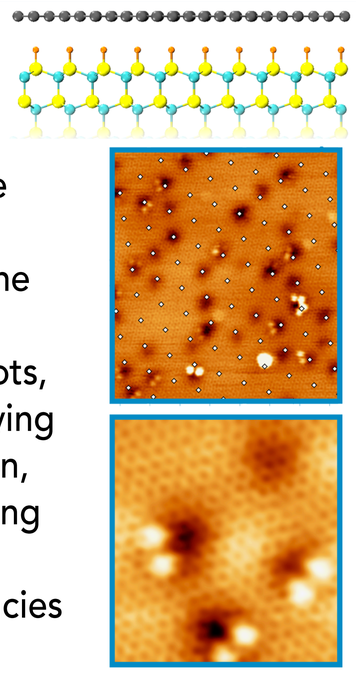
H coverage defects in Quasi Free Standing Graphene

T. Cavallucci, Y. Murata, S. Heun, V. Tozzini
NEST-Scuola Normale Superiore and Istituto Nanoscienze-CNR, Pisa, Italy

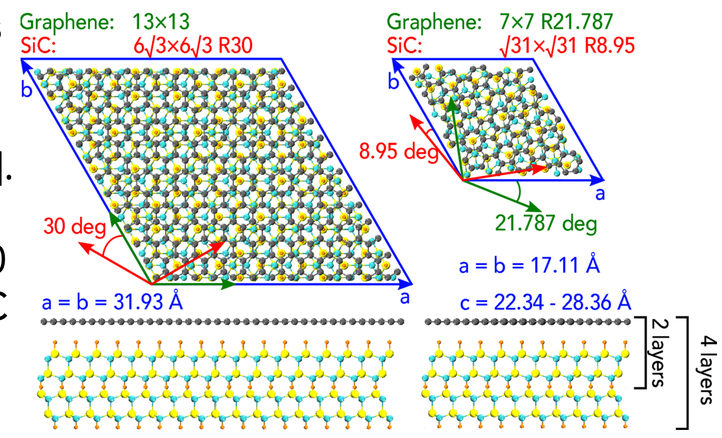
Introduction

Quasi Free Standing Graphene (QFSG) on SiC is obtained by intercalating H atoms at the interface between the carbon rich buffer layer obtained by Si evaporation and SiC(0001) substrate. The procedure produces a flat and completely sp^2 hybridized honeycomb lattice [1]. The regularity of this graphene sheet is however interrupted by localised features appearing in the STM images as bright and dark spots, whose brightness depends on the bias voltage. Varying the temperature of measurement and H intercalation, the amount and distribution of spots varies, appearing in some cases located on a lattice with ~6×6 SiC periodicity. These features were attributed to vacancies in the H coverage [2].

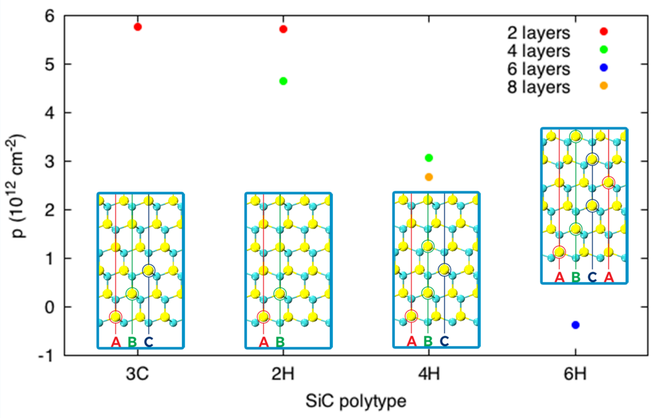


Methods and models

DFT calculations using USPPs (PBE + Grimme vdW correction), performed with Quantum ESPRESSO 5.3.0 [3]. Two model systems: small (~280 atoms) and large (~980 atoms). In the smaller one SiC and graphene are rotated by ~0.73 deg.

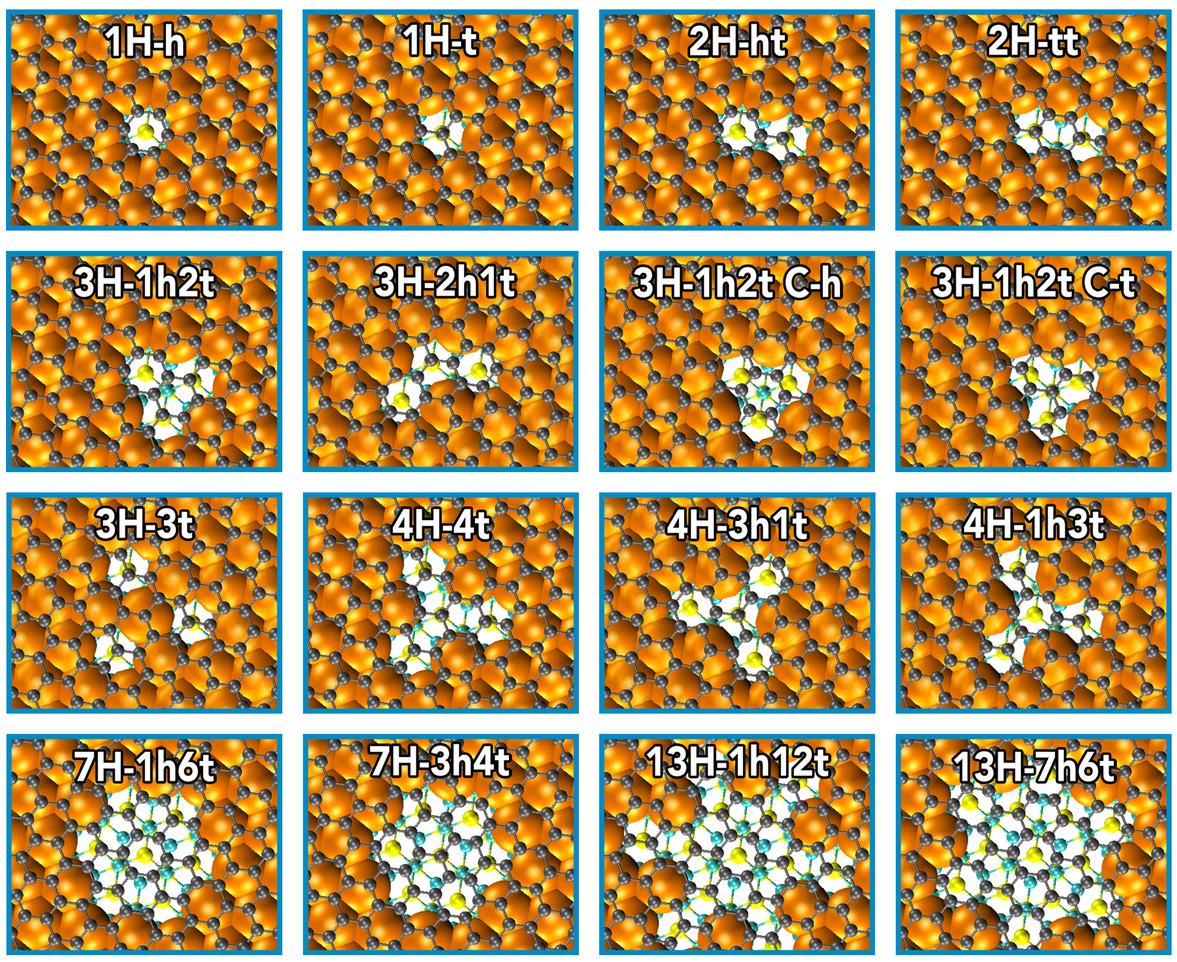


QFSG doping

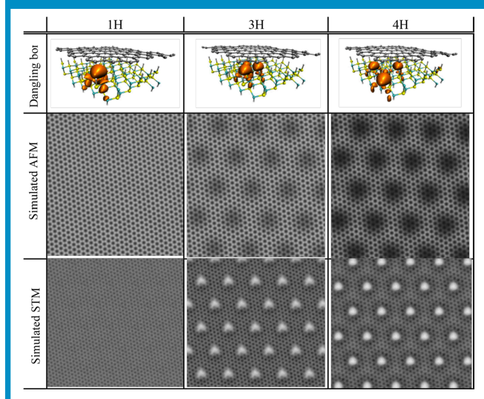


Intrinsic SiC polarization induces p doping (~10^{12} cm^{-2}) on QFSG. SiC polarization depends on its polytype [4]. 3C-SiC with two layers was chosen in our models since it has a similar doping level with respect to experiments and allows to simulate the smallest number of atoms.

H vacancies studied

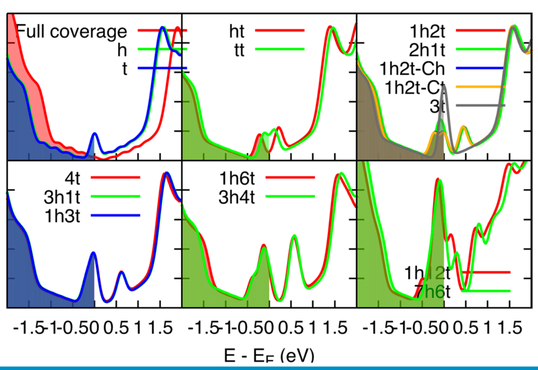


Results: STM images and DoS



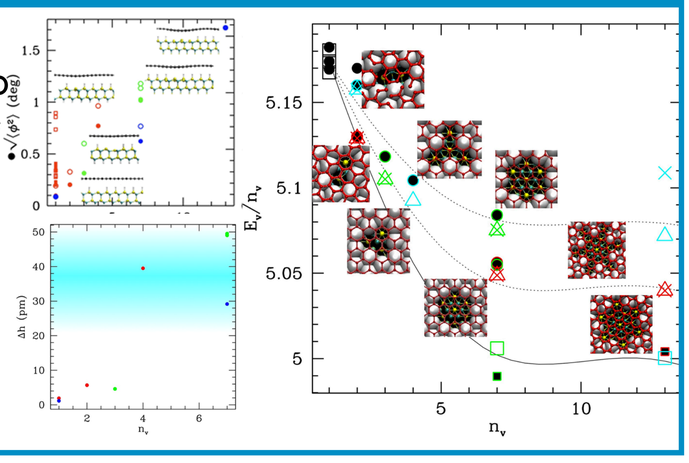
STM simulated images of vacancies show the bright spots due to "dangling bonds" states localized between graphene and SiC. The dark/bright spots are due to different size of vacancies and not to their location [5]. Comparing theoretical and experimental data, the most favourable ones are the 3H and the 4H.

DoS spectra show localized states. With two or more missing H a second peak appears, which slighly shifts towards high energy in larger vacancies. First peak is always pinned at the Fermi level and does not move much from the Dirac point.



Results: Vacancies stability

Vacancies tend to aggregate and their energy decreases up to 7 H missing. Comparing vacancy height, size and curvature with AFM measurement, experimental vacancies should range from 3H to 7H. This is supported also by STM-like images and DoS calculations.



Conclusions

- We have built two model systems for the representation of the QFSG, and examined their reliability on the basis of the comparison with experimental data.
- Systematic evaluation of the system properties allows to clarify the interpretation of experimental data in three specific aspects:

1) Polarization induced doping of QFSG depends on the SiC polytype and on the number of layers included in the model.
2) Calculations show a decrease of energy formation of vacancy as the vacancy size increases. This indicates a tendency of vacancies to aggregate at least up to the size of 7 H atoms.
3) Comparison of DoS and STM-like images of vacancies and combination with AFM data indicates that the most probable candidates for the features appearing in the STM images are the 3H and 4H vacancies, distinguishable among each other by different contrast behavior as a function of the applied voltage.

[1] Riedl, C., Coletti, C., Iwasaki, T., Zakharov, A. A., & Starke, U. (2009). PRL, 103(24), 246804.
[2] Murata, Y., Mashoff, T., Takamura, M., Tanabe, S., Hibino, H., Beltram, F., & Heun, S. (2014). APL, 105(22), 221604.
[3] Cavallucci, T., & Tozzini, V. (2016). JPCC, 120(14), 7670-7677.
[4] Ristein, J., Mammadov, S., & Seyller, T. (2012). PRL, 108(24), 246104.
[5] Murata, Y., Cavallucci, T., Tozzini, V., Pavliček, N., Gross, L., Meyer, G., Takamura, M., Hibino, H., Beltram, F., & Heun, S. (2017) (submitted).

CINECA SCAI SuperComputing Applications and Innovation
H2020 Core1 GRAPHENE FLAGSHIP
MusCaDe Multi-scale modeling and simulation Devices http://www.muscade-lab.it
PRACE