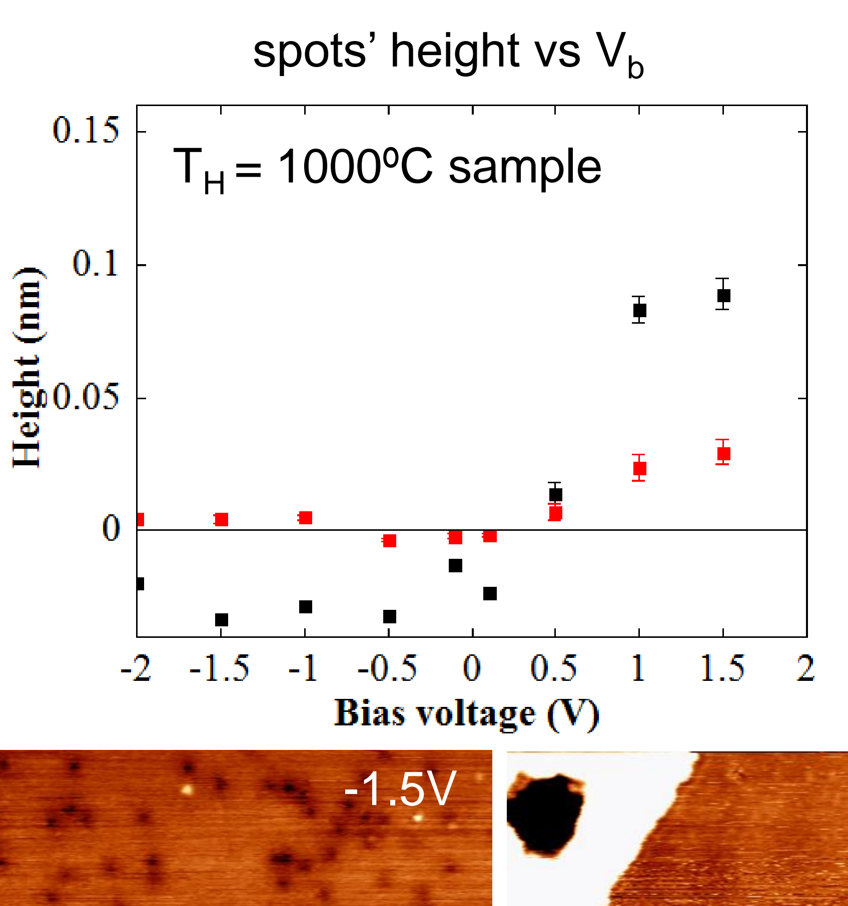
dark blue: the least favored H adsorption site

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

Si dangling bonds distribute along a periodicity of moiré pattern

Murata, Appl. Phys. Lett. 105, 221604 (2014)

spots' height vs V_b



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

0.1nA 100nm

-1.5V

0.5V

1.5V

Si dangling bonds

CNRNANO PISA NEST

STM and STS at 6K

B
A
flat

1.8V, 0.01nA, 20 nm

dI/dV / I/V

A
B
flat area

-1.5 -1 -0.5 0 0.5 1 1.5

V (V)

A
B
flat area

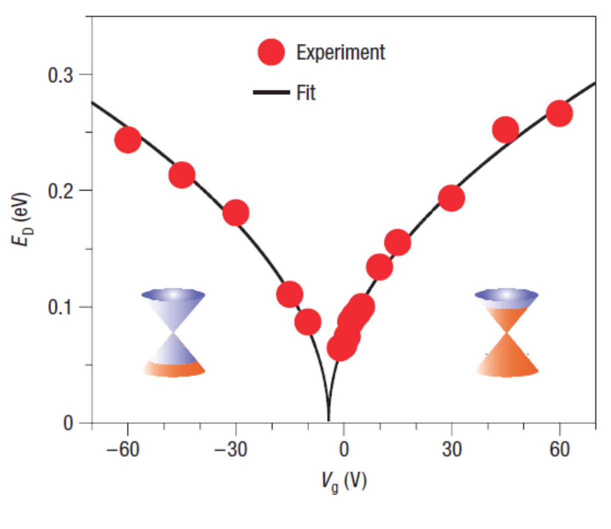
0.2 -0.1 0 0.1 0.2 0.3 0.4 0.5

V (V)

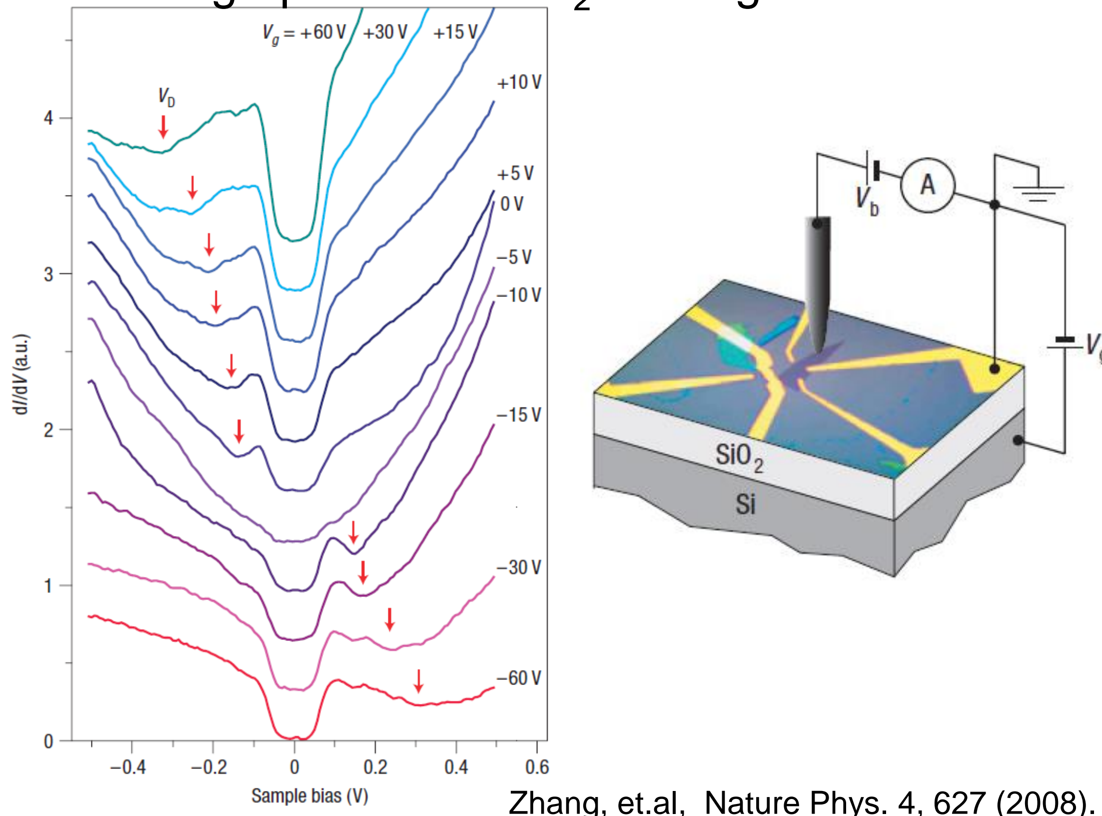
gap like feature at 0 V
and a dip at 0.25 eV

Si dangling bonds

Energy position of Dirac point vs Vg



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



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

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

Si dangling bonds

1.8V, 0.01nA, 20 nm

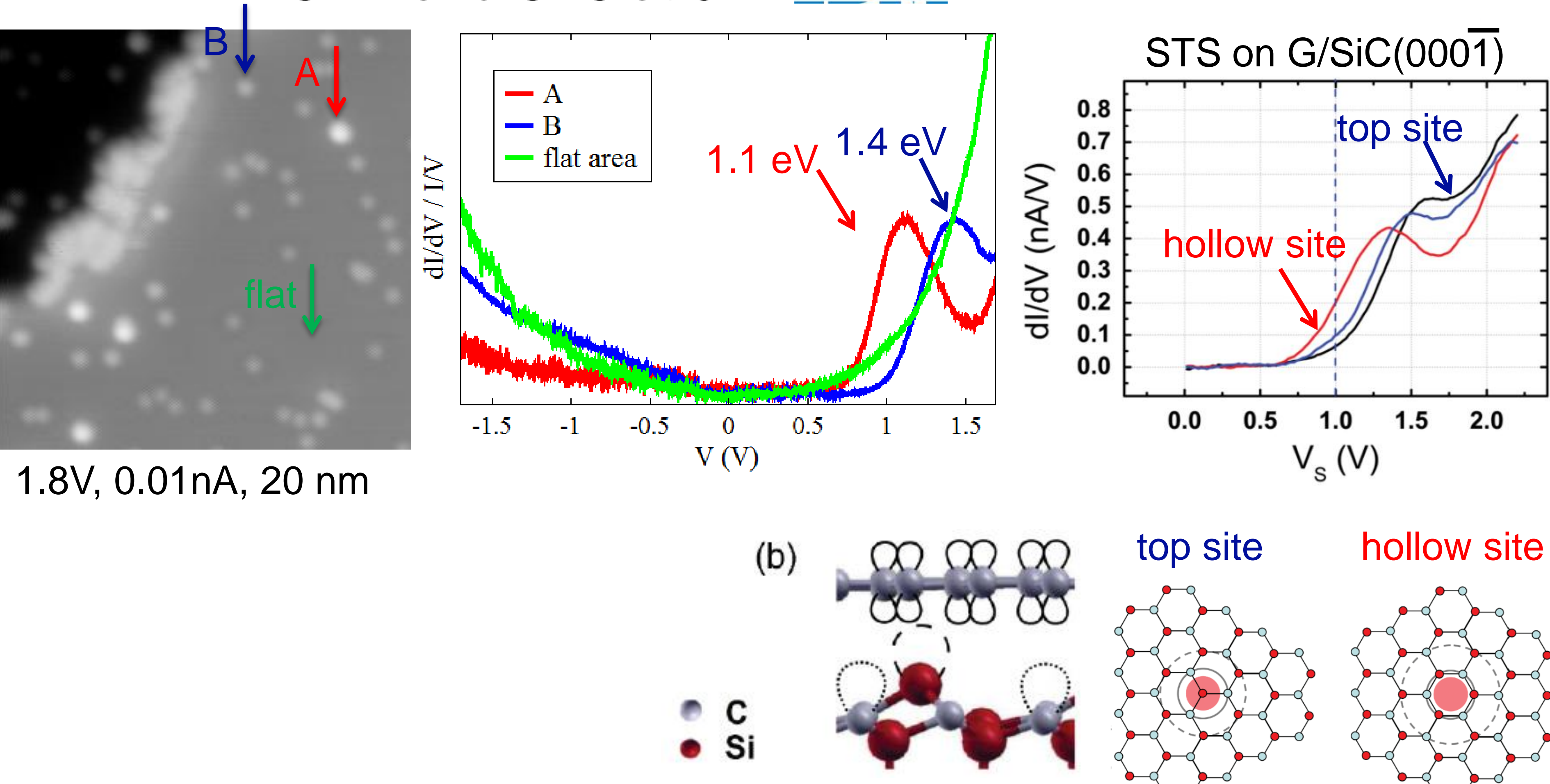
- p doping of QFMLG

- consistent with other experimental (ARPES) and theoretical reports
  Riedl, et.al., Phys. Rev. Lett. **103**, 246804 (2009) Sławińska, et.al., Carbon, 93, 88 (2015)

- spontaneous polarization of polar surface on SiC substrate
  Ristein, et.al., PRL, 108, 246104 (2012)

Si dangling bonds

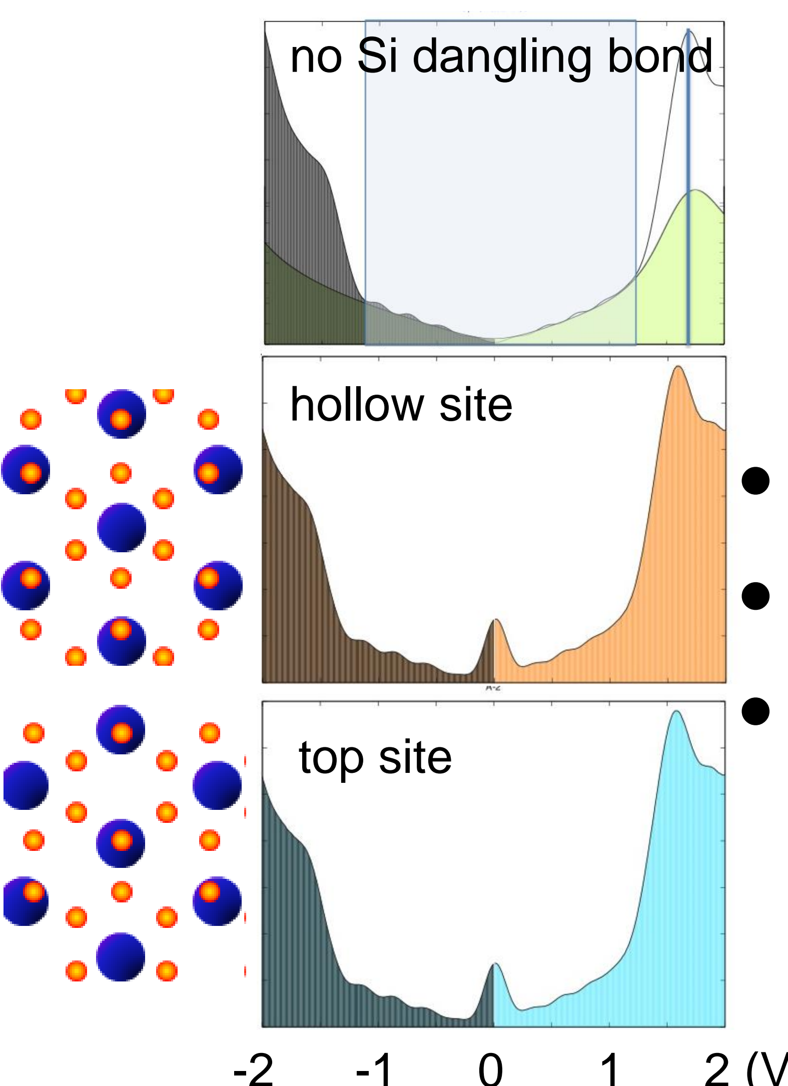
STM and STS at 6K

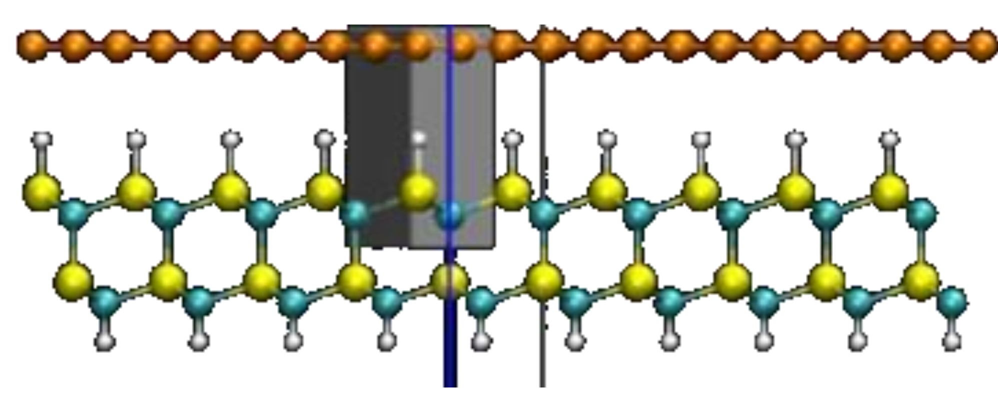


- 2 types of Si dangling bonds at different graphene / Si stacking configurations

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

DFT calculation of local density of states of QFMLG models with single Si dangling bond

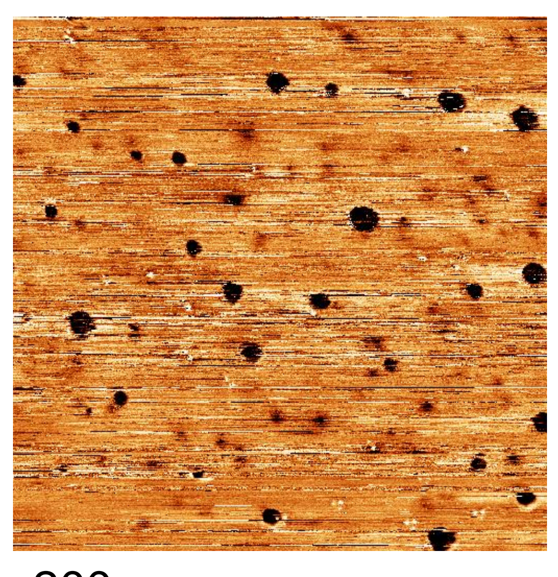




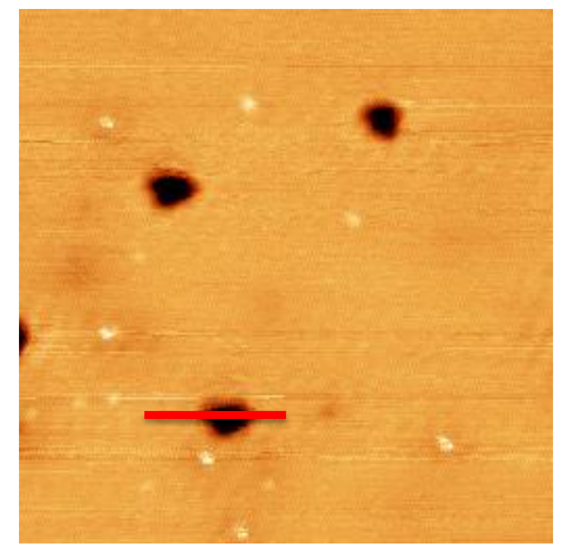
- The 1.1-1.4 eV peaks in STS are not reproduced.
- The results of hollow and top sites are almost same.
- The dangling bond state appears as a half-filled state at E_F. why?
  - doping
  - multiple Si dangling bonds may induce more buckling of graphene and more interaction

performed by Tommaso Cavallucci, Valentina Tozzini, NEST

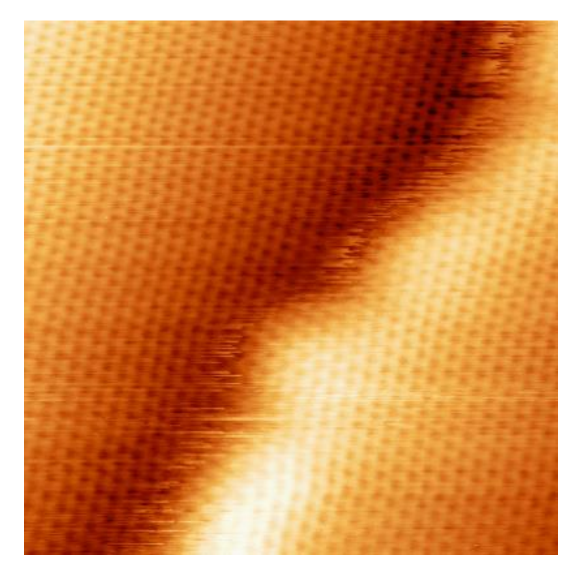
etch pit in SiC: $T_H = 1000^oC$



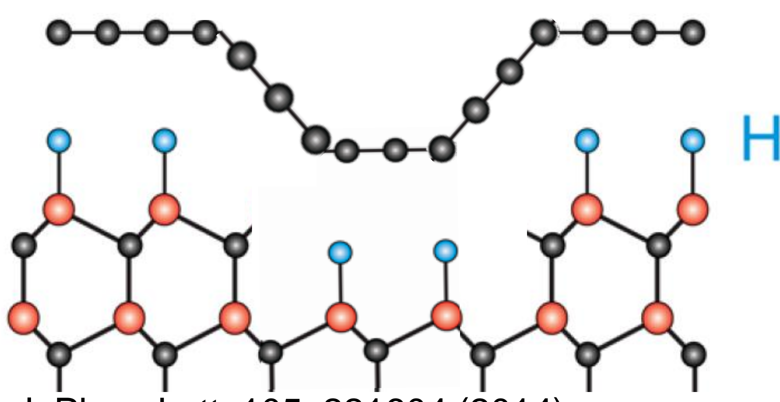
200 nm

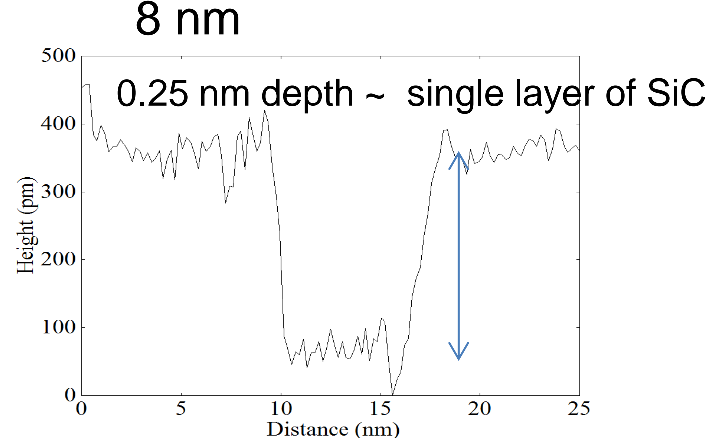


50 nm



8 nm

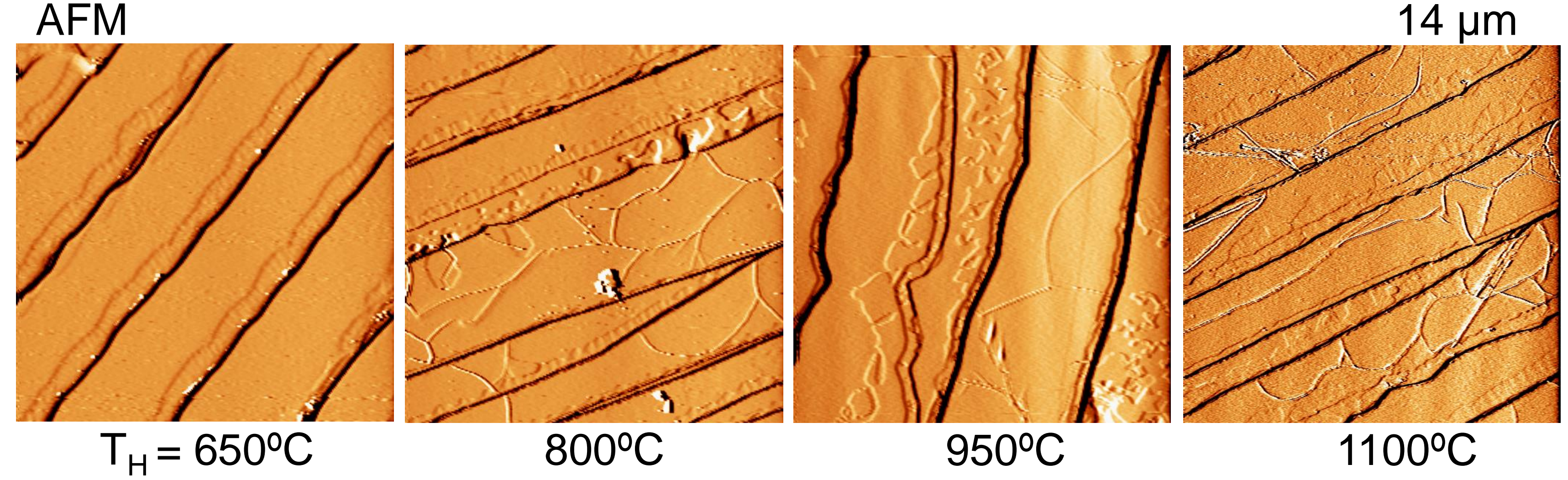


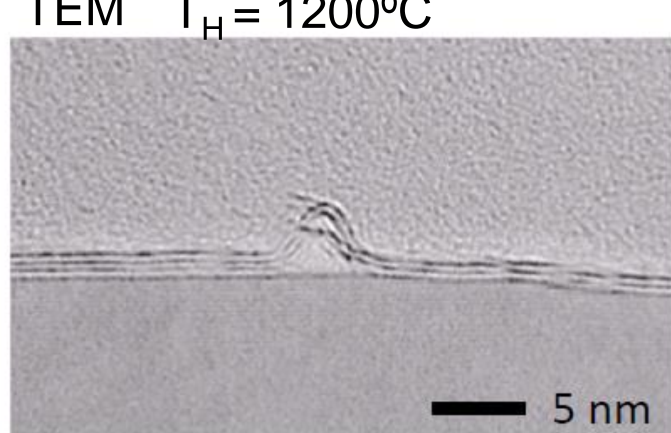


Murata, Appl. Phys. Lett. 105, 221604 (2014)

$$1/5SiC + H = 1/5SiH_4 + 1/10C_2H_2$$

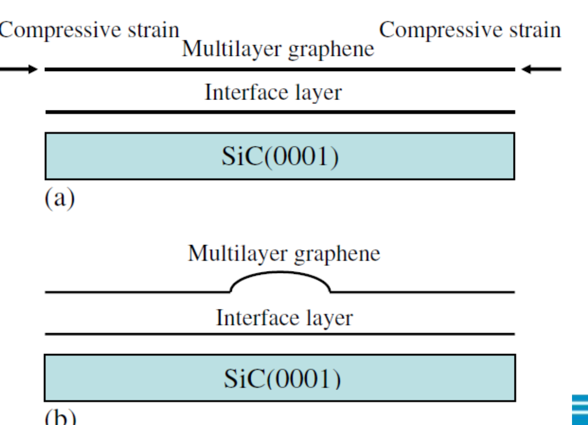
graphene wrinkle: $T_H = 1000^oC$





Murata, Appl. Phys. Lett. 105, 221604 (2014)

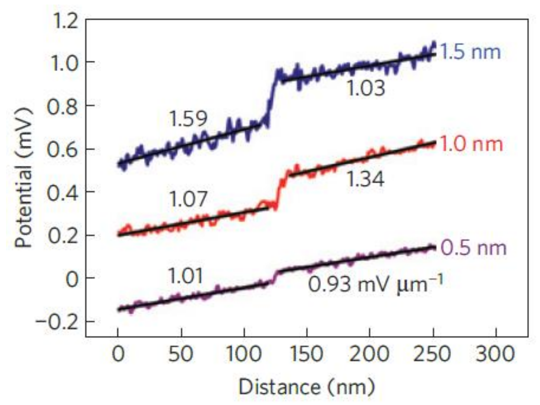
difference in thermal expansion coefficients between graphene and SiC induces the wrinkle



Sun, et.al., Nanotechnology 20, 355701 (2009)

etch pit in SiC, and graphene wrinkle

Scanning tunneling potentiometry



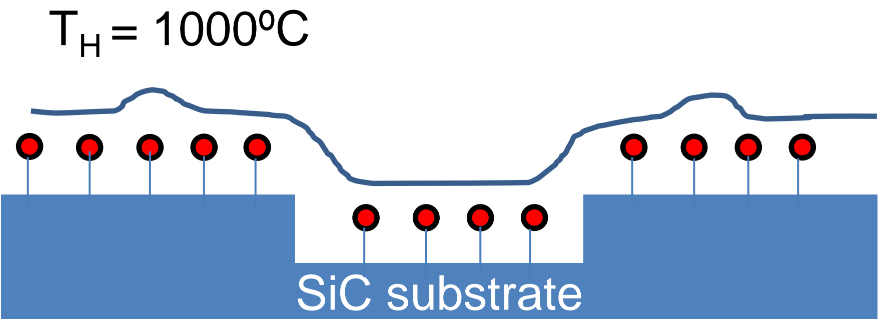
Ji, et.al., Nature Materials 11, 114 (2012)

EMLG resistance increases over SiC substrate steps

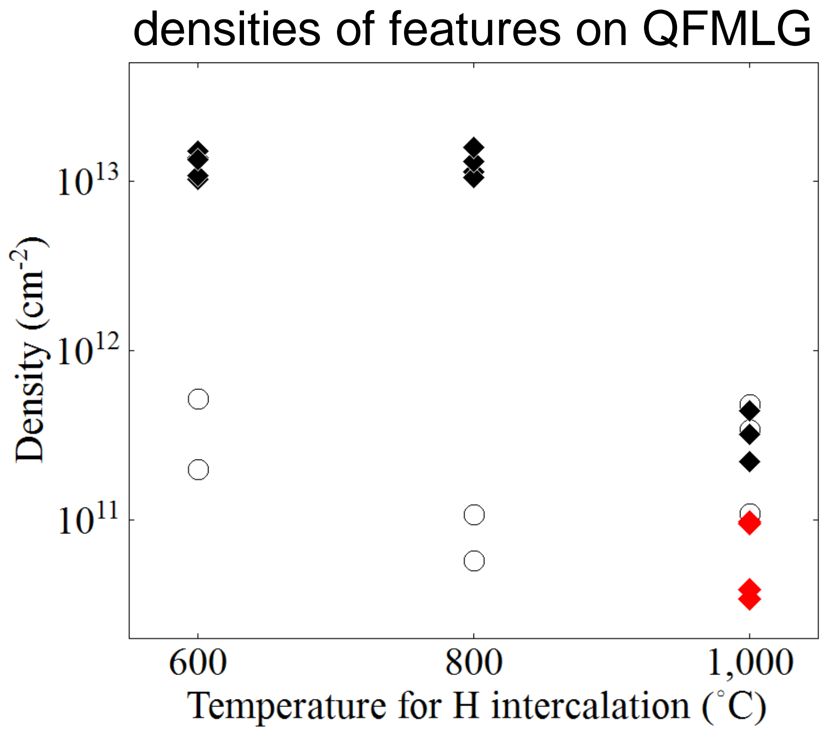
- π-σ hybridization by curvature of graphene
- strain of graphene
- reduced doping due to a larger distance at the interface

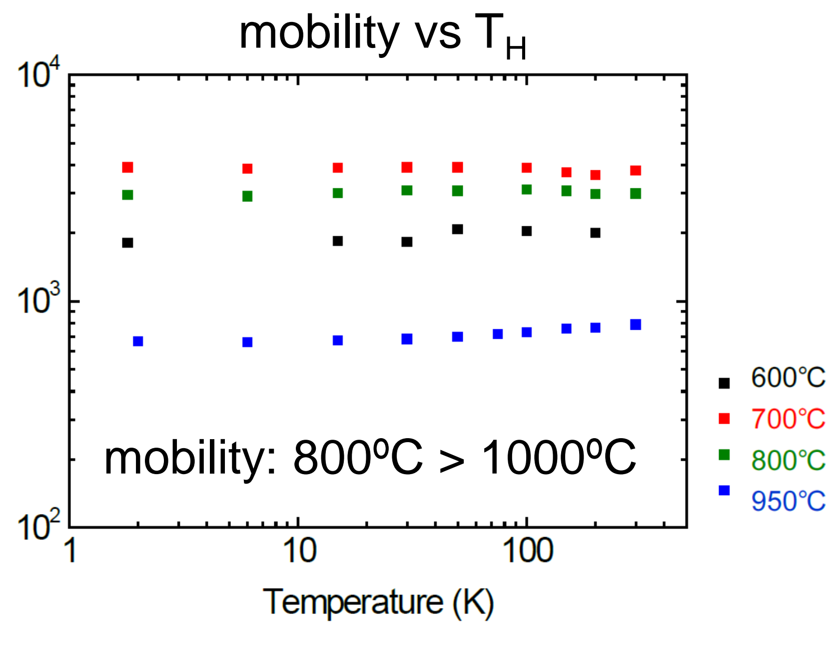
T. Low, V. Perebeinos, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. 108, 096601 (2012)

$T_H = 1000^oC$



Morphology and transport





S. Tanabe, Jpn. J. Appl. Phys. **53**, 04EN01 (2014).

		• influence on mobility
graphene defect ----------------	constant with T_H	
Si dangling bond ---------------	decrease with T_H	small increase
etch pit in SiC (and G wrinkle)	increase with T_H	large decrease

Murata, Appl. Phys. Lett. 105, 221604 (2014)

Conclusion

- We investigated the atomic and electronic structures of QFMLG formed at different temperatures for H intercalation with STM, AFM, and TEM.

- Si dangling bonds align along SiC6x6 periodicity.

- Si dangling bonds show two different types of contrasts in STM image.

- The two types of Si dangling bonds have a peak at 1.1 eV and 1.4 eV in STS. The difference may be attributed to different graphene-Si configurations.

- SiC holes and graphene wrinkle appear on T_H = 1000ºC sample

- In order to obtain a high mobility QFMLG, we need to optimize H intercalation condition to intercalate more H, below the temperature at which SiC holes and graphene wrinkles appear.

Murata, Appl. Phys. Lett. 105, 221604 (2014)

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