The influence of graphene curvature on hydrogen adsorption

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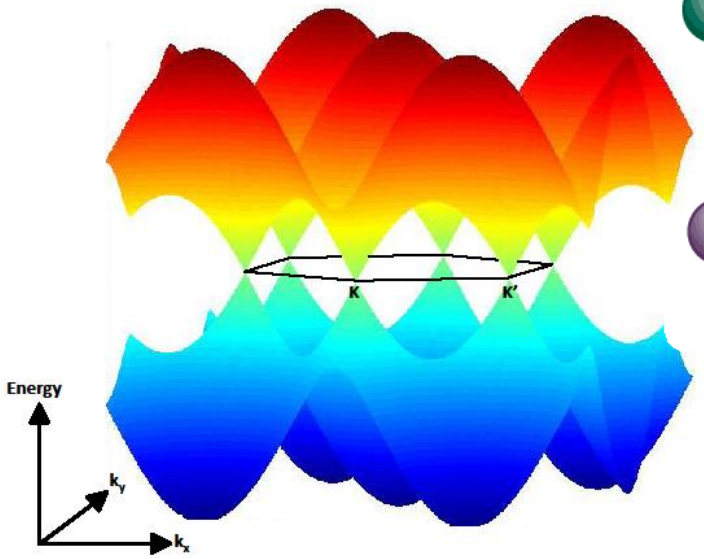
Outline

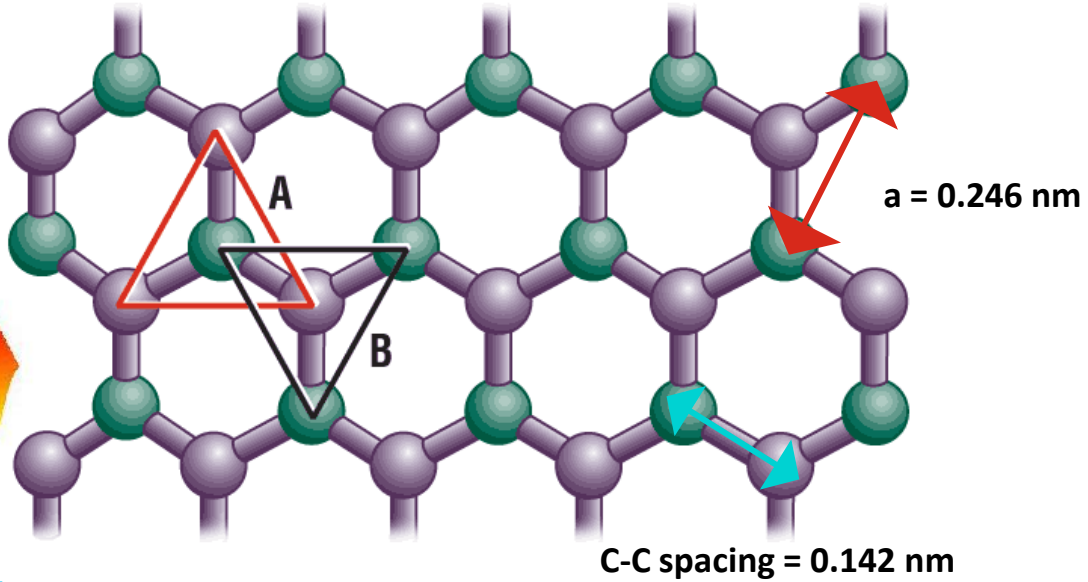
- Why graphene and hydrogen?
- The role of graphene curvature from theoretical calculations
- Finding a suitable graphene system with intrinsic curvature
- Characterizing the samples
  - Raman spectroscopy
  - Scanning tunneling microscopy
- Hydrogenating the samples
- Dehydrogenating the samples
- Conclusions

What is graphene?

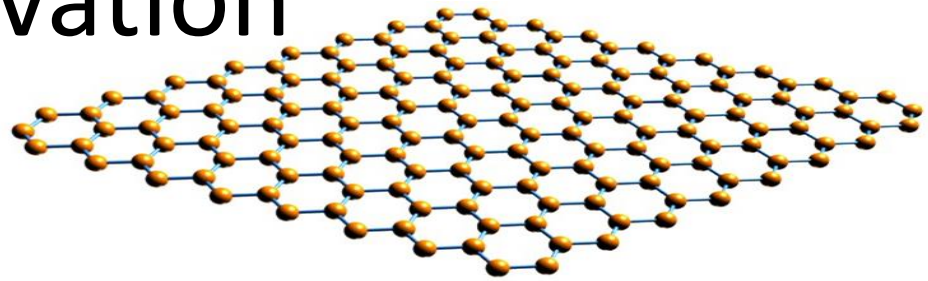
A SINGLE sheet of carbon atoms.

The atoms are arranged in a honeycomb lattice composed of two intertwined equivalent sublattices.





Motivation

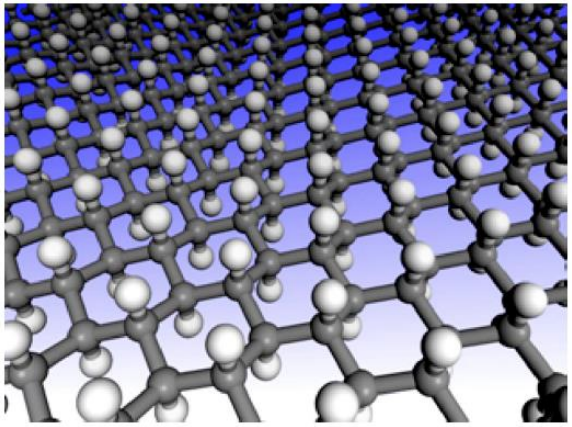


Possible to change the electronic properties by H adsorption.

Open a band gap of 3.5eV. (Sofo (2007))

Possibly useful for hydrogen storage.

We are interested in the interaction of hydrogen as a function of local curvature since graphene is a flexable membrane.



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

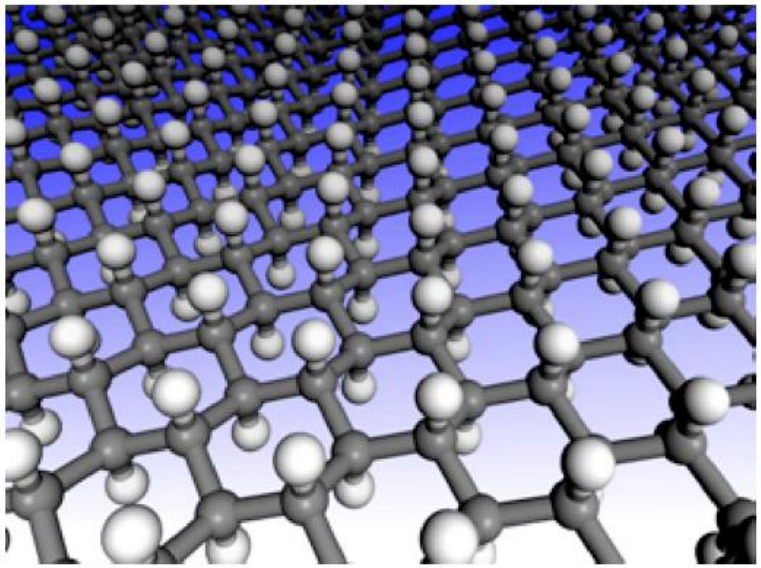
Graphene + Hydrogen →Graphane

Chemisorption: Formation of a covalent chemical bond between the hydrogen atoms and the scaffold.

Adsorption of hydrogen opens a bandgap of 3.5eV.
J. O. Sofo et al. Phys. Rev. B 75, 153401 (2007)

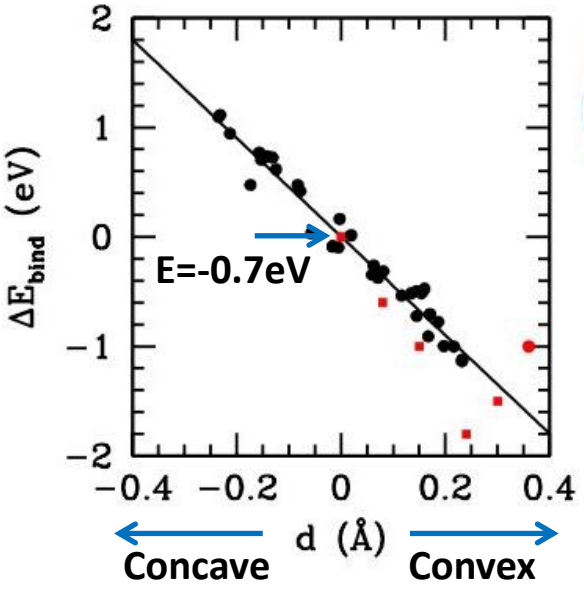
First experimental evidence of hydrogen adsorption on graphene in 2009.
D.C. Elias et al. Science 323 5914 (2009)

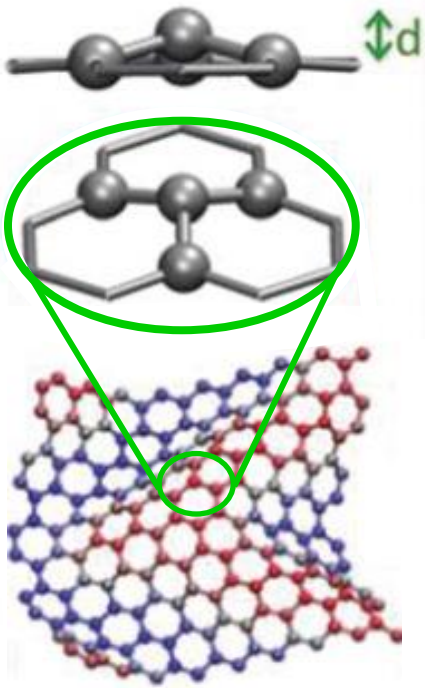
EXPLORE THE INTERACTION OF GRAPHENE CURVATURE FOR HYDROGEN ADSORBTION AND RELEASE

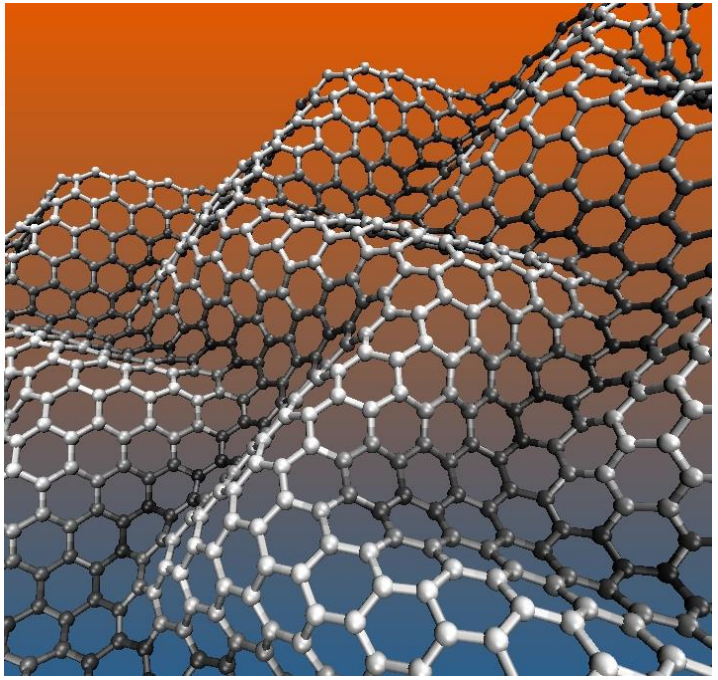


J. O. Sofo et al. Phys. Rev. B 75, 153401 (2007)

Hydrogen binding energy depends on graphene curvature







V. Tozzini and V. Pellegrini, Journal Physical Chemistry C **115**, 25523 (2011)

The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts

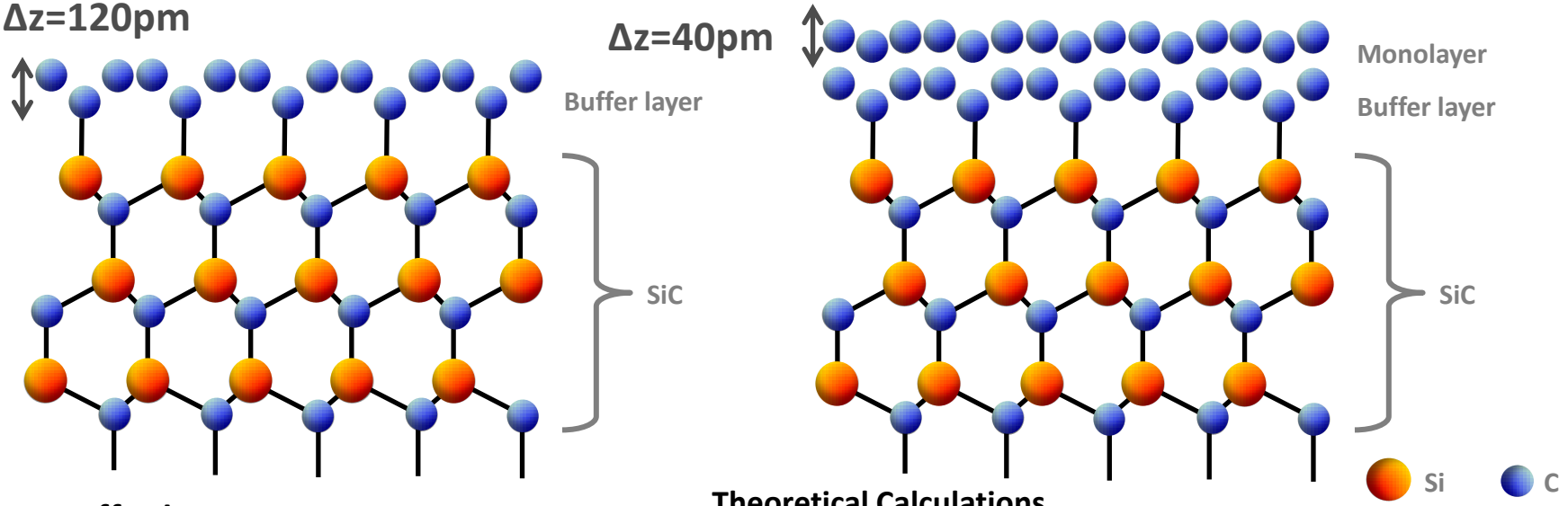
Finding a suitable graphene system to test the interaction of hydrogen and graphene as a function of curvature

Monolayer graphene on SiC(0001)

Buffer layer on SiC(0001)

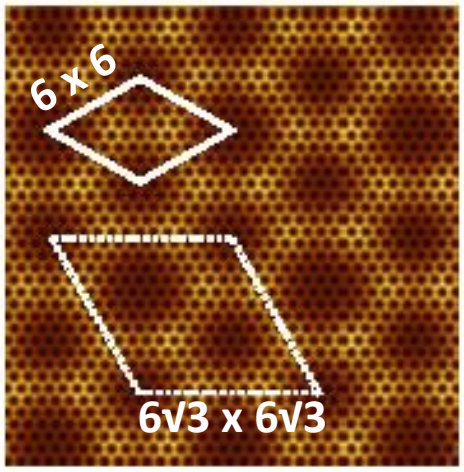
Quasi-free-standing monolayer graphene on SiC(0001)

Graphene 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.

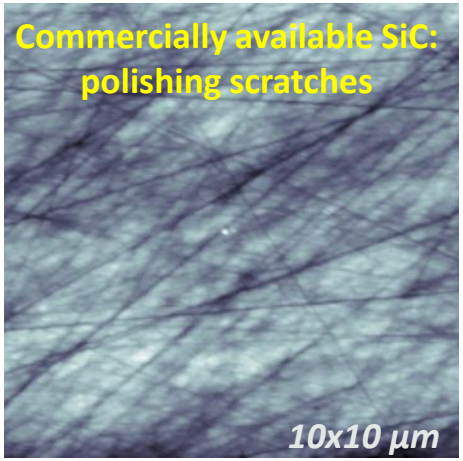
Theoretical Calculations



Superperiodicity of both the Buffer layer (Δz=120pm) and monolayer (Δz=40pm) graphene on the Si face from the periodic interaction with the substrate.

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

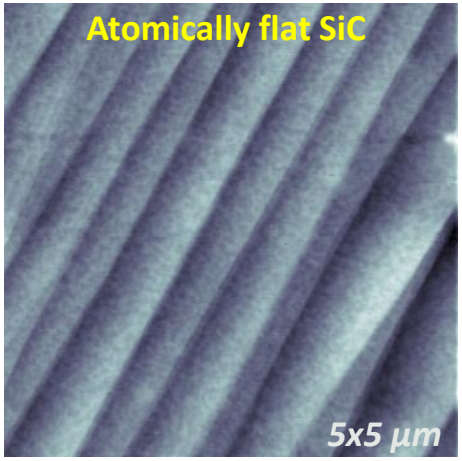
Graphene growth on SiC(0001)

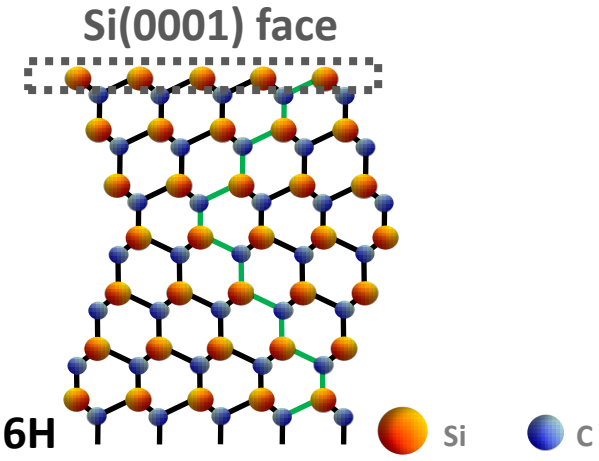


Growth Chamber
P ~ atmospheric pressure
T > 1400°C

H_2 Etching

C. Coletti et al., *Appl. Phys. Lett.* 91, 061914 (2007)

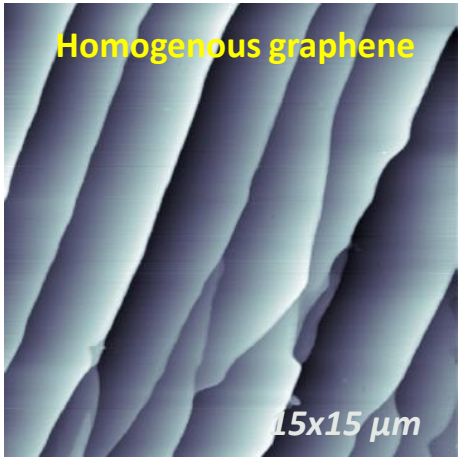




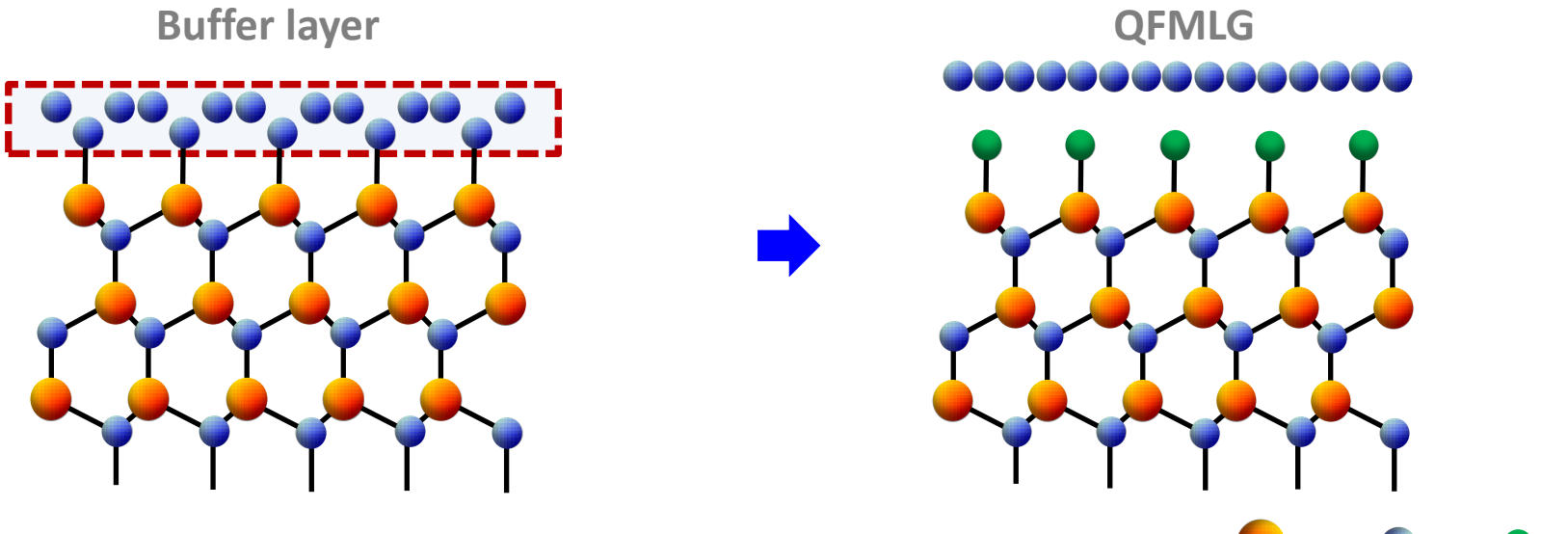
Growth Chamber
P ~ atmospheric pressure
T ~ 1400°C (BL) ~ 1480°C (ML)

Ar-Annealing

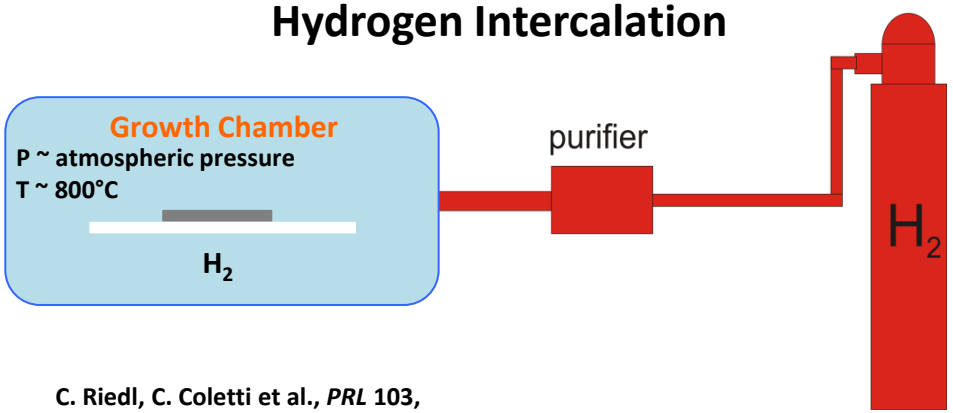
K.Emtsev et al., Nature Mater. 8, 203 (2009)



Quasi-free-standing monolayer graphene (QFMLG)

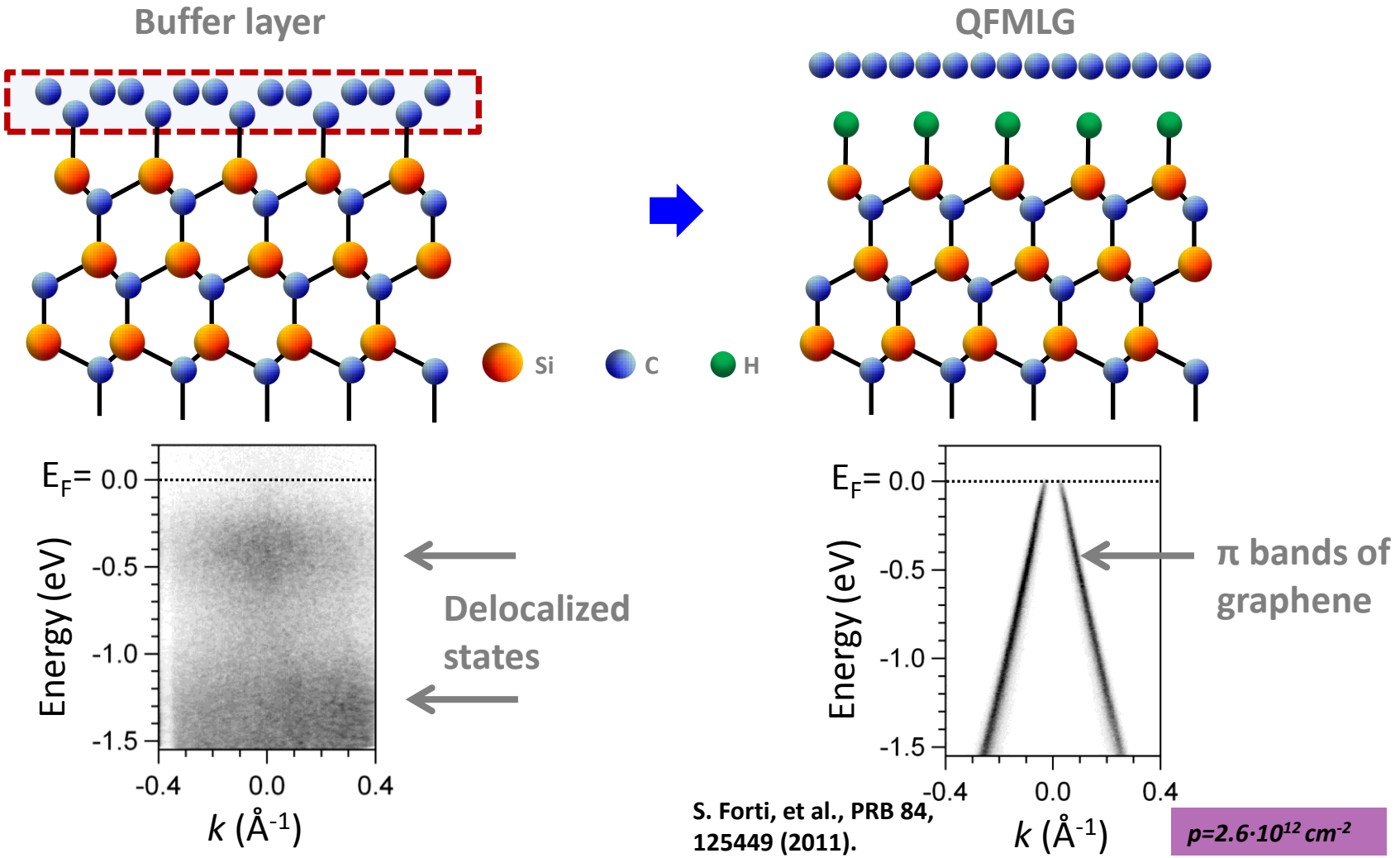


Hydrogen Intercalation



C. Riedl, C. Coletti et al., *PRL* 103, 246804 (2009)

Hydrogen intercalation of the buffer layer and ARPES



S. Forti, et al., PRB 84, 125449 (2011).

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

Material Characterization

Monolayer graphene on SiC(0001)

Buffer layer on SiC(0001)

Quasi-free-standing monolayer graphene on SiC(0001)

Techniques

- Raman spectroscopy
- Scanning Tunneling Microscopy

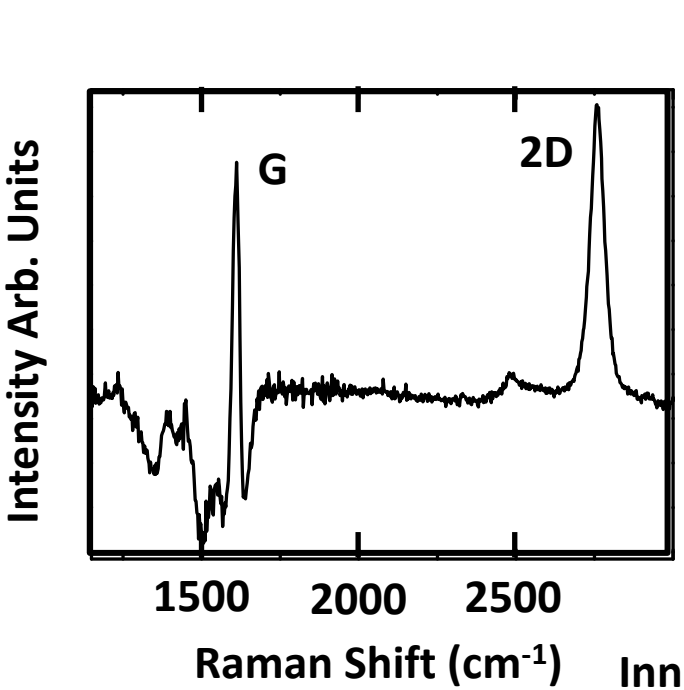
Scanning tunneling microscope

in

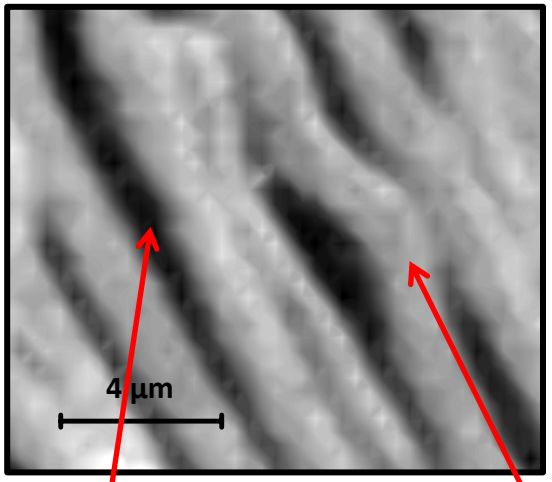
he

Photographs courtesy of Massimo Brega.

Raman spectrum on monolayer graphene SiC(0001)



Intensity map of 2D peak

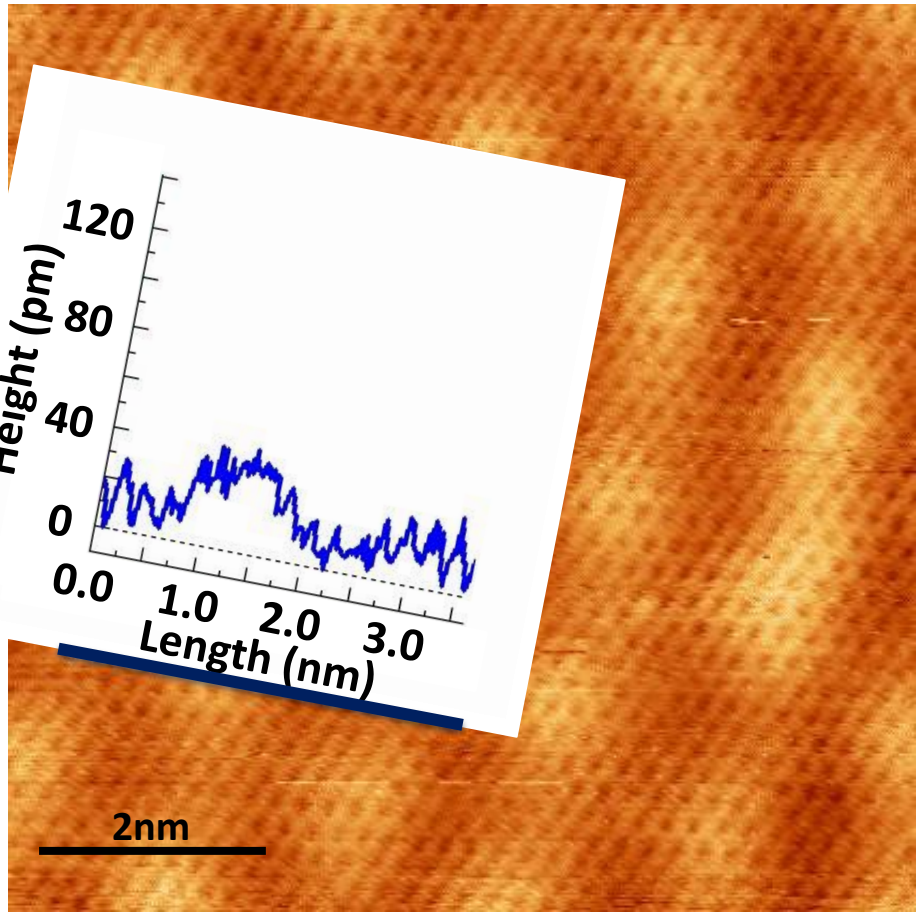


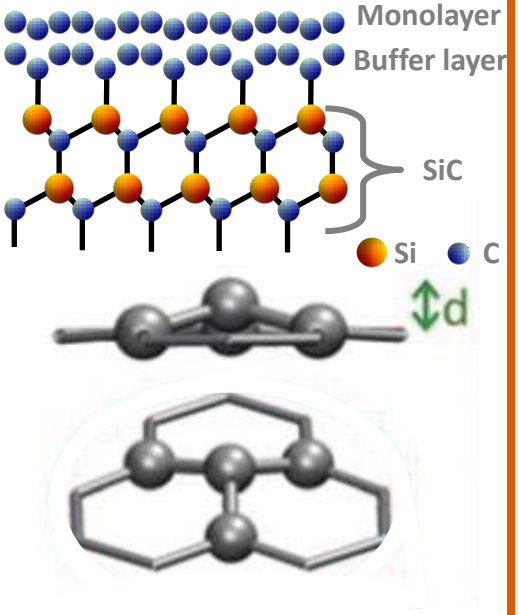
Inner most step area
Dark areas (No 2D)
Buffer layer

Step area
Light areas (2D)
Monolayer graphene

STM imaging should be in the steps not at the step edges.

STM image of monolayer graphene on SiC

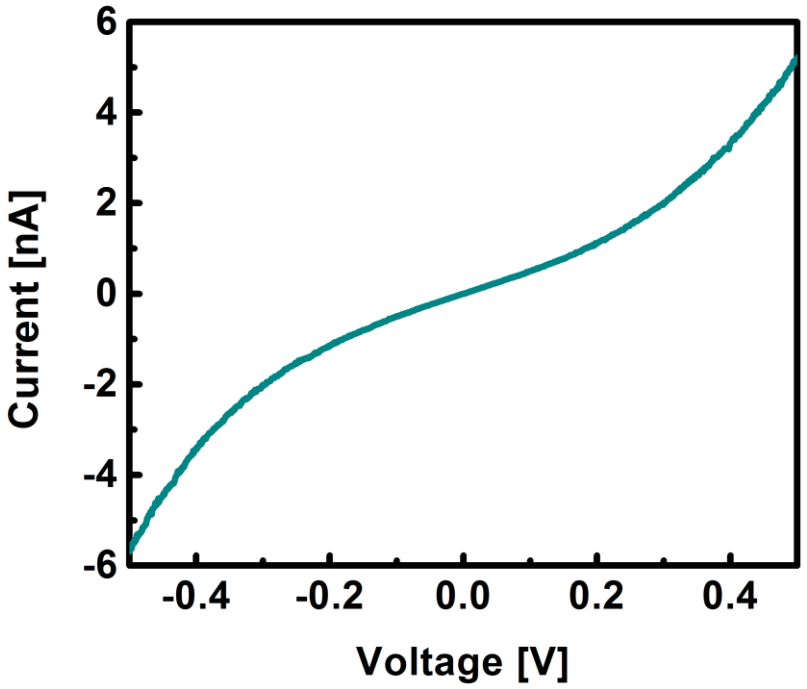


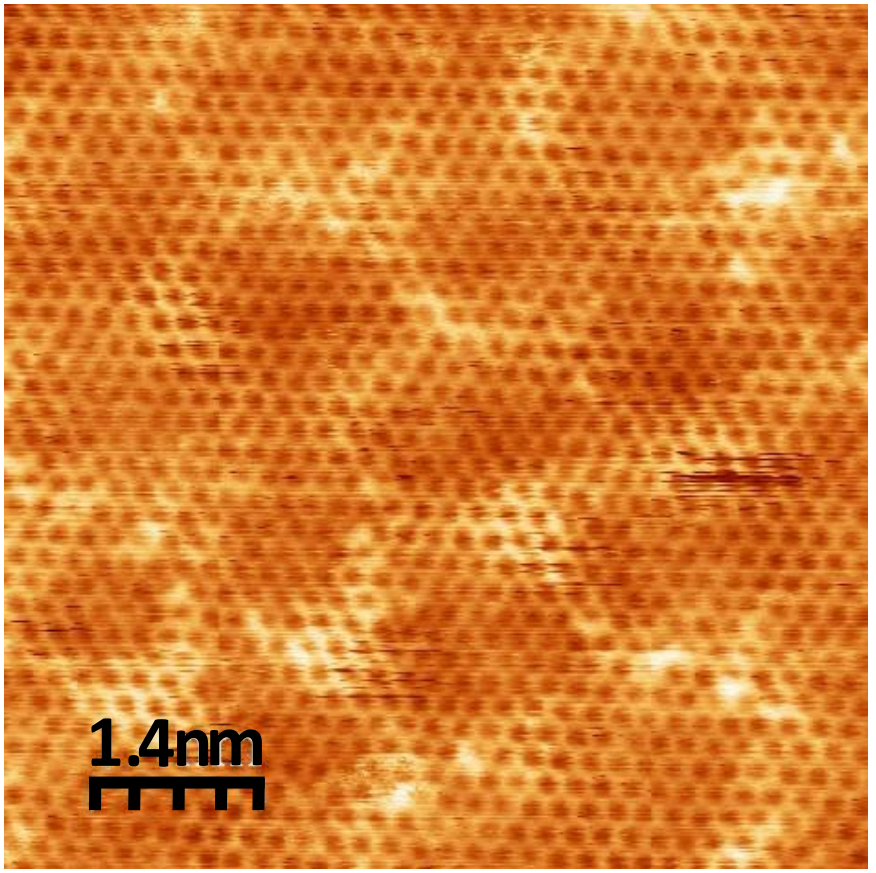


d = 0.008Å
Increase in binding energy of ~-0.04eV
E = -0.74eV

Bias = 115mV, Current = 0.3nA

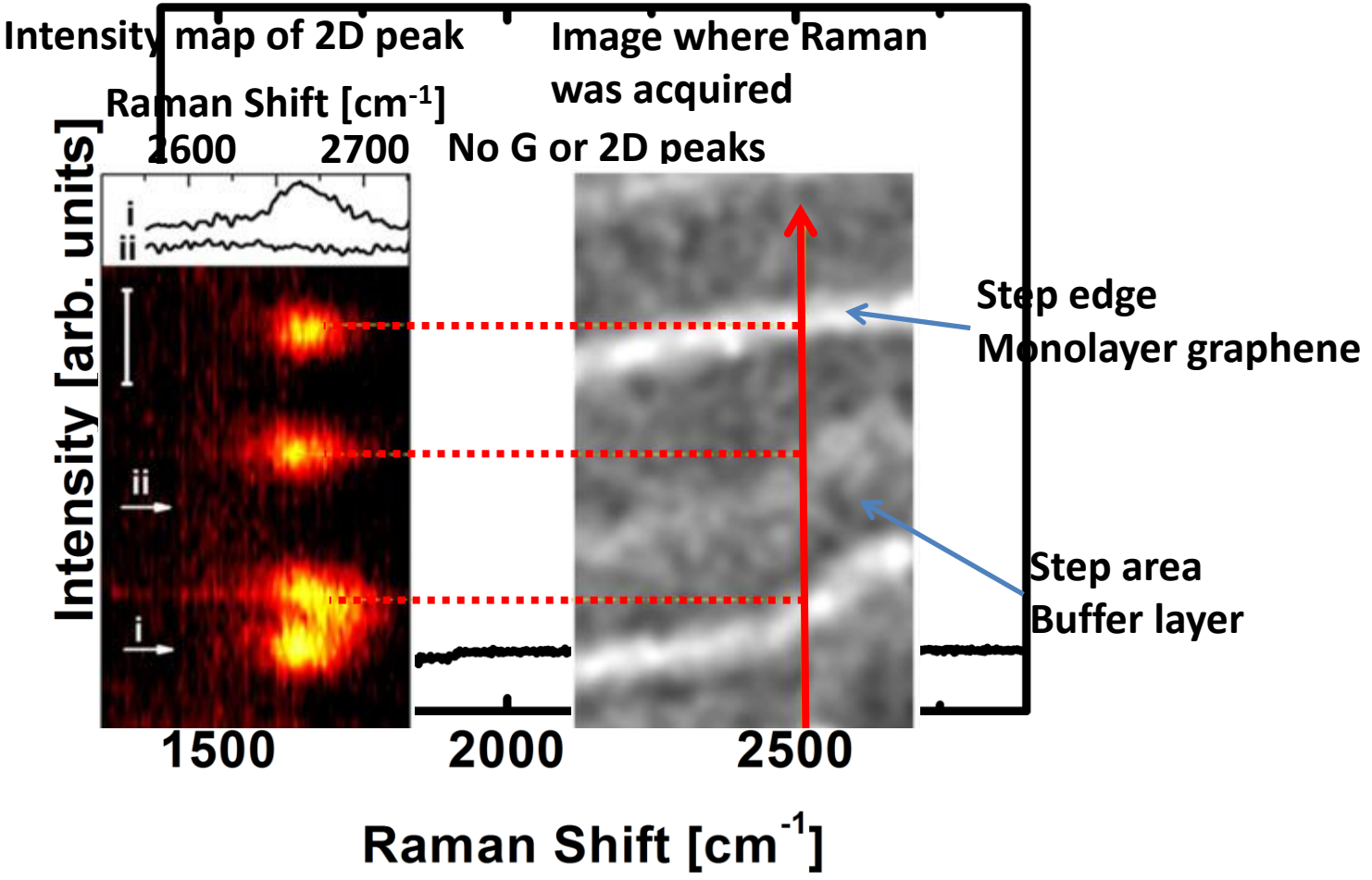
Scanning tunneling spectroscopy (STS) of monolayer graphene on SiC



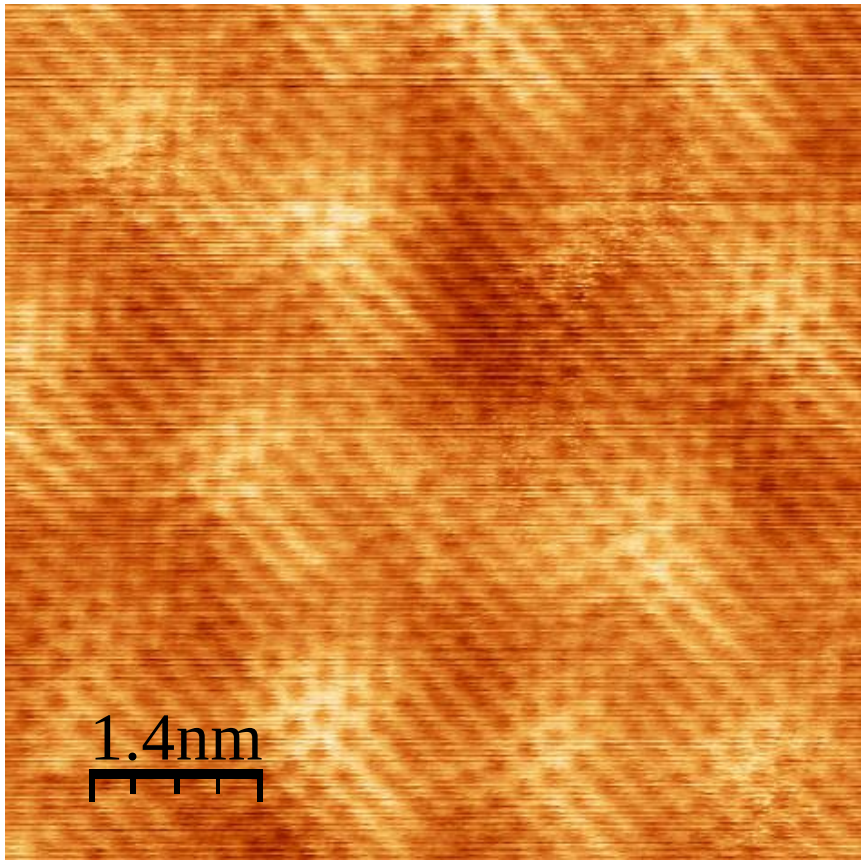


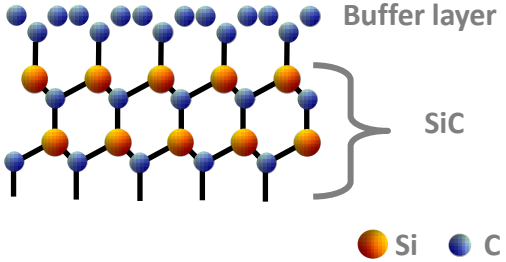
Bias = -0.292V, Current = 0.3nA

Raman spectrum on buffer layer SiC(0001)



STM image of buffer layer on SiC

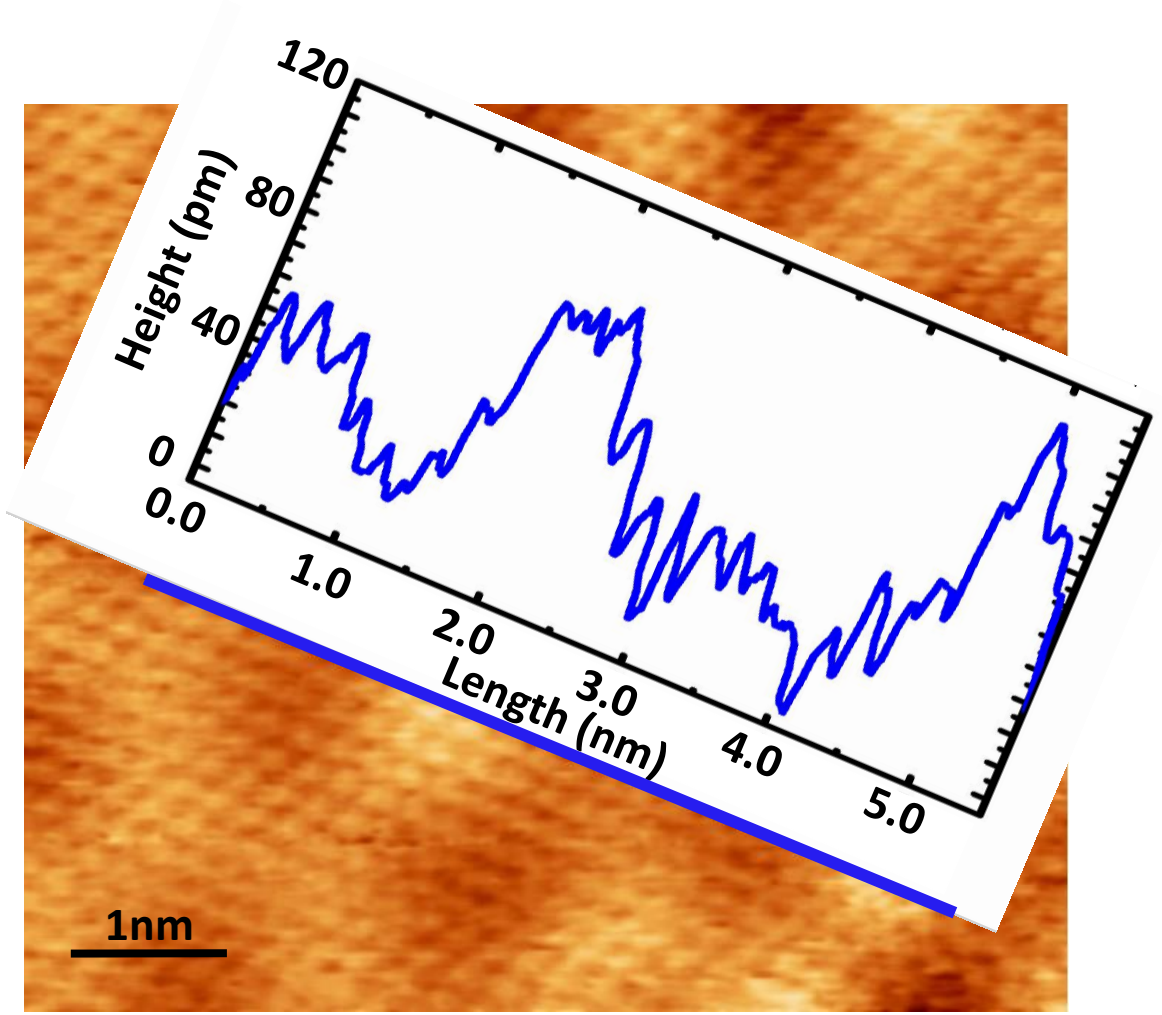


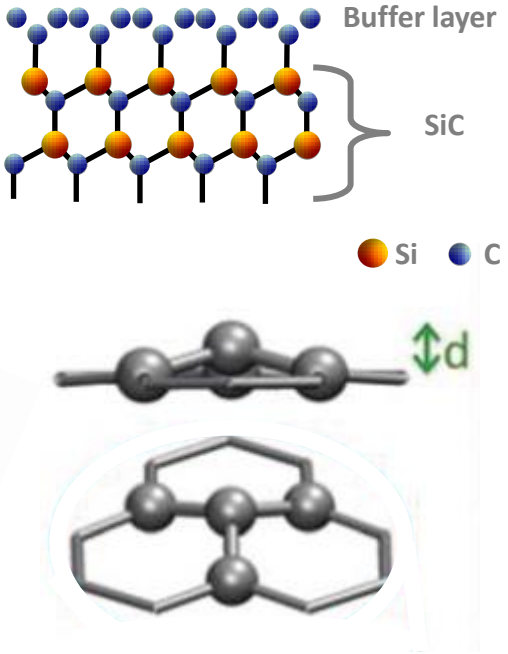


Bias = -0.22V, Current = 0.3nA

S. Goler, et al. Carbon, 51: 249-254, 2013.

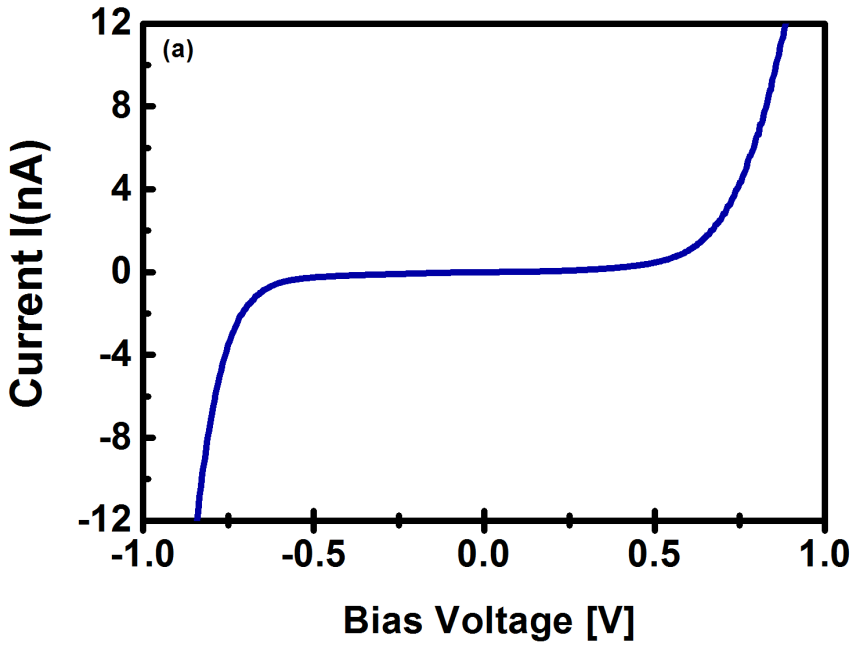
STM image of buffer layer on SiC

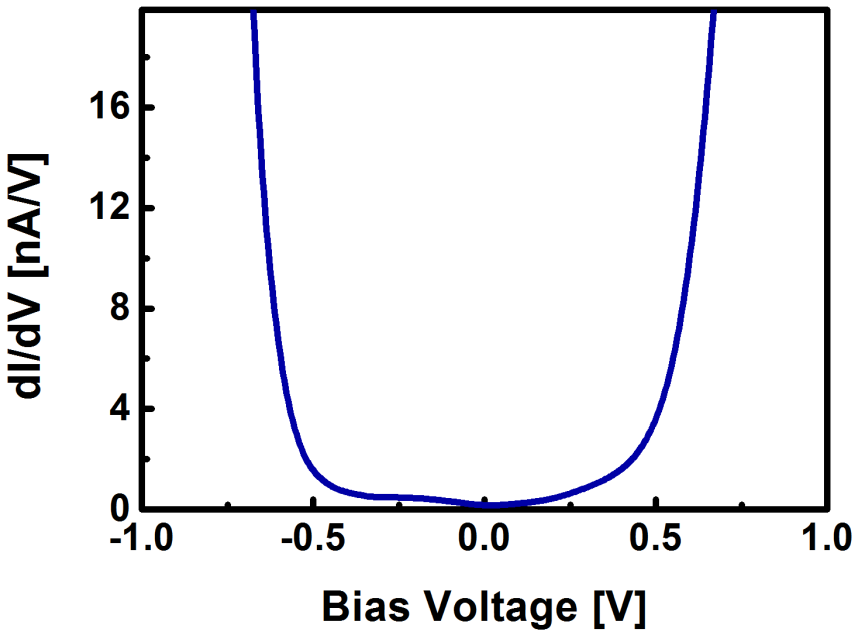




d = 0.13Å
Increase in binding energy of ~-0.63eV
E = -1.33eV

STS of buffer layer on SiC

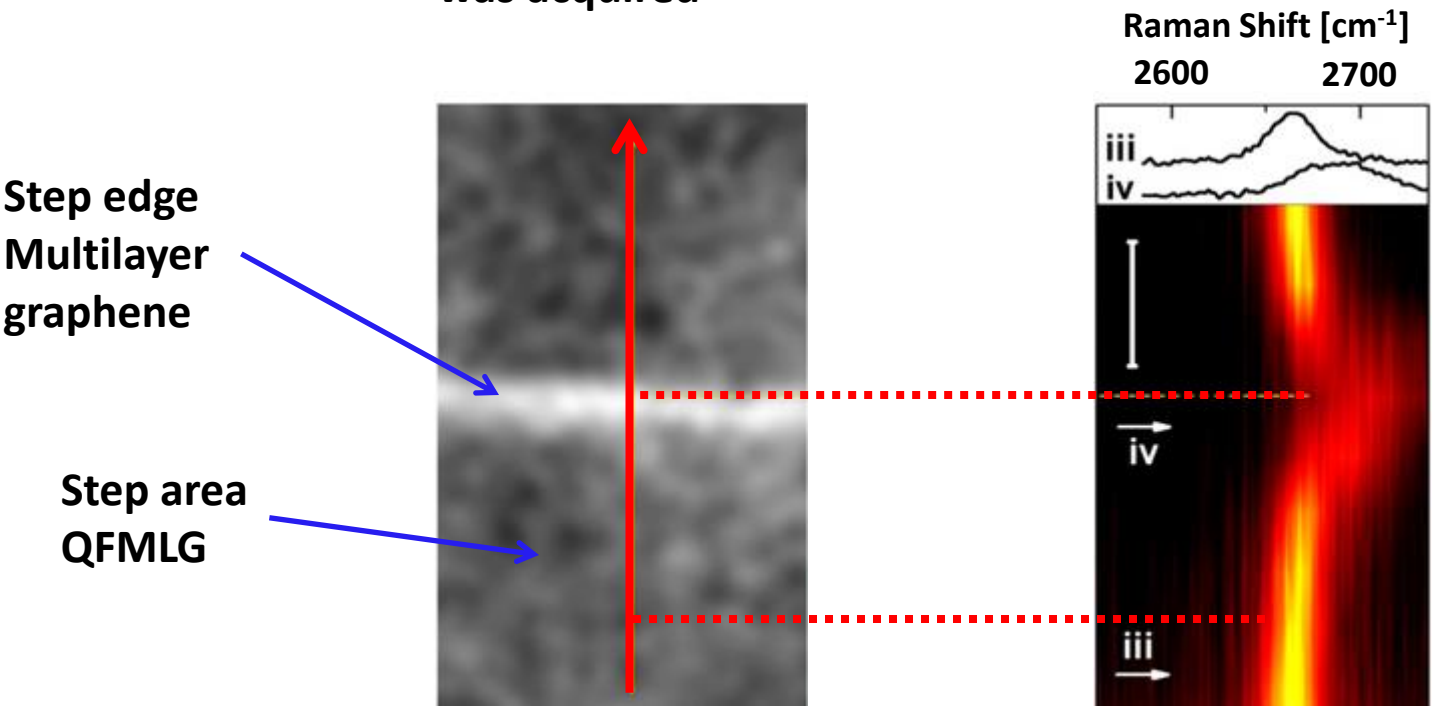




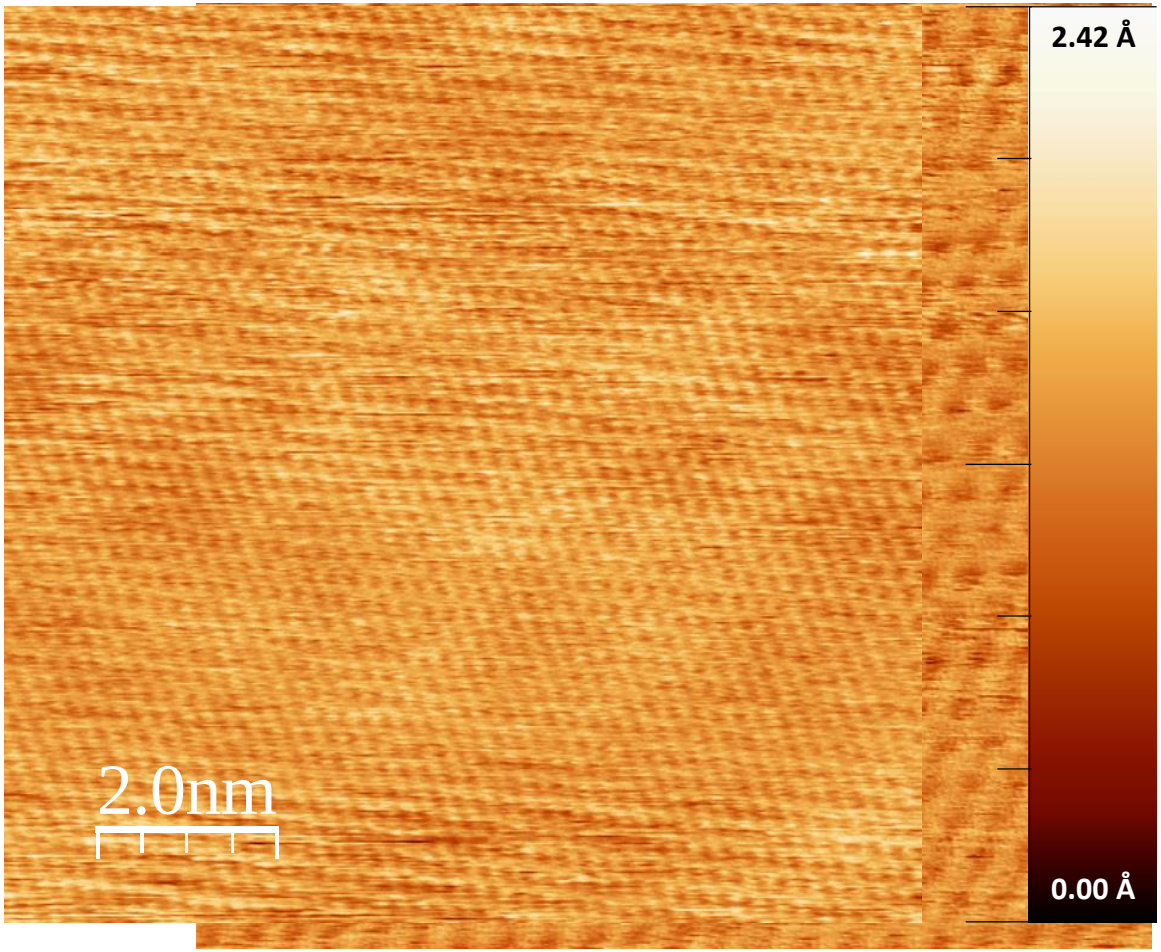
Raman spectrum on quasi-free-standing monolayer graphene

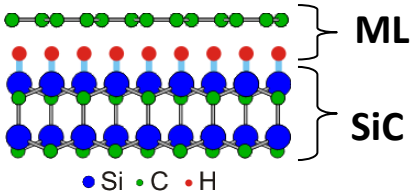
Image where Raman was acquired

Intensity map of 2D peak

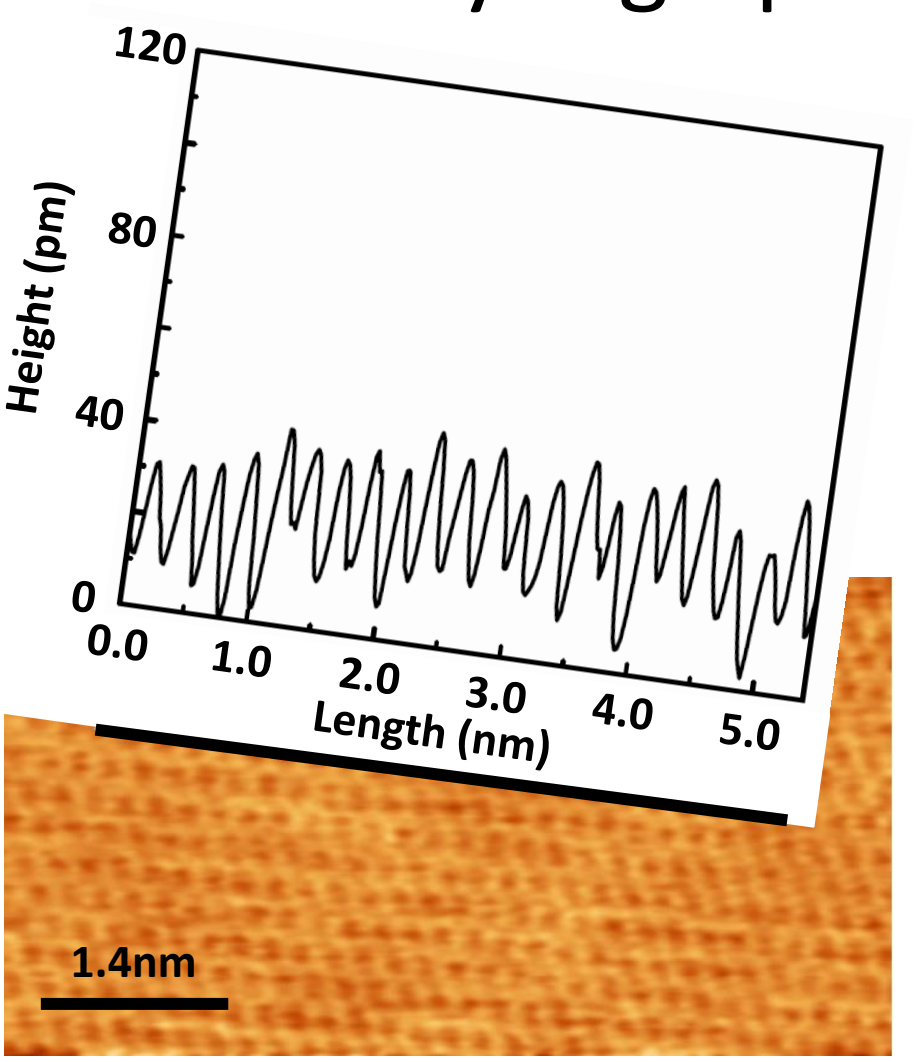


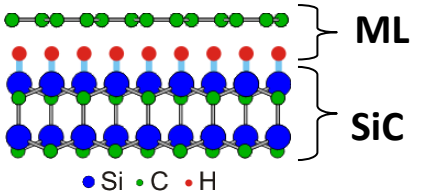
STM image quasi-free standing monolayer graphene on SiC

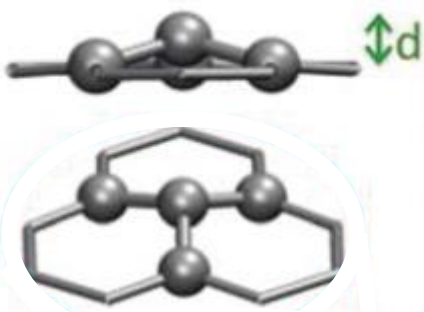




STM image quasi-free-standing monolayer graphene on SiC

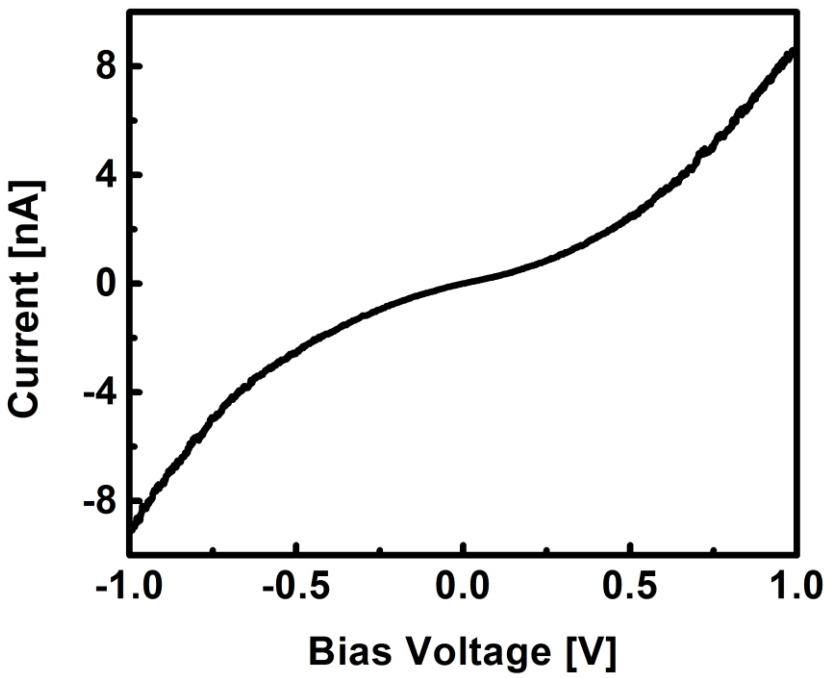


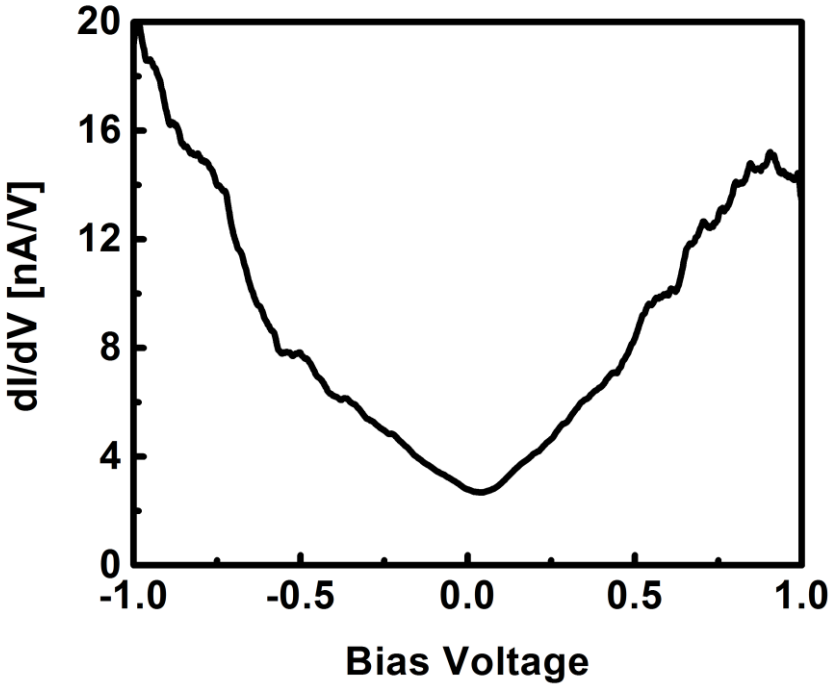




d = 0. 0Å
Increase in binding energy of 0.0eV
E = -0.7eV

STS of quasi-free-standing monolayer graphene on SiC

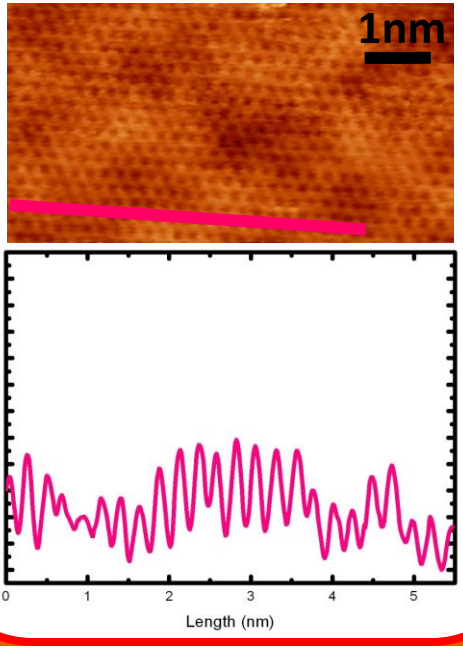




Summary of graphene systems

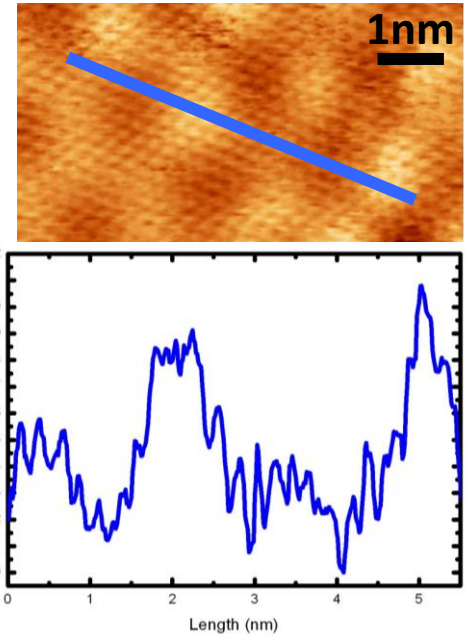
Monolayer on SiC(0001)

Peak to Peak corrugation: ~40pm
Periodicity: ~2nm
Bonds to substrate: no



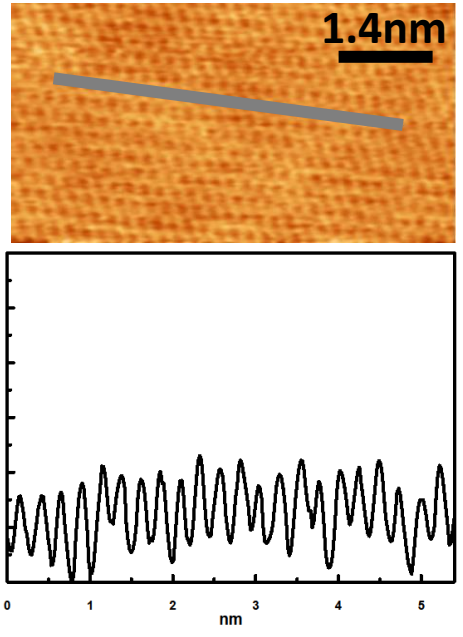
Buffer layer on SiC(0001)

Peak to Peak corrugation: ~110pm
Periodicity: ~2nm
Bonds to substrate: yes



Quasi-free-standing monolayer graphene

Peak to Peak corrugations: ~40pm from atomic contribution
Periodicity: none
Bonds to substrate: no



Hydrogenation Experiments

Experiments on monolayer graphene

Parameters

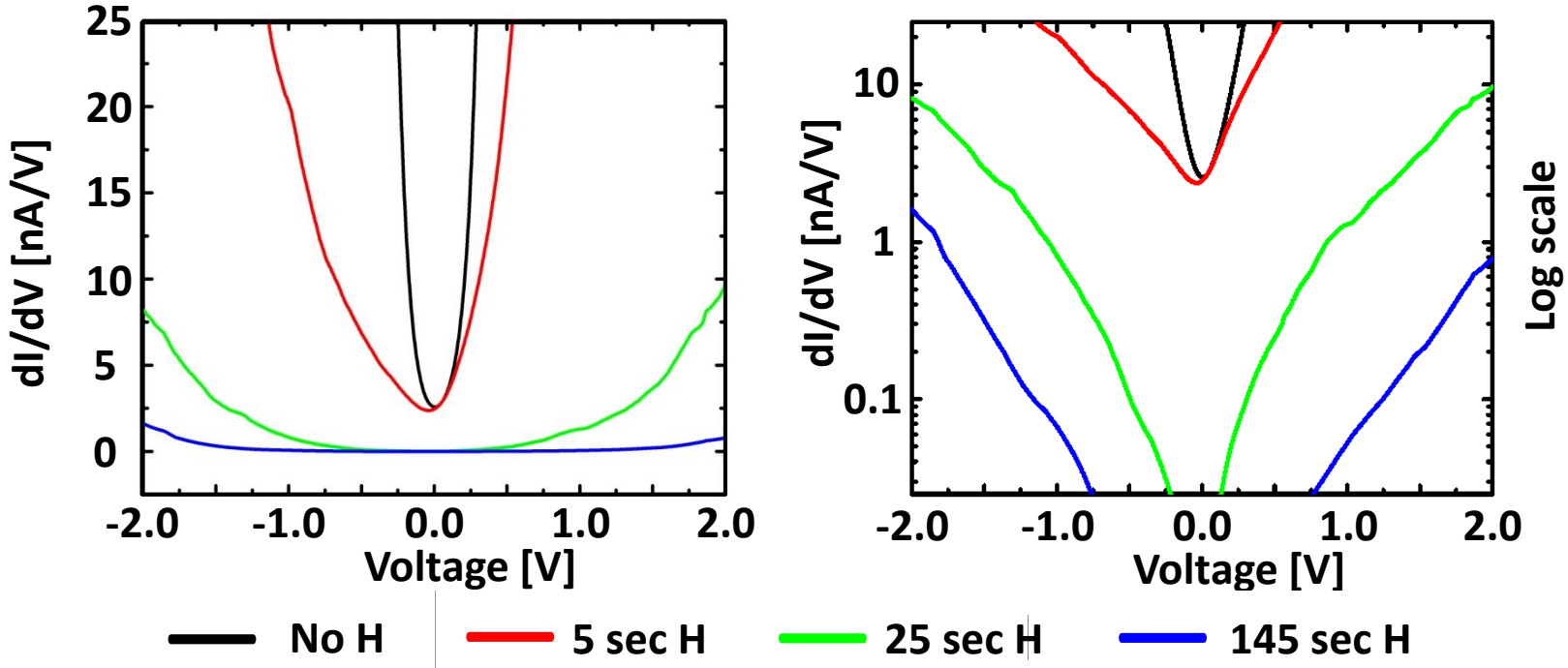
Atomic hydrogenation parameters:
Chamber base pressure: 5×10^{-10} mbar
Atomic hydrogen flux: 5.1×10^{12} atoms/cm^{2}s
Sample temperature: Room temperature

Experiments

STS measurements after atomic hydrogen exposure for 5, 25 and 145 seconds.

STM imaging after 5 second hydrogenation and subsequent heating in steps of 50°C for 5 minutes followed by STM imaging after each heating to observe at what temperature the hydrogen desorbs.

STS on monolayer graphene as a function of atomic hydrogen exposure time



Best monolayer images were acquired at <200mV so STM imaging experiments were done after 5 sec. H exposure

25 sec H = 0.8% coverage and 0.4eV gap opens

145 sec H = 3.8% coverage and 1.5eV gap opens

S. Goler, et al. J. Phys. Chem. C, 117: 11506-11513, 2013.

Experiments on monolayer graphene

Parameters

Atomic hydrogenation parameters:
Chamber base pressure: 5×10^{-10} mbar
Atomic hydrogen flux: 5.1×10^{12} atoms/cm^{2}s
Sample temperature: Room temperature

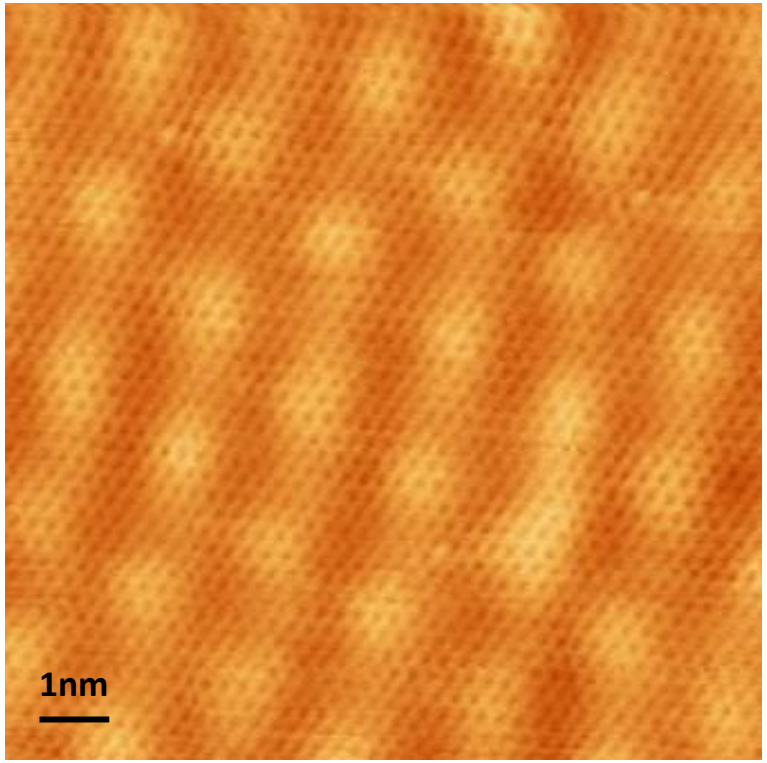
Experiments

STS measurements after atomic hydrogen exposure for 5, 25 and 145 seconds.

STM imaging after 5 second hydrogenation and subsequent heating in steps of 50°C for 5 minutes followed by STM imaging after each heating to observe at what temperature the hydrogen desorbs.

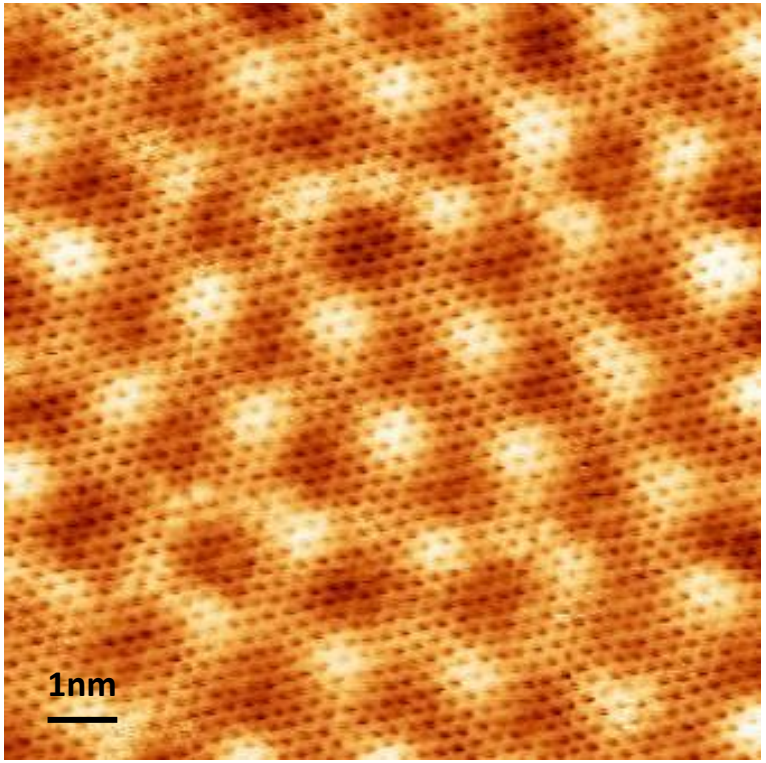
STM image of monolayer graphene after atomic hydrogen exposure of 5 seconds

Before Hydrogenation



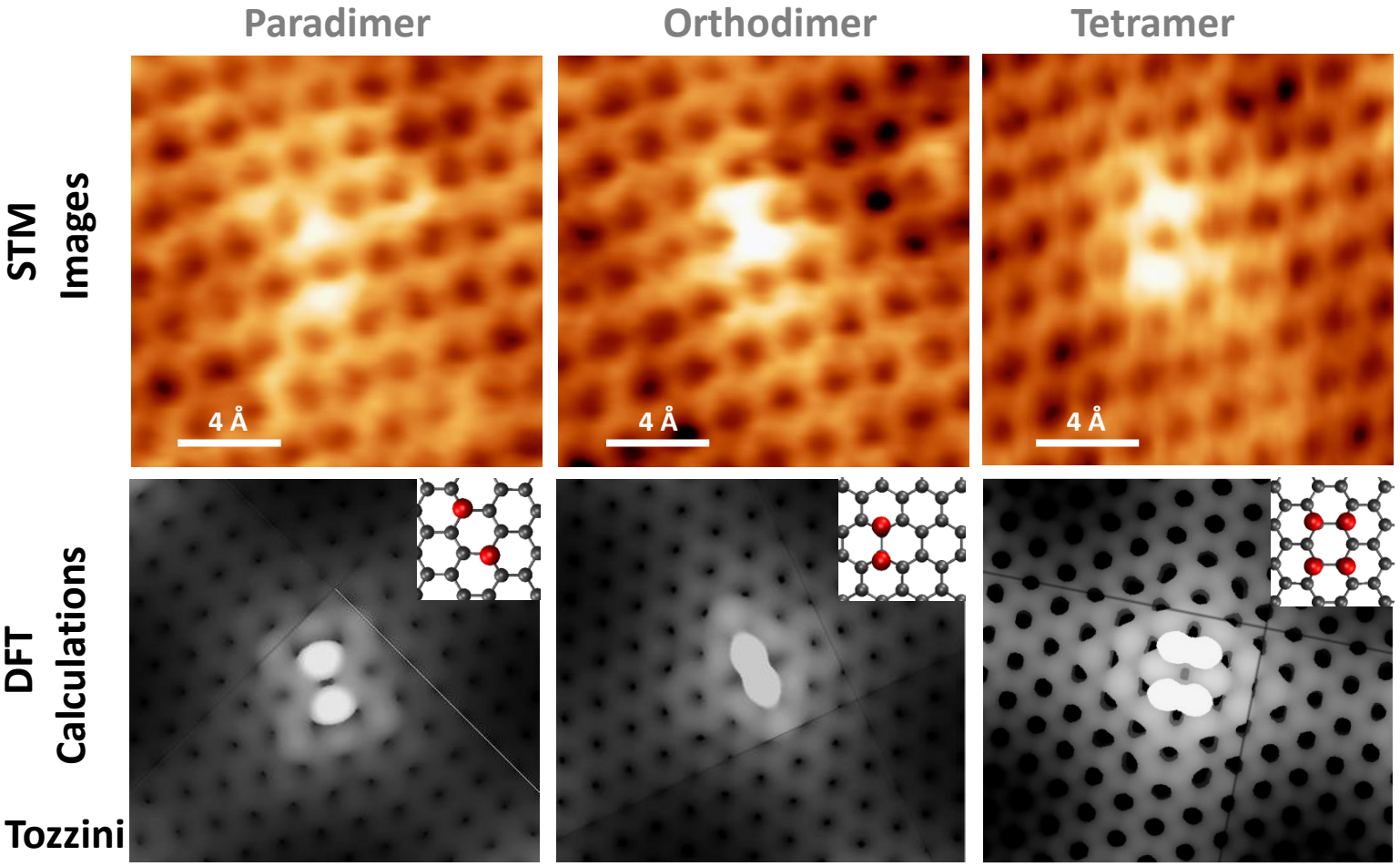
Bias = 115mV, Current = 0.3nA

After Hydrogenation



Bias = 50mV, Current = 0.3nA

Identifying stable hydrogen configurations on monolayer graphene



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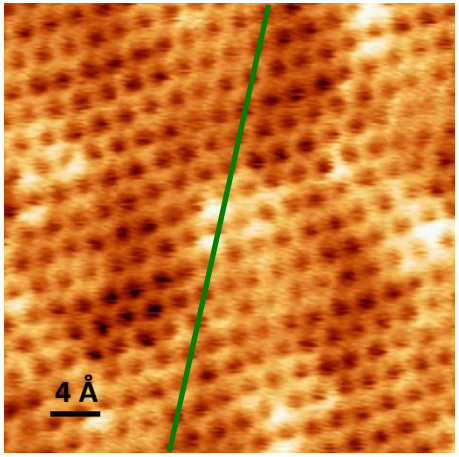
STM imaging parameters at Bias = 50mV, Current = 0.3nA

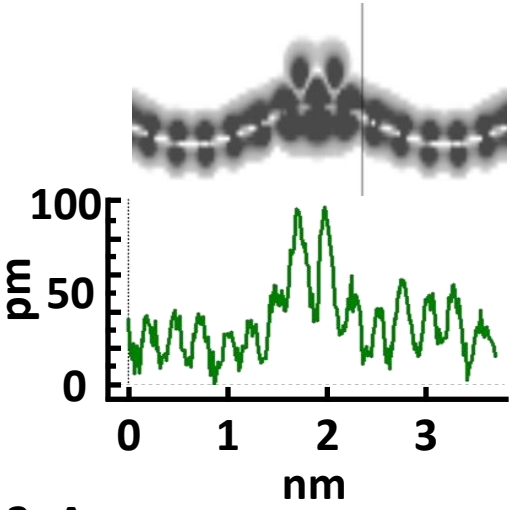
S. Goler, et al. J. Phys. Chem. C, 117: 11506-11513, 2013.

Tetramer on monolayer graphene after 5 second hydrogenation

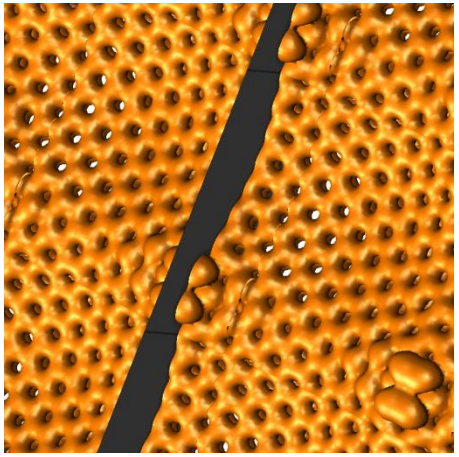
STM measurements



Cross section



Theoretical calculations



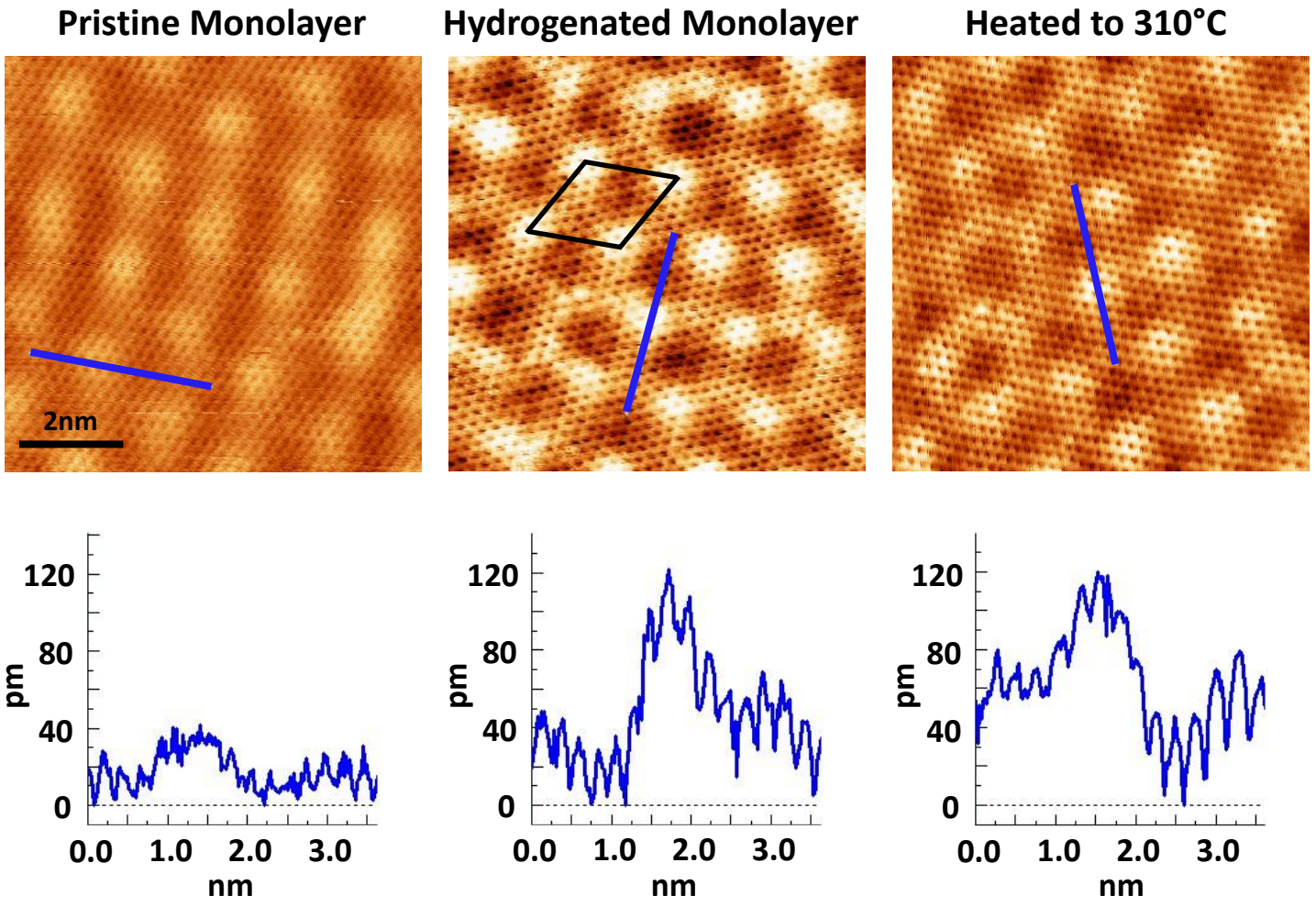
Bias = 50mV, Current = 0.3nA

V. Tozzini

C-H bond length is expected to be 1.1Å and instead we measure 50pm. Carbon atom is slightly more electronegative than hydrogen pulling the electronic wavefunction towards the graphene surface. Agreement with theory.

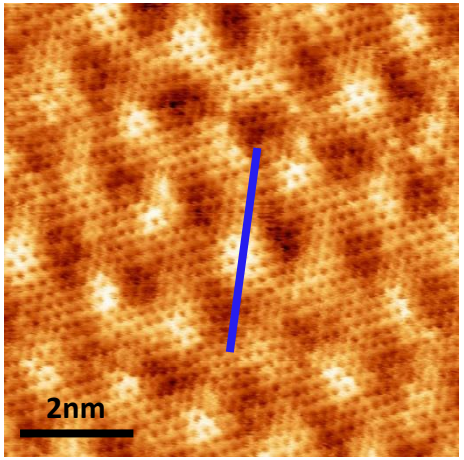
S. Goler, et al. J. Phys. Chem. C, 117: 11506-11513, 2013.

Heating the monolayer graphene

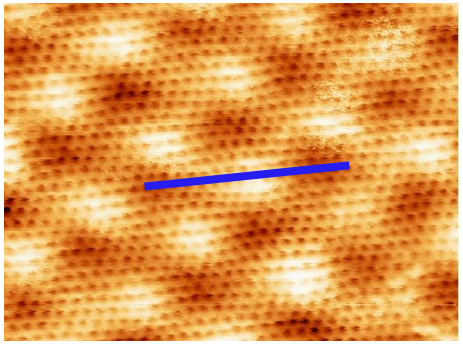


Heating the monolayer graphene

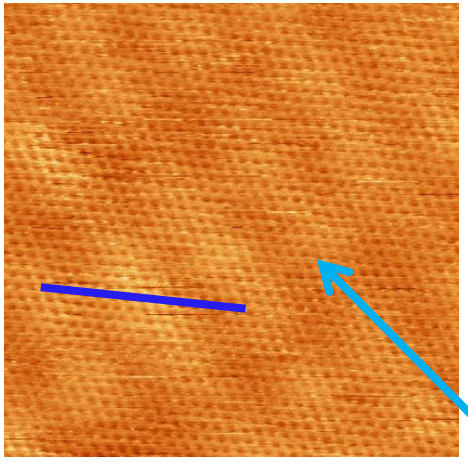
Heated to 420°C



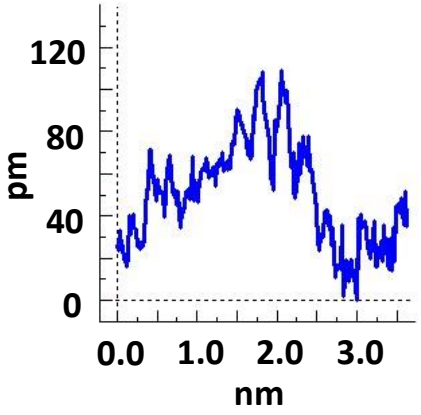
Heated to 630°C

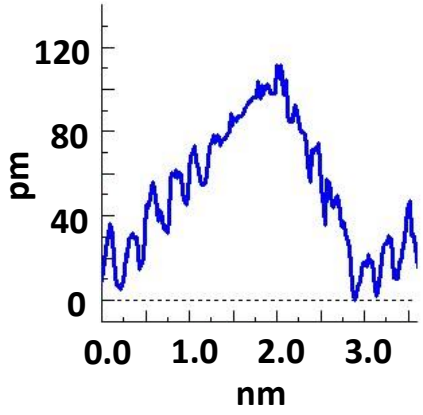


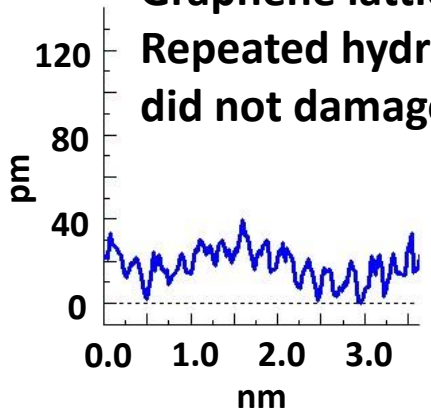
Heated to 680°C



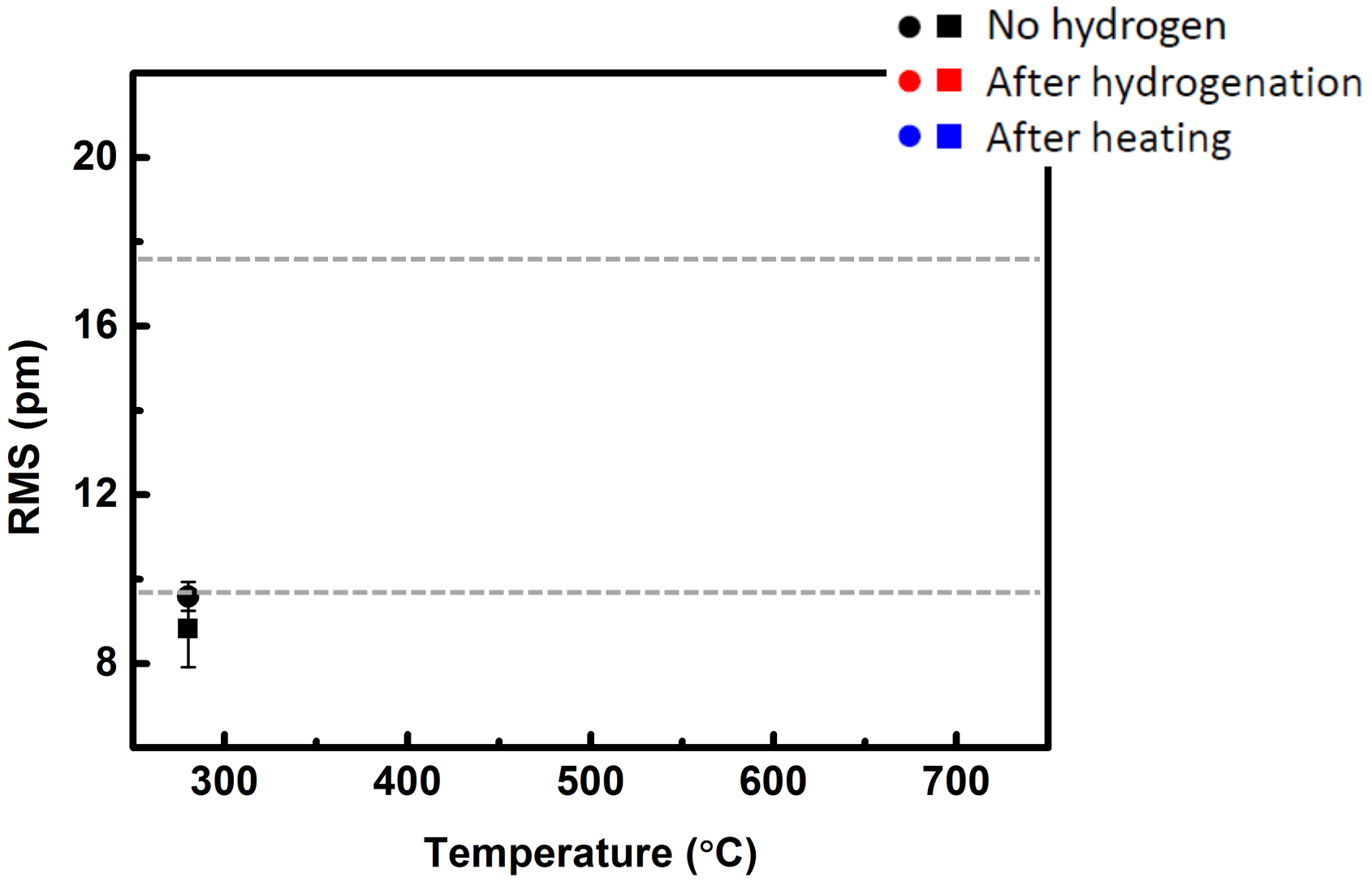
Graphene lattice is intact. Repeated hydrogenation did not damage.







RMS values from images



Estimating the desorption energy barrier from Arrhenius equation

$$\frac{E_d}{kT_m} = A\tau_m e^{\frac{-E_d}{kT_m}}$$

E_d = 2.8eV/molecule or 1.4eV/atom

E_d = Desorption energy barrier

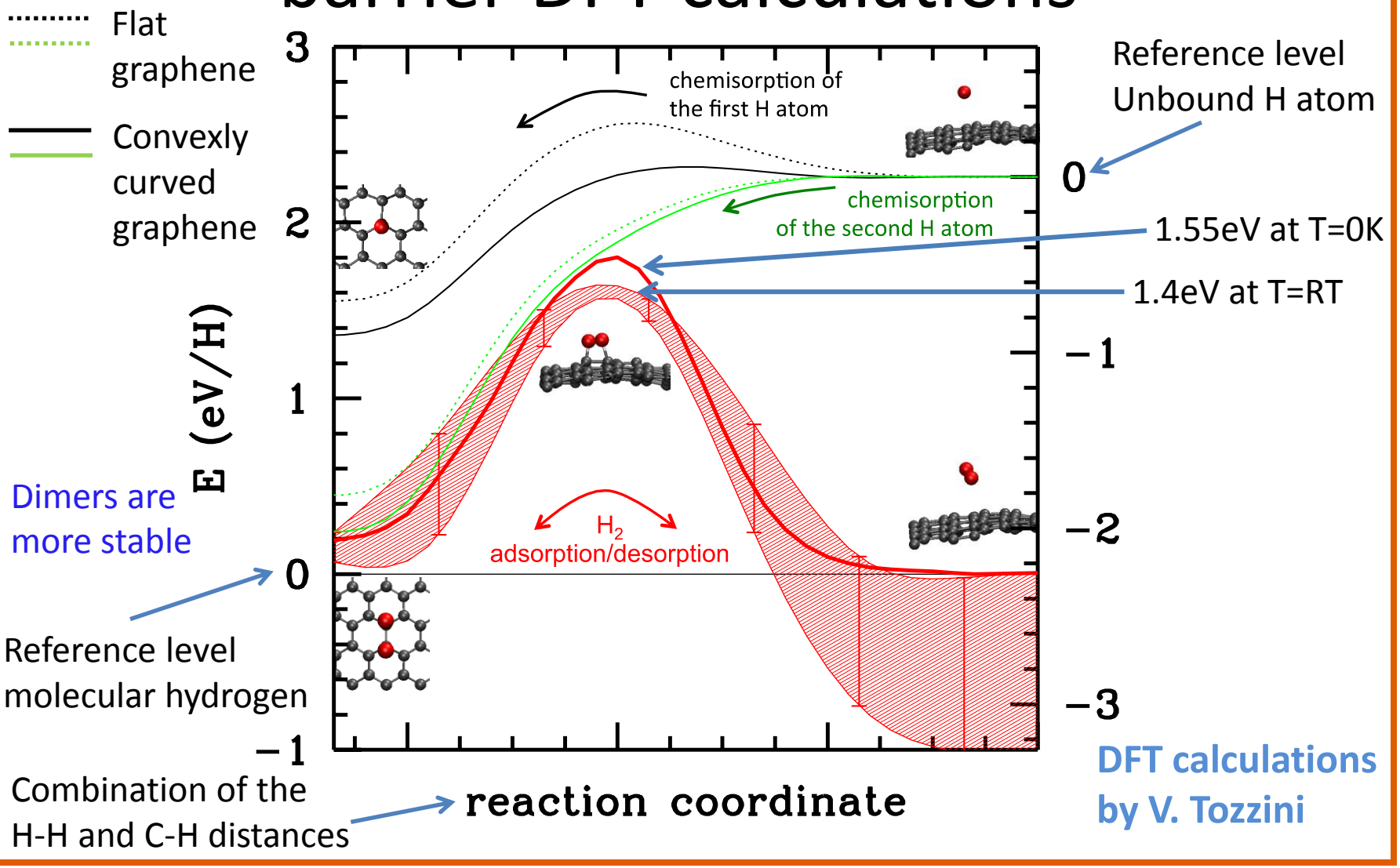
k = Boltzman's constant (8.617 x 10^{-5}eV/K)

T_m = Temperature of desorption (650°C, ~930K)

A = Arrhenius constant ($10^{13}s^{-1}$)

τ_m = Heating time (10^3s)

Desorption energy barrier DFT calculations



Summary of results

- Thorough characterization of buffer layer, monolayer and quasi-free-standing monolayer graphene on SiC(0001).
- First clear atomic resolution STM images of the buffer layer.
- Preferential adsorption of atomic hydrogen on locally convex areas of graphene.
- First observation of dimers and tetramers on graphene on SiC(0001).
- The atomic hydrogen on the maximally convex areas is stable up to ~650°C and agrees with the DFT calculations for the desorption energy barrier of ~1.4eV.
- The graphene layer is not destroyed following multiple hydrogen exposure and heating cycles.

People who contributed to this work

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Thank you