Hydrogen Storage in Graphene

Stefan Heun

NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore

Pisa, Italy

National Enterprise for nanoScience and nanoTechnology

NEST

Outline

- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Corrugation (Chemisorption)
- Hydrogen Storage by Functionalization (Physisorption)

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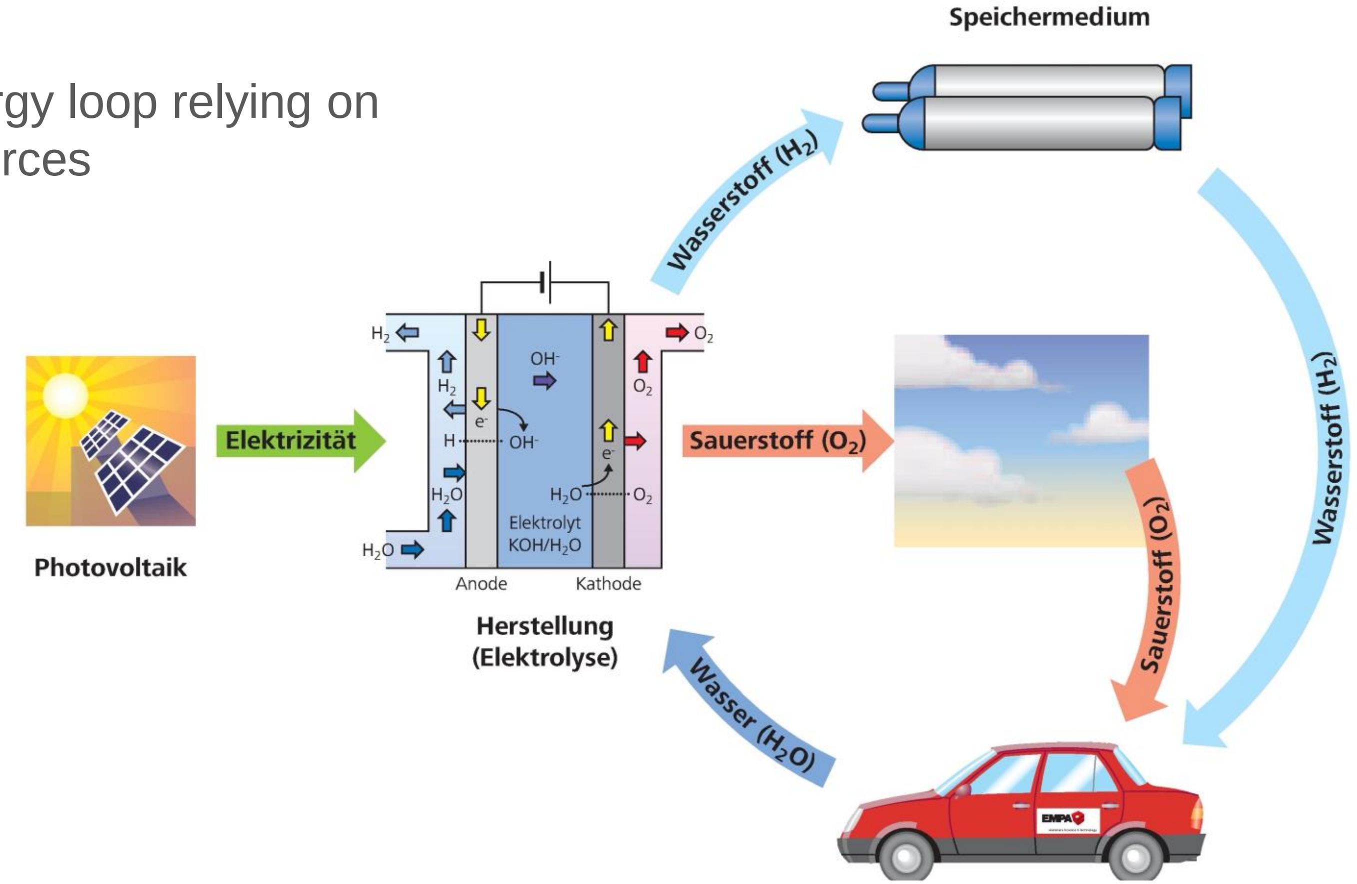
Hydrogen Life Cycle

Complete energy loop relying on renewable sources



Hydrogen Storage in a safe and cheap way is **a critical issue**

Hydrogen-fuelled vehicles

Hydrogen-fuelled vehicles

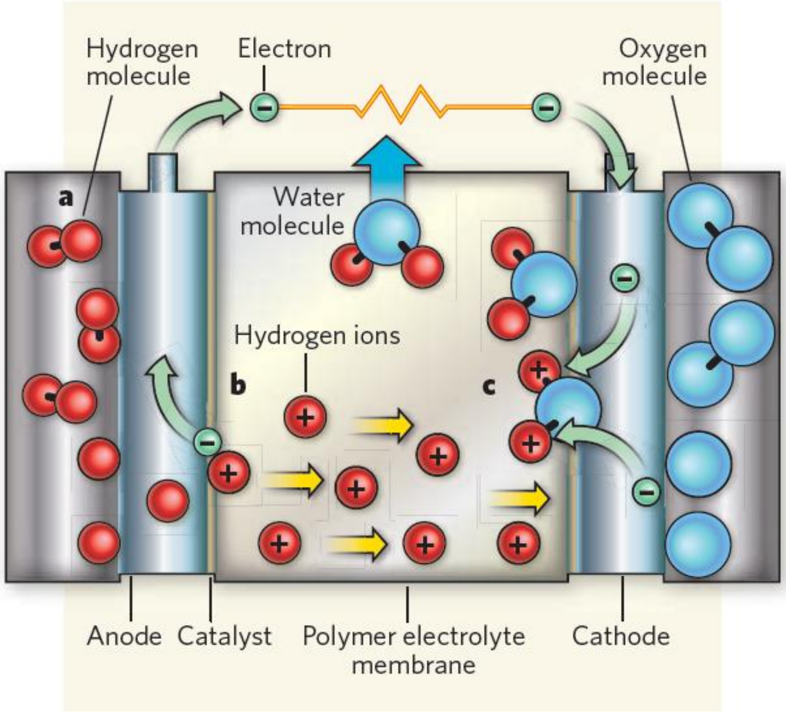
Sales launch of Fuel Cell sedan in Japan before April 2015

Hydrogen & energy

As a fuel, hydrogen has advantages:

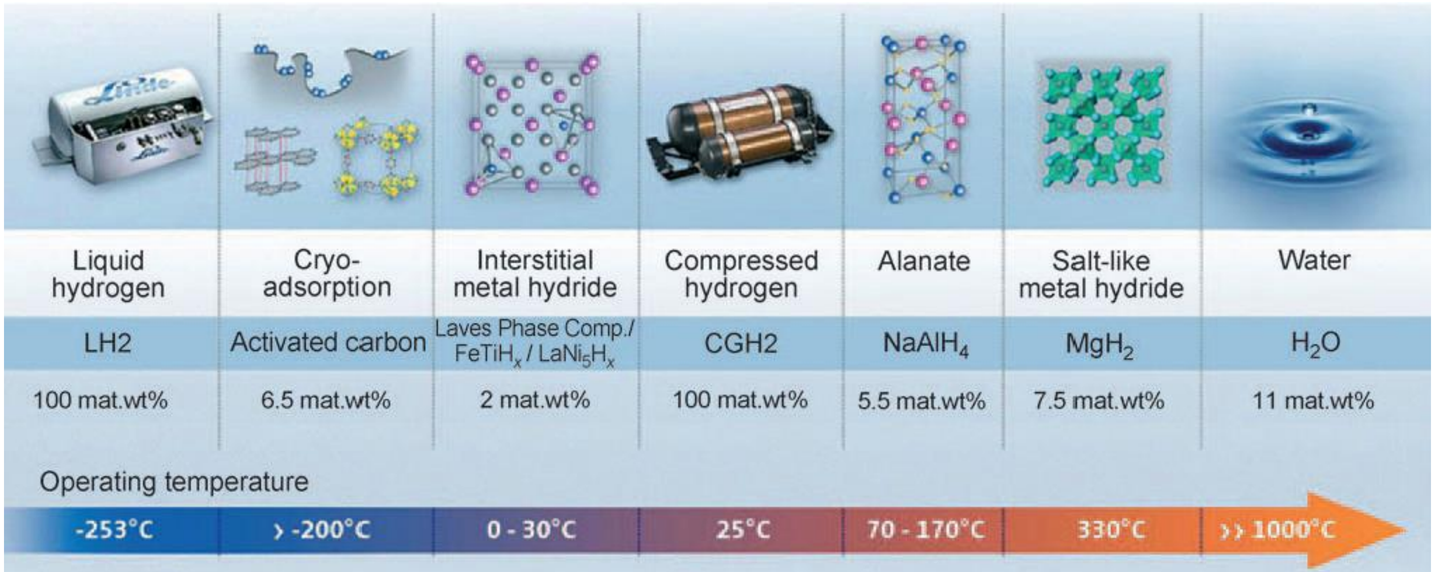
- Highest energy-to-mass ratio
- $H_2 + 1/2\ O_2 \rightarrow H_2O$ $\Delta H = -2.96eV$
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency

However, hydrogen is NOT an energy source: it must be produced e.g. by electrolysis, needing +2.96 eV, with zero balance with respect to energy production.



Hydrogen fuel cell

Hydrogen Storage



Targets for **transport applications** not reached yet:

$\rho_m > 5.5$ wt%

$\rho_V > 50$ kg H_2 /m^3

$P_{eq} \approx 1$bar at T< 100°C

Compressed H_2:
High pressure and heavy container to support such pressure

Solid State:
Physisorption
Chemisorption

Liquid H_2:
Liquefation needs energy and consumes more than 20% of the recoverable energy

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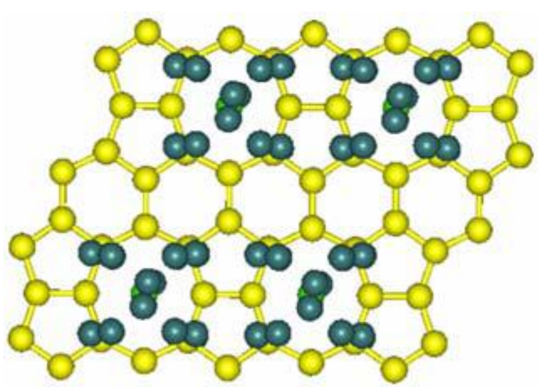
Graphene for hydrogen storage

- Graphene is lightweight, inexpensive, robust, chemically stable
- Large surface area (~ 2600 m^2/g)
- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen

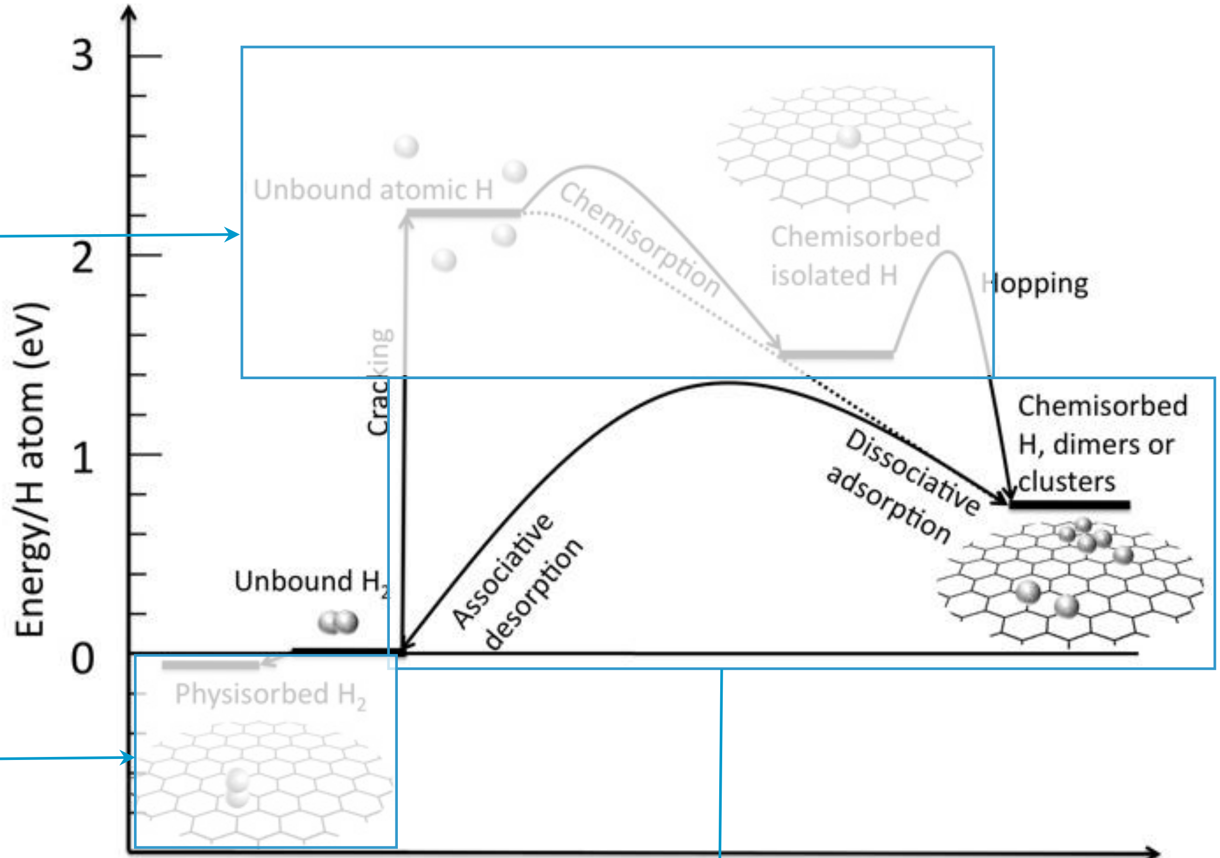


Yang et al., PRB 79 (2009) 075431

H storage in graphene

❖ Atomic hydrogen chemisorption has a small or negligible chemisorption barrier ⇒
feasible but H_2 must be cracked

❖ Physisorption weakly bounds hydrogen ⇒ acceptable storage densities only at low temperatures and/or high pressure



❖ Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate ~eV) ⇒ chemisorbed H is stable for transportation etc, but catalytic mechanisms are necessary in the loading-release phases

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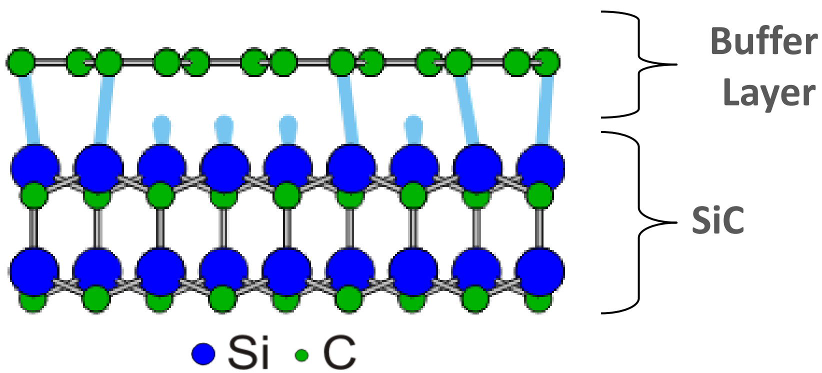
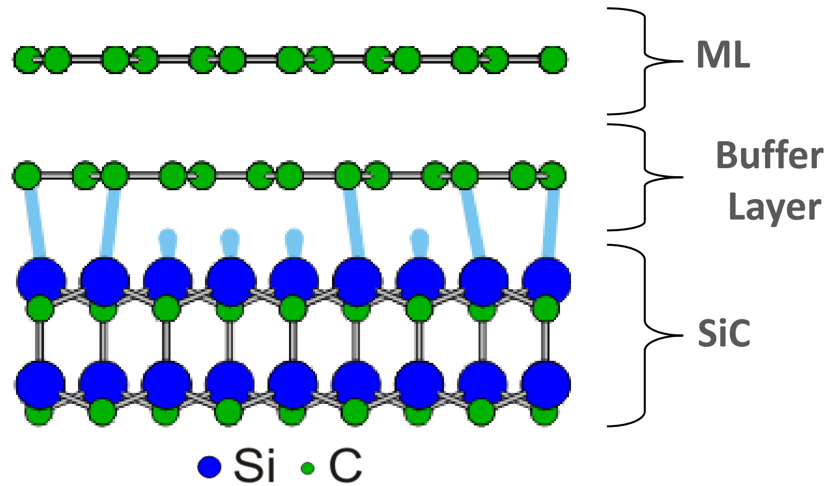
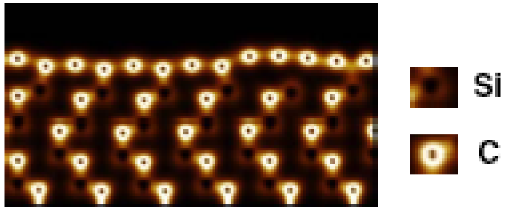
Graphene growth on SiC(0001)



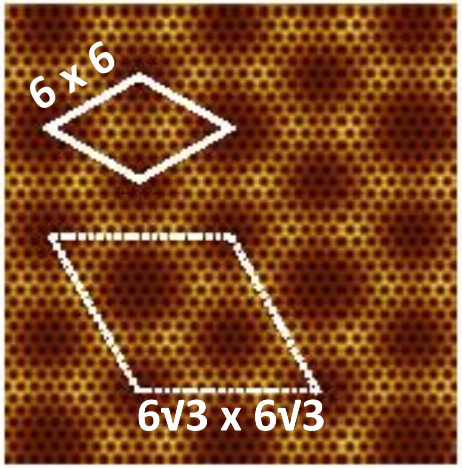


Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp^3 C-Si bonds.



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

Theoretical Calculations



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

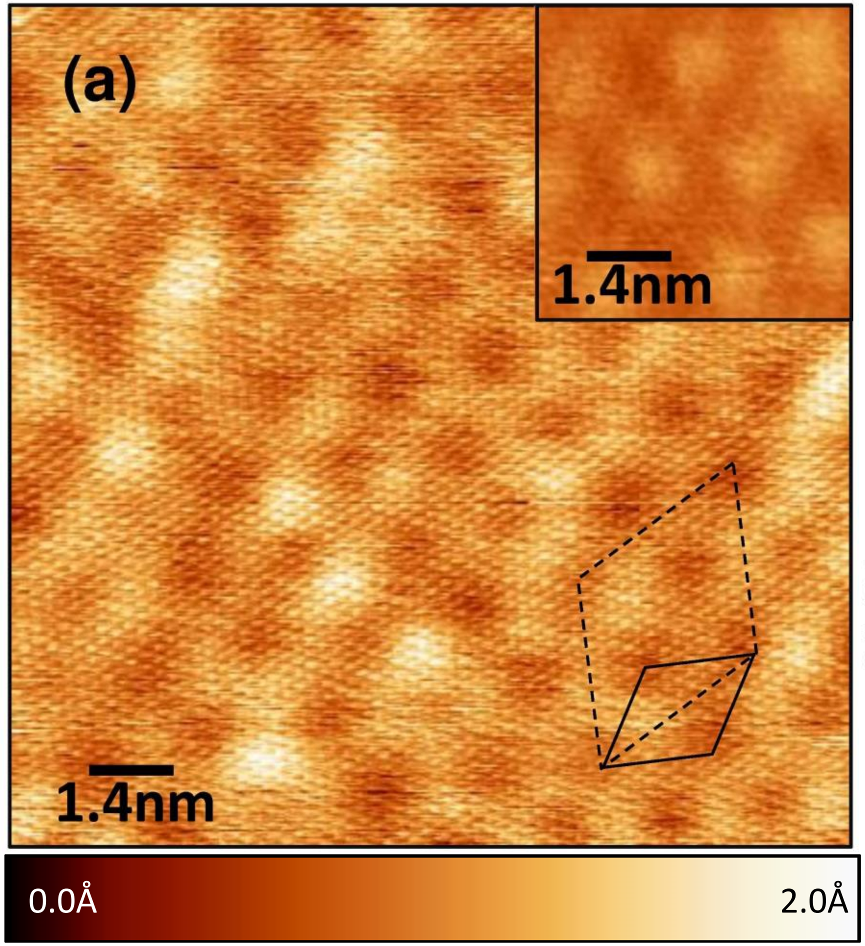
Superstructure of both the buffer layer and monolayer graphene on the Si face from the periodic interaction with the substrate.

Buffer Layer

Bias: +1.7V
Current: 0.3nA

$6\sqrt{3} \times 6\sqrt{3}$ -----

quasi-(6x6) ——



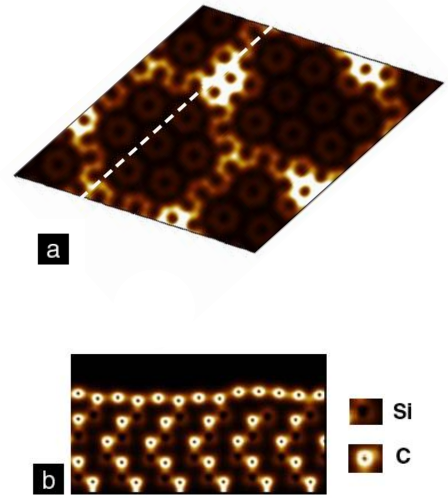
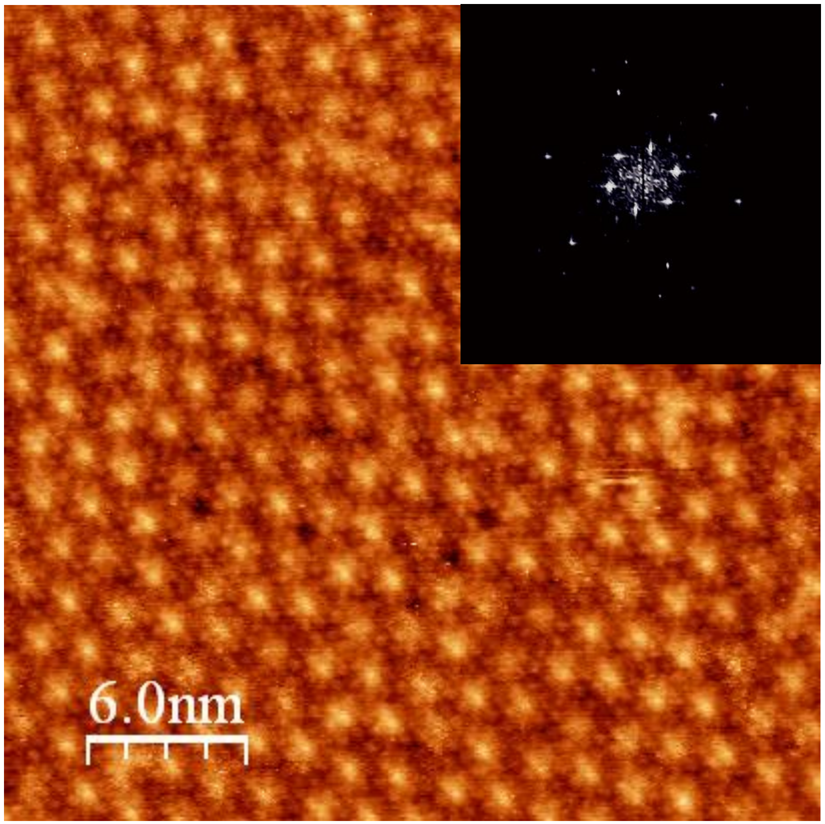


FIG. 2. (Color online) Total charge density of the buffer layer on SiC(001). (a) total charge density in the 6*R*3-SiC unit cell. (b) cross section of the total charge density along the line defined in (a). The black dots that appear when the cross section goes through the middle of an atom are due to the use of pseudopotentials (no core electrons).

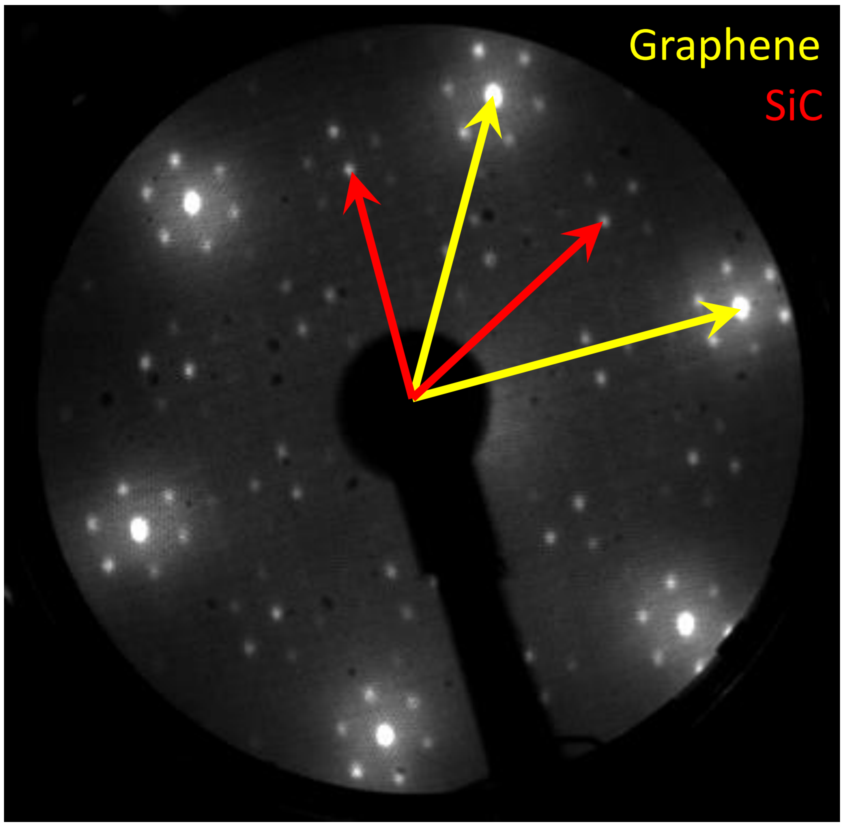
F. Varchon, et al., PRB 77, 235412 (2008).

S. Goler *et al.*: Carbon **51**, 249 (2013).

$6\sqrt{3}x6\sqrt{3}$-Superstructure

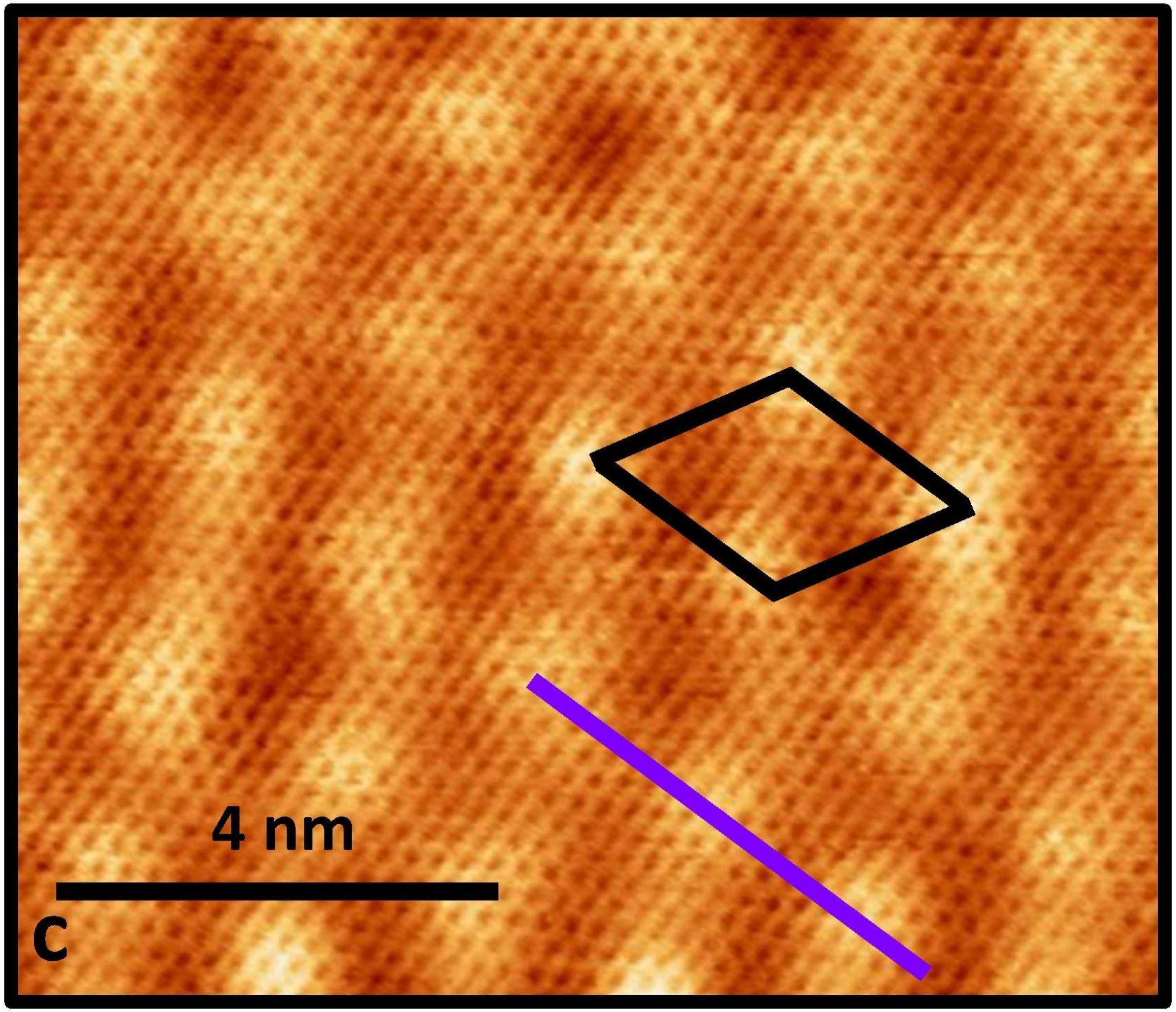


30 nm, 1V, 100 pA

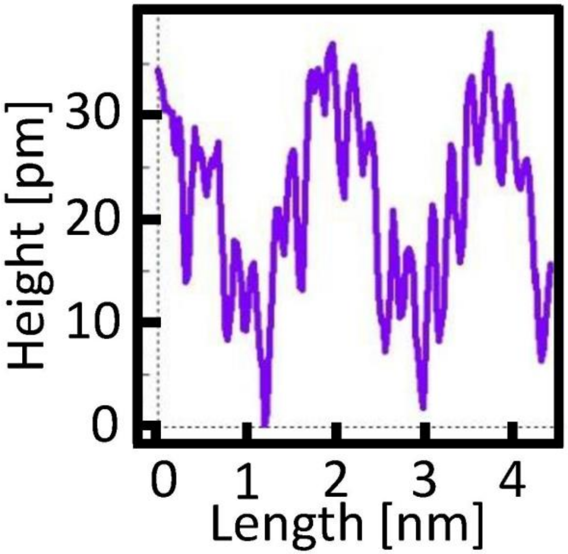


E= 75 eV

Monolayer Graphene

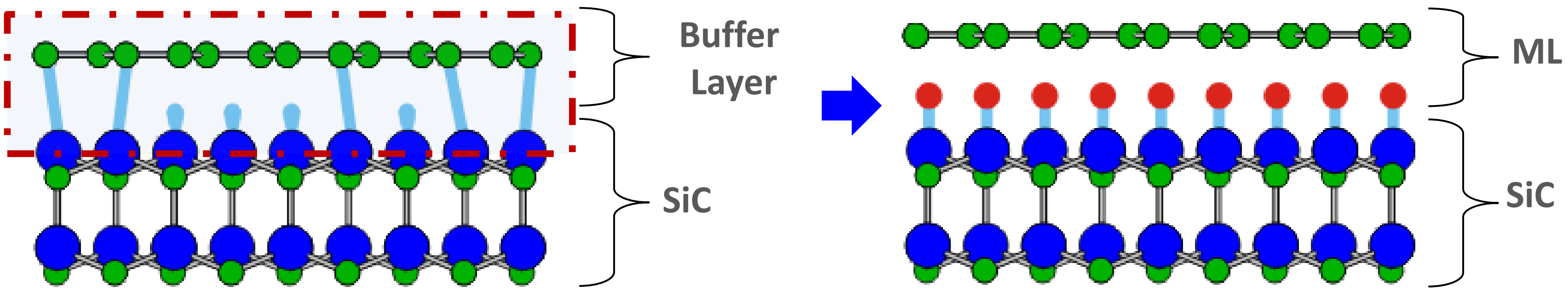


STM



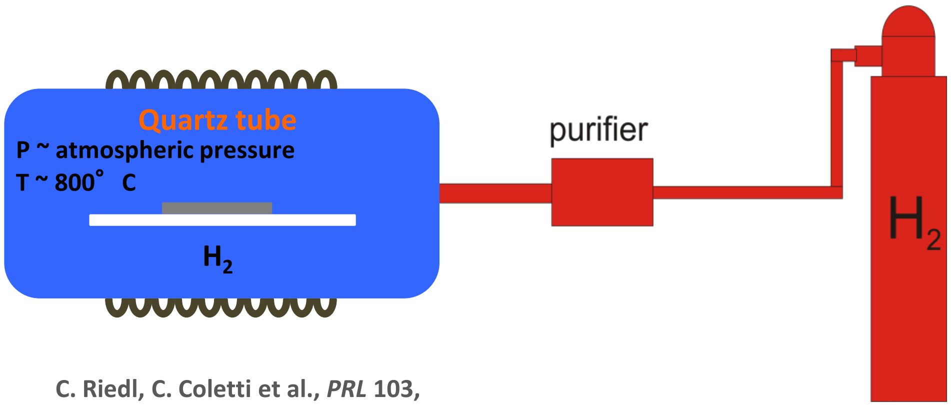
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

Hydrogen Intercalation



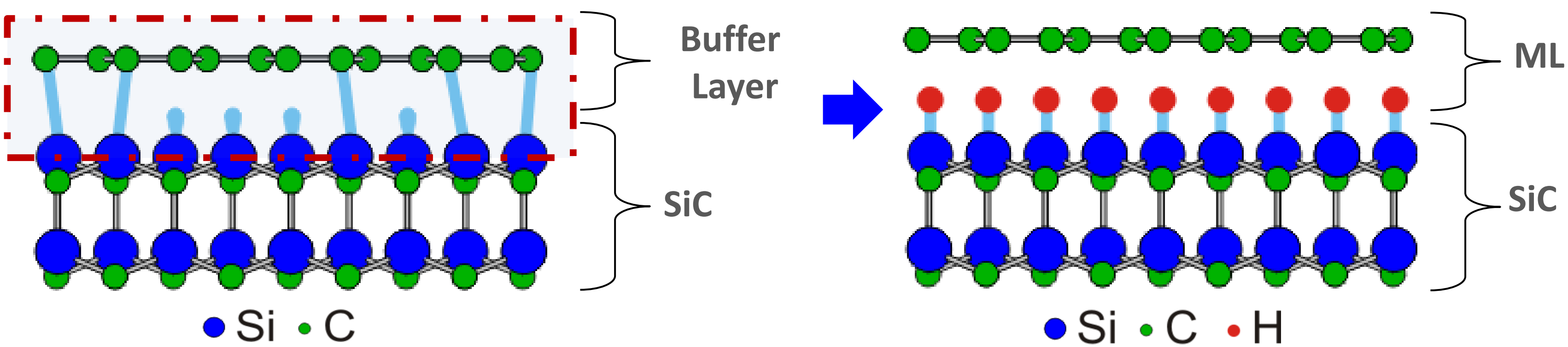
Buffer Layer (BL)

Quasi-free standing monolayer graphene



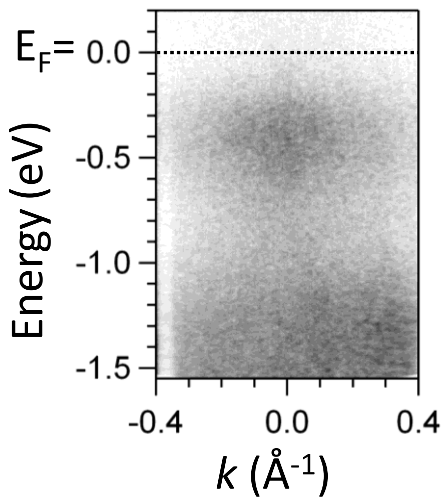
C. Riedl, C. Coletti et al., *PRL* 103, 246804 (2009)

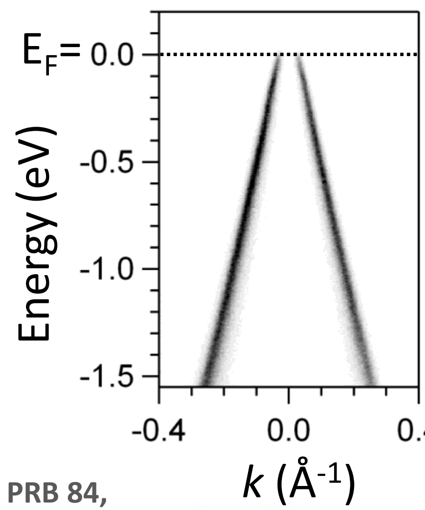
Hydrogen Intercalation



Buffer Layer (BL)

Quasi-free standing monolayer graphene

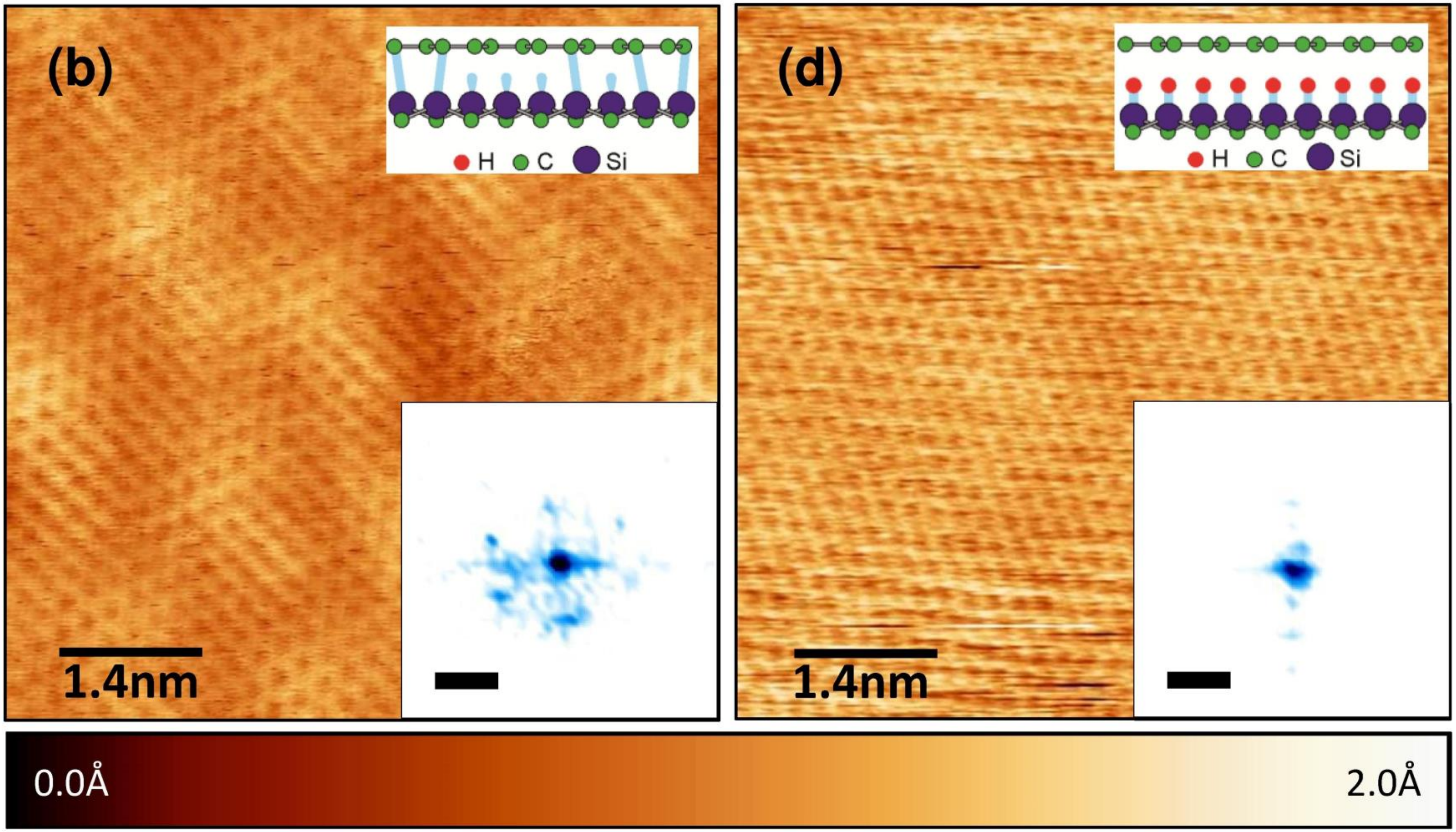




$p=2.6\cdot10^{12}\ cm^{-2}$

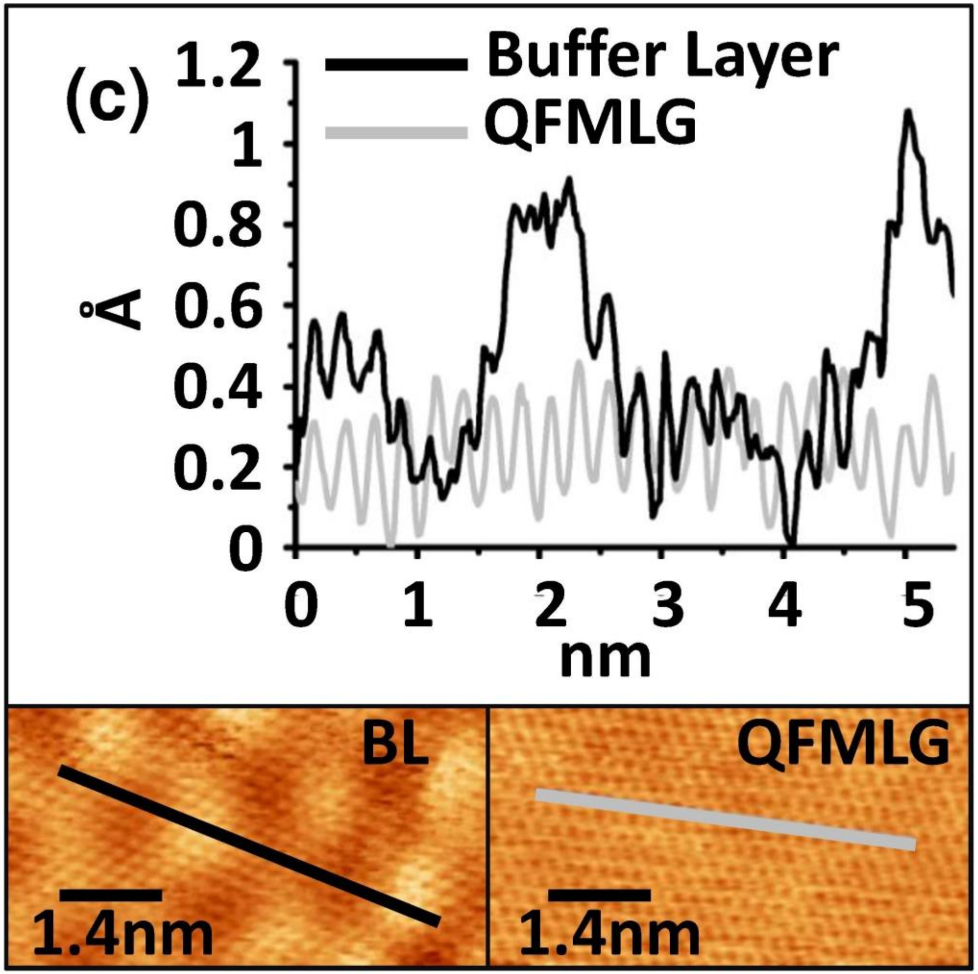
S. Forti, et al., PRB 84, 125449 (2011).

BL vs. QFMLG



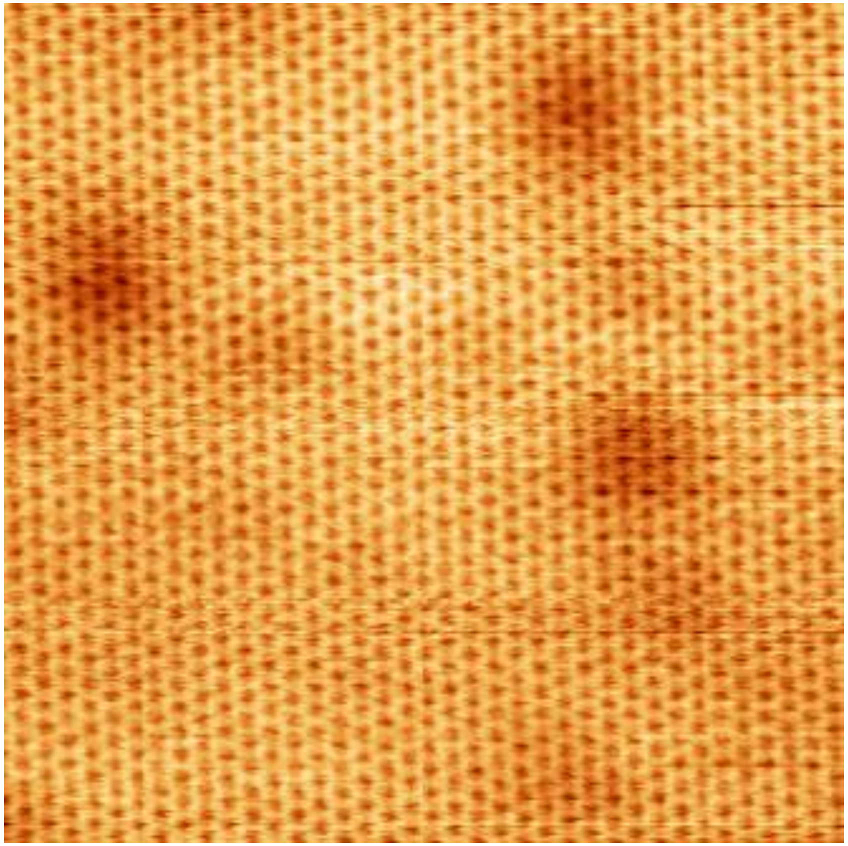
S. Goler *et al.*: Carbon **51**, 249 (2013).

BL vs. QFMLG



S. Goler *et al.*: Carbon **51**, 249 (2013).

QFMLG



- Dangling bonds in SiC
- Contribute to carrier scattering as charged imputities
- Reduce mobility

Y. Murata *et al.*: arXiv 1409.0457

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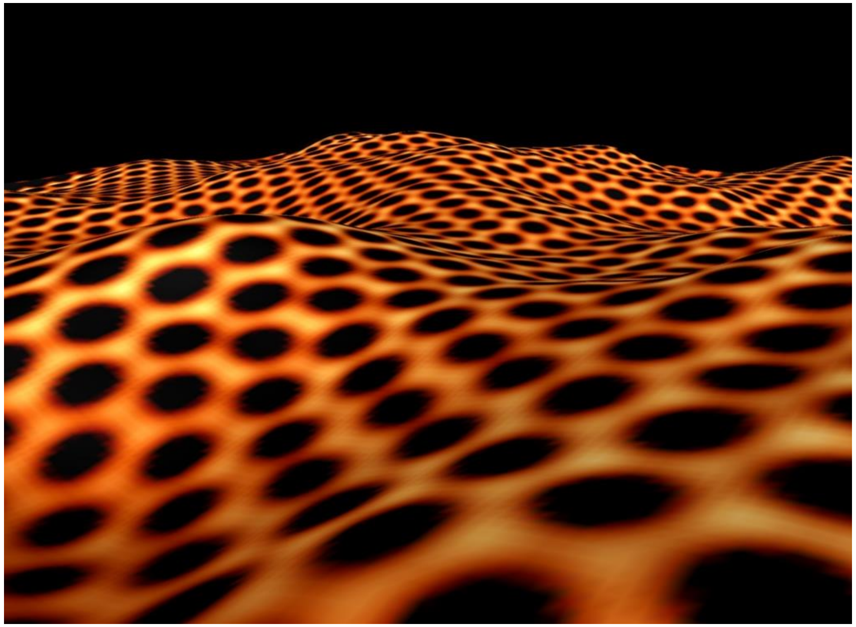
Graphene Curvature

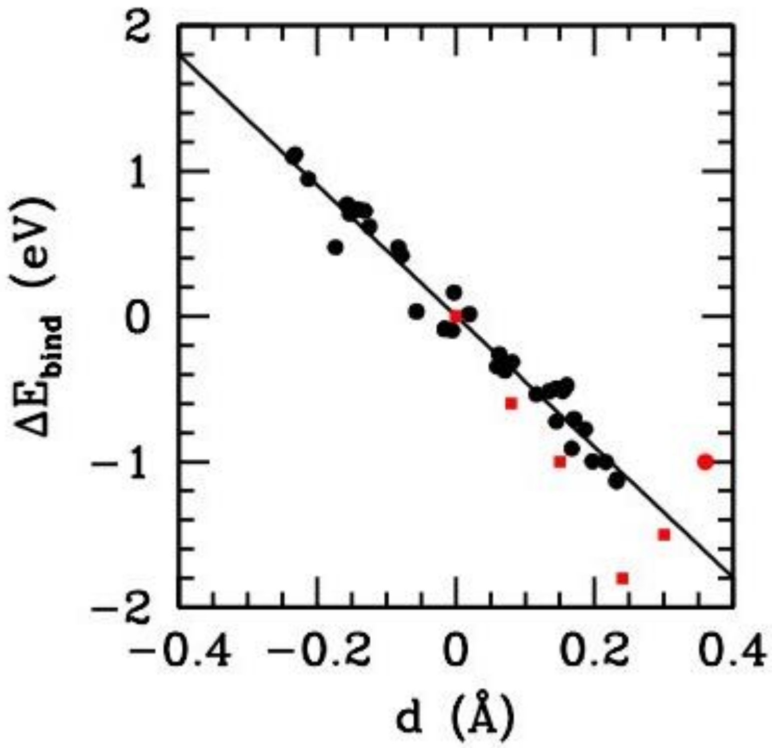
- Exploit graphene curvature for hydrogen storage at room temperature and pressure



V. Tozzini and V. Pellegrini: J. Phys. Chem. C **115**, 25523 (2011).

Graphene Curvature

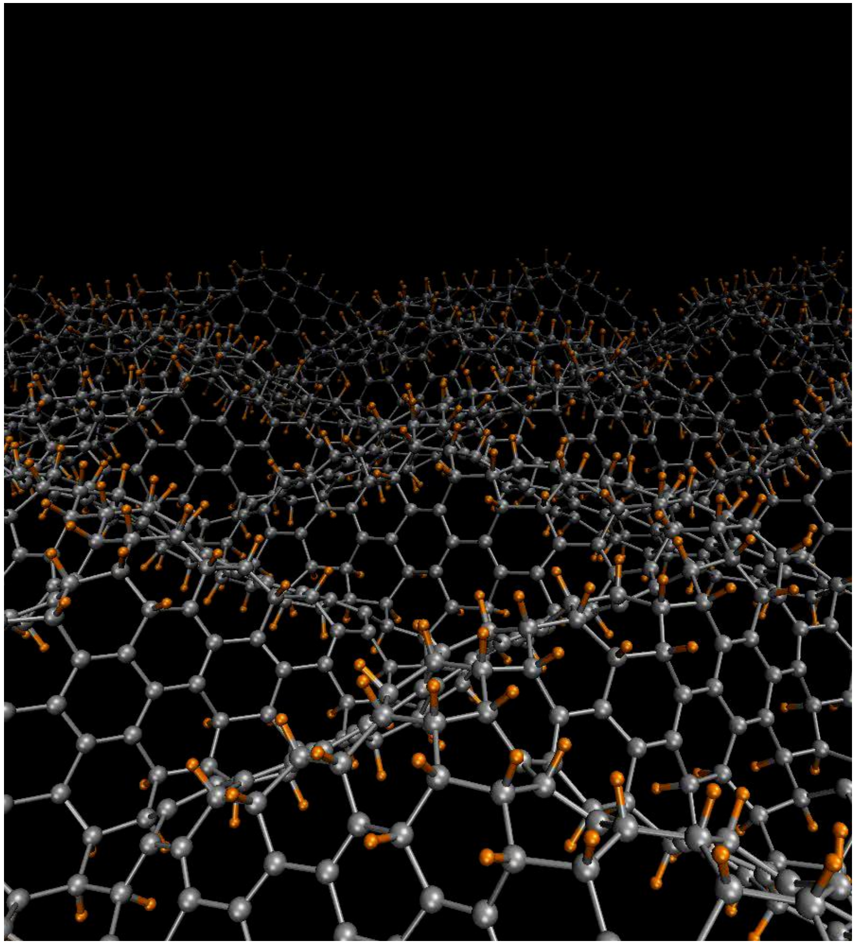
- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts



V. Tozzini and V. Pellegrini: J. Phys. Chem. C **115**, 25523 (2011).

Graphene Curvature

- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts
- Atomic hydrogen spontaneously sticks on convex parts; inverting curvature H is expelled



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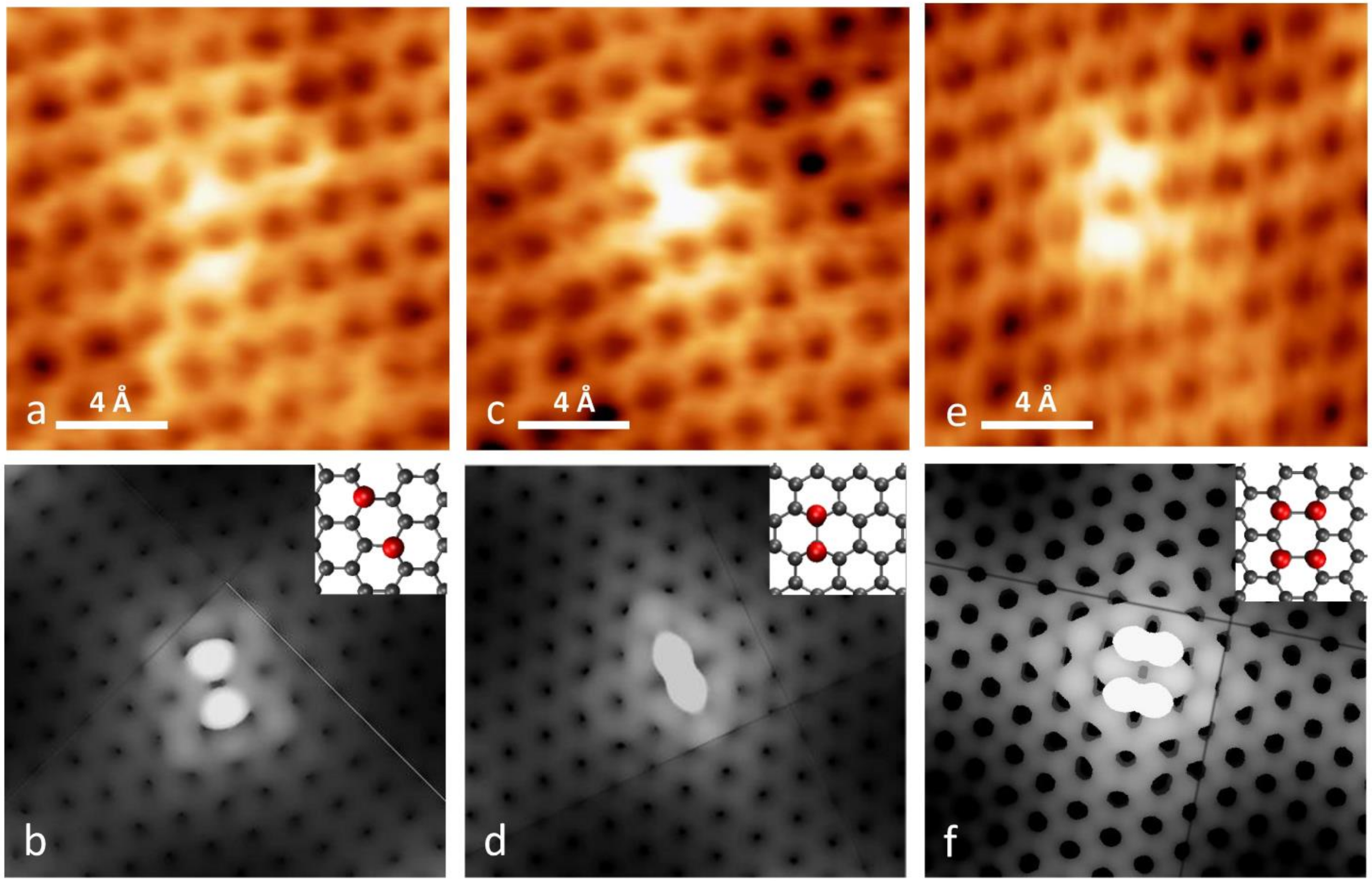
H-dimers and tetramers



Para-dimer   Ortho-dimer   Tetramer

S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

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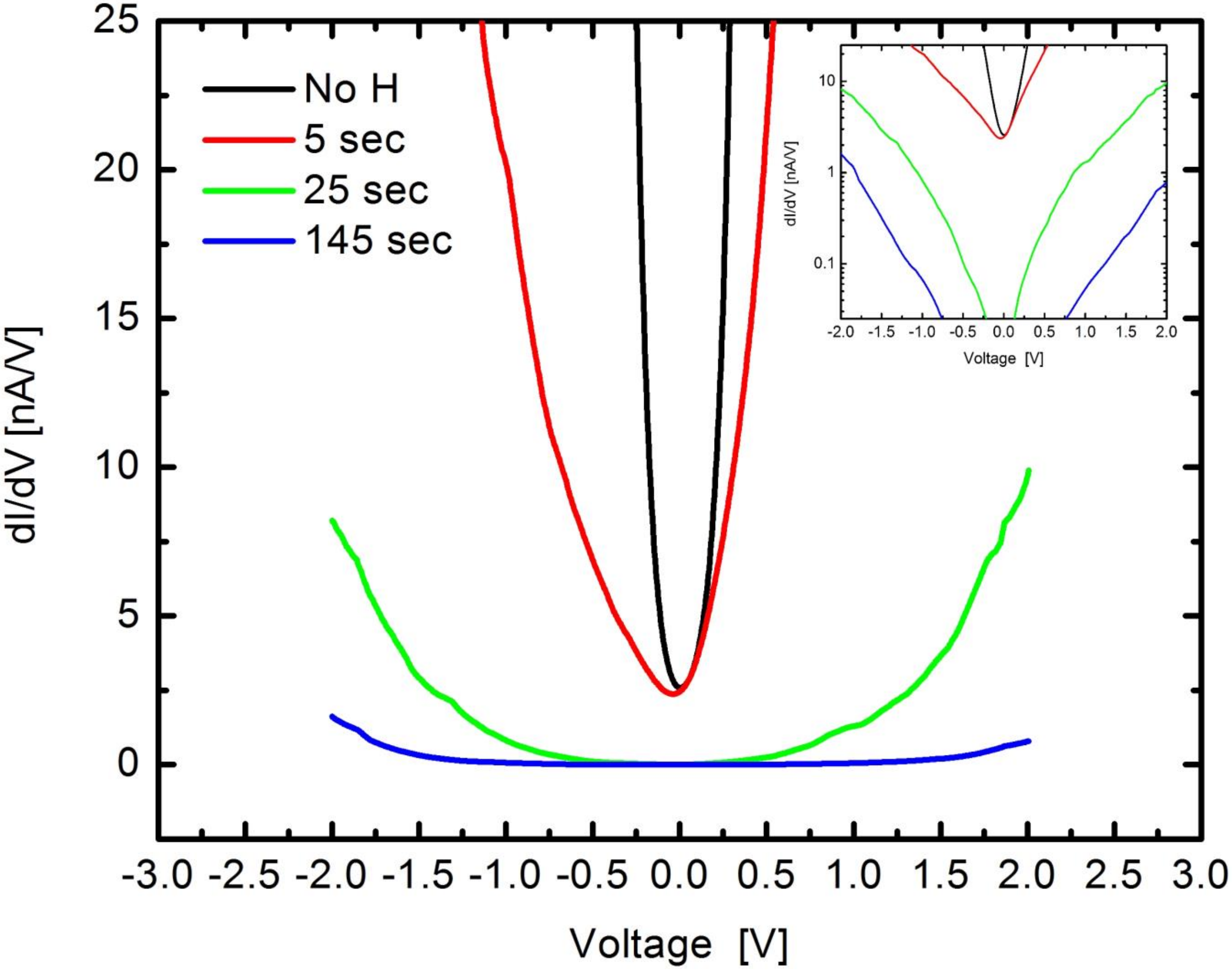
STS after hydrogenation



S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

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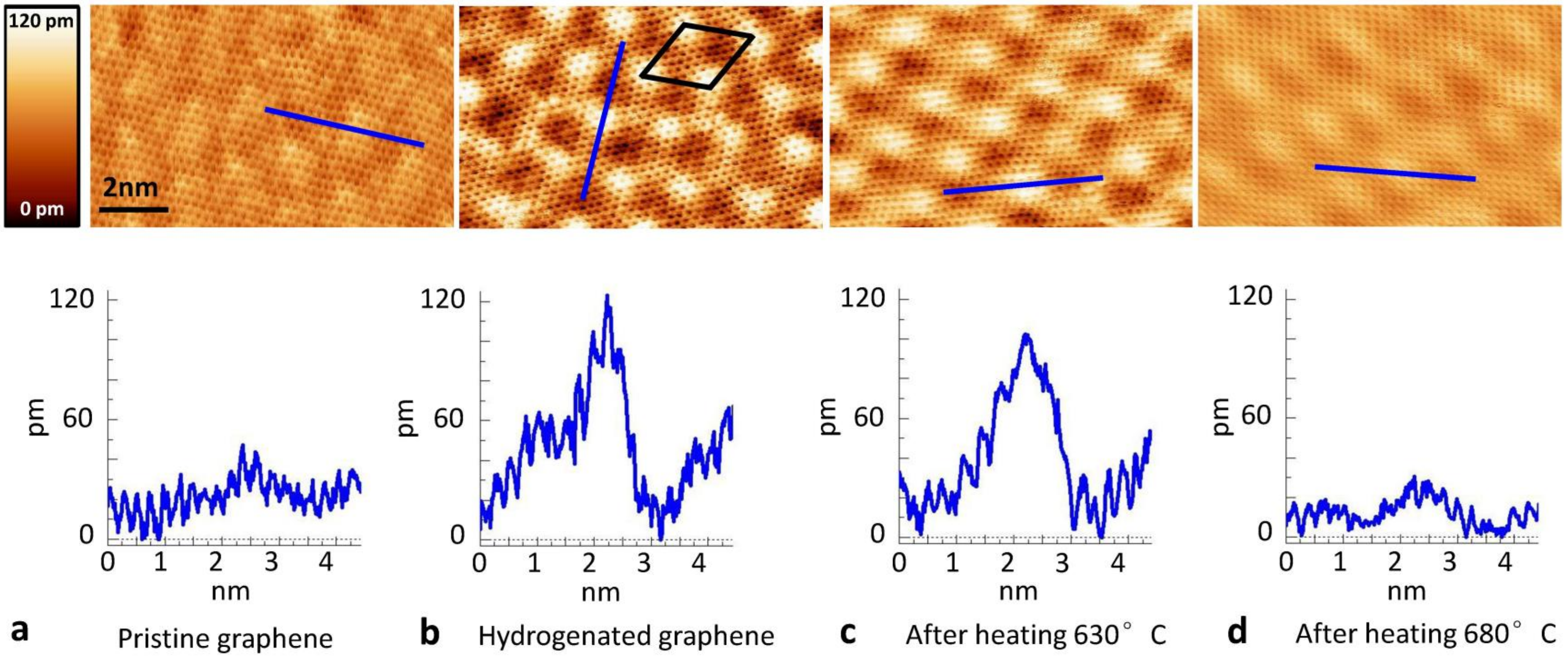
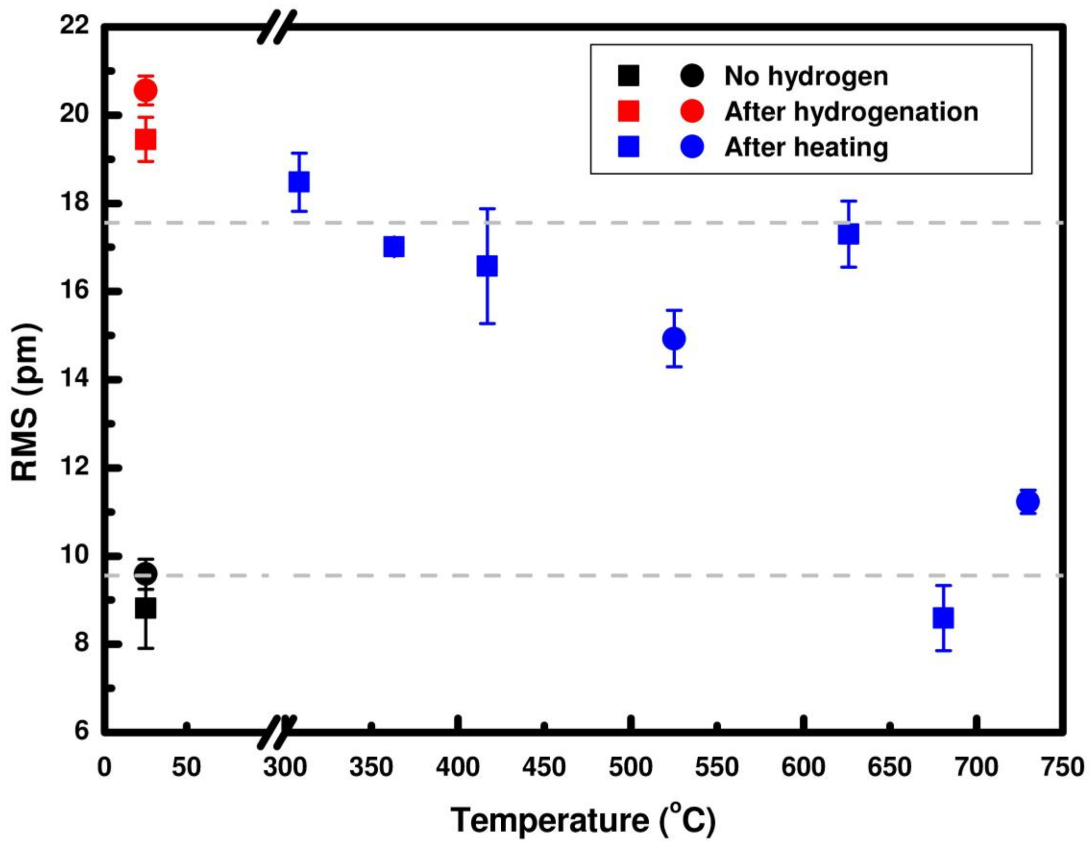
H adsorption and desorption



S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

RMS roughness



S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

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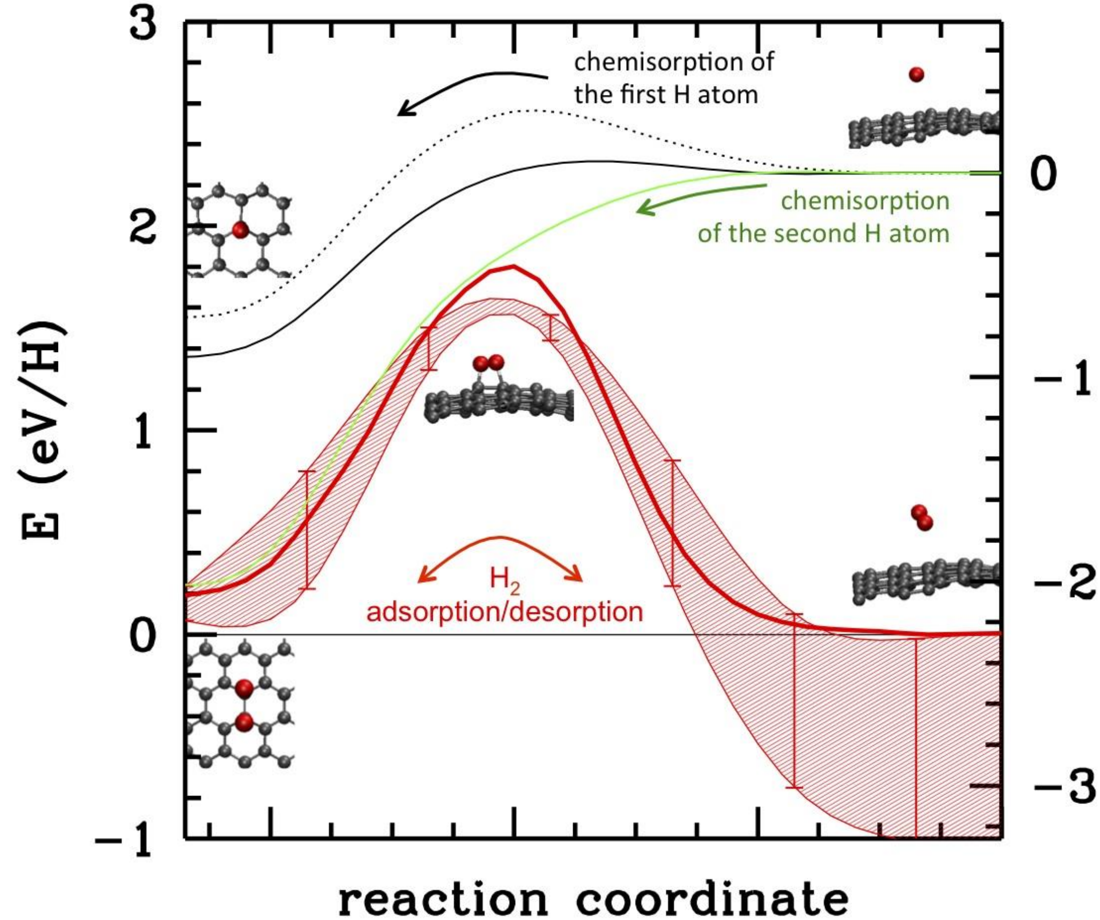
DFT calculations



S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

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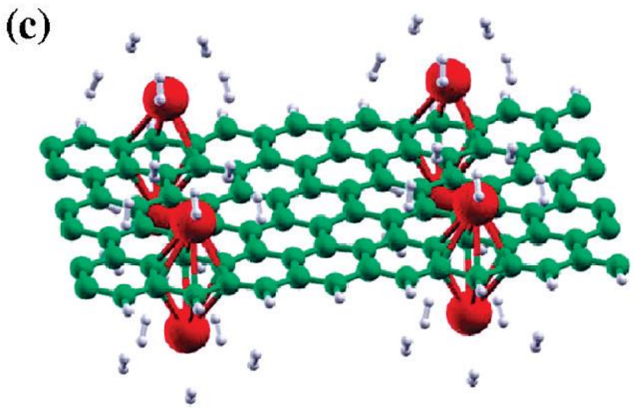
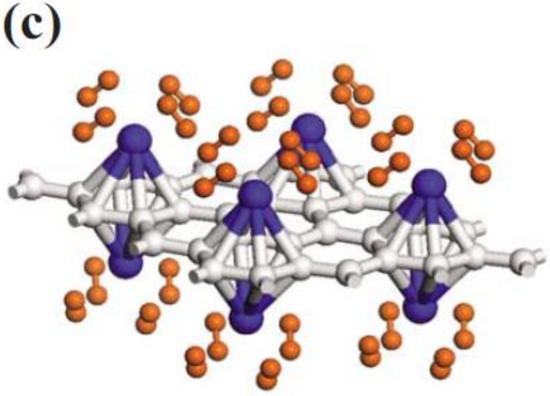
Functionalized Graphene

- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen
- Modify graphene with various chemical species, such as calcium or transition metals (Titanium)

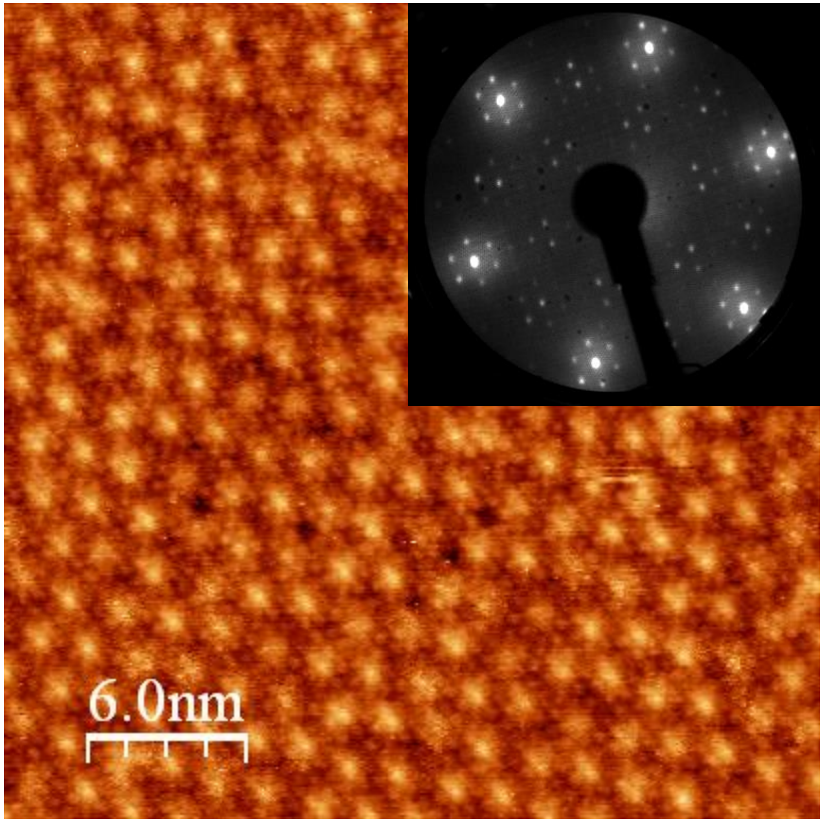


Lee et al., Nano Lett. 10 (2010) 793

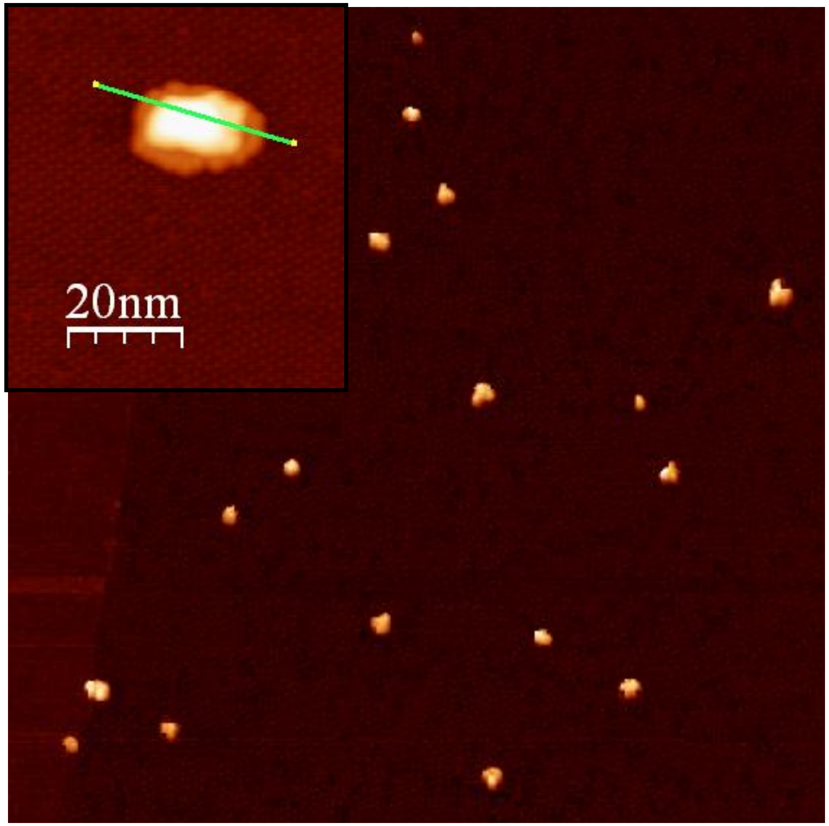


Durgen et al., PRB 77 (2007) 085405

Titanium on graphene



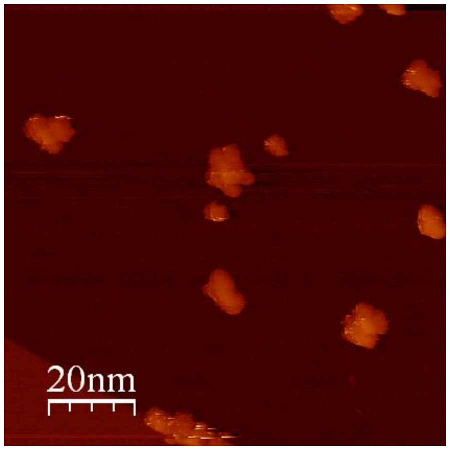
ML graphene on SiC(0001)
with reconstruction



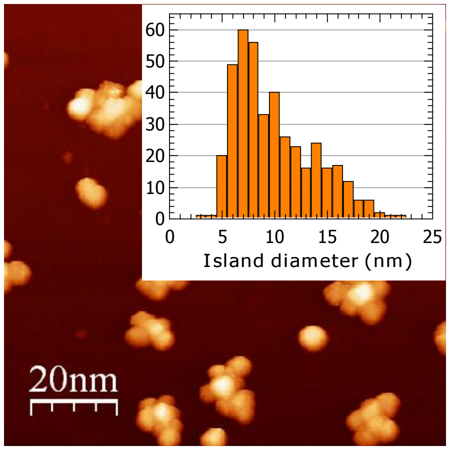
After deposition of Ti at RT

T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

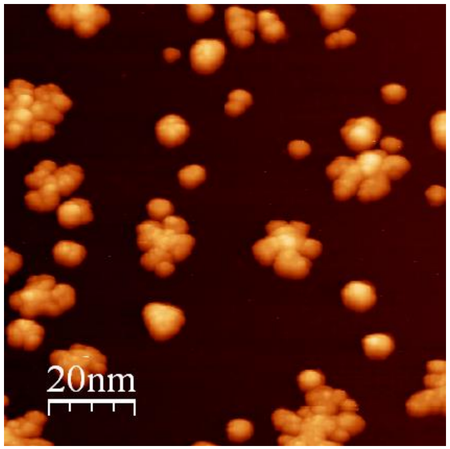
Titanium island growth



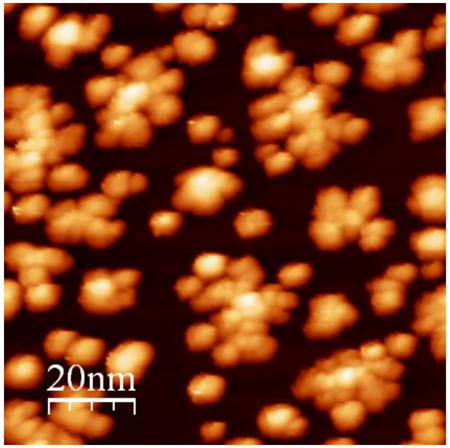
6% Coverage



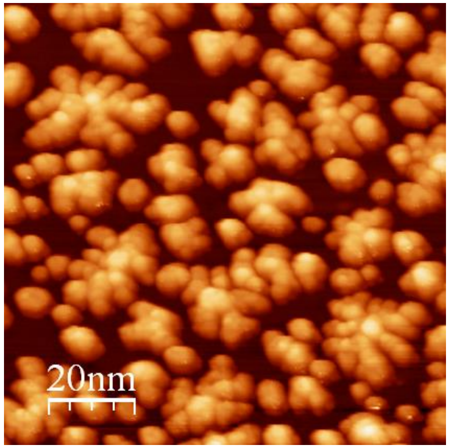
16% Coverage



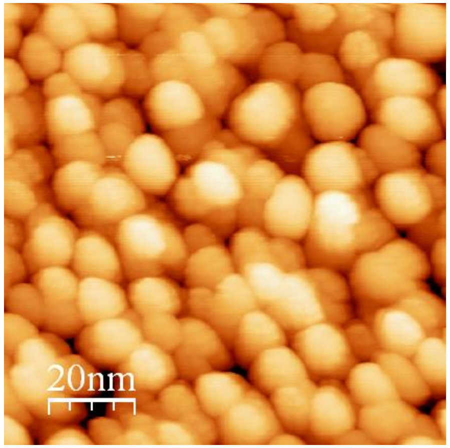
29% Coverage



53% Coverage



79% Coverage



100% Coverage

T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

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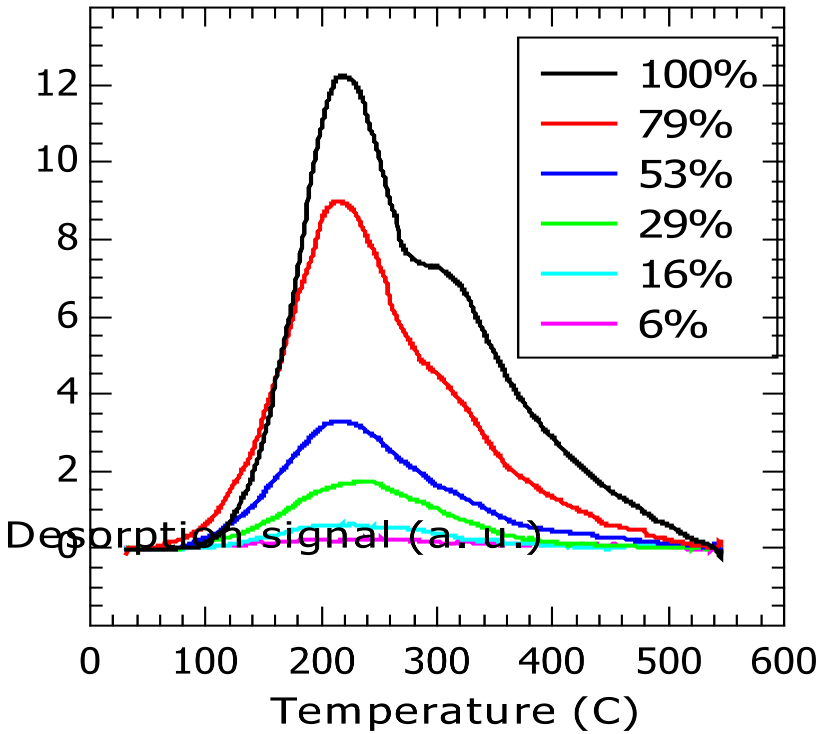
Thermal desorption spectroscopy

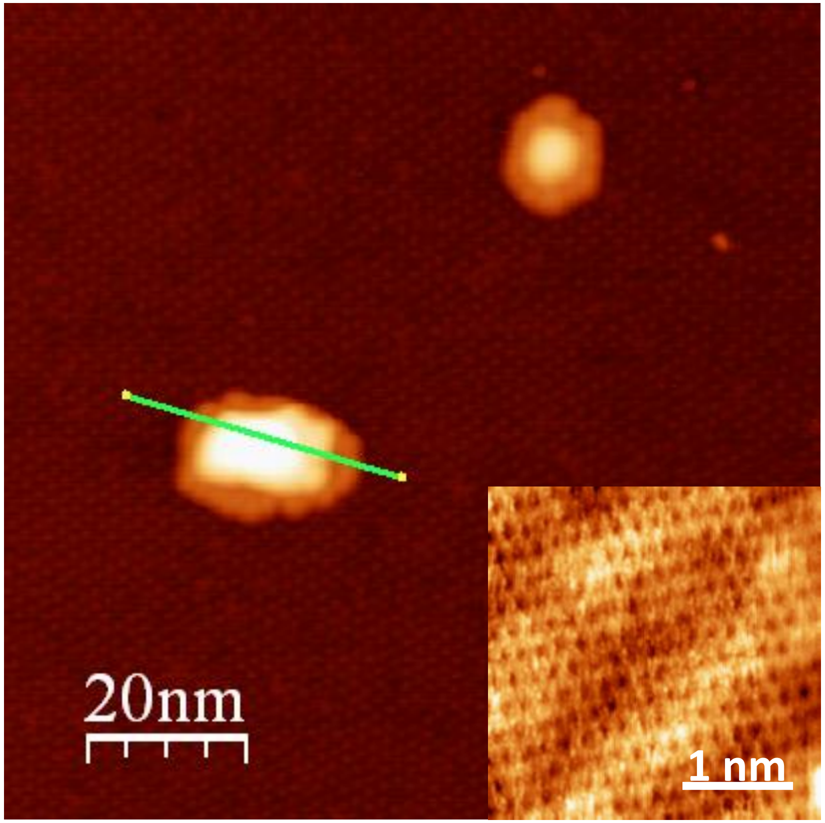
- Deposition of different amounts of Titanium
- Offering Hydrogen (D_2)
- ($1x10^{-7}$ mbar for 5 min)
- Heating sample with constant rate (10K/s) up to 550° C
- Measuring mass-sensitive desorption with a mass spectrometer

Spectra for different Ti-coverages

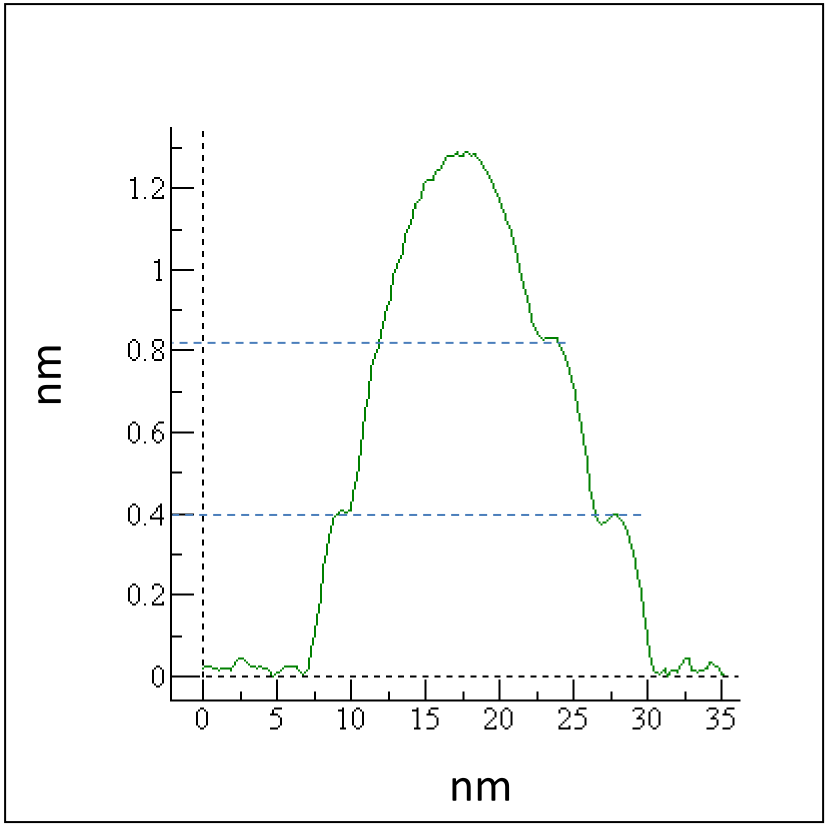


T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

Forming of Islands



100 nm, 1 V, 82 pA



PHYSICAL REVIEW B **87**, 014102 (2013)

Hydrogen adsorption capacity of adatoms on double carbon vacancies of graphene: A trend study from first principles

K. M. Fair,[1,2] X. Y. Cui,[3,4,*] L. Li,[1] C. C. Shieh,[1] R. K. Zheng,[1,3] Z. W. Liu,[3,5] B. Delley,[6] M. J. Ford,[2] S. P. Ringer,[3,4] and C. Stampfl[1,7]

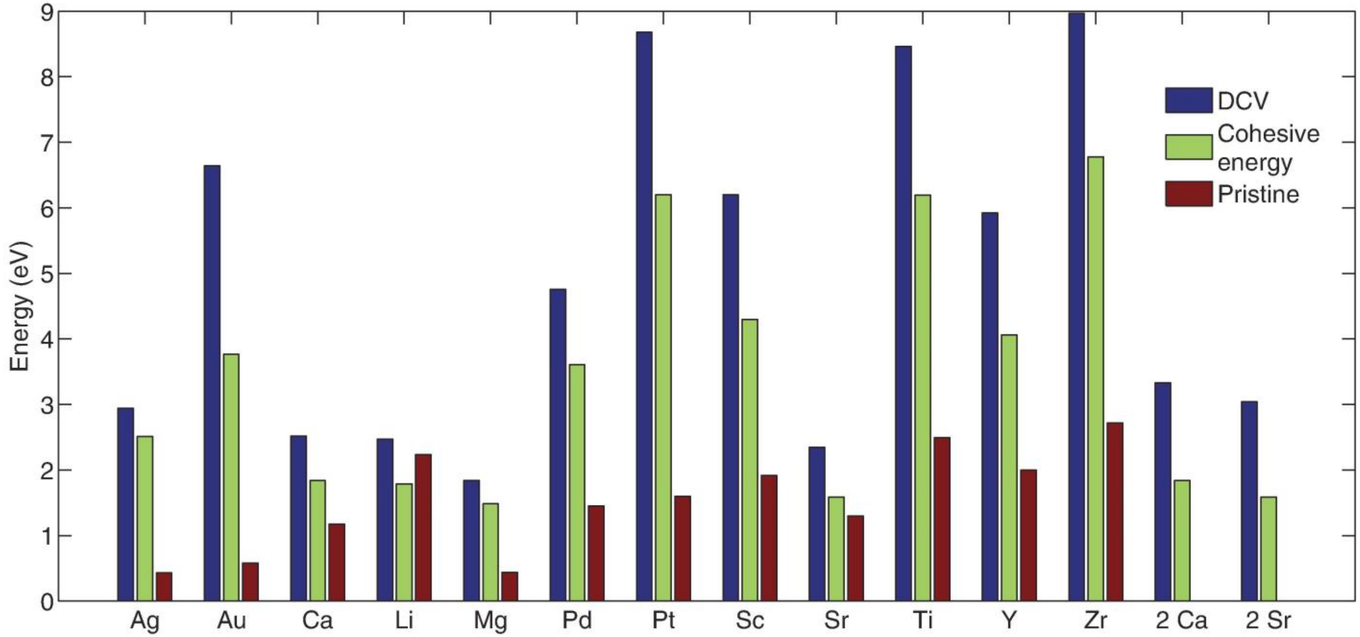
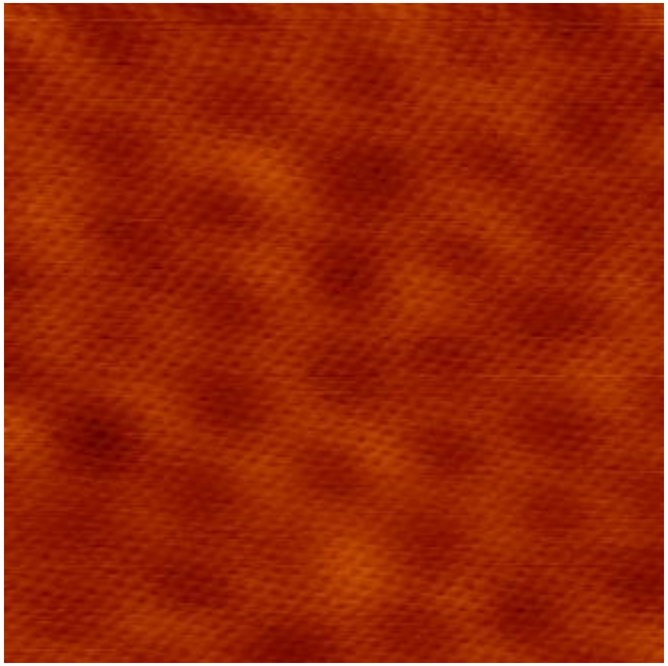


FIG. 1. (Color online) The binding energy of adatoms to graphene DCVs (blue), and pristine graphene (red), as well as the cohesive energy of the respective metal (green). Also included are the binding energies per adatom of two Ca and Sr ("2Ca" and "2Sr") adatoms with one on either side of the DCV.

DCV = Double Carbon Vacancy

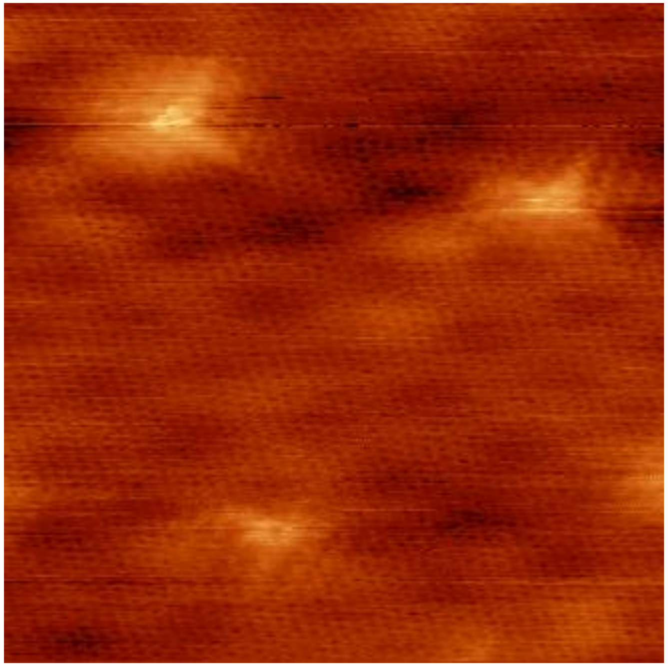
N_2 - sputtering of the graphene surface

Clean graphene surface



$10x10\ nm^2$, 1V, 0.8nA

Sputtered 150s @100eV



$10x10\ nm^2$, 1V, 0.8nA

Defects in the graphene film should reduce the mobility of Ti-atoms and lead to more and smaller islands.

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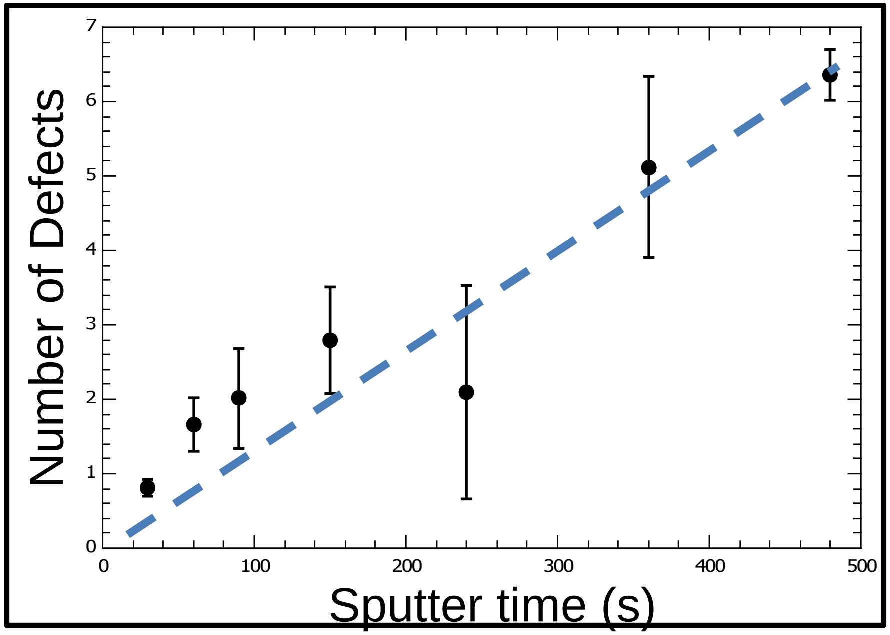
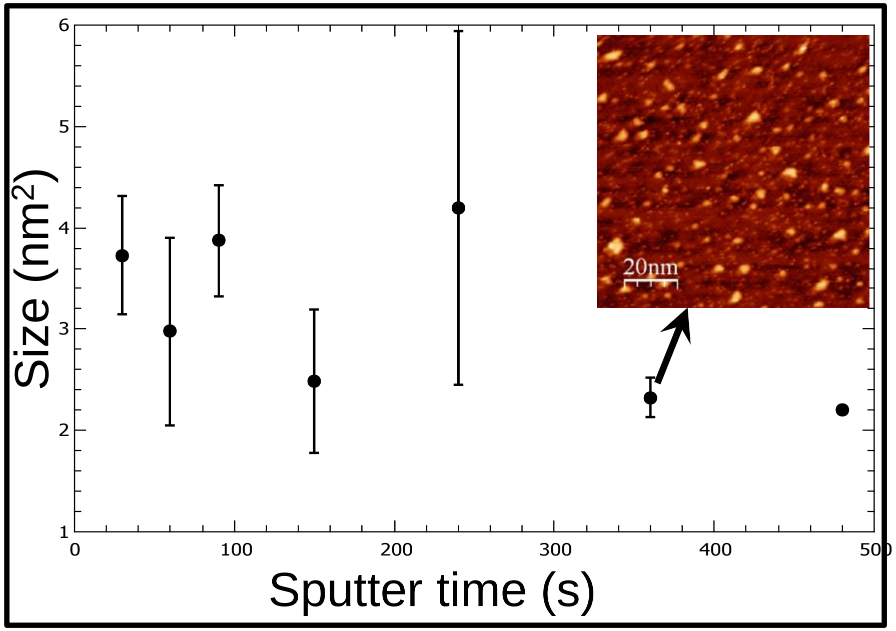
Distribution of defects in graphene

Number of Defects per 100nm^2

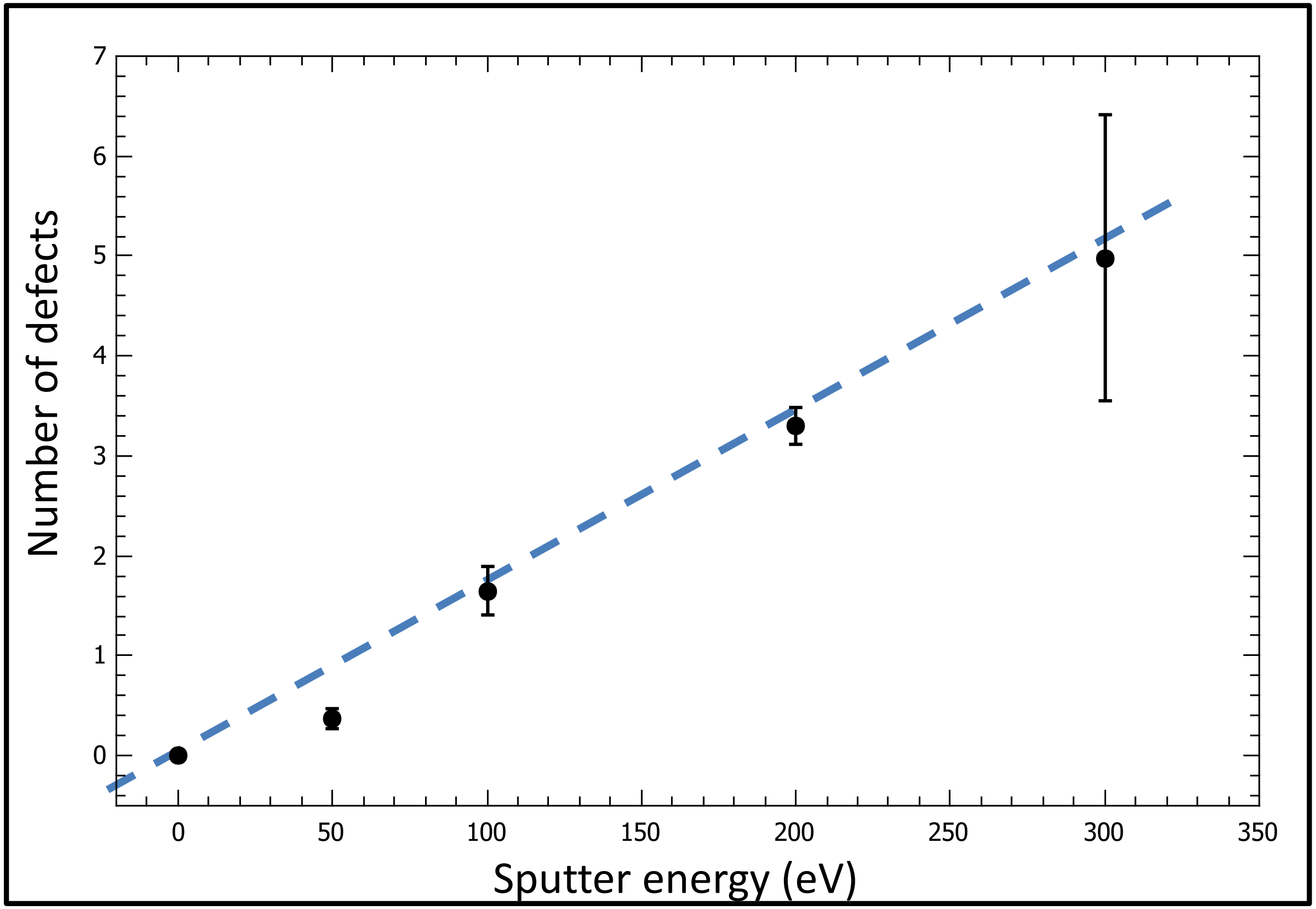


Average size of defects



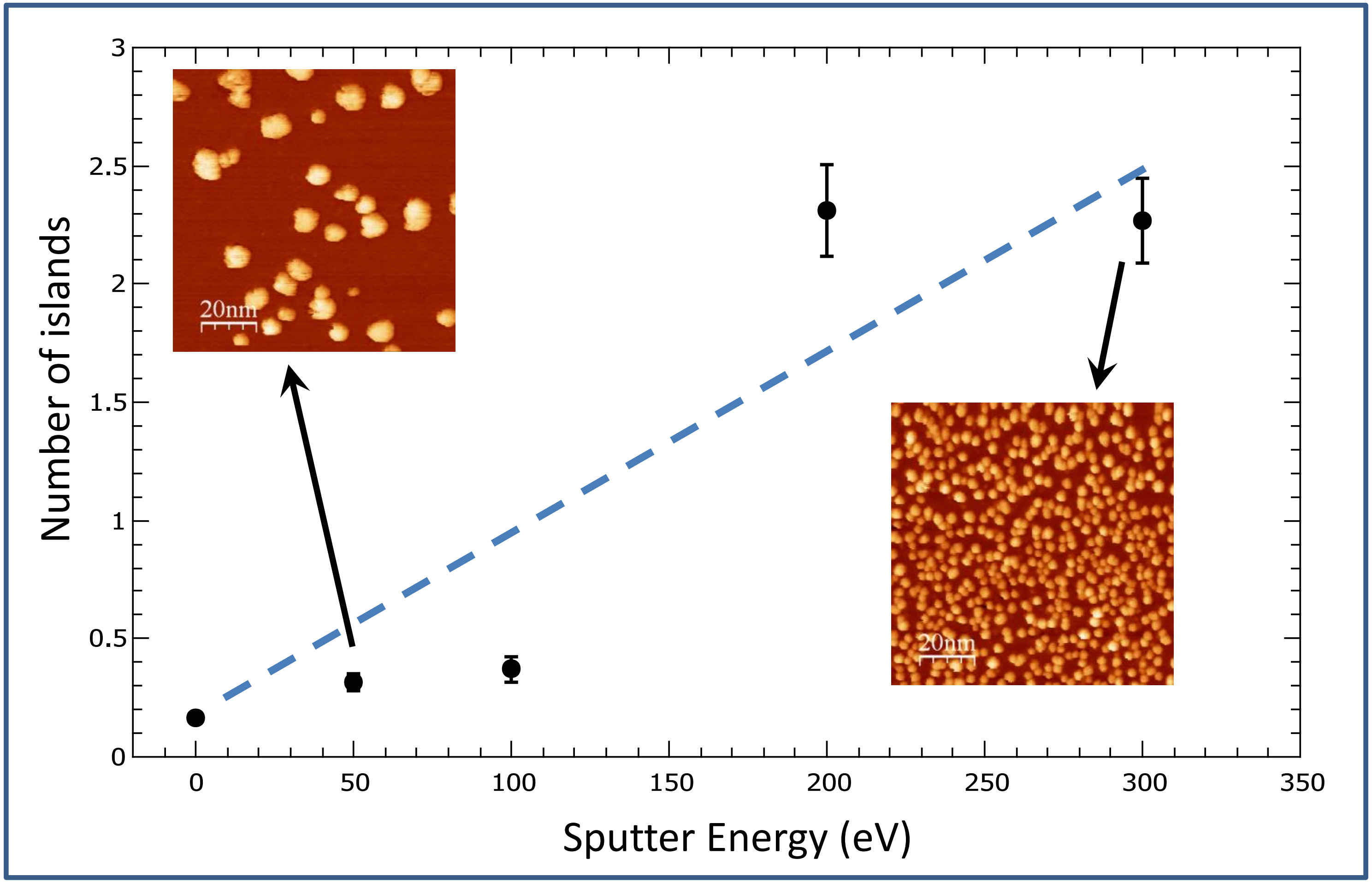
Energy: 200eV, Ion Current: (5.7 +/- 1) nA

Average number of induced defects per 100nm^2



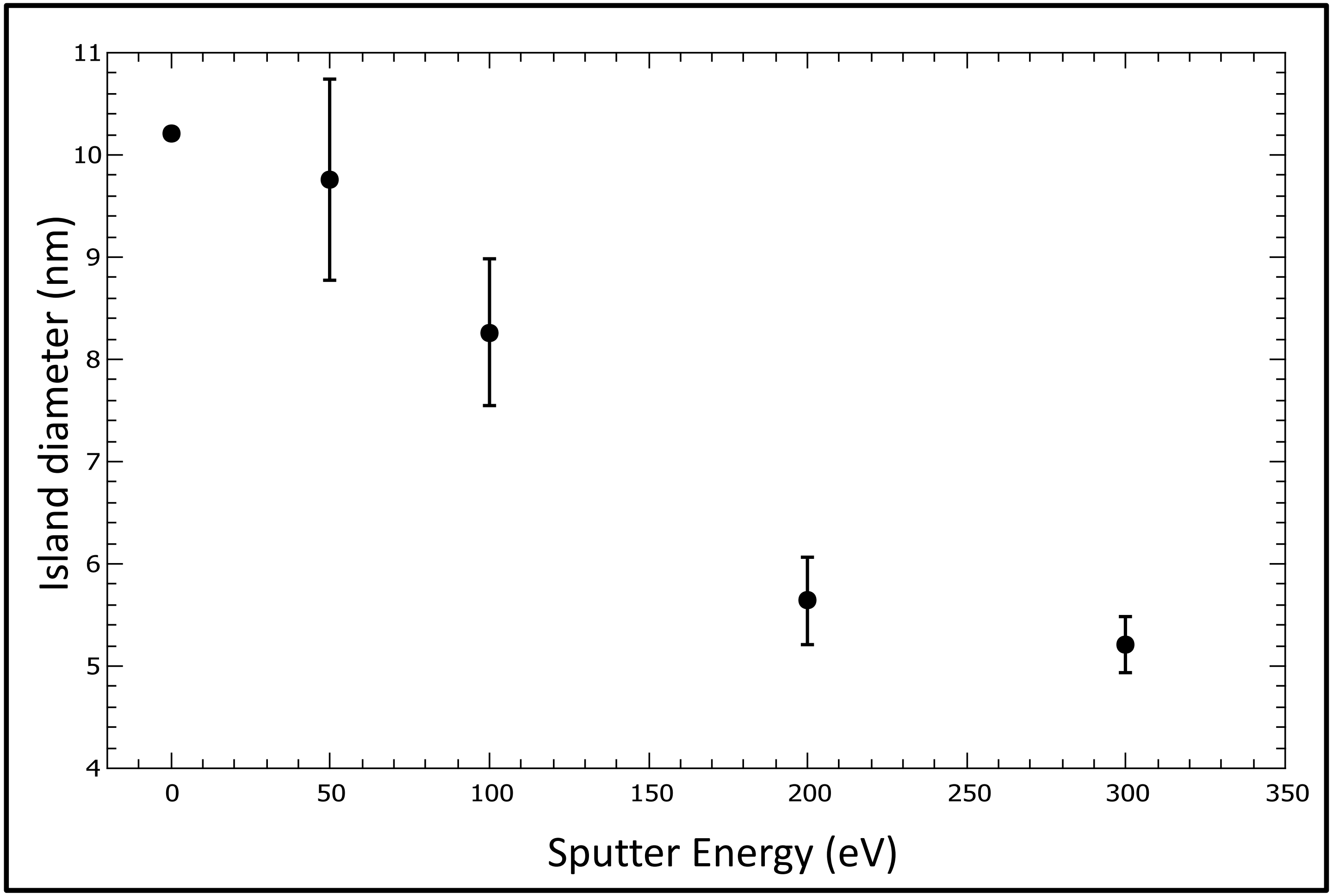
Sputter time: 150s

Average Number of Islands per 100 nm^2



Sputtered 150 s and Deposition of 0.5 ML Titanium

Average diameter of individual Ti-Islands



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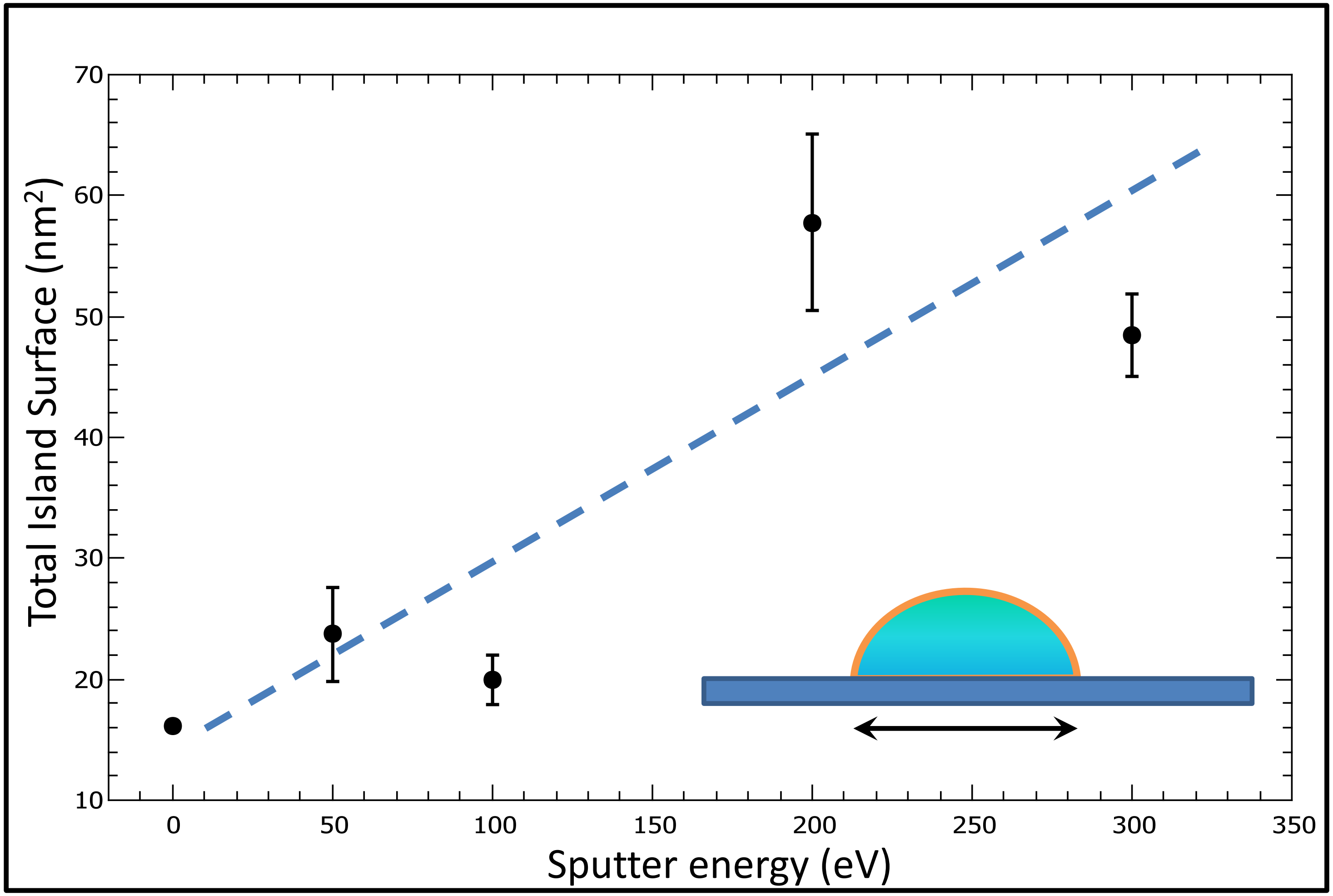
“Active” 3D-surface per 100nm^2



Conclusions

- Graphene is a promising material for hydrogen storage
- Curvature-dependent adsorption and desorption of hydrogen
  - reusable hydrogen storage devices that do not depend on temperature or pressure changes.
- Graphene functionalized by Ti:
  - Stability of hydrogen binding at room temperature
  - Hydrogen desorbes at moderate temperatures
  - Modifying the size and distribution of Islands by sputtering and increasing the active surface

Coauthors


S. Goler


T. Mashoff


Y. Murata


D. Convertino


V. Miseikis


C. Coletti

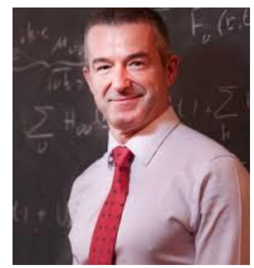

V. Piazza


V. Tozzini


P. Pingue


F. Colangelo


V. Pellegrini


F. Beltram

K. V. Emtsev, U. Starke,
S. Forti


M. Takamura


S. Tanabe


H. Hibino

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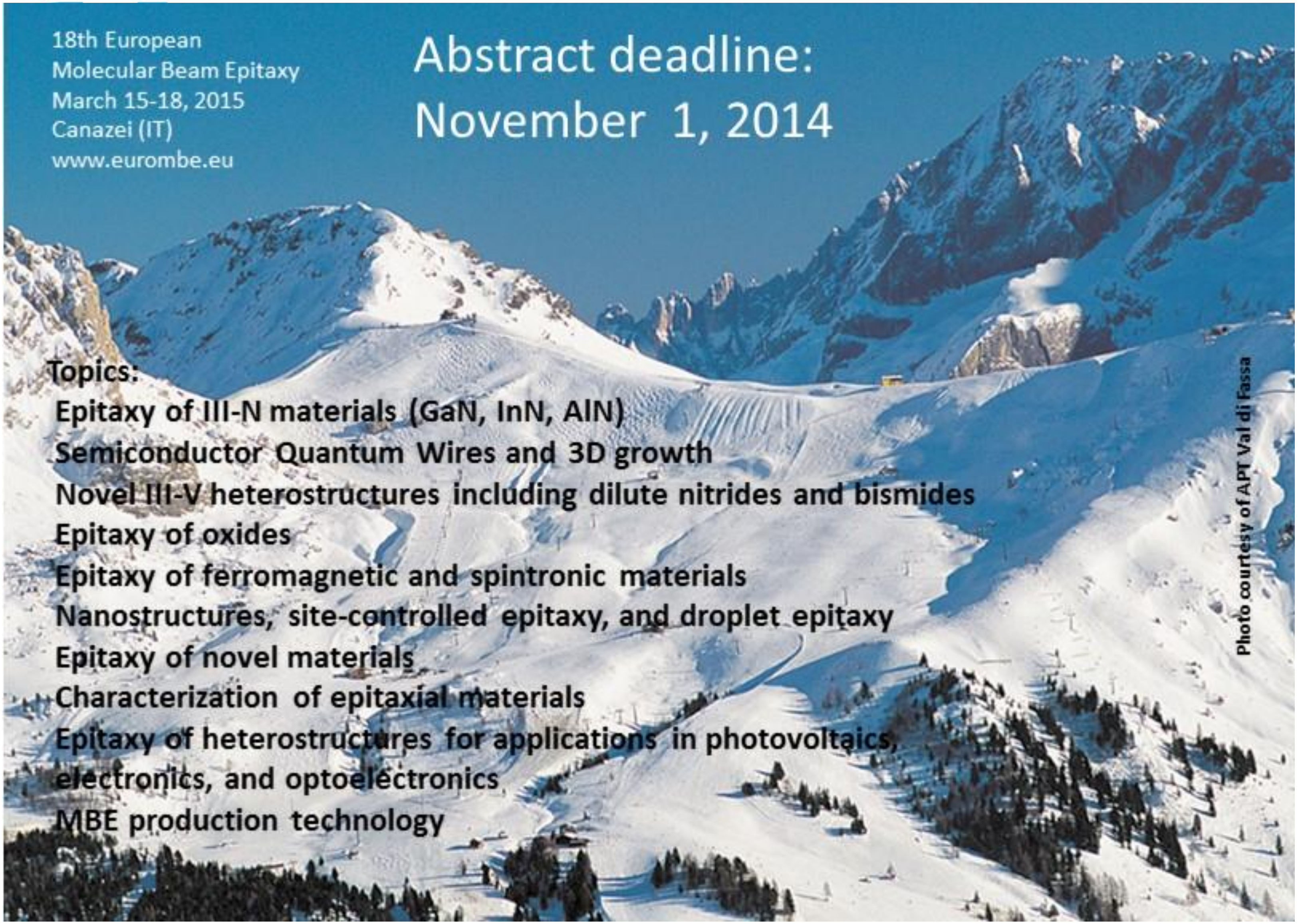
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Semiconductor Quantum Wires and 3D growth
Novel III-V heterostructures including dilute nitrides and bismides
Epitaxy of oxides
Epitaxy of ferromagnetic and spintronic materials
Nanostructures, site-controlled epitaxy, and droplet epitaxy
Epitaxy of novel materials
Characterization of epitaxial materials
Epitaxy of heterostructures for applications in photovoltaics, electronics, and optoelectronics
MBE production technology
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