Atomic and electronic structures of Si-dangling bonds in quasi-free standing monolayer graphene (QFMLG)

Yuya Murata, Tommaso Cavallucci, Valentina Tozzini, Fabio Beltram, Stefan Heun

Niko Pavliček, Leo Gross, Gerhard Mayer

Makoto Takamura, Hiroki Hibino

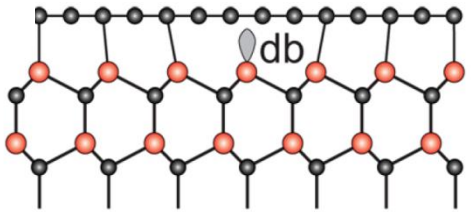
GRAPHENE FLAGSHIP

National Enterprise for nanoScience and nanoTechnology

NEST

graphene on SiC(0001)

side view



buffer layer

Si

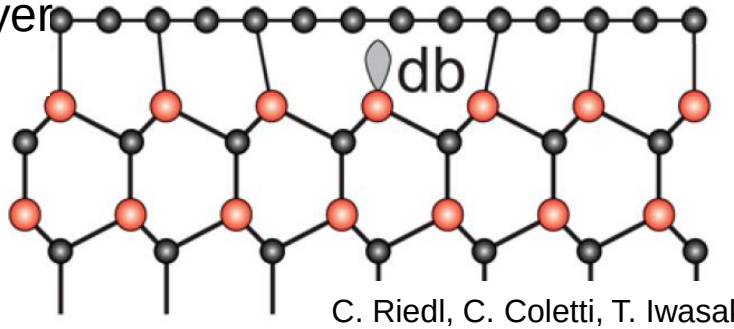
C

annealing in vacuum
or inert gas

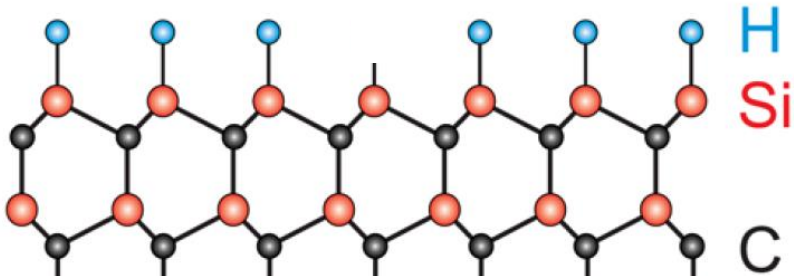
H intercalation

epitaxial monolayer graphene (EMLG)

buffer layer



quasi-free-standing monolayer graphene (QFMLG)



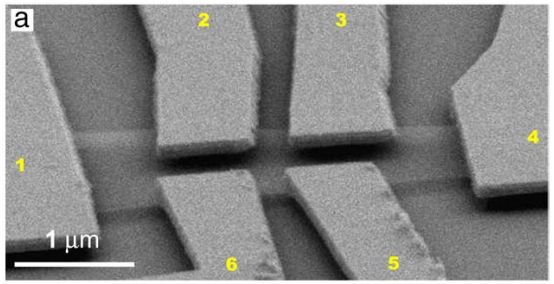
C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009)

mobility of graphene

free standing graphene

: mobility = 2×10^5 $cm^2 \cdot V^{-1} \cdot s^{-1}$

- difficult to handle, make contacts



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

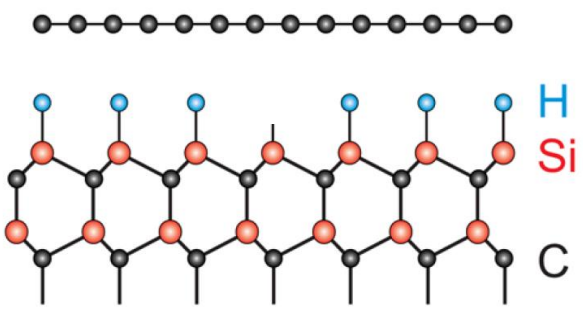
graphene on SiO_2: mobility = 4.6×10^4 $cm^2 \cdot V^{-1} \cdot s^{-1}$ Chen, et.al., Nature Nanotech. 3, 206 (2008).

graphene on hBN: mobility = 1.4×10^5 $cm^2 \cdot V^{-1} \cdot s^{-1}$ Wang, et.al., Science 342, 614 (2013).

- mobility decreases due to substrate's phonon, charged impurity, and disorder
- Graphene needs to be transferred from graphite or growth substrate.

quasi-free-standing monolayer graphene (QFMLG)

graphene epitaxially grown on H-terminated SiC(0001) surface



graphene

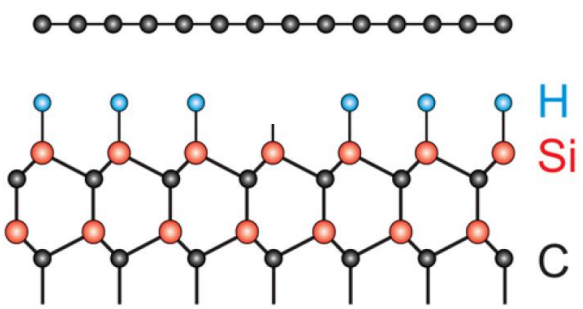
SiC substrate

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

- H atoms are intercalated at the interface to terminate Si bonds of SiC
- the reported highest mobility 6000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ Ciuk et al., Carbon 101, 431 (2016).
- Si dangling bonds (= H vacancies) may remain at the interface and act as carrier scattering centers?

quasi-free-standing monolayer graphene (QFMLG)

graphene epitaxially grown on H-terminated SiC(0001) surface



graphene

SiC substrate

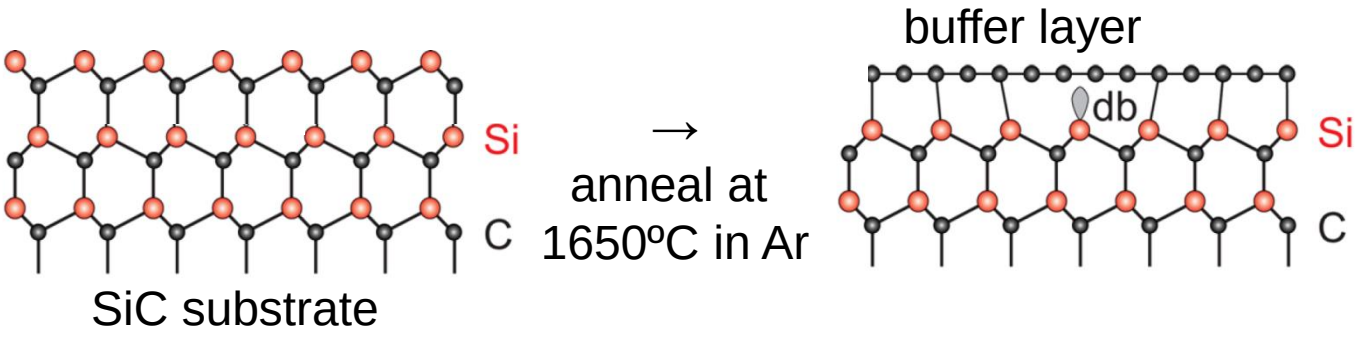
In this work, we studied:

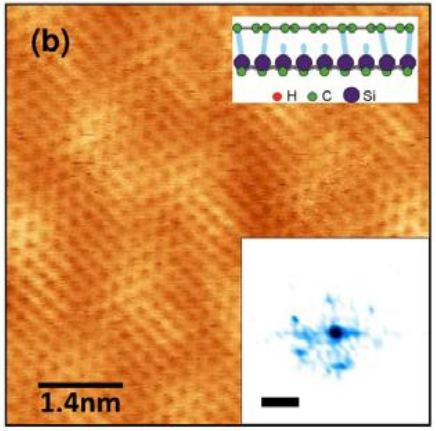
the atomic/electronic structure of Si dangling bonds (= H vacancies) at the interface of QFMLG

by scanning tunneling microscopy (STM), atomic force microscopy (AFM), and DFT calculation.

experiment

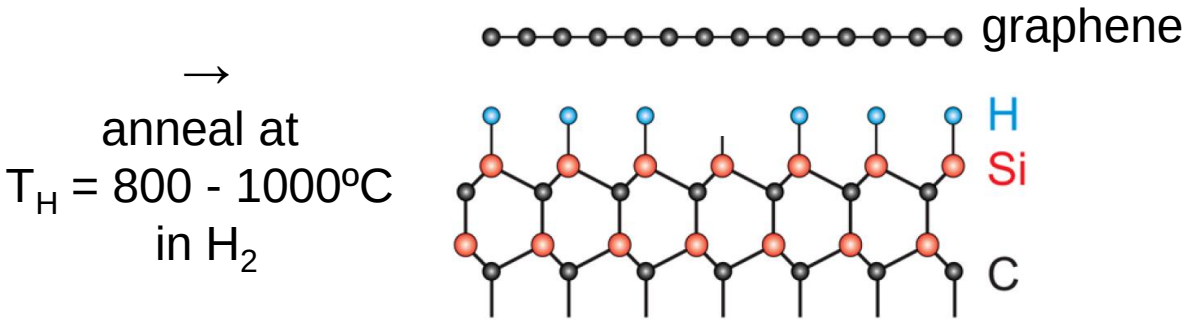
1. formation of buffer layer





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

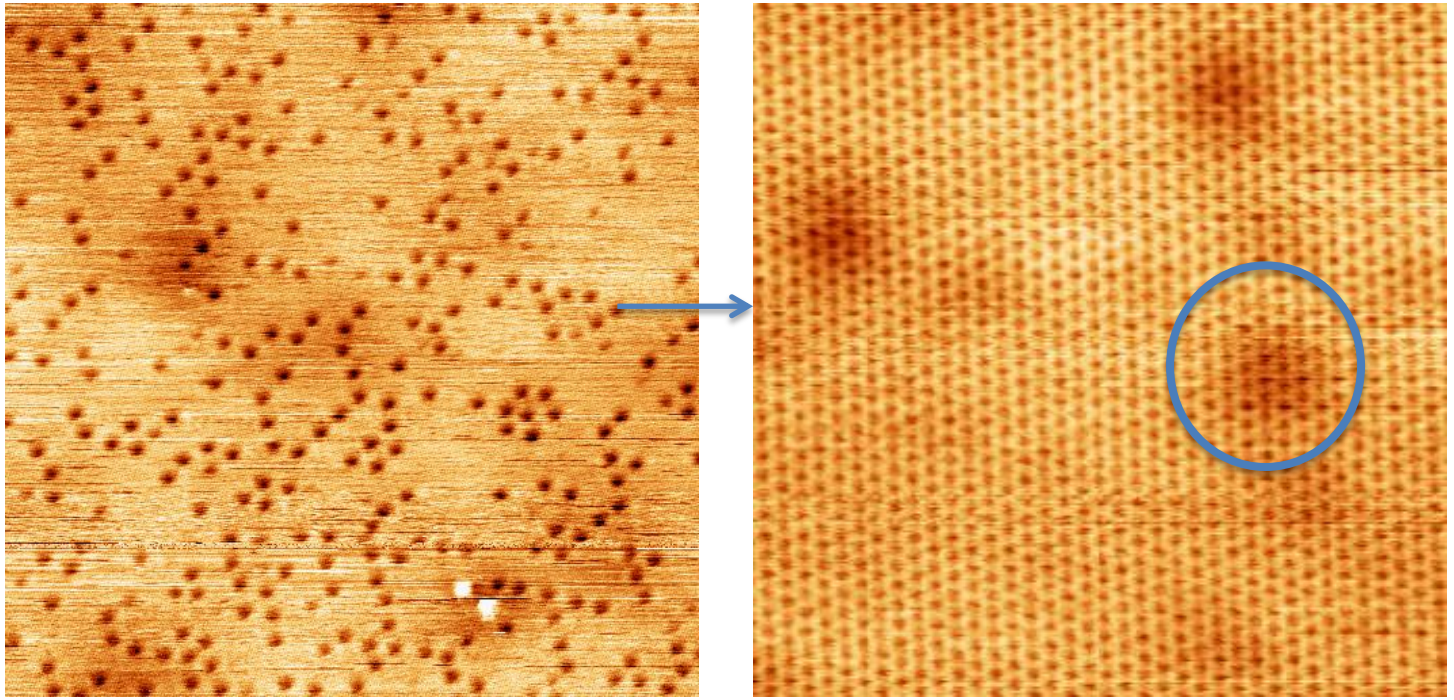
2. H intercalation



3. characterization

- RT-STM
- LT-STM/AFM (5K)

RT-STM on QFMLG (T_H = 800ºC)



50 nm, 0.6 V, 0.4 nA

8 nm, 0.5 V, 0.1 nA

- dark features

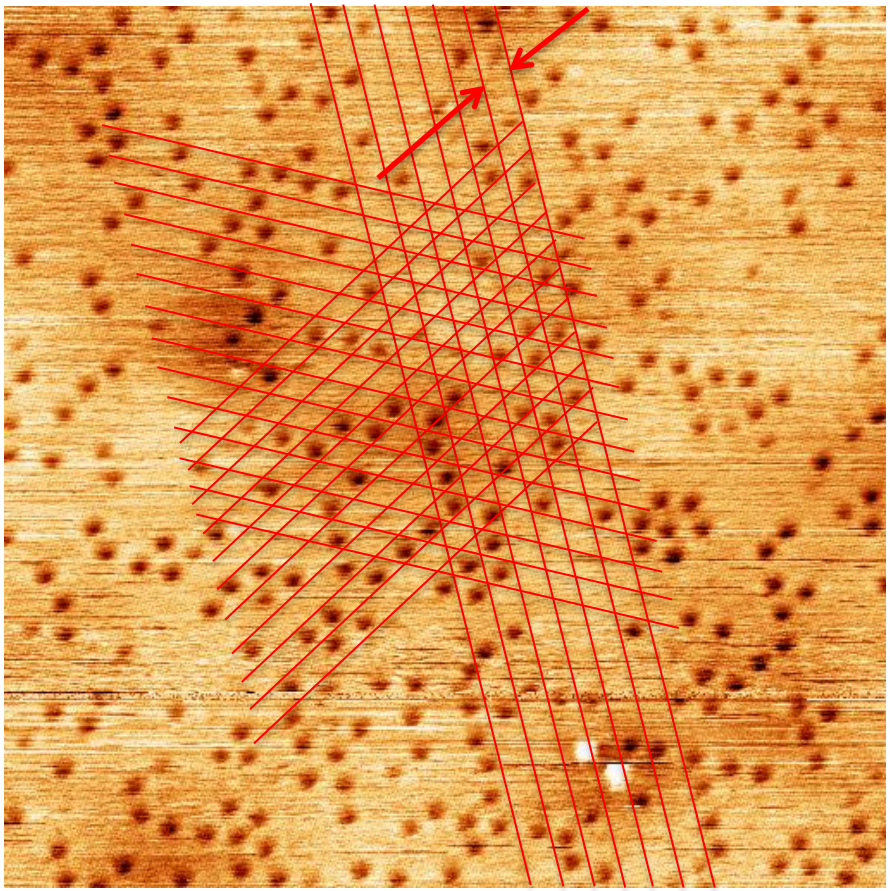
  width: 1.5 nm
  density: 10^{13} cm^{-2}

  -> Si dangling bonds?

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

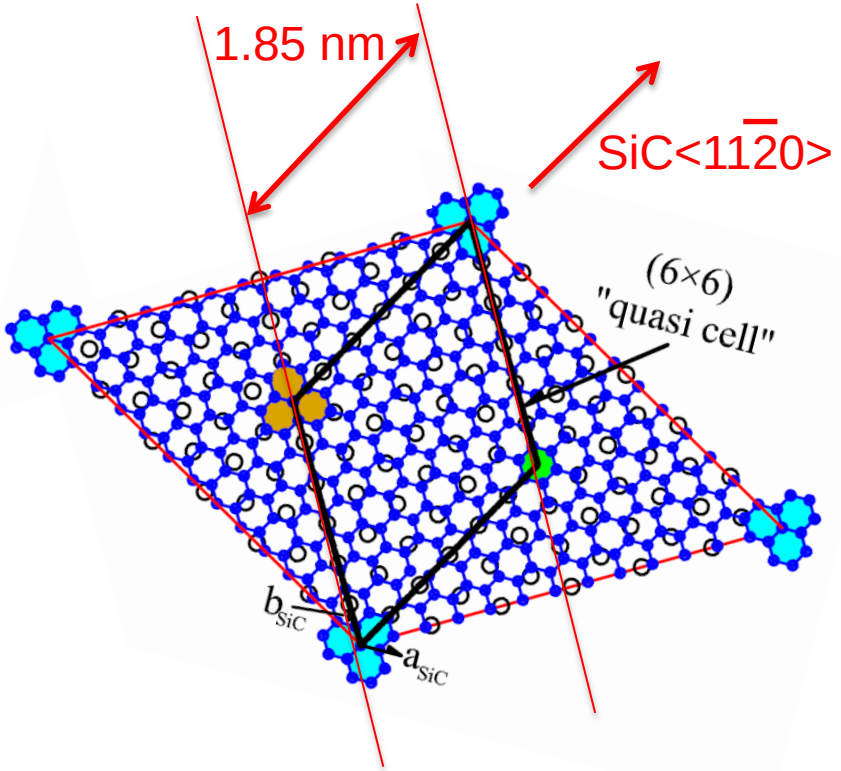
distribution of the features

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



50 nm

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

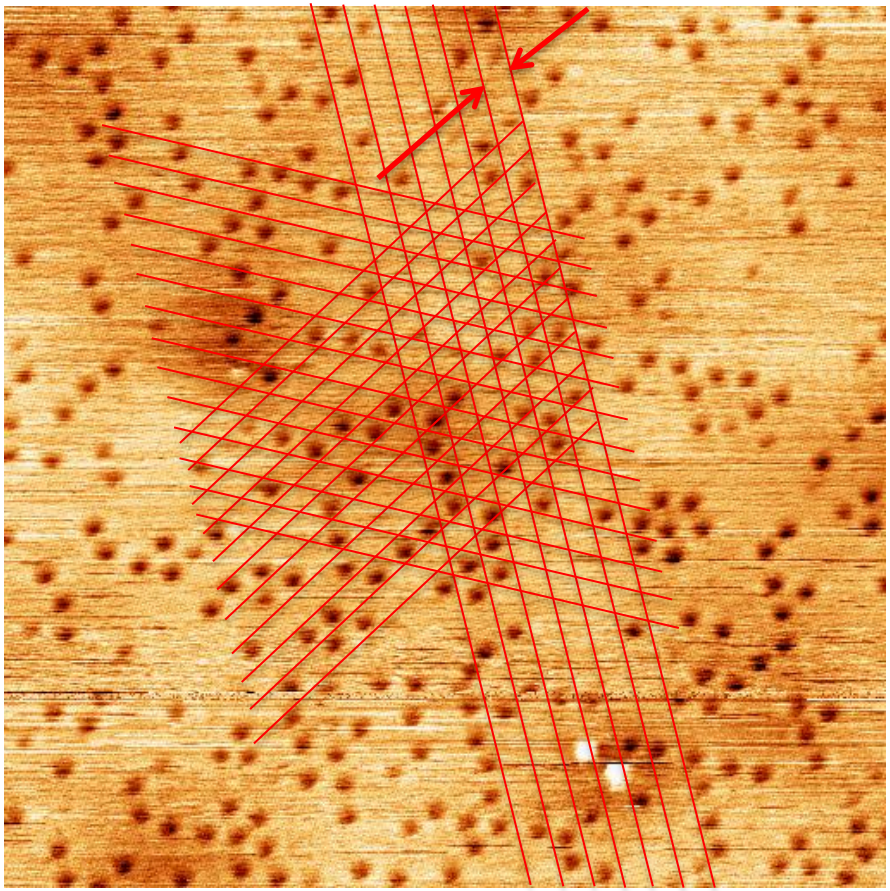


blue: graphene a = 0.24589 nm
white: a = Si 0.30805 nm

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

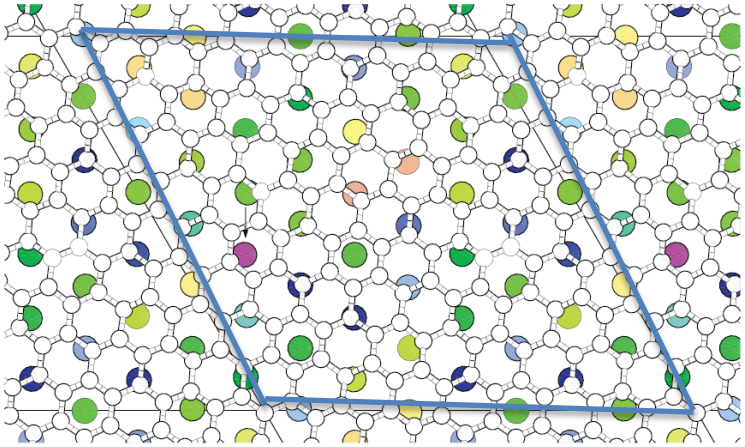
distribution of the features

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



50 nm

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



variation ~ 1 eV

dark blue: the least favored H adsorption sites

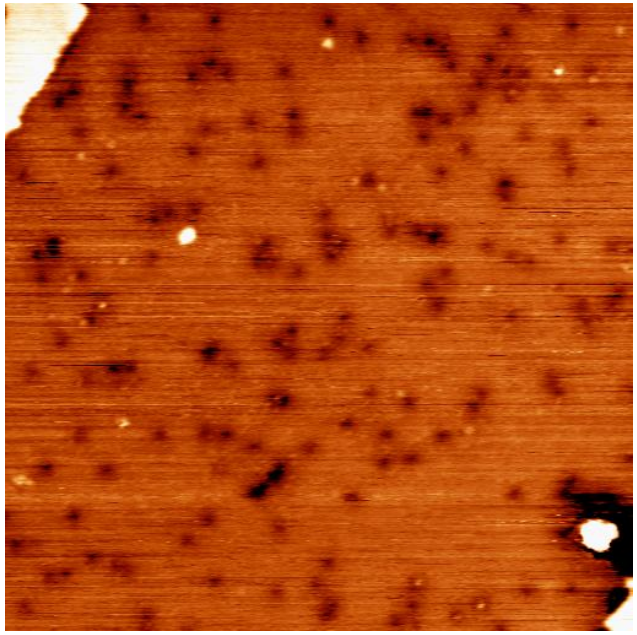
G. Sclauzero, A. Pasquarelo, Appl. Surf. Sci. 291, 64 (2014).

The least favored H adsorption site remain vacant in each quasi cell, and they are observed as the dark features.

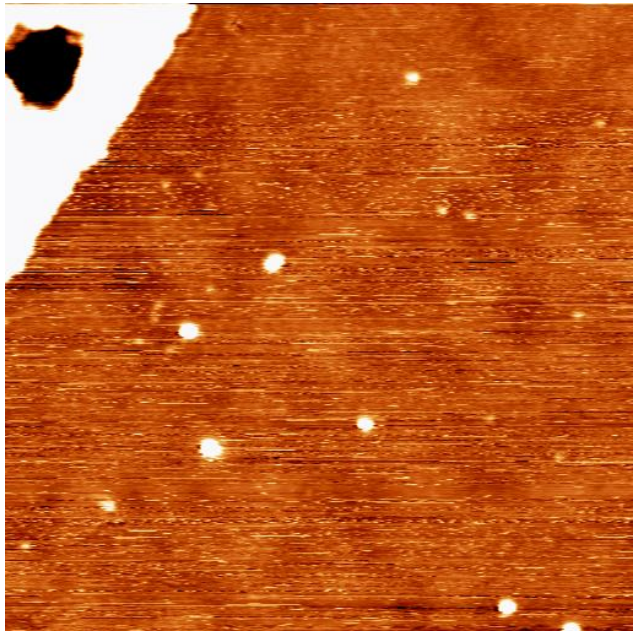
Murata, Appl. Phys. Lett. 105, 221604 (2014)

RT-STM on QFMLG (T_H = 1000ºC)

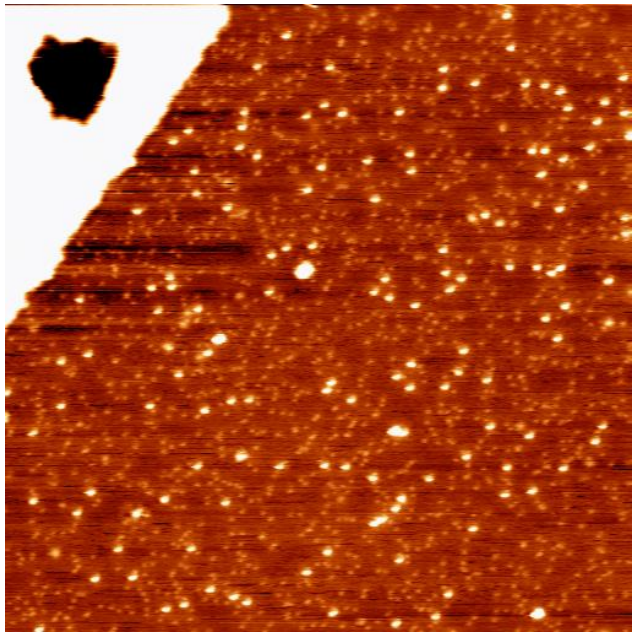
bias V = -1.5V



0.5V



+1.5V



0.1nA 100nm

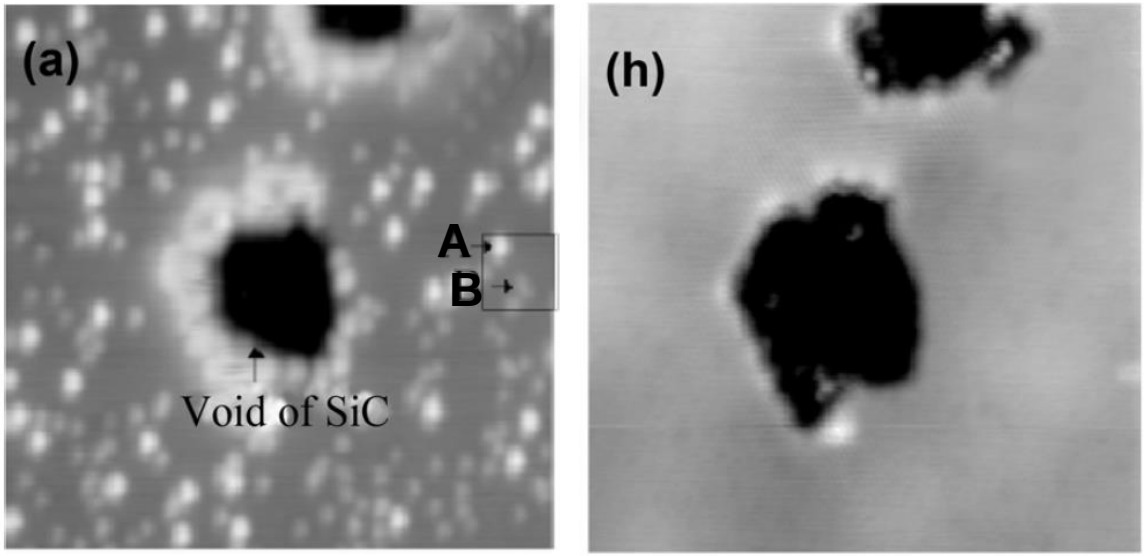
- The density of the features is 5×10^{11} cm^{-2}, less than the sample T_H = 800ºC.

- The contrasts of the features vary with bias V.
- There are 2 types of features. (brighter and less bright)

LT-STM on QFMLG (T_H = 1000ºC)

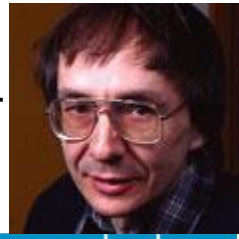
at 5K

bias V = +1.5V -0.05V



5pA 30nm

- There are two types of features. (brighter A and less bright B)
- The contrasts vary with bias V.

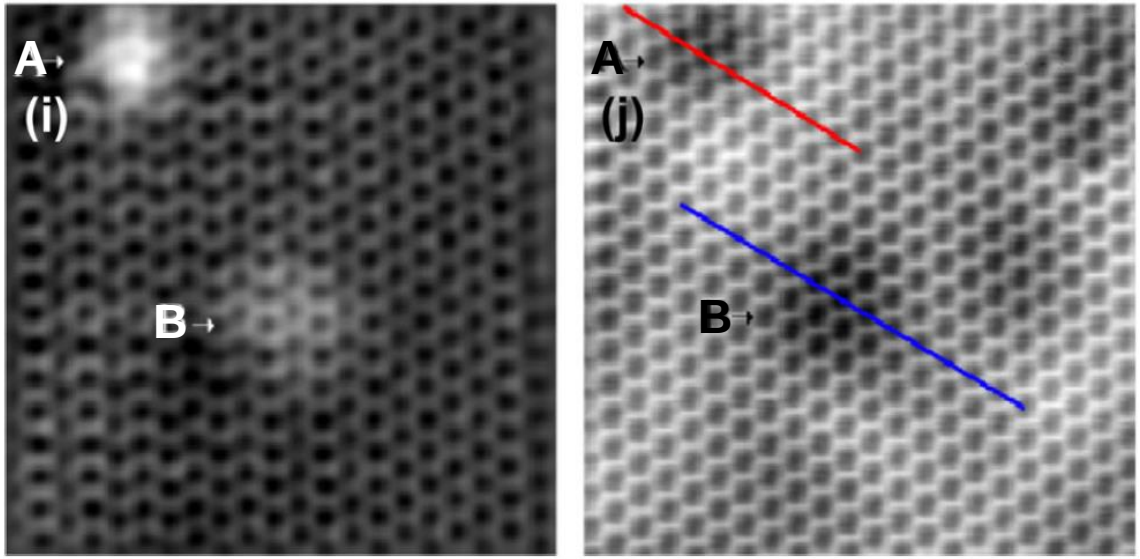


Dr. Gerhard Mayer
IBM Zurich

Murata, Nano Research, DOI:10.1007/s12274-017-1697 (2017)

- High magnification images

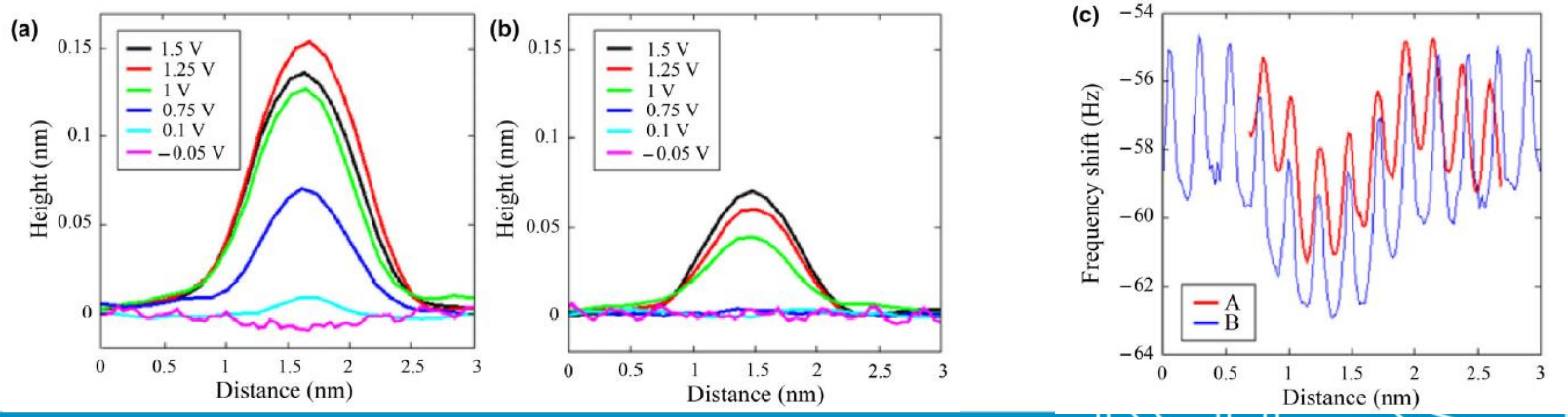
STM AFM



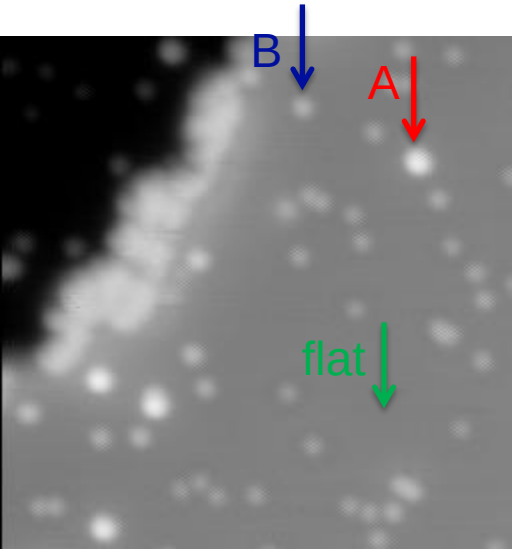
0.1V, 20pA, 4nm 4nm

- profiles on features

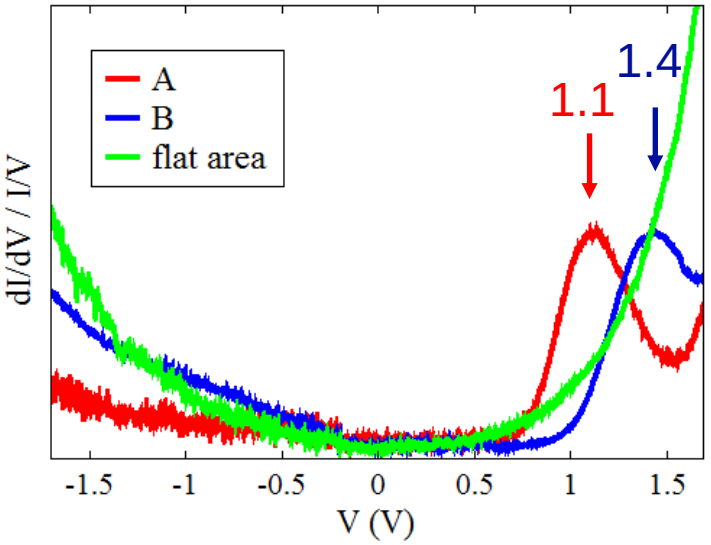
STM – feature A STM – feature B AFM – features A and B

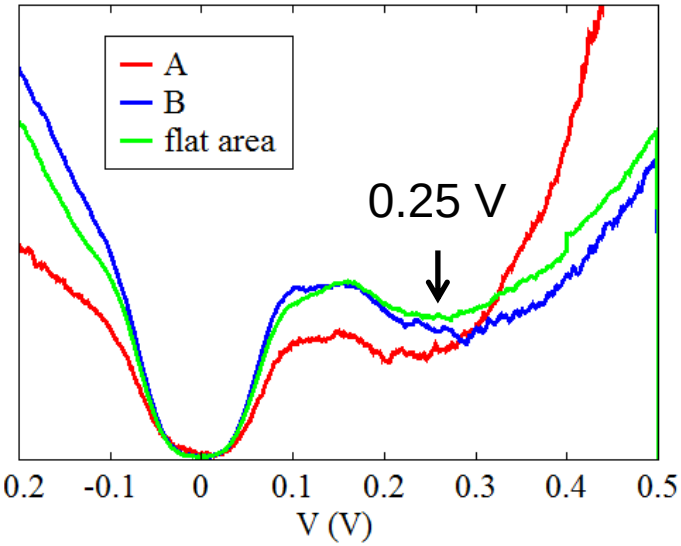


STS



1.8V, 0.01nA, 20 nm





peak at 1.1 V
1.4 V

gap like feature at 0 V
dip at 0.25 V

-> p doping of QFMLG

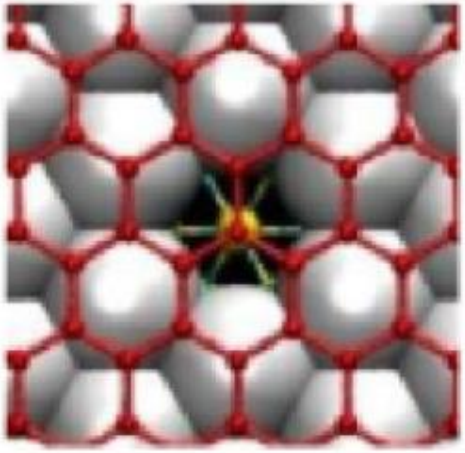
Sławińska, et.al., Carbon, 93, 88 (2015)

DFT calculation: models

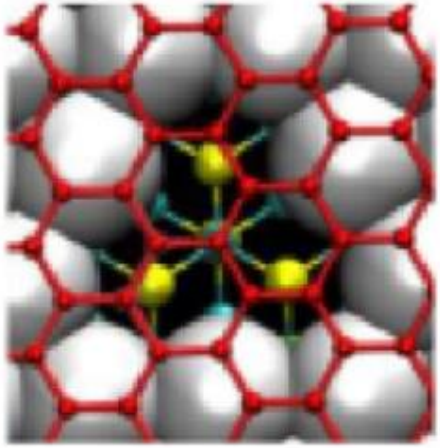
Si dangling bonds' cluster (H vacancies)

Dr Valentina Tozzini
CNR Pisa

1 H vacancy

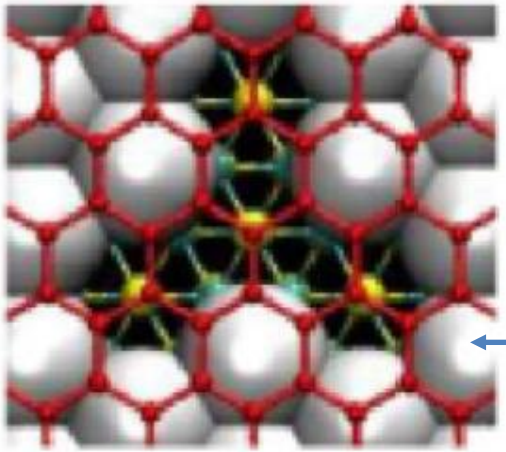


3 H vacancies



-> feature A

4 H vacancies



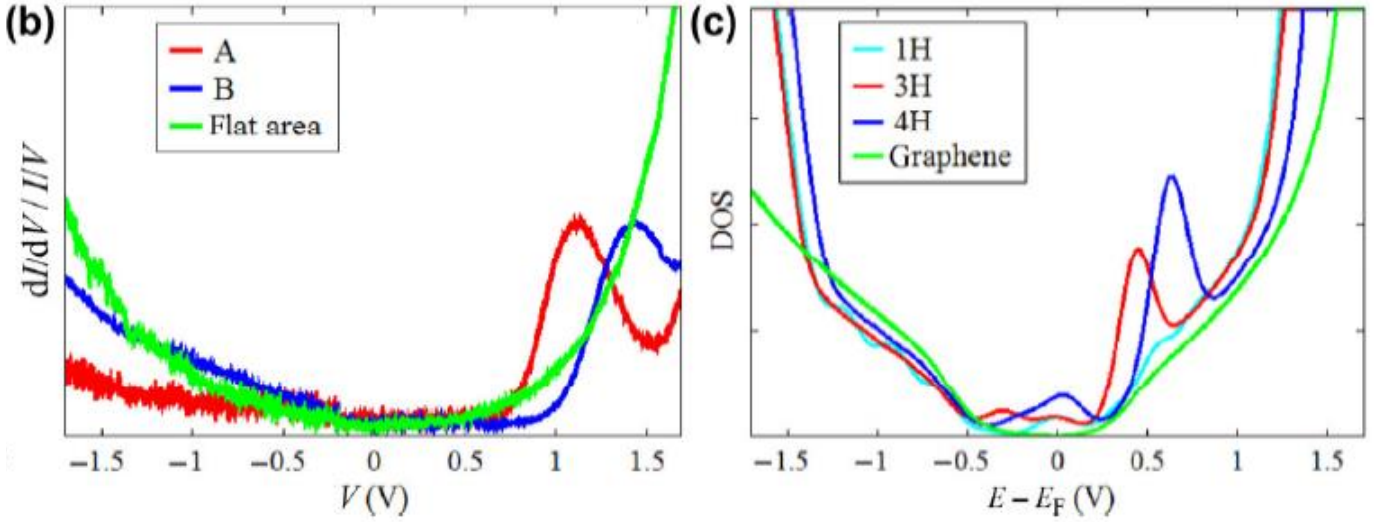
-> feature B

- Even in the 4 H vacancies, Si atoms do not covalently bond to graphene C, remaining dangling bonds. It acts as a charged scattering center.

DFT calculation: DOS

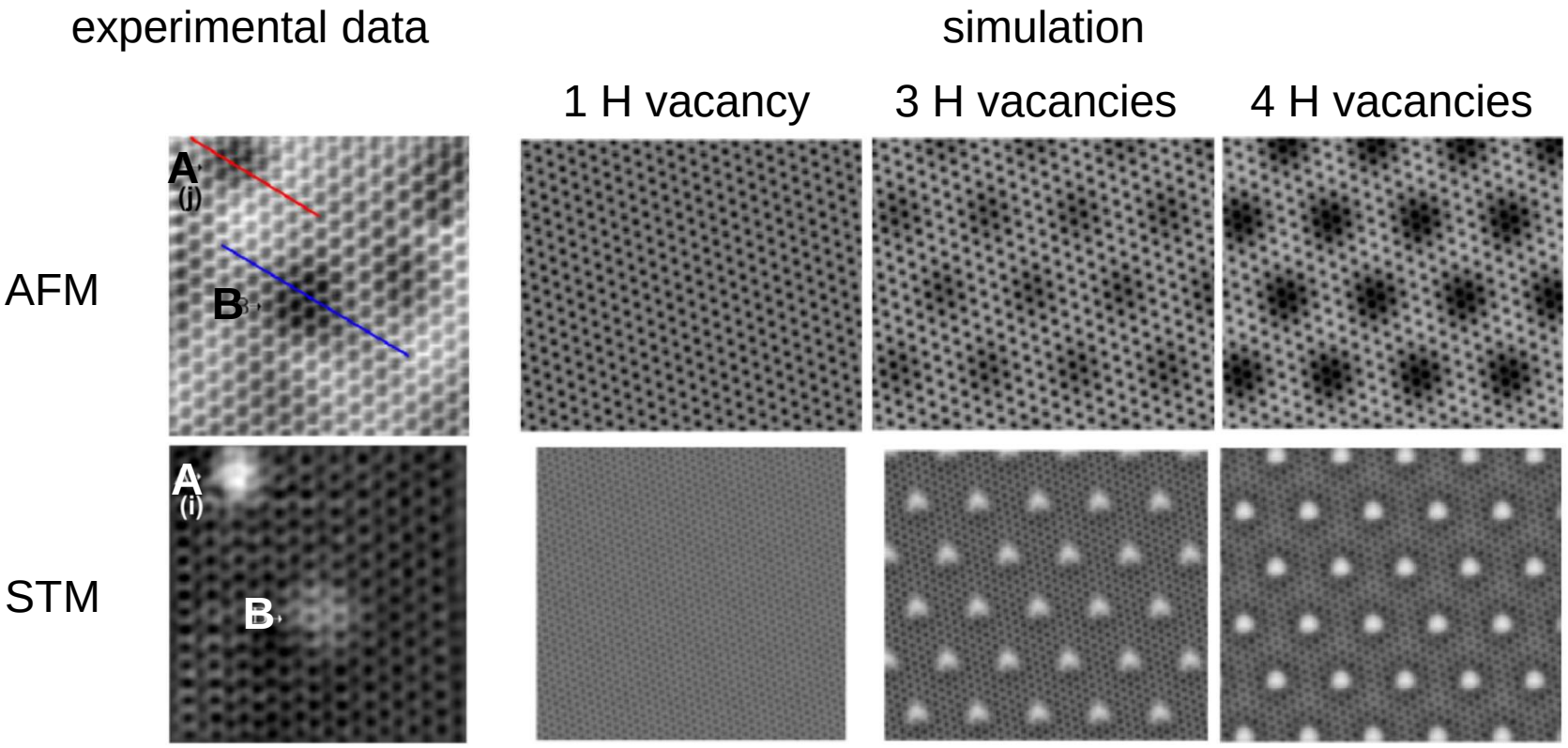
experimental data of STS

calculated DOS



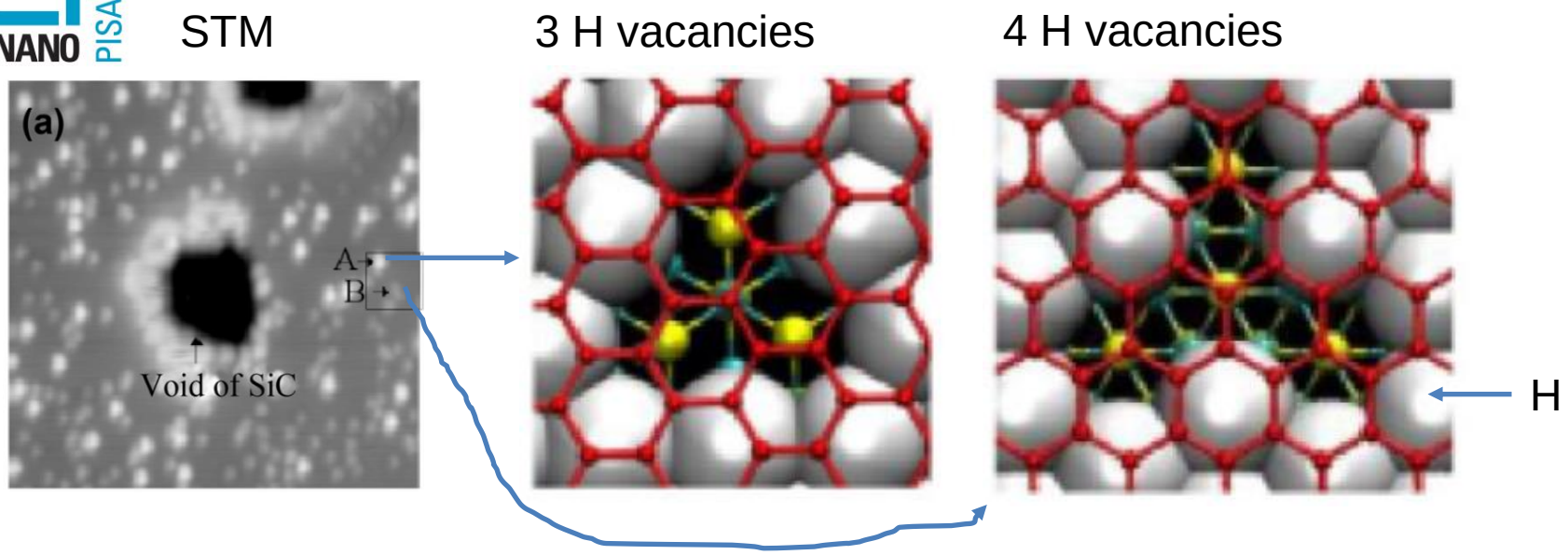
- 1H model: no peak
- 3H and 4H models have peaks in the empty state, originating from the Si dangling bonds.
- The relative energy positions represent the peaks in experimental data on the features A and B, respectively.

DFT calculation: simulated AFM/STM



- The simulated STM/AFM images of 3H and 4H best fit the experimental data on the features A and B, respectively.

conclusion



- We investigated the structure of Si dangling bonds (H vacancies) of QFMLG by STM, AFM and DFT calculation.
- We could identify 2 types of Si dangling bonds' clusters (H vacancies) including 3H and 4H vacancies.
- Even in the 4H vacancies, Si atoms do not covalently bond to graphene C, remaining dangling bonds.
- the density of Si dangling bonds: the sample formed at T_H = 800ºC > 1000ºC

CNRNANO PISA NEST

National Enterprise for nanoScience and nanoTechnology

NEST

Yuya Murata, Stefan Heun, RT STM

Tommaso Cavallucci, Valentina Tozzini DFT calculation

Fabio Beltram

NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Pisa, Italy

Torge Mashoff RT STM

Domenica Convertino, Ameer Al-Temimy, Camilla Coletti graphene growth

Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Pisa, Italy

Niko Pavliček, Gerhard Meyer LT STM

IBM Zurich Research Laboratory, Zurich, Switzerland

Makoto Takamura, Shinichi Tanabe, Hiroki Hibino graphene growth

NTT Basic Research Laboratories, NTT Corporation, Japan

CNRNANO PISA NEST

National Enterprise for nanoScience and nanoTechnology

NEST