H coverage defects in quasi-free-standing monolayer graphene on SiC

Tommaso Cavallucci

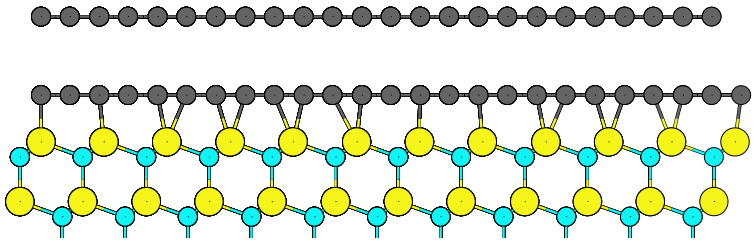
tommaso.cavallucci@sns.it

Outline

- Introduction
  - Epitaxial graphene growth on SiC(0001)
  - Spots on quasi free standing monolayer graphene
  - H vacancy's AFM, STM and STS data
- DFT methods
  - Model systems
  - Studied vacancies
- Results
  - Energy and structure of vacancies
  - Vacancy's DoS
  - STM-like images
  - STM and STM-like comparison
- Conclusions

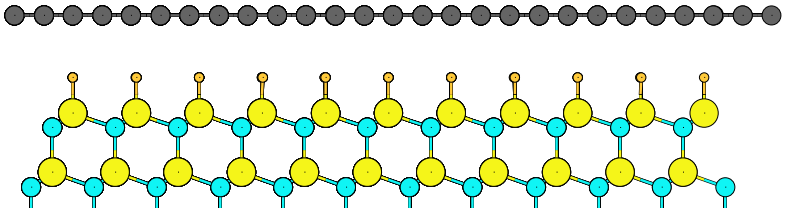
Epitaxial graphene on silicon carbide

Monolayer graphene



- First carbon layer is covalently bonded to SiC (buffer layer)
- Further evaporation of Si leads to monolayer graphene
- Monolayer is corrugated due to lattice mismatch

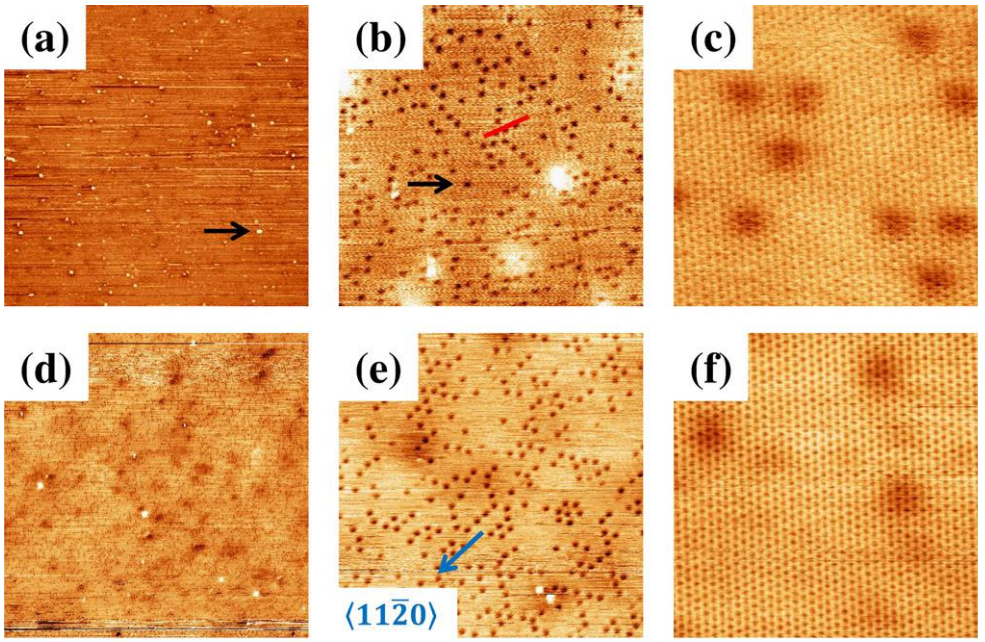
Quasi free standing monolayer graphene (QFSMG)



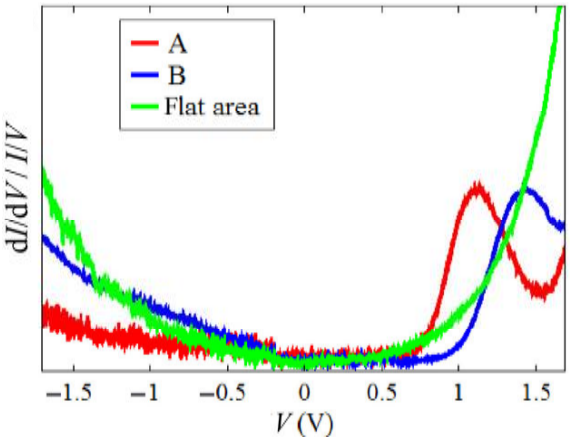
- Buffer layer is detached by hydrogen intercalation (QFSMG)
- QFSMG is flatter and less interacting with SiC than monolayer

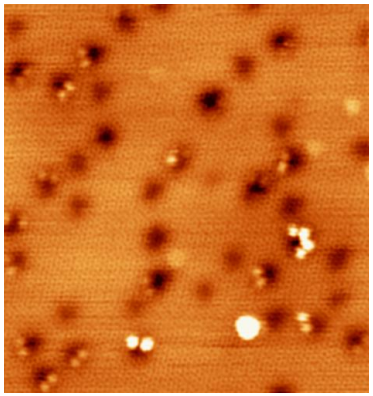
Quasi free standing monolayer graphene

- STM and STS analysis show several “spots” in a ~6×6 periodicity
- Spots are associated to vacancies in the intercalated layer, Si dangling bonds
- Size, shape and peak energy of spots depend on intercalation conditions:
  - High T_H → smaller spots
  - Low T_H → larger spots

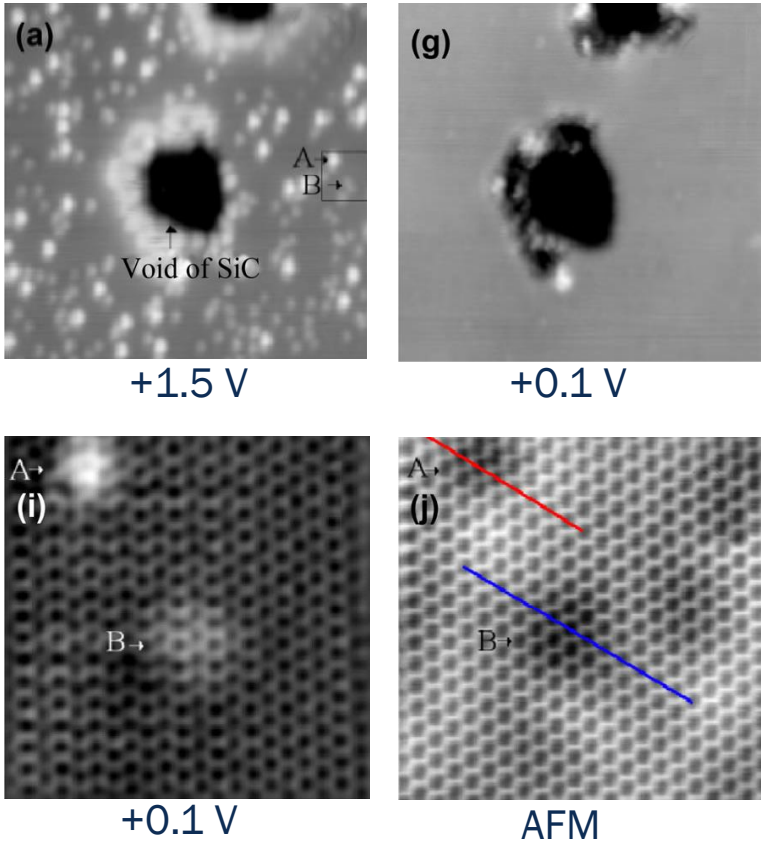


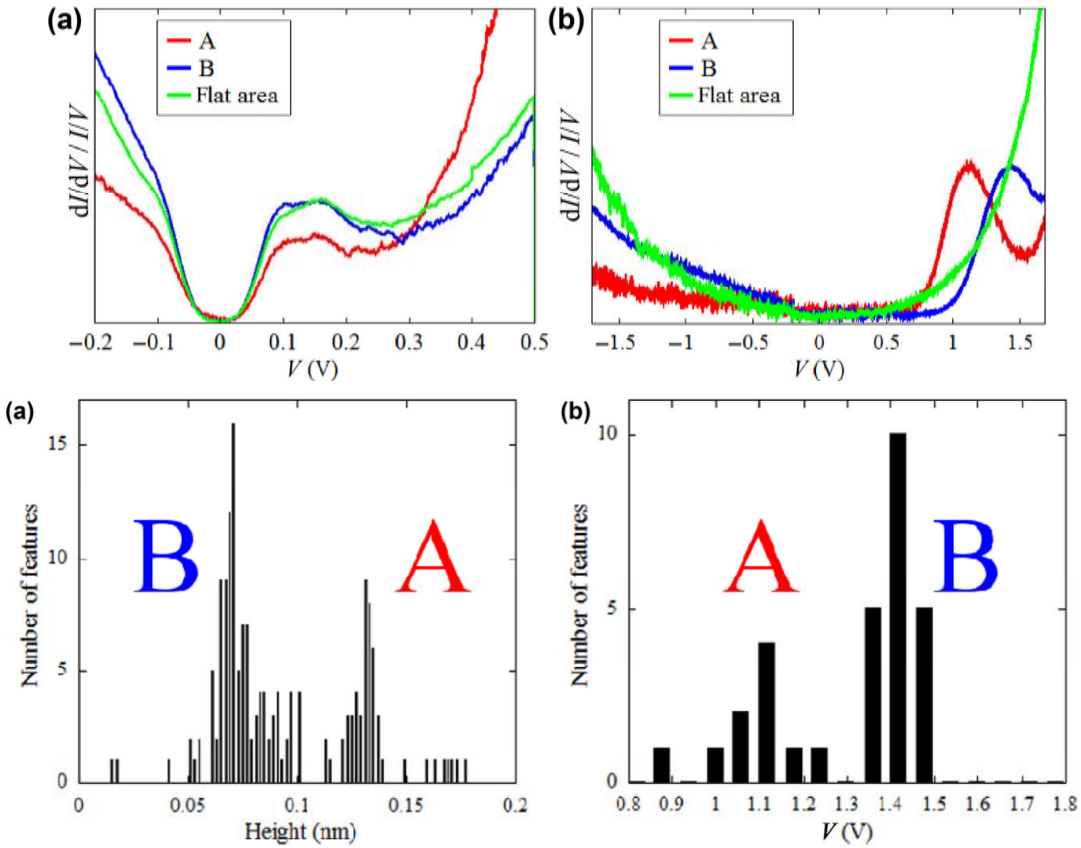
Murata, Y., et al. (2014), APL 105.22:221604





Smallest spots can be grouped in two classes, A and B





Murata, Y., et al. (2017), "Atomic and Electronic Structure of Si Dangling Bonds in Quasi-Free-Standing Monolayer Graphene", in press

- A: deeper, STS peak at +1.1 V
- B: less deep, STS peak at +1.4 V

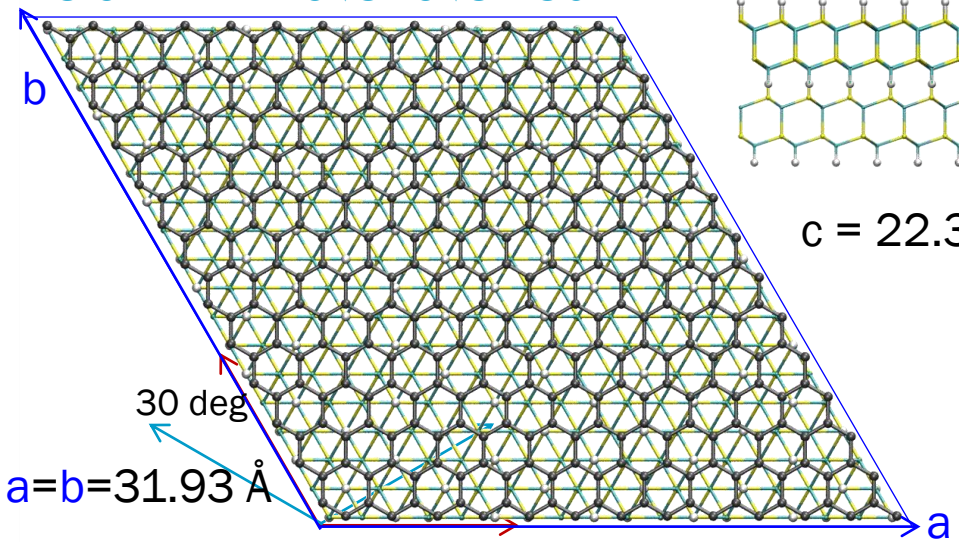
Motivations

- Difference between small A and B spots:
  - Does it depends on graphene location with respect to dangling bond?
  - Does it depends on vacancy's size or shape?
- Is vacancies aggregation favorable?
- More complex and larger spots, combination of dark and bright spots:
  - From which vacancy's size and shape they arise?
  - What's the shape and electronic structure of localized these localized states?
- Check the reliability of our models and DFT setup to describe H coverage defects

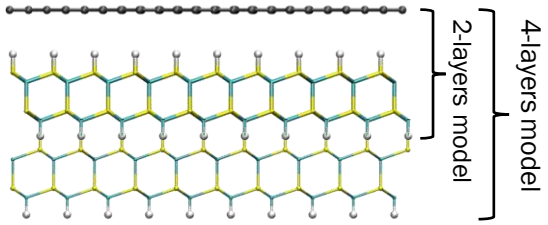
Methods and Results

Large model (L)

graphene 13×13
SiC 6√3×6√3 R30



a=b=31.93 Å

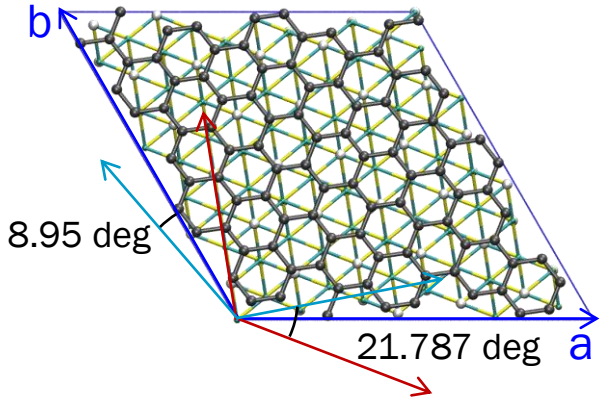


c = 22.34-28.36 Å

- It reproduces the exact SiC-graphene periodicity
- It contains more than 1000 atoms, calculations are very expensive
- Used for few selected cases
- Can host from 0 to 3 vacancies

Small model (S)

graphene 7×7 R21.787
SiC √31×√31 R8.95

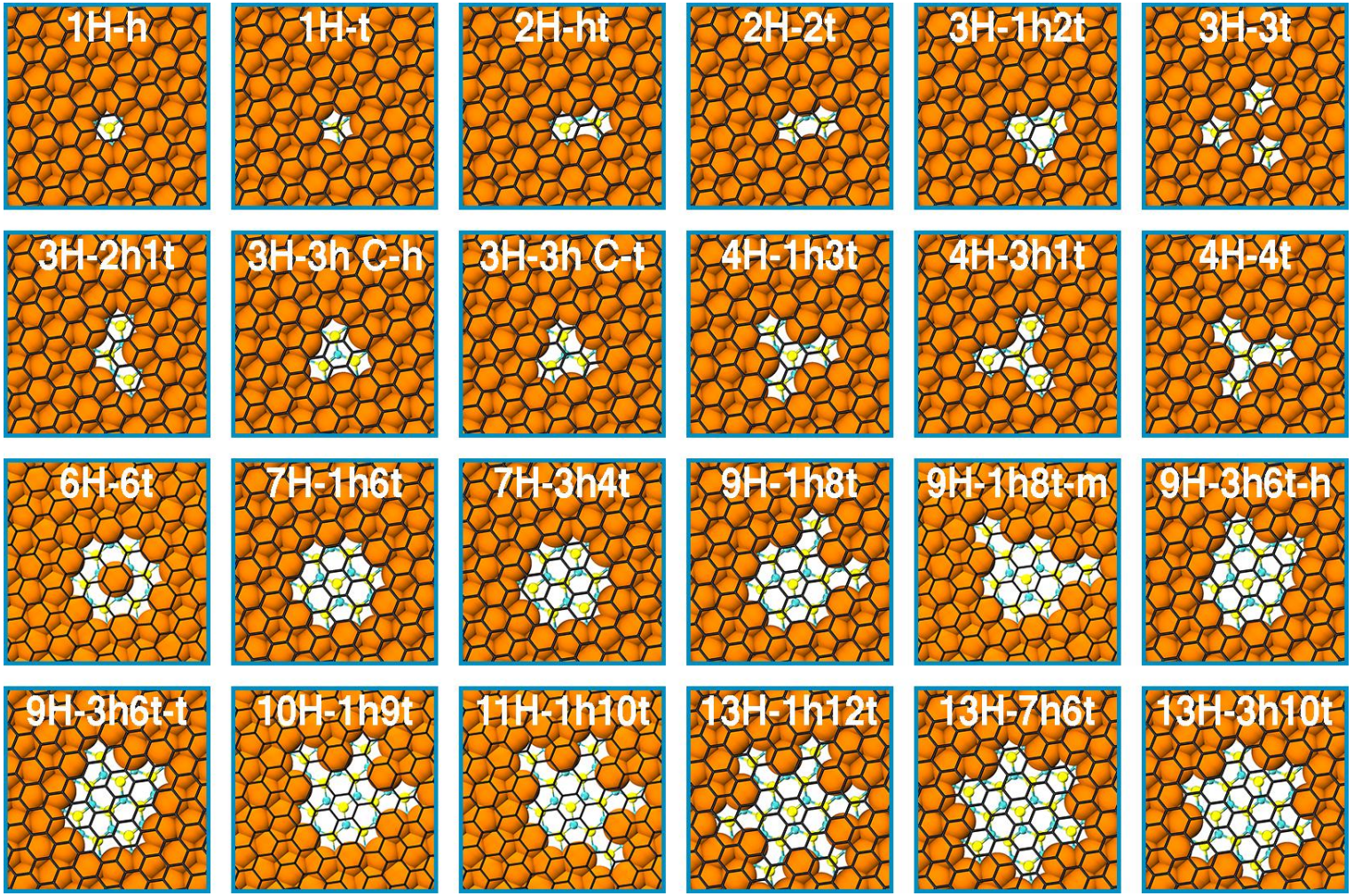


a=b=17.11 Å

- Small SiC-graphene misalignment (~0.7°)
- Graphene is slightly contracted (~0.4%)
- It contains 300-400 atoms, thus was used for extensive calculations
- Can host 0 or 1 vacancy

Methods: structural variations

Vacancies size ranges from 1 to 13 missing H atoms



Labelling:

9H 1h8t m

N. of vacant H

Vacancy location:

- h = hollow (hexagon center)
- t = top (below C atom)

Additional info

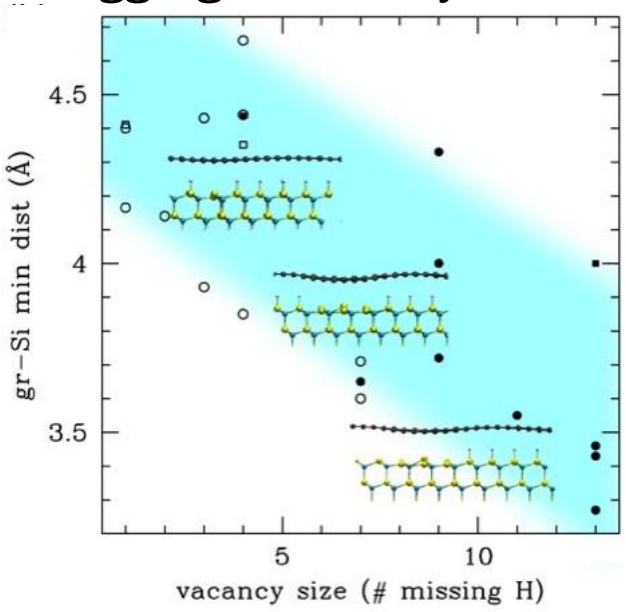
DFT calculations using QE:

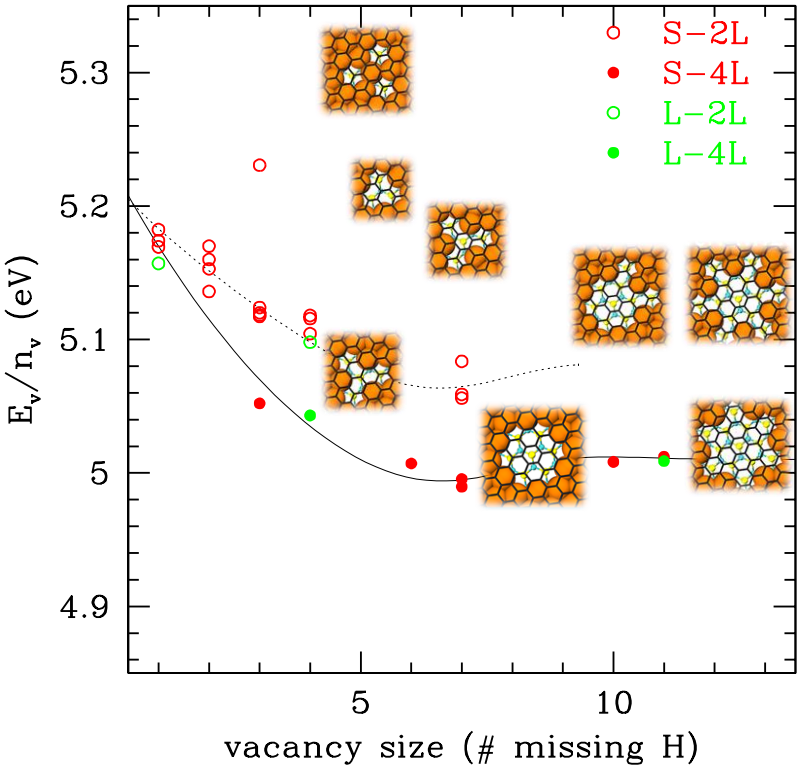
XC-func.	PBE-D2
Pseudopot.	Ultrasoft
PW cutoff	30 Ry
Den. cutoff	300 Ry
Brillouin zone sampling	Γ
	5×5×1 (DoS, L model)
	10×10×1 (DoS, S model)

Energetics of vacancy aggregation

$$E_{\mathrm{V}}/n_{\mathrm{V}} = \left(E_{\mathrm{part}} + n_{\mathrm{V}}E_{\mathrm{H}} - E_{\mathrm{full}}\right)/n_{\mathrm{V}}$$

- Neighbor vacancies are energetically favored: small vacancies tend to aggregate up to 4H-7H size
- Beyond 4H, vacancies have a small energy difference (~10 meV): hopping and aggregation likely

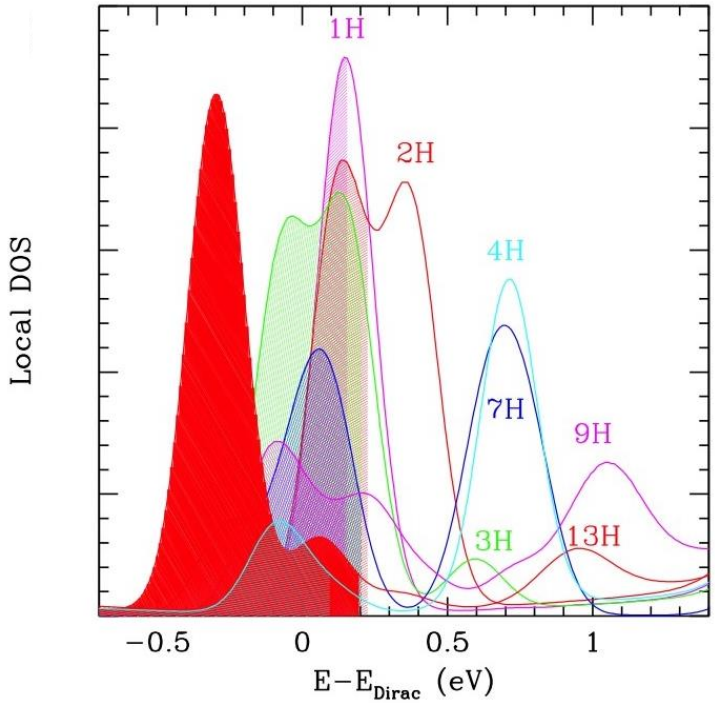


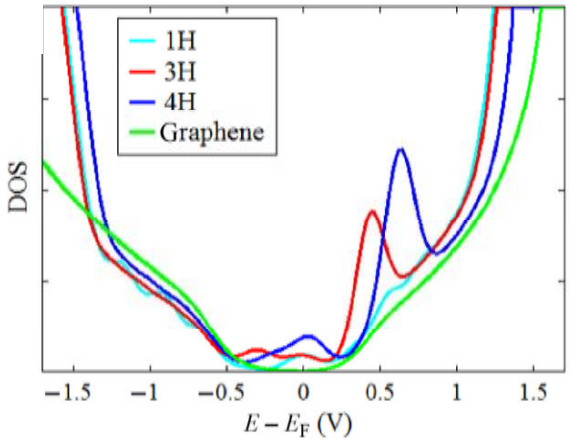


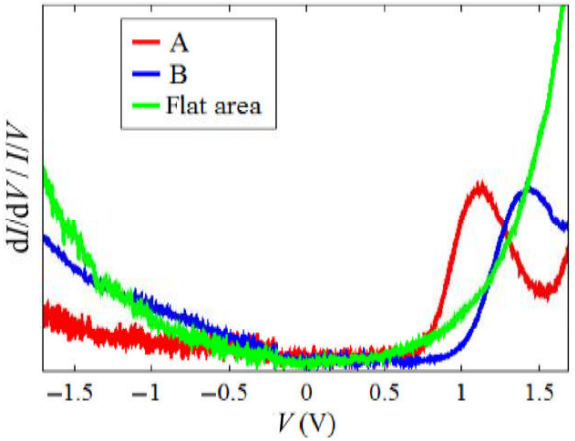
- Graphene inward bending due to vacancies visible as dark spots in AFM images
- Vacancy energy results from a balance between bending penalty and the attraction of Si

Vacancy localized states

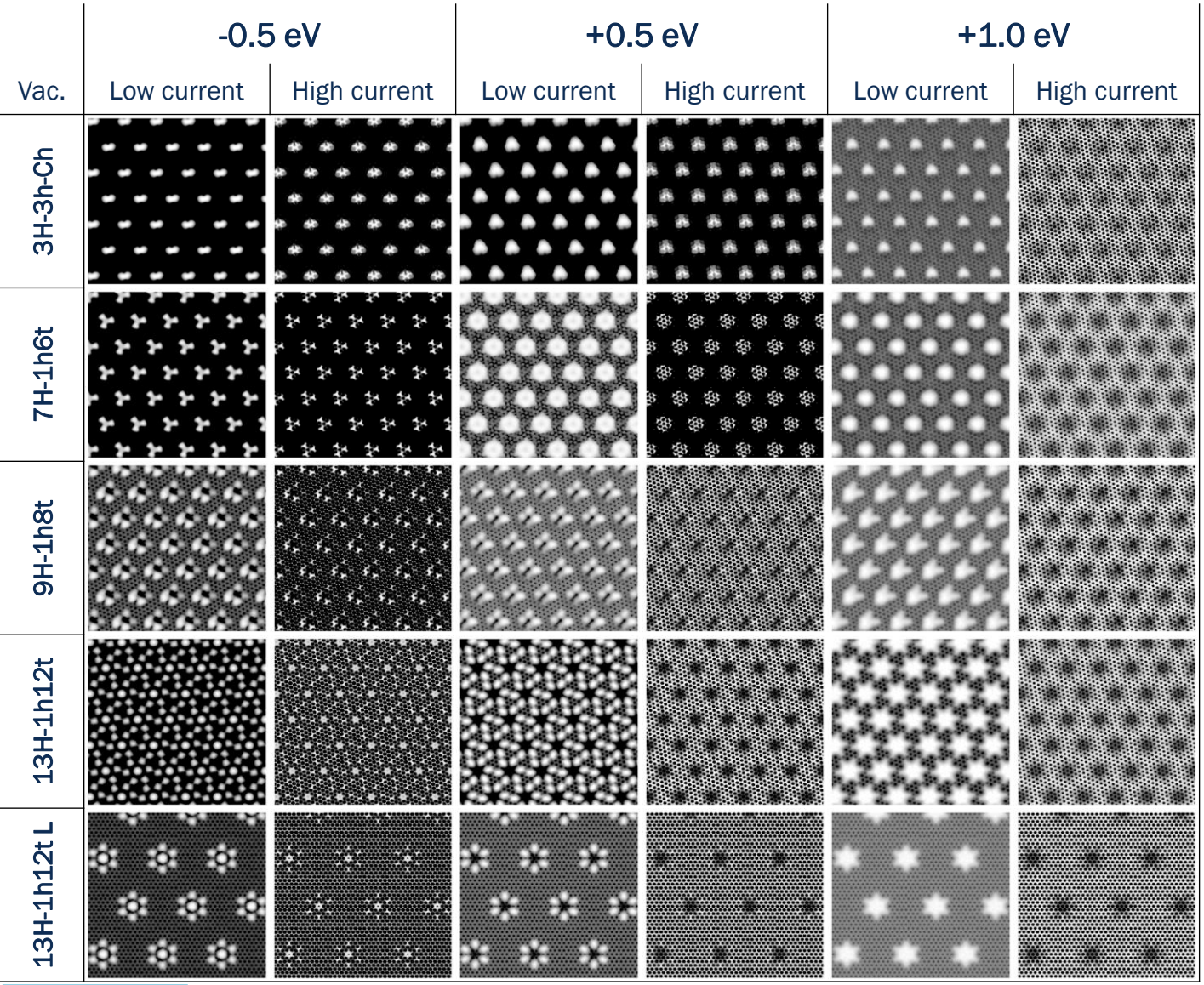
- Localized states are visible as peaks in DoS
- Peak number, shape and location depend on vacancy type
- Generally vacancies can have 1, 2 or 3 peaks, one pinned at the Dirac point, one empty and one filled
- Peaks mainly depend on vacancy shape and size than on graphene position





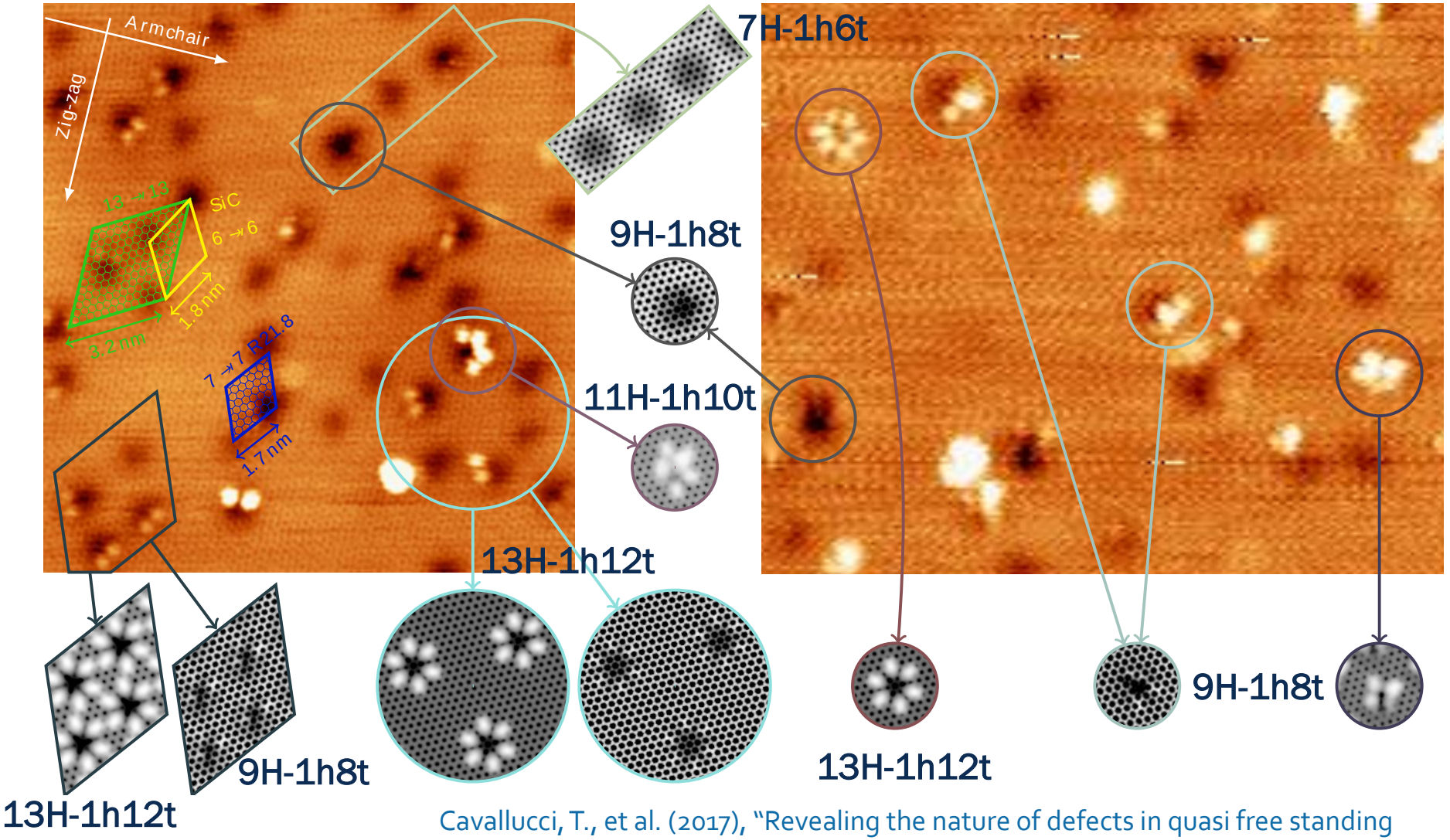


Simulated images



- STM-like images generated using Tersoff-Hamann theory
- Empty and filled states have different shape and symmetry

Defects in quasi free standing graphene



Cavallucci, T., et al. (2017), "Revealing the nature of defects in quasi free standing monolayer graphene on SiC by means of Density Functional Theory", in preparation

Conclusions

- Size vacancy depends on intercalation conditions:
  - Most probable vacancy size for small dark/bright spots is 3 and 4 missing atoms, due to STS and structural data
  - Comparison with STM images allows assigning larger spots to vacancies in the 7H-13H range, recognizable by their typical shape and different contrast
- Larger vacancies could be generated at lower H saturation: H mobility is allowed and single vacancies tends to aggregate to lower the formation energy
- Both Small ($\sqrt{31}\times\sqrt{31}$ R8.95) and Large ($6\sqrt{3}\times6\sqrt{3}$ R30) models seem compatible with experimental STM images:
  - Large model reproduces the exact graphene-SiC symmetry
  - Graphene rotations and contractions cannot be excluded locally, with a symmetry more similar to the Small model which facilitates larger vacancies
- For larger vacancies, DoS calculations show two or three peaks associated to dangling bonds, one empty and one filled or half filled; empty peak location can be tuned with vacancy size

Acknowledgements

- NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore:
  - Valentina Tozzini
  - Yuya Murata
  - Stefan Heun
  - Fabio Beltram
- NTT Basic Research Laboratories:
  - Makoto Takamura
  - Hiroki Hibino
- IBM Research-Zurich:
  - Niko Pavliček
  - Leo Gross
  - Gerhard Meyer