The influence of graphene curvature on hydrogen adsorption

Sarah Goler

Laboratorio NEST, Istituto Nanoscienze – CNR and Scuola Normale Superiore, Piazza San Silvestro 12, 56127 Pisa, Italy
Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy
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.
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 flexible membrane.

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.

First experimental evidence of hydrogen adsorption on graphene in 2009.

EXPLORE THE INTERACTION OF GRAPHENE CURVATURE FOR HYDROGEN ADSORPTION AND RELEASE

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 sp³ C-Si bonds.

Δz=120pm

Δz=40pm

SiC

Buffer layer

Monolayer

SiC

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


NOTE: What does the charge density map tell you?
Graphene growth on SiC(0001)

Commercially available SiC: polishing scratches

Atomically flat SiC

Homogenous graphene

Si(0001) face


Growth Chamber
P ~ atmospheric pressure
T > 1400°C

H₂ Etching

Ar-Annealing

P ~ atmospheric pressure
T ~ 1400°C (BL) ~ 1480°C (ML)
Quasi-free-standing monolayer graphene (QFMLG)

Buffer layer

QFMLG

Hydrogen Intercalation

Growth Chamber

\[ P \sim \text{atmospheric pressure} \]
\[ T \sim 800^\circ\text{C} \]

\[ \text{H}_2 \]

C. Riedl, C. Coletti et al., *PRL* 103, 246804 (2009)
Hydrogen intercalation of the buffer layer and ARPES

Buffer layer

\[ E_F = \frac{k}{\text{Å}^{-1}} \]

Delocalized states

\[ \pi \text{ bands of graphene} \]


\[ p = 2.6 \times 10^{12} \text{ cm}^2 \]
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
NOTE: We bias the sample: +empty states and – filled states

$\Psi_n$ = sample state

$E_n$ = energy (for tunneling must be between $E_F$ - eV)

$\Phi$ = -$E_F$ (ignoring thermal excitations)  Work function needed to remove the electron from the bulk to the vacuum.

NOTE: Should I write chemical potential instead of Fermi level?

Base pressure of ~5 x 10$^{-11}$ mbar

Measurements acquired in constant current mode. Bias voltage and tunneling current are constant.

The distance between the sample and the tip is modified to maintain a constant tunneling current.

Room temperature.

Photographs courtesy of Massimo Brega.
Raman spectrum on monolayer graphene SiC(0001)

STM imaging should be in the steps not at the step edges.
STM image of monolayer graphene on SiC

Bias = 115mV, Current = 0.3nA

$\Delta d = 0.008\,\text{Å}$

Increase in binding energy of $\sim -0.04\,\text{eV}$

$E = -0.74\,\text{eV}$
Scanning tunneling spectroscopy (STS) of monolayer graphene on SiC

Bias = -0.292V, Current = 0.3nA
Raman spectrum on buffer layer

SiC(0001)

No G or 2D peaks

Raman spectrum on buffer layer

No G or 2D peaks
STM image of buffer layer on SiC

Bias = -0.22V, Current = 0.3nA

STM image of buffer layer on SiC

$d = 0.13\text{Å}

Increase in binding energy of $\sim-0.63\text{eV}$

$E = -1.33\text{eV}$
STS of buffer layer on SiC
Raman spectrum on quasi-free-standing monolayer graphene

Image where Raman was acquired

Intensity map of 2D peak

Step edge
Multilayer graphene

Step area
QFMLG

Raman Shift [cm\(^{-1}\)]
2600
2700
STM image quasi-free standing monolayer graphene on SiC
STM image quasi-free-standing monolayer graphene on SiC

\[ E = -0.7 \text{eV} \]

Increase in binding energy of 0.0 eV

\[ d = 0.0 \text{Å} \]

1.4 nm
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:  $5 \times 10^{-10}$ mbar
Atomic hydrogen flux: $5.1 \times 10^{12}$ 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

Experiments on monolayer graphene

Parameters

Atomic hydrogenation parameters:
Chamber base pressure: $5 \times 10^{-10}$ mbar
Atomic hydrogen flux: $5.1 \times 10^{12}$ 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

After Hydrogenation

Bias = 115mV, Current = 0.3nA

Bias = 50mV, Current = 0.3nA
Identifying stable hydrogen configurations on monolayer graphene

Paradimer

Orthodimer

Tetramer

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

Tetramer on monolayer graphene after 5 second hydrogenation

STM measurements

Cross section

Theoretical calculations

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.

Heating the monolayer graphene

Pristine Monolayer  Hydrogenated Monolayer  Heated to 310°C
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

- No hydrogen
- After hydrogenation
- After heating

Temperature (°C) vs. RMS (pm)
Estimating the desorption energy barrier from Arrhenius equation

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

\(E_d = 2.8\text{eV/molecule} \text{ or } 1.4\text{eV/atom}

\(E_d = \text{Desorption energy barrier}\)
\(k = \text{Boltzman’s constant (8.617 x } 10^{-5}\text{eV/K)}\)
\(T_m = \text{Temperature of desorption (650}^\circ\text{C, } \sim 930\text{K)}\)
\(A = \text{Arrhenius constant (10}^{13}\text{s}^{-1})\)
\(\tau_m = \text{Heating time (10}^3\text{s)}\)
Desorption energy barrier DFT calculations

- $1.55\text{eV at } T=0\text{K}$
- $1.4\text{eV at } T=RT$

Combination of the $\text{H-H}$ and $\text{C-H}$ distances

Dimers are more stable

Reference level molecular hydrogen

Reference level Unbound H atom

$H_2$ adsorption/desorption

DFT calculations by V. Tozzini
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

• Vittorio Pellegrini$^{1,4}$
• Stefan Heun$^1$
• Fabio Beltram$^1$
• Camilla Coletti$^{2,3}$
• Valentina Tozzini$^1$
• Vincenzo Piazza$^2$
• Pasqualantonio Pingue$^1$
• Angelo Bifone$^2$
• Torge Mashoff$^2$
• Massimo Morandini$^1$
• Ulrich Starke$^3$
• Konstantin V. Emtsev$^3$
• Stiven Forti$^3$

1) Laboratorio NEST, Istituto Nanoscienze – CNR and Scuola Normale Superiore, Piazza San Silvestro 12, I-56127 Pisa, Italy
2) Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy
3) Max-Planck-Institut fuer Festkoerperforschung, Heisenbergstr. 1, D-70569, Stuttgart, Germany
4) IIT Graphene labs, Genova, Italy
Thank you