Prospects for Hydrogen Storage in Graphene

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National Enterprise for nanoScience and nanoTechnology

NEST

Outline

- The NEST lab in Pisa
- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Corrugation (Chemisorption)
- Hydrogen Storage by Functionalization (Physisorption)

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NEST Pisa

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NEST Pisa

National **E**nterprise for nano**S**cience and nano**T**echnology

NEST is an interdisciplinary research and training centre where physicists, chemists and biologists investigate scientific issues at the nanoscale.

Research themes @ NEST Pisa

NanoPhysics

1. Quantum transport and phase coherent effects in superconductors

2. Physics of low-dimensional semiconductor systems

3. Graphene (**Flagship**)

Advanced Photonics

4. Intersubband polaritonics

5. Silicon-Germanium optoelectronics

6. THz photonics

7. OptoElectronics Materials: from nanoscale to bulk single crystals

NanoBioScience

8. Visualizing brain function and structure in the living mouse

9. Lab-on-a-chip technologies

10. Nanoscale and single-molecule spectroscopy and imaging of soft matter

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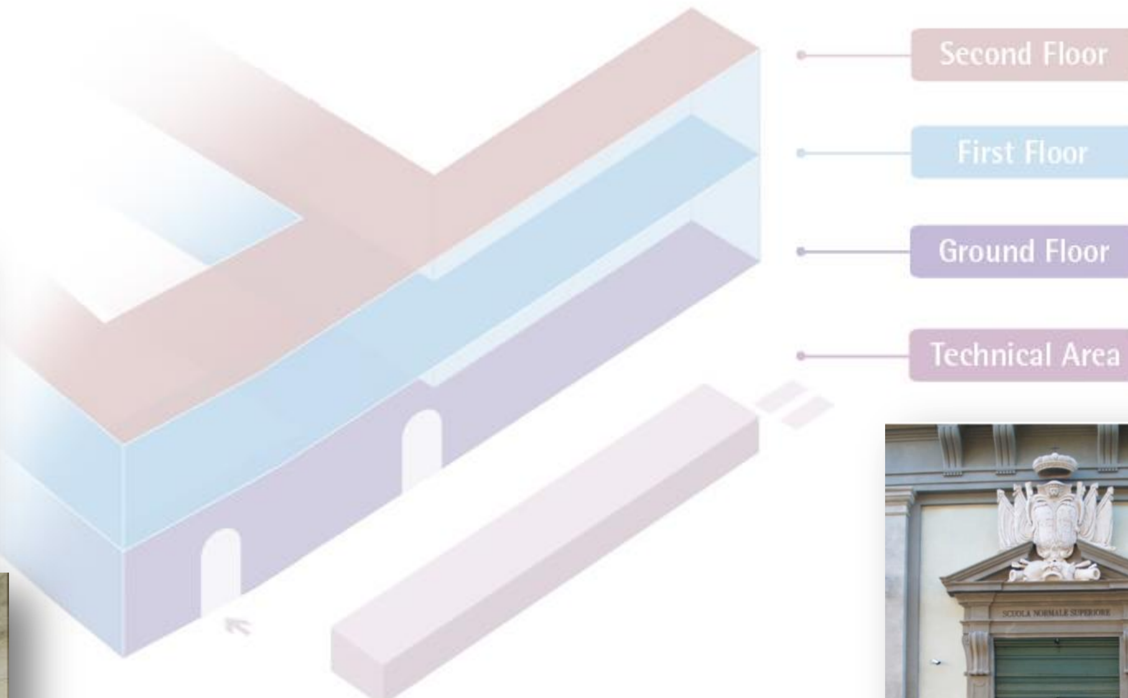
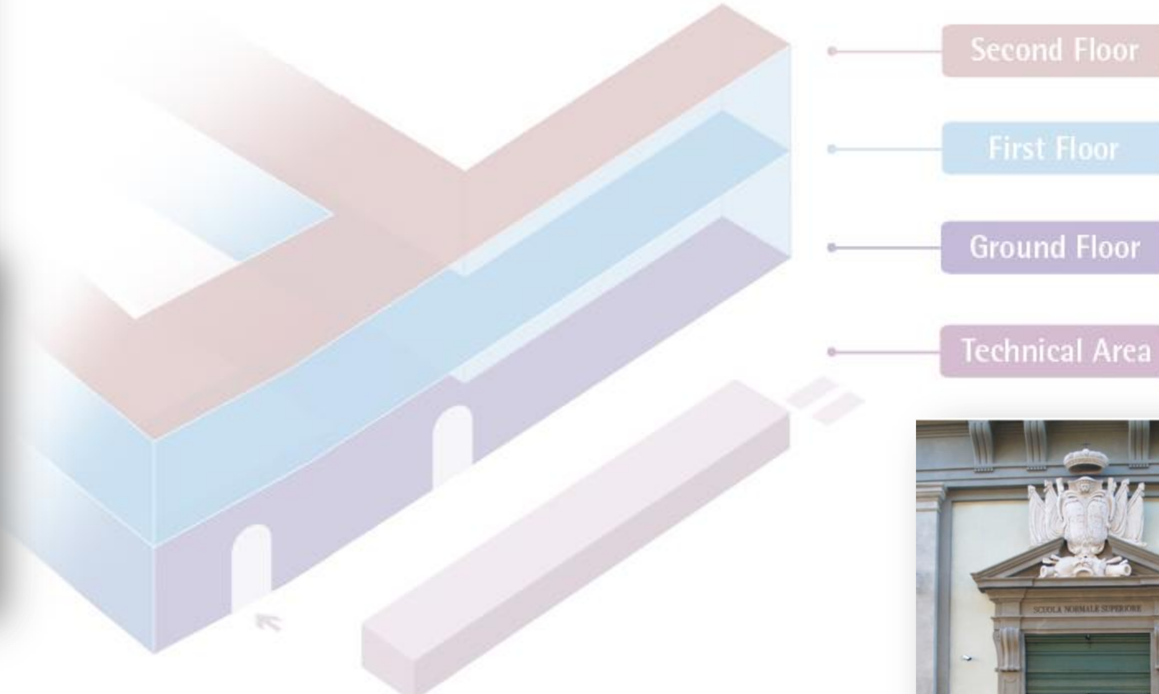

Second Floor
First Floor
Ground Floor
Technical Area

NEST Pisa



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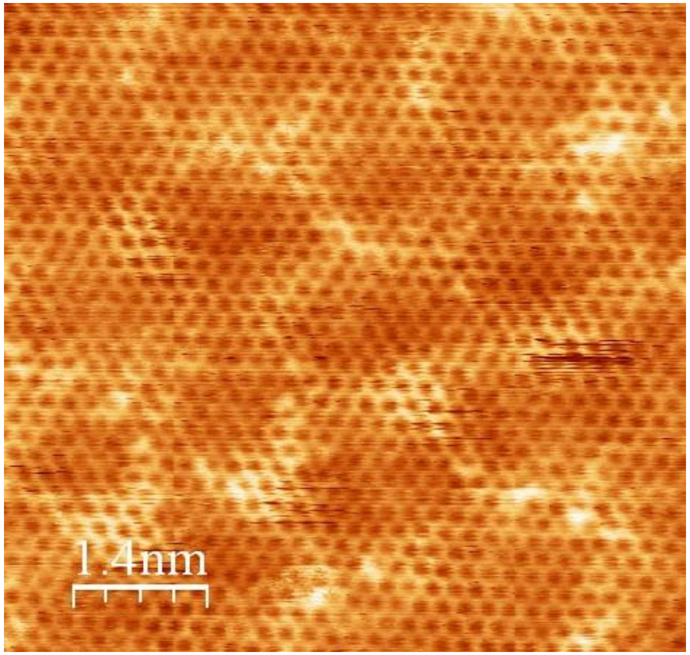
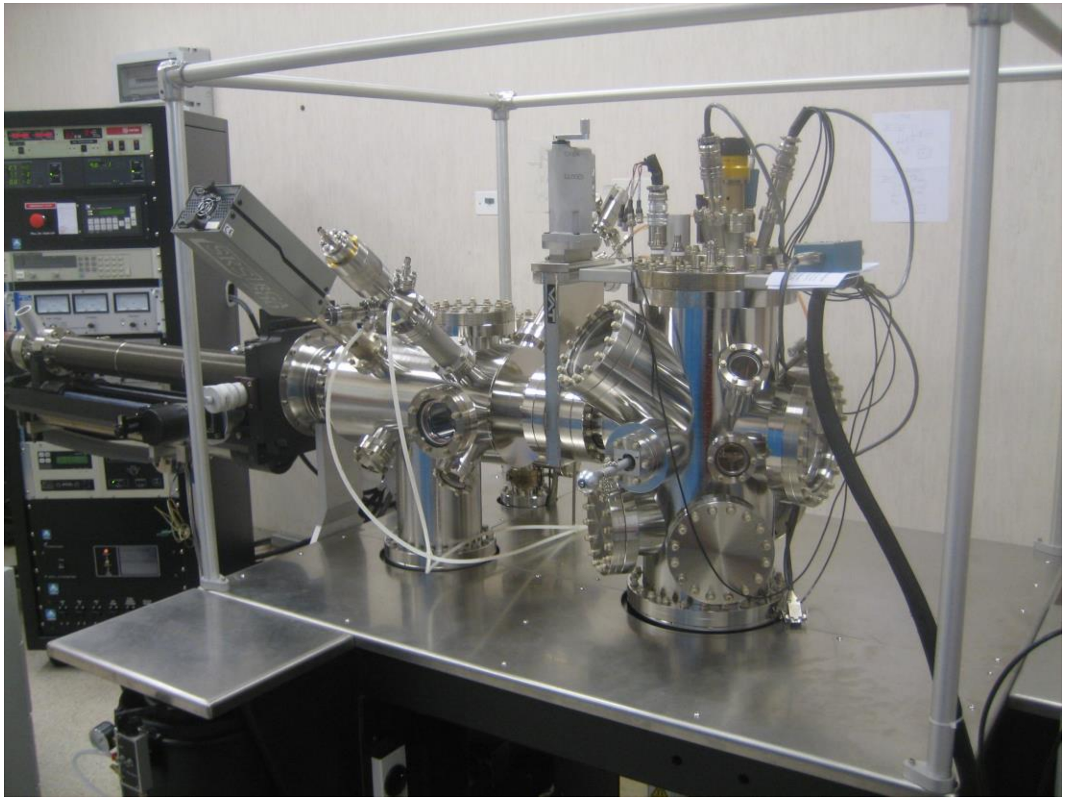
NEST facilities

- UHV STM
  - 1 VT and 1 LT





S. Goler et al., arXiv:1111.4918v1

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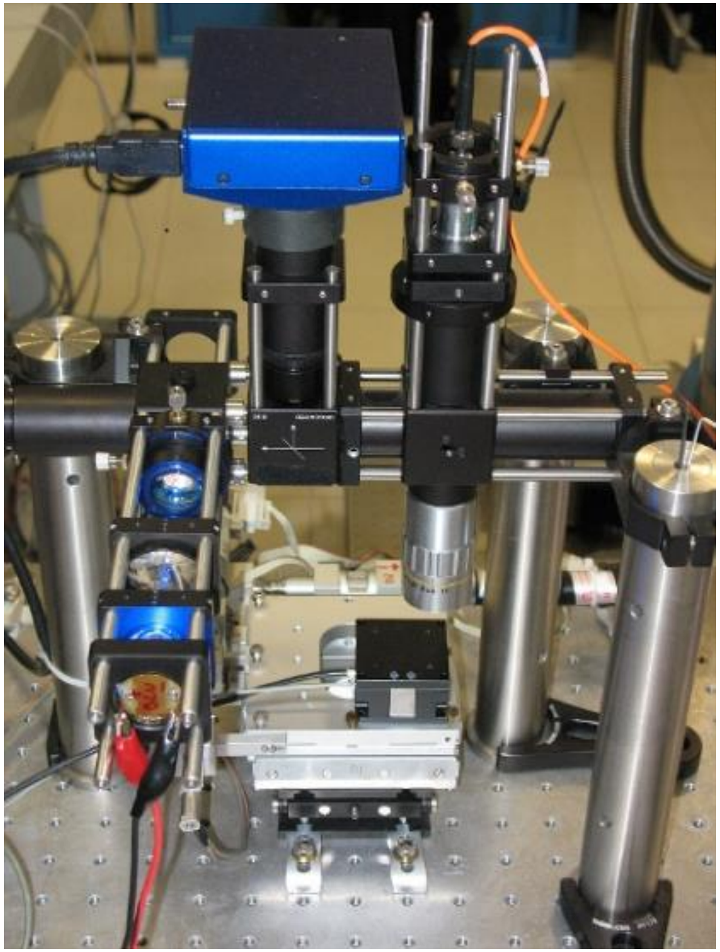
NEST facilities

- UHV STM
- Graphene Growth

NEST facilities

- UHV STM
- Graphene Growth
- Micro-Raman



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NEST facilities

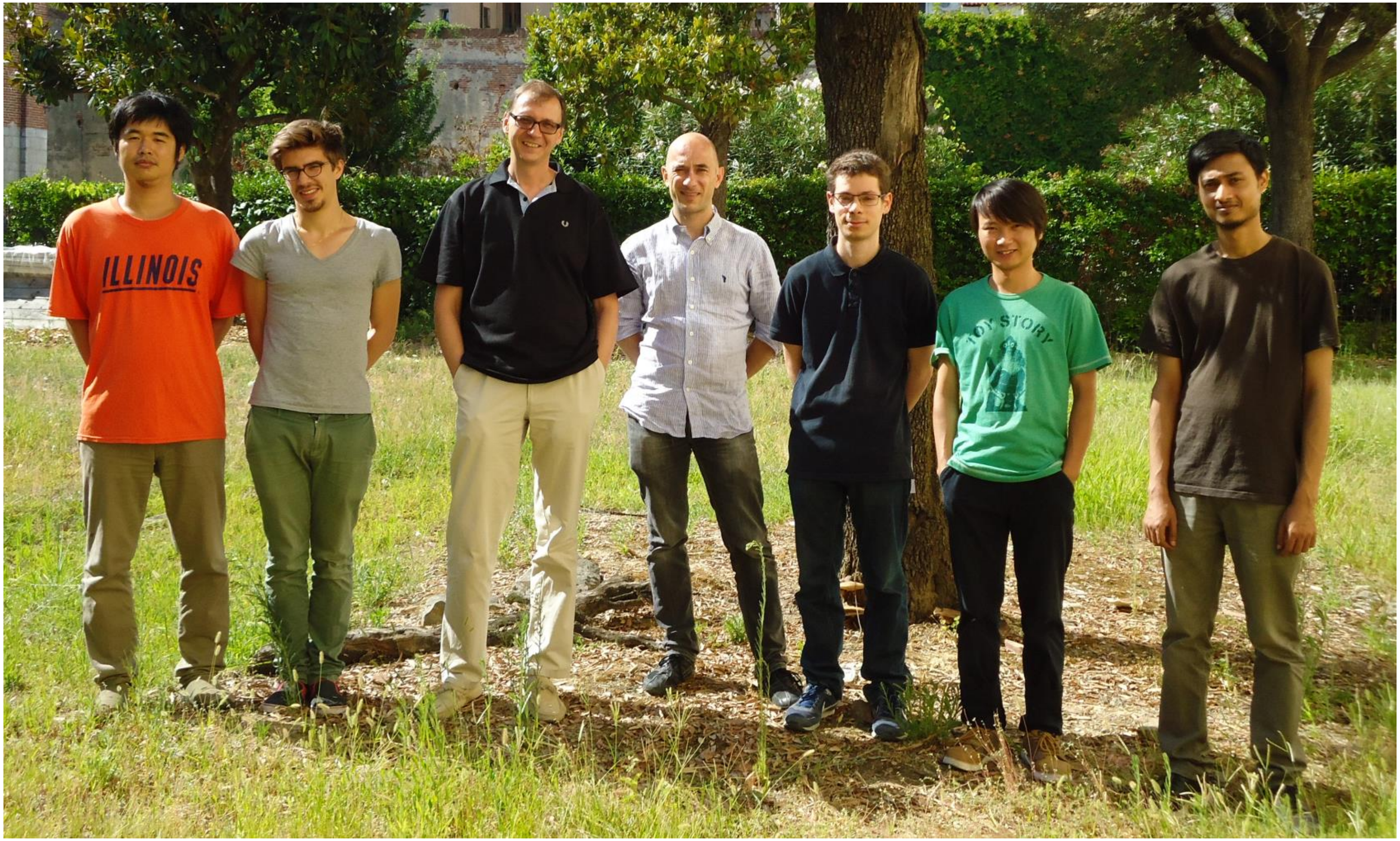
- UHV STM
- Graphene Growth
- Micro-Raman
- AFM

NEST facilities

- UHV STM
- Graphene Growth
- Micro-Raman
- AFM
- SEM

NEST facilities

- UHV STM
- Graphene Growth
- Micro-Raman
- AFM
- SEM
- Theory



Yuya Murata Stefan Heun Stefano Guiducci Abhishek Kumar

Luca Planat Stefano Roddaro Shaohua Xiang

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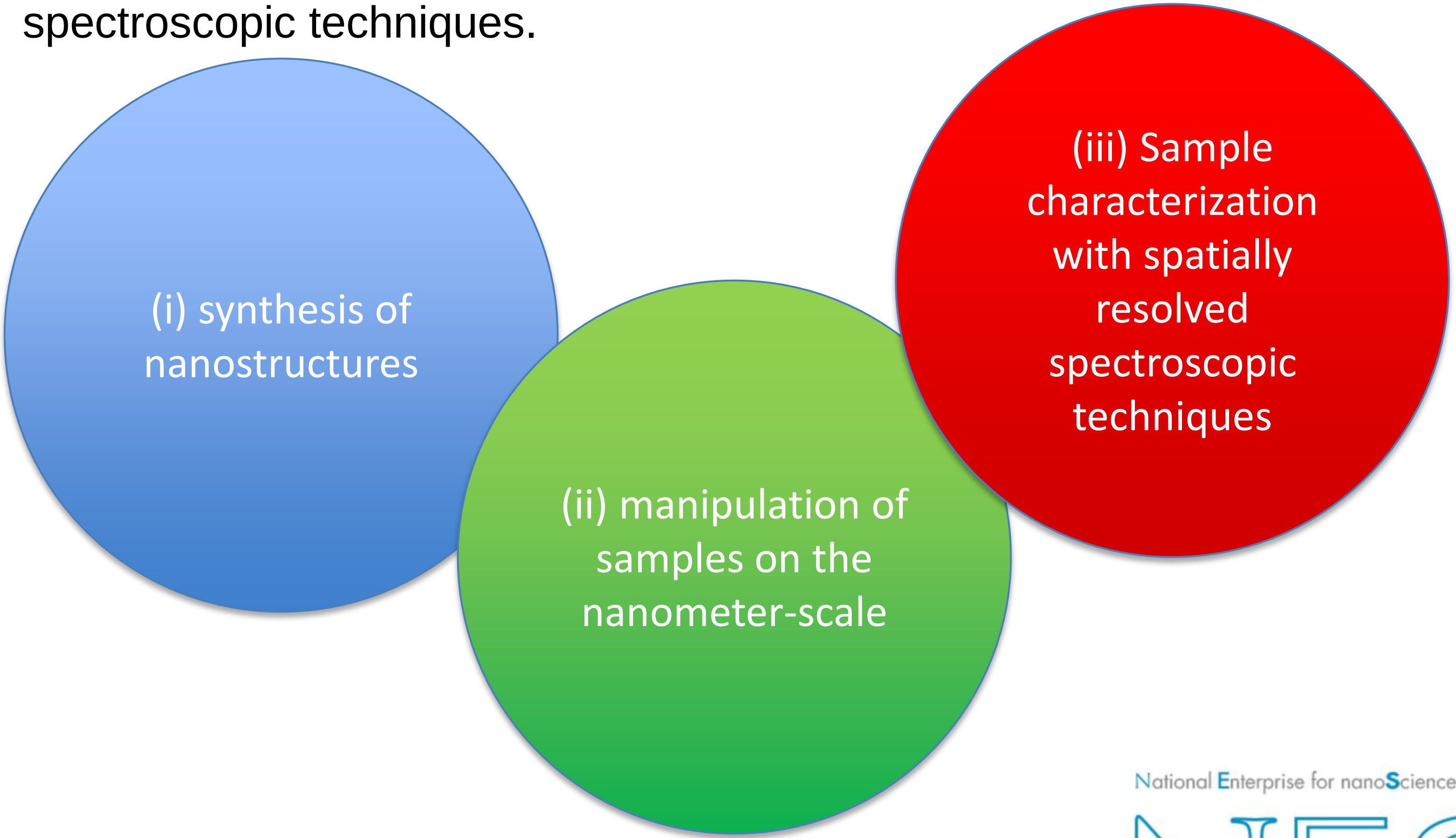
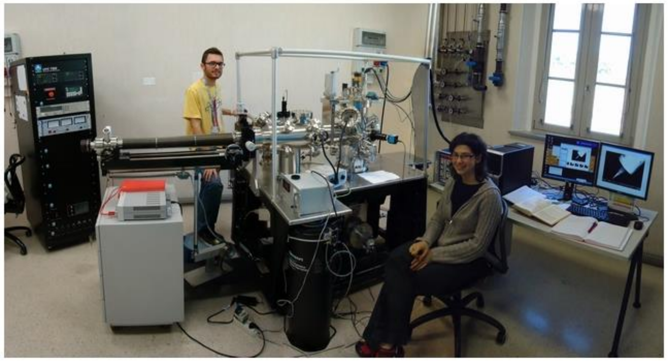
Research Activities

The physics of low-dimensional systems. This includes three aspects: (i) the synthesis of nanostructures, (ii) the manipulation of samples on the nanometer-scale, and (iii) their characterization with spatially resolved spectroscopic techniques.



Surface Science & Magneto-Transport



UHV-VT-STM

UHV-LT-STM

Scanning Gate Microscopy
300 mK, 9 T

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Projects

GRAPHENE FLAGSHIP

Graphene for Hydrogen Storage

erc

Phosphorene

Ministero degli Affari Esteri
e della Cooperazione Internazionale

G. Gervais, Mc Gill University,
Montreal, Canada
2D Materials

Consiglio Nazionale delle Ricerche

JAPAN SOCIETY FOR THE PROMOTION OF SCIENCE
日本学術振興会

S. Suzuki, NTT
High-mobility Graphene

Recent Activities

- SGM on QPCs in III-V 2DEGS
- Magneto-transport in Graphene
- Hydrogenated Graphene
- Hydrogen Storage in Graphene
- Phosphorene

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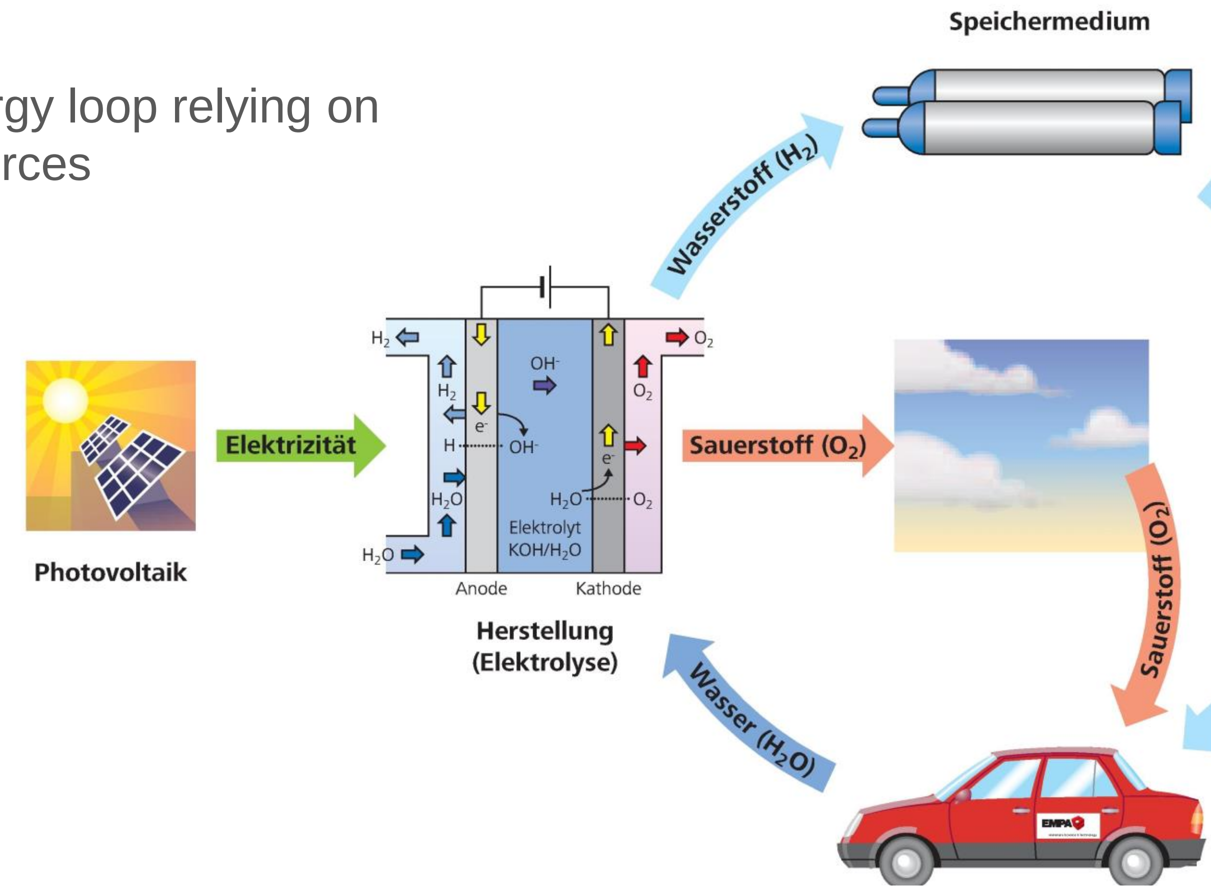
Hydrogen Life Cycle

Complete energy loop relying on renewable sources



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

Hydrogen-fuelled vehicles

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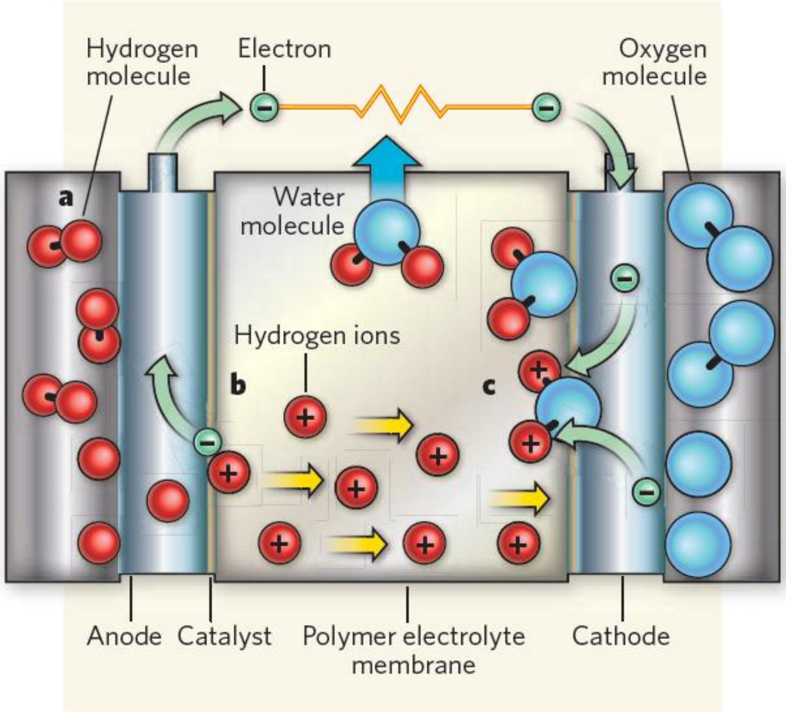
Hydrogen-fuelled vehicles

Hydrogen & energy

As a fuel, hydrogen has advantages:

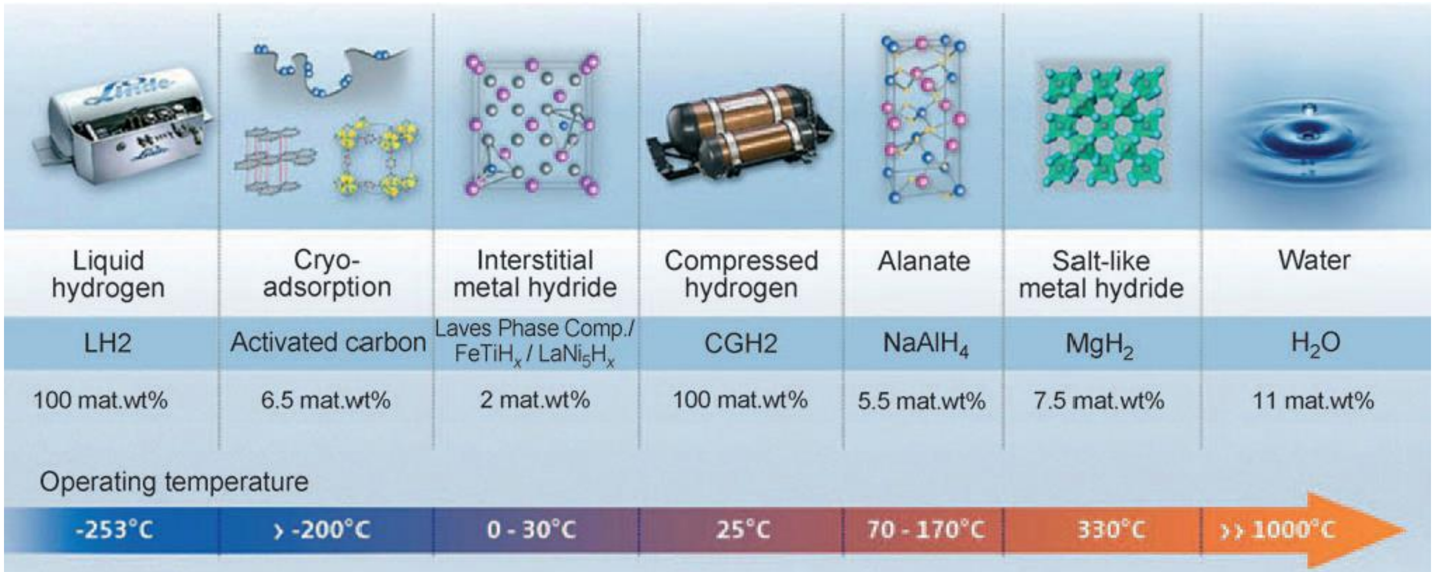
- Highest energy-to-mass ratio
- $H_2 + 1/2\ O_2 \rightarrow H_2O$ $\Delta H = -2.96eV$
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency



Hydrogen fuel cell

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 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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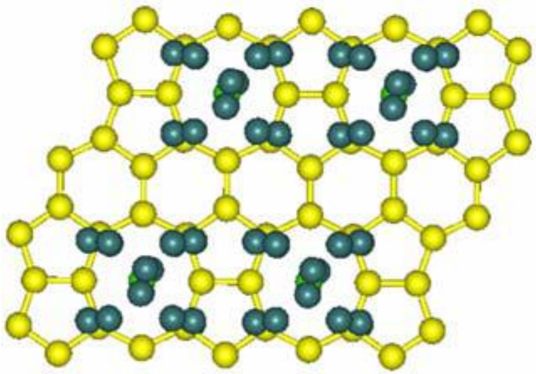
Graphene for hydrogen storage

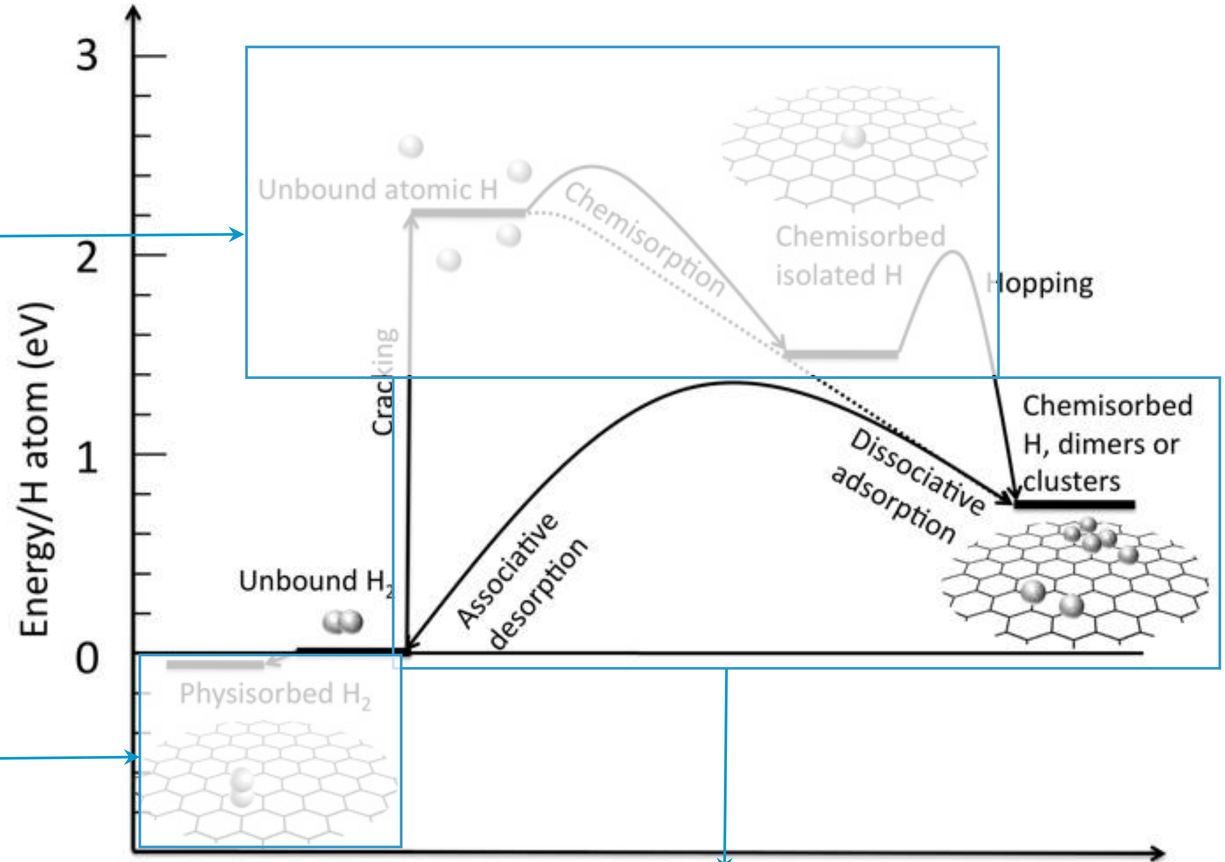
- Graphene is lightweight, inexpensive, robust, chemically stable
- Large surface area (~ 2600 m^2/g)
- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen



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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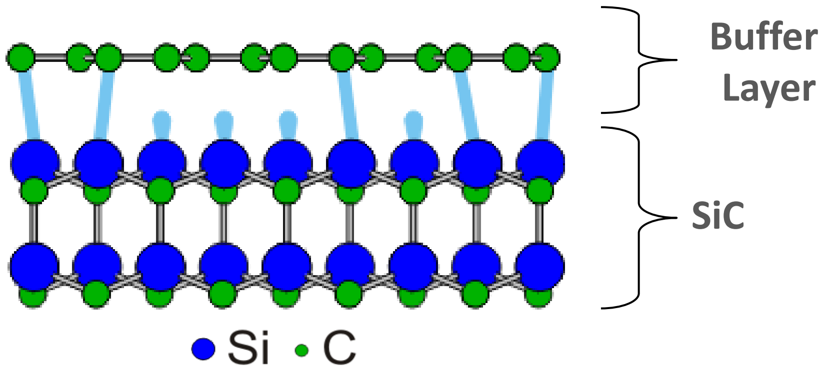
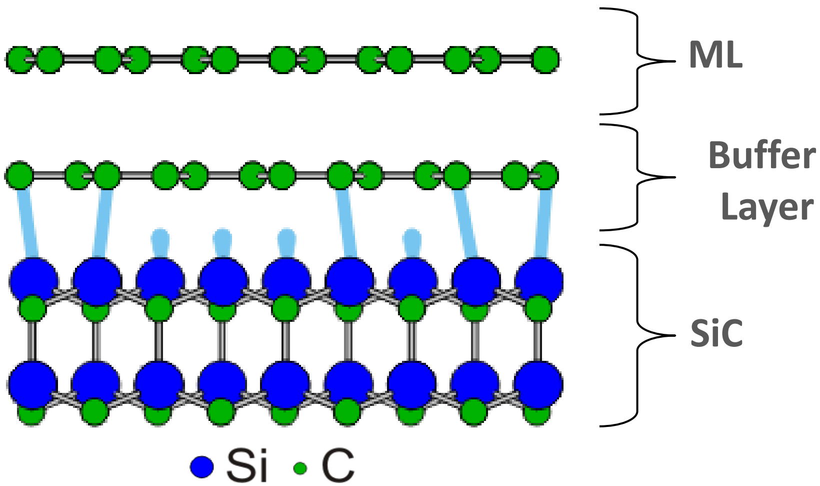
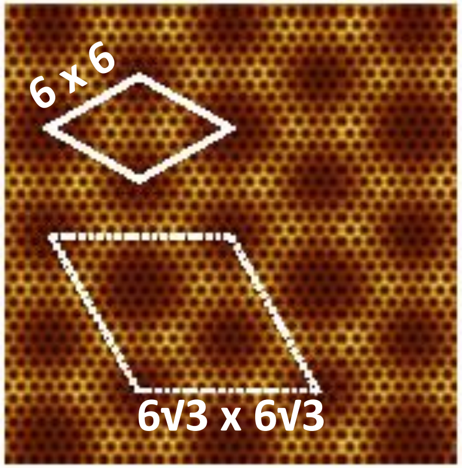
Graphene growth on SiC(0001)



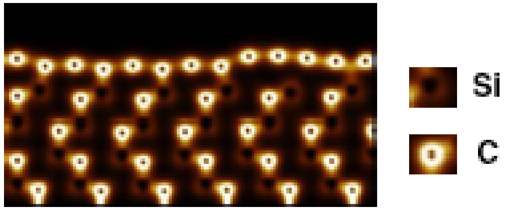


Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp^3 C-Si bonds.

Theoretical Calculations



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



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

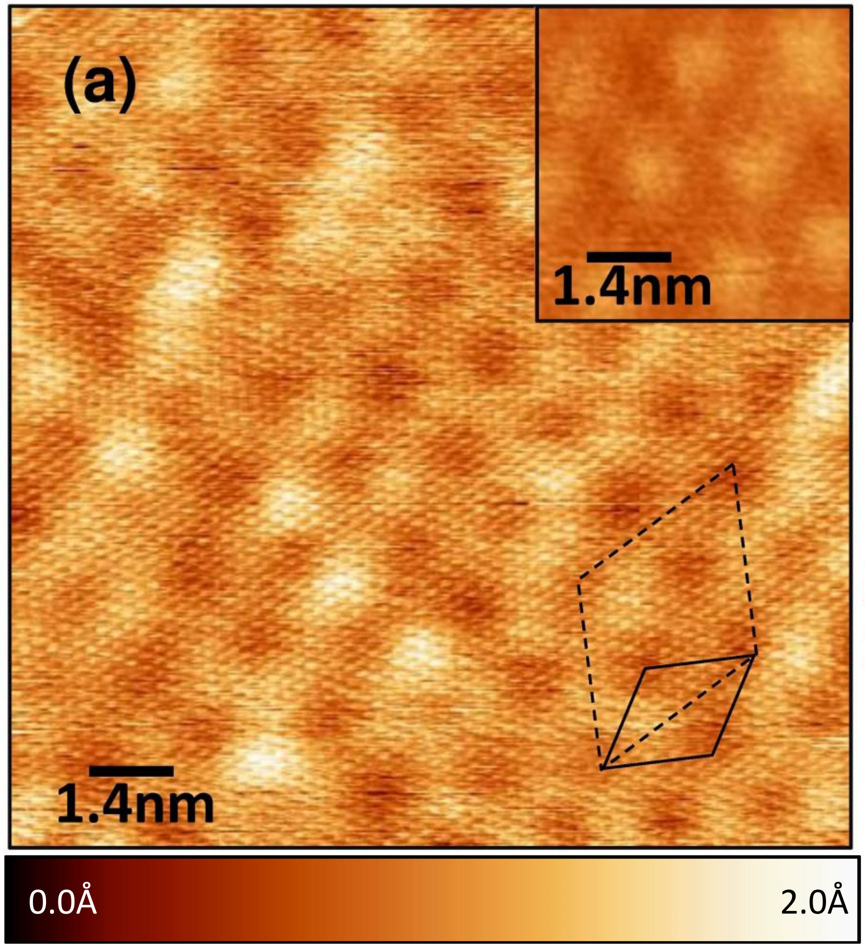
F. Varchon, et al., PRB 77, 235412 (2008).

Buffer Layer

Bias: +1.7V
Current: 0.3nA

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

quasi-(6x6) ——



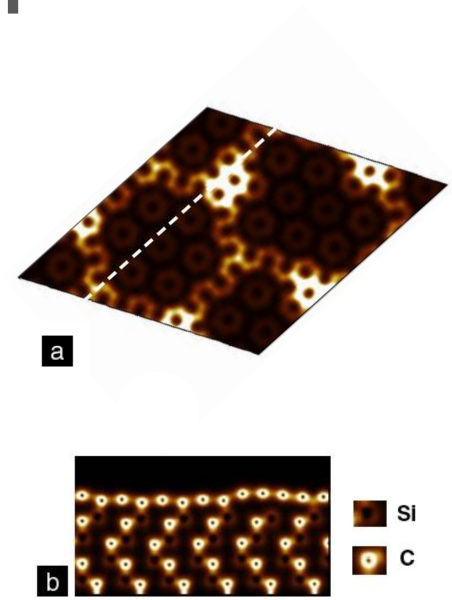


FIG. 2. (Color online) Total charge density of the buffer layer on SiC(001). (a) total charge density in the 6*R*3-SiC unit cell. (b) cross section of the total charge density along the line defined in (a). The black dots that appear when the cross section goes through the middle of an atom are due to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

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

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

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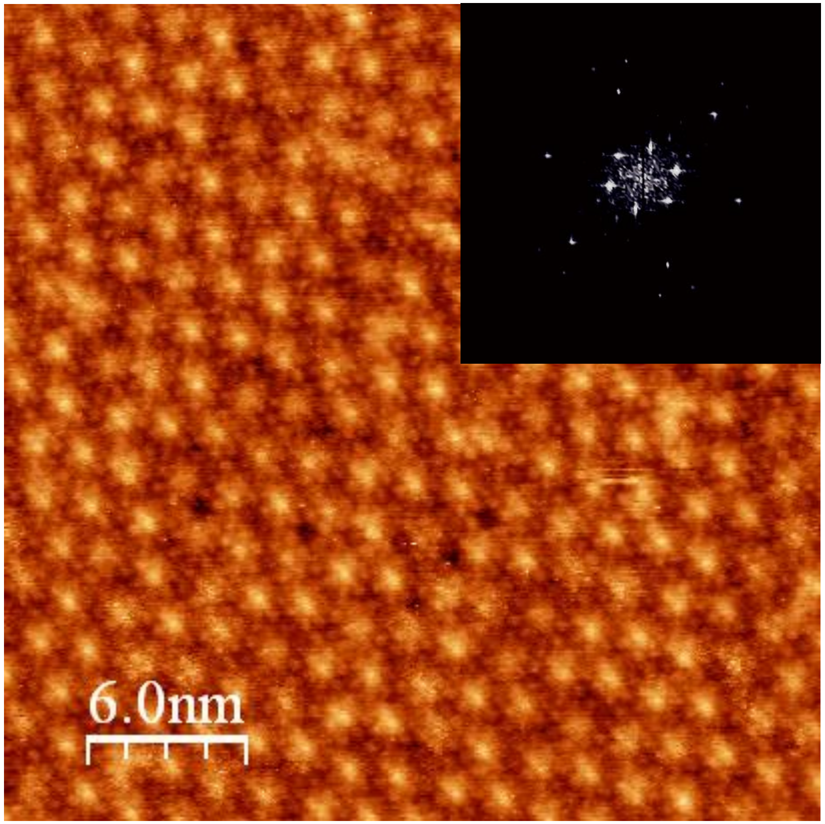
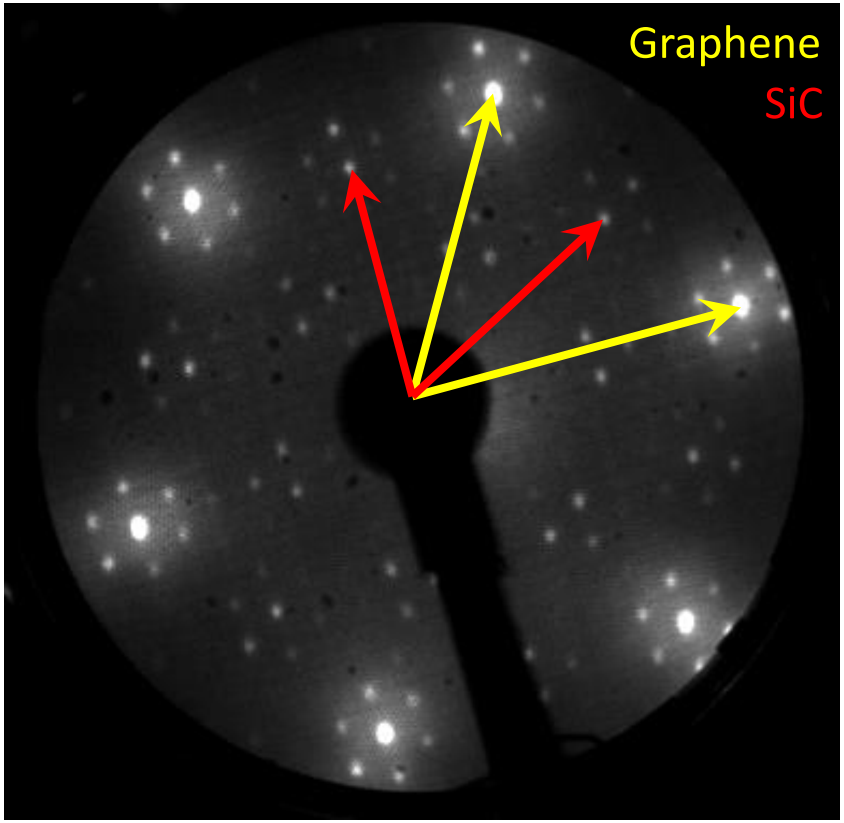
6√3x6√3-Superstructure



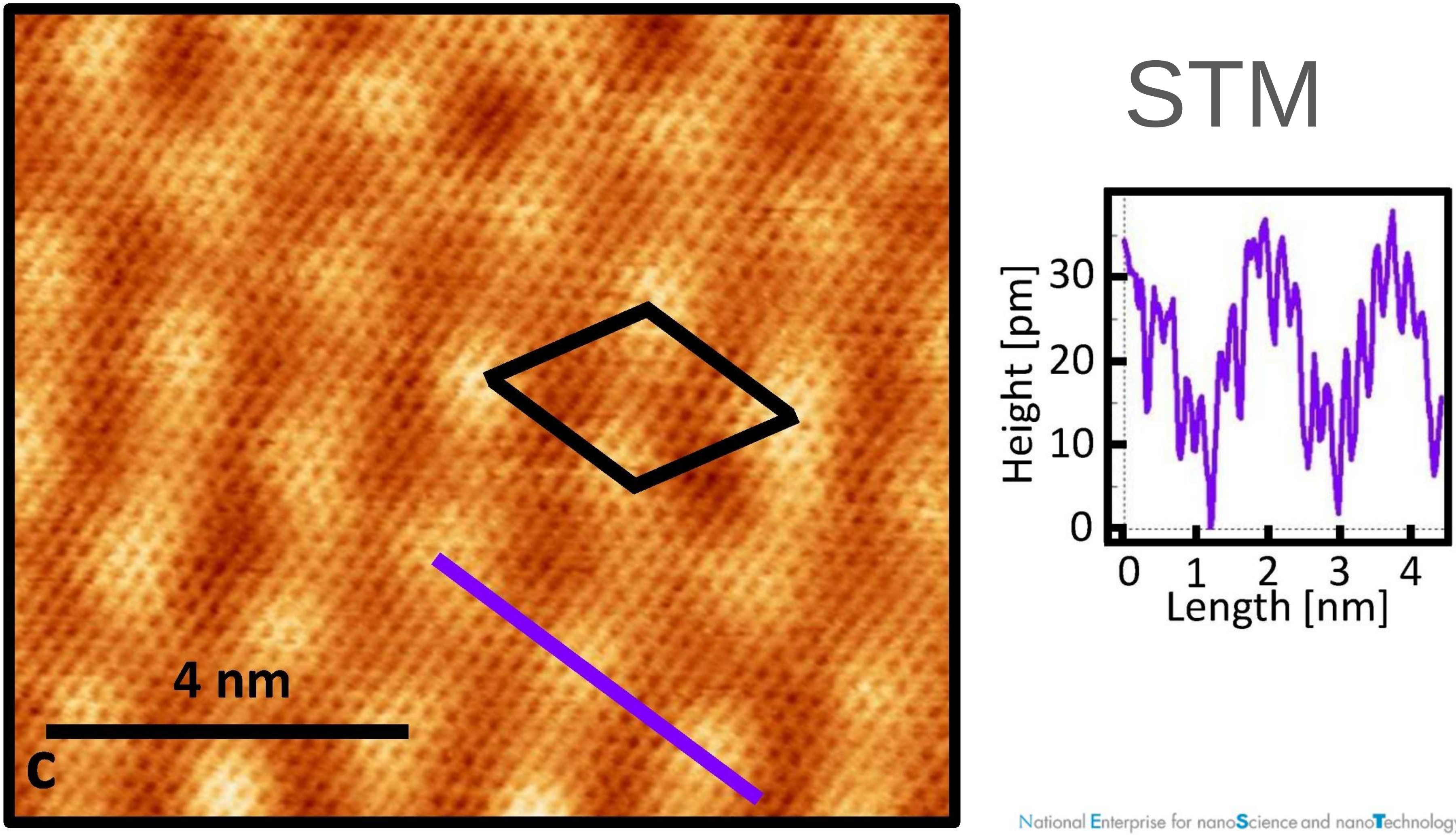
30 nm, 1V, 100 pA



E= 75 eV

Monolayer Graphene

STM



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

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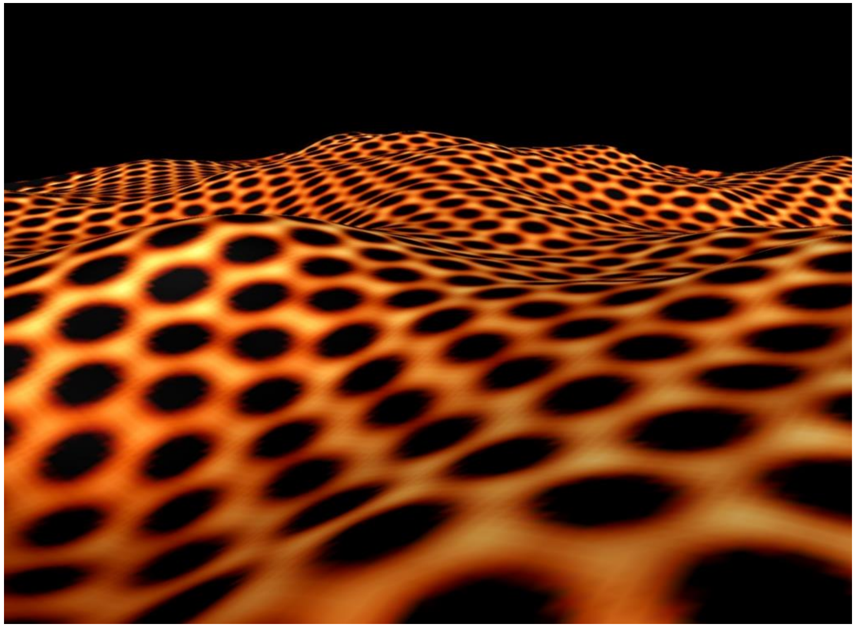
Graphene Curvature

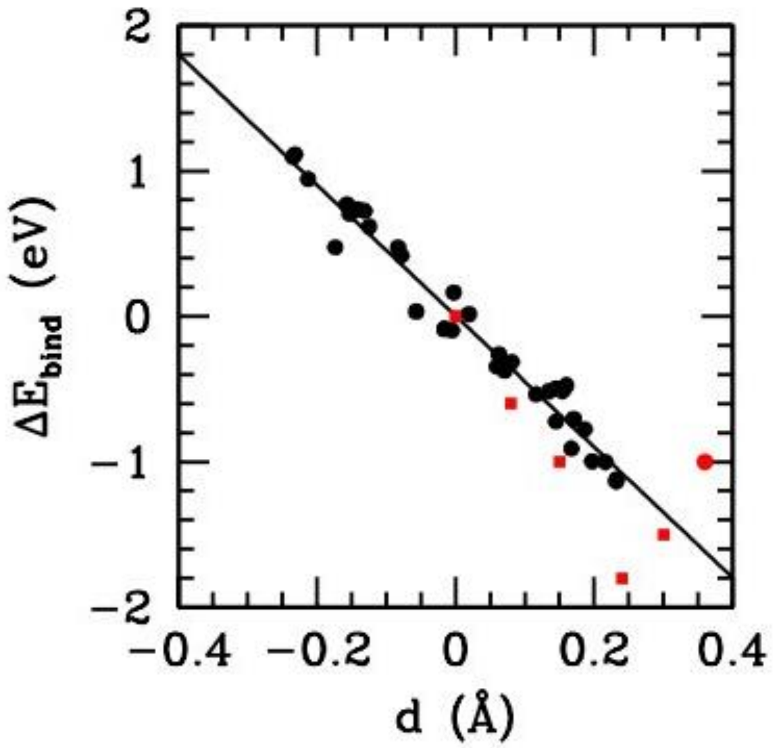
- Exploit graphene curvature for hydrogen storage at room temperature and pressure



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

Graphene Curvature

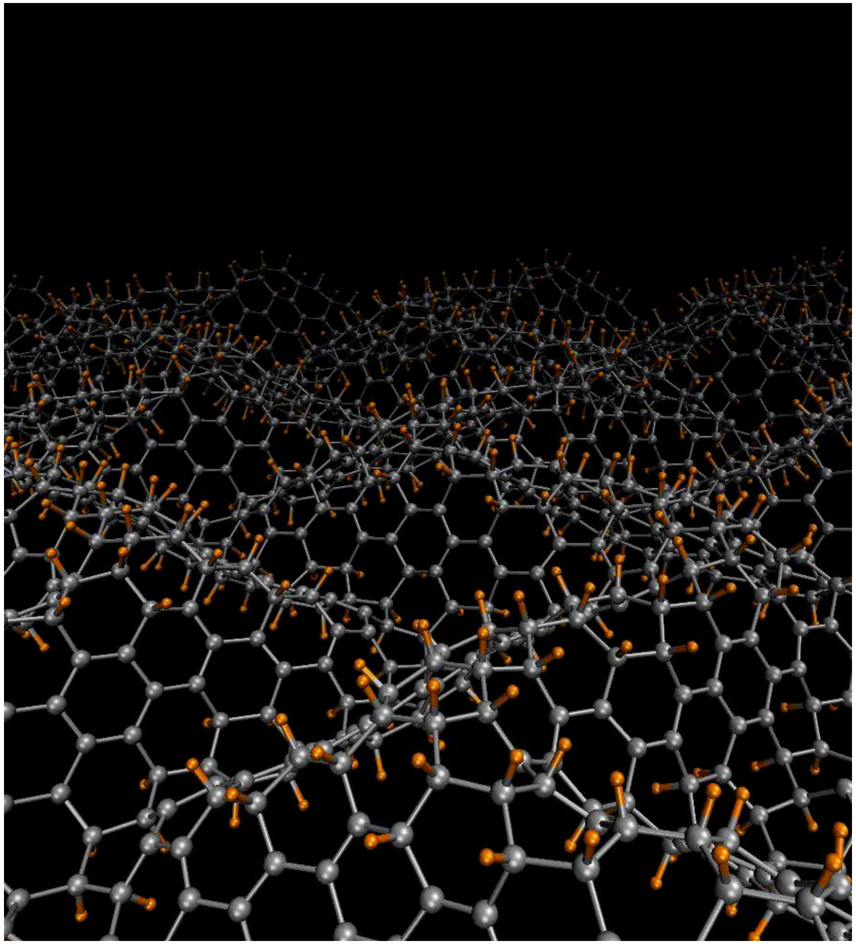
- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts



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

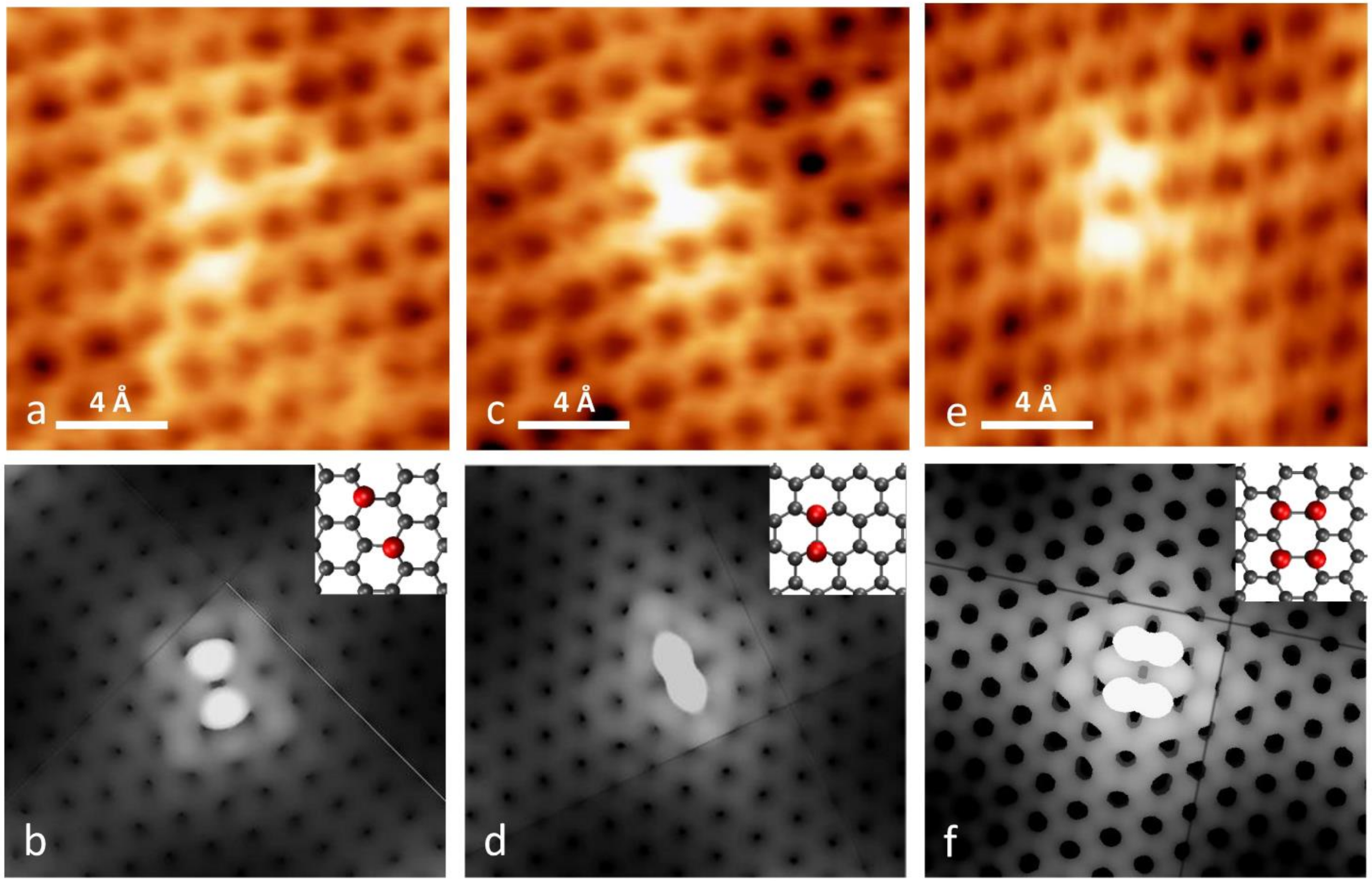
Graphene Curvature

- 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



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

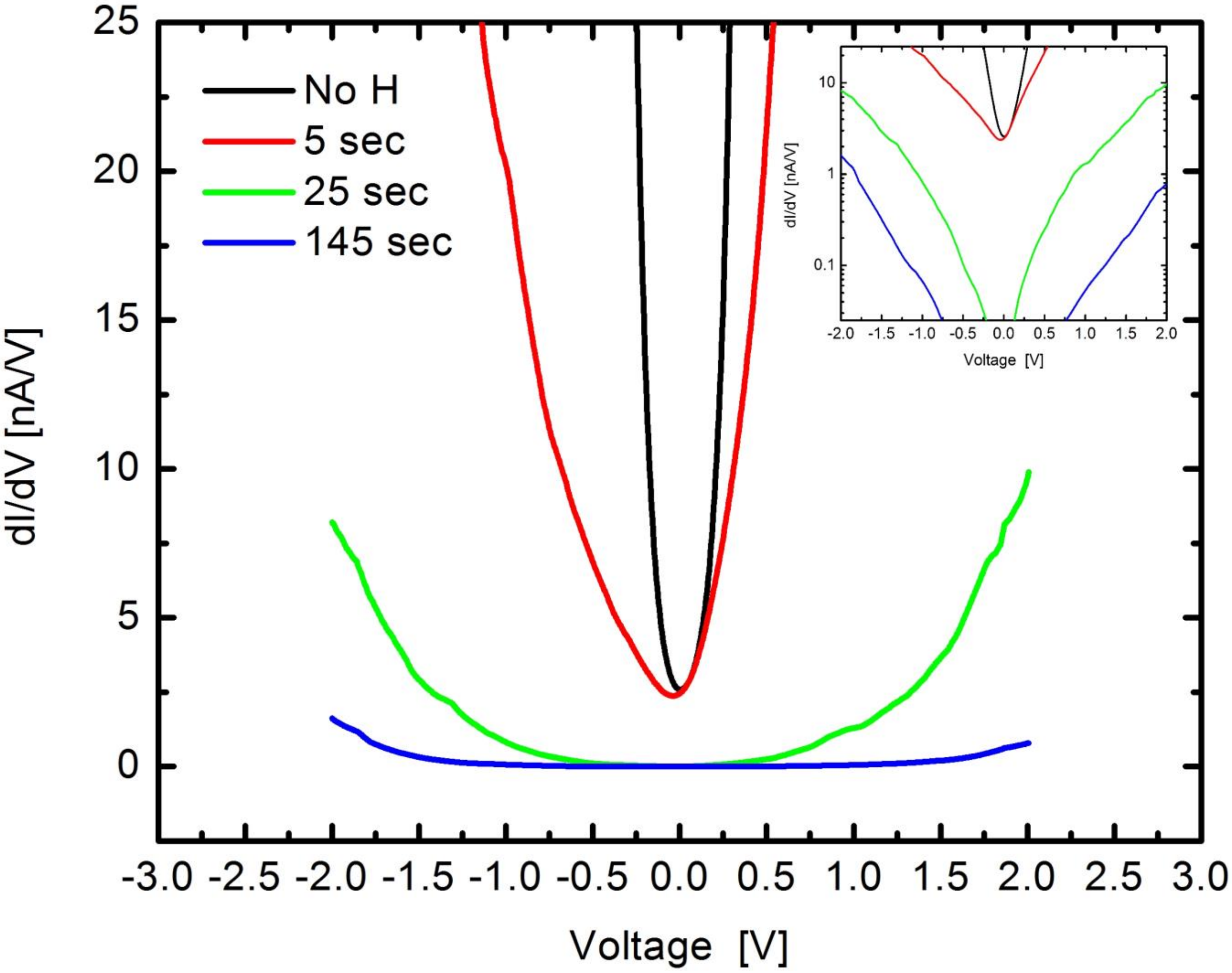
H-dimers and tetramers



Para-dimer Ortho-dimer Tetramer

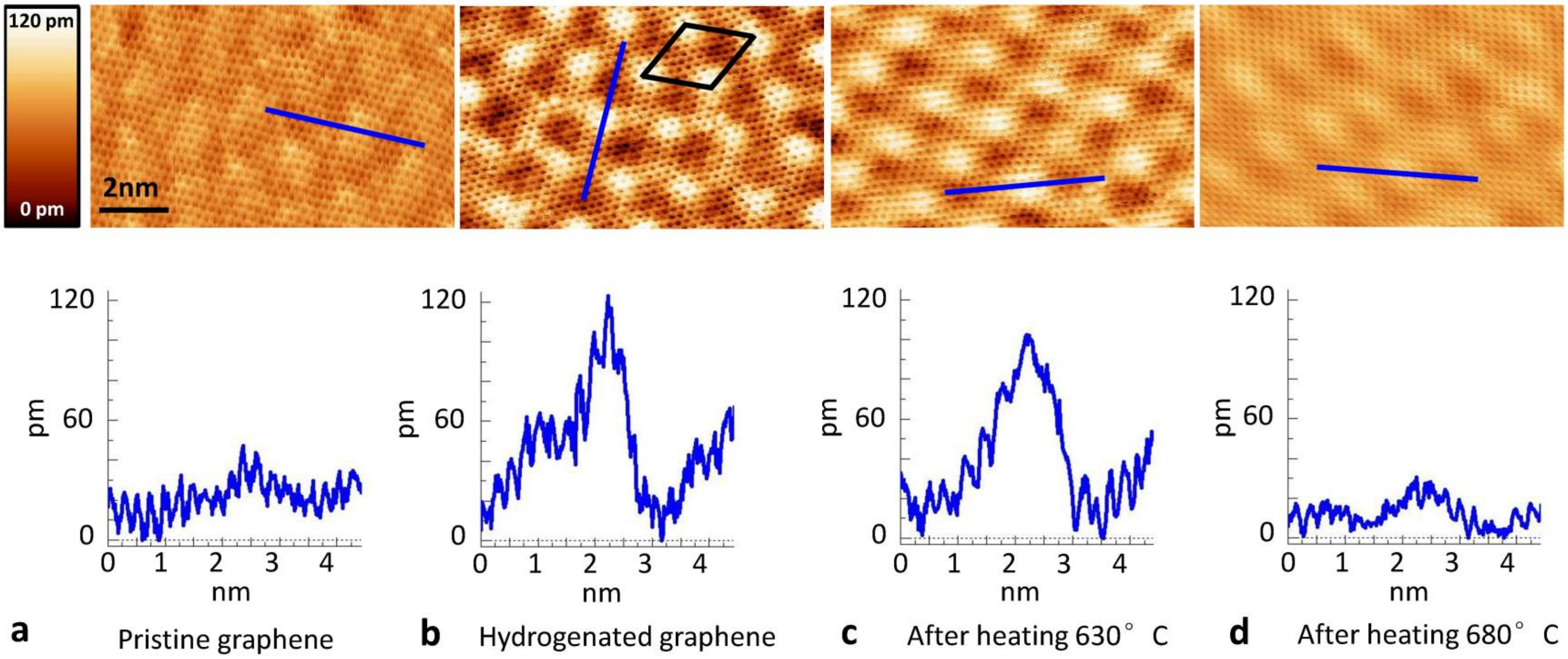
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

STS after hydrogenation



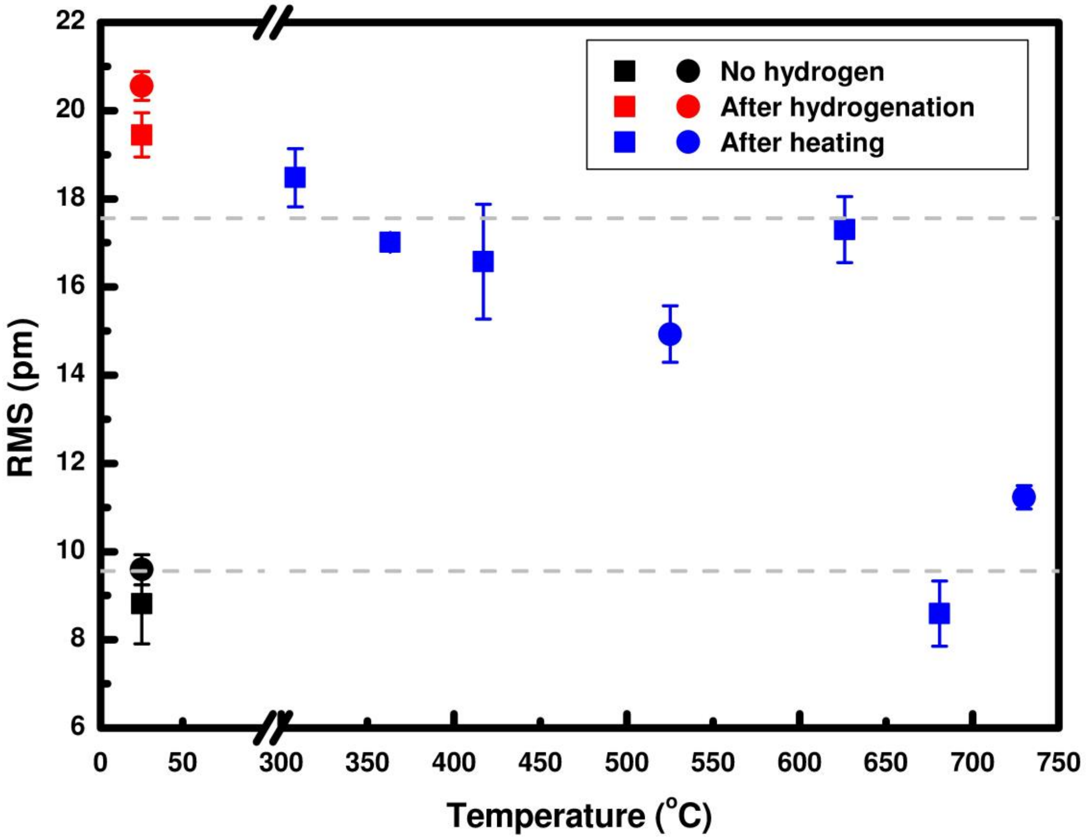
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

H adsorption and desorption



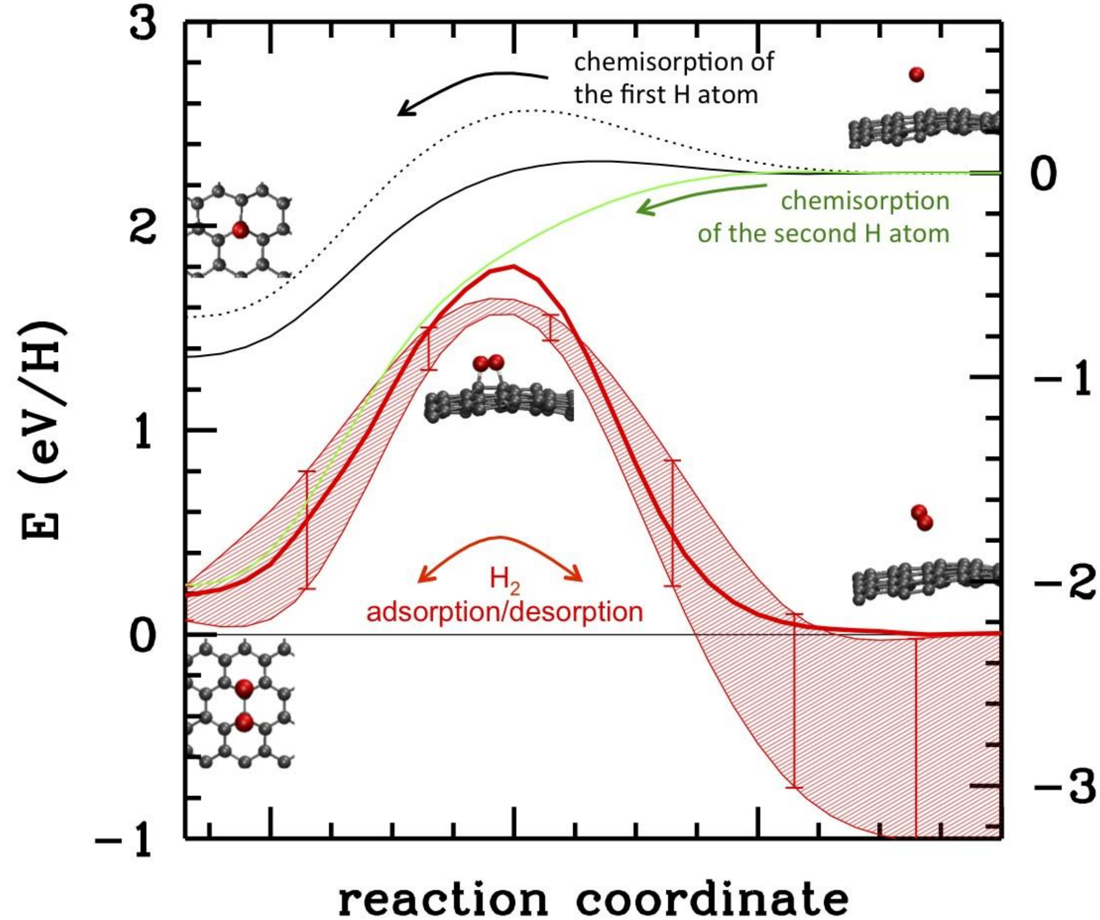
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

RMS roughness



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

DFT calculations



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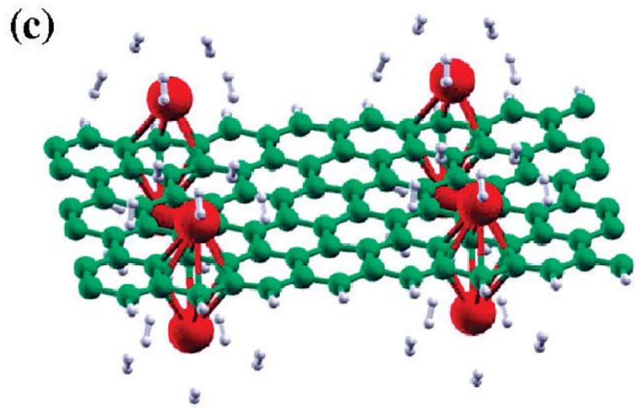
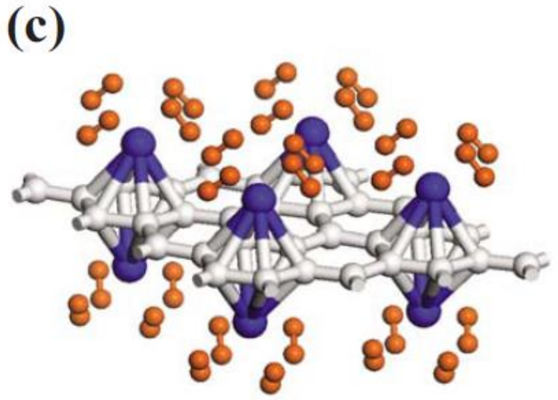
Functionalized Graphene

- 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)

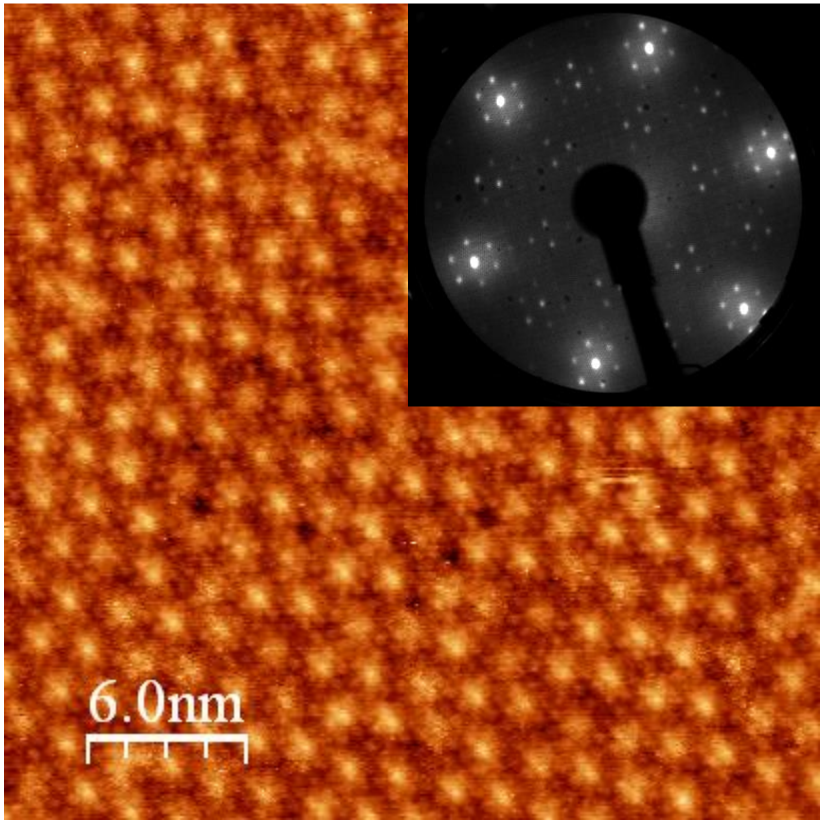


Lee et al., Nano Lett. 10 (2010) 793

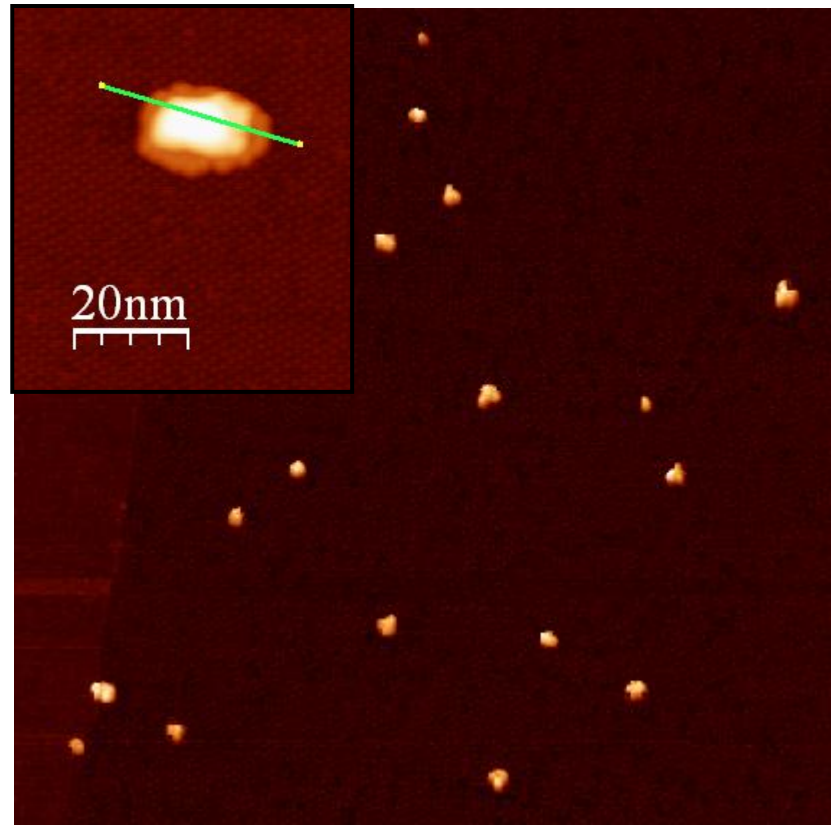


Durgen et al., PRB 77 (2007) 085405

Titanium on graphene



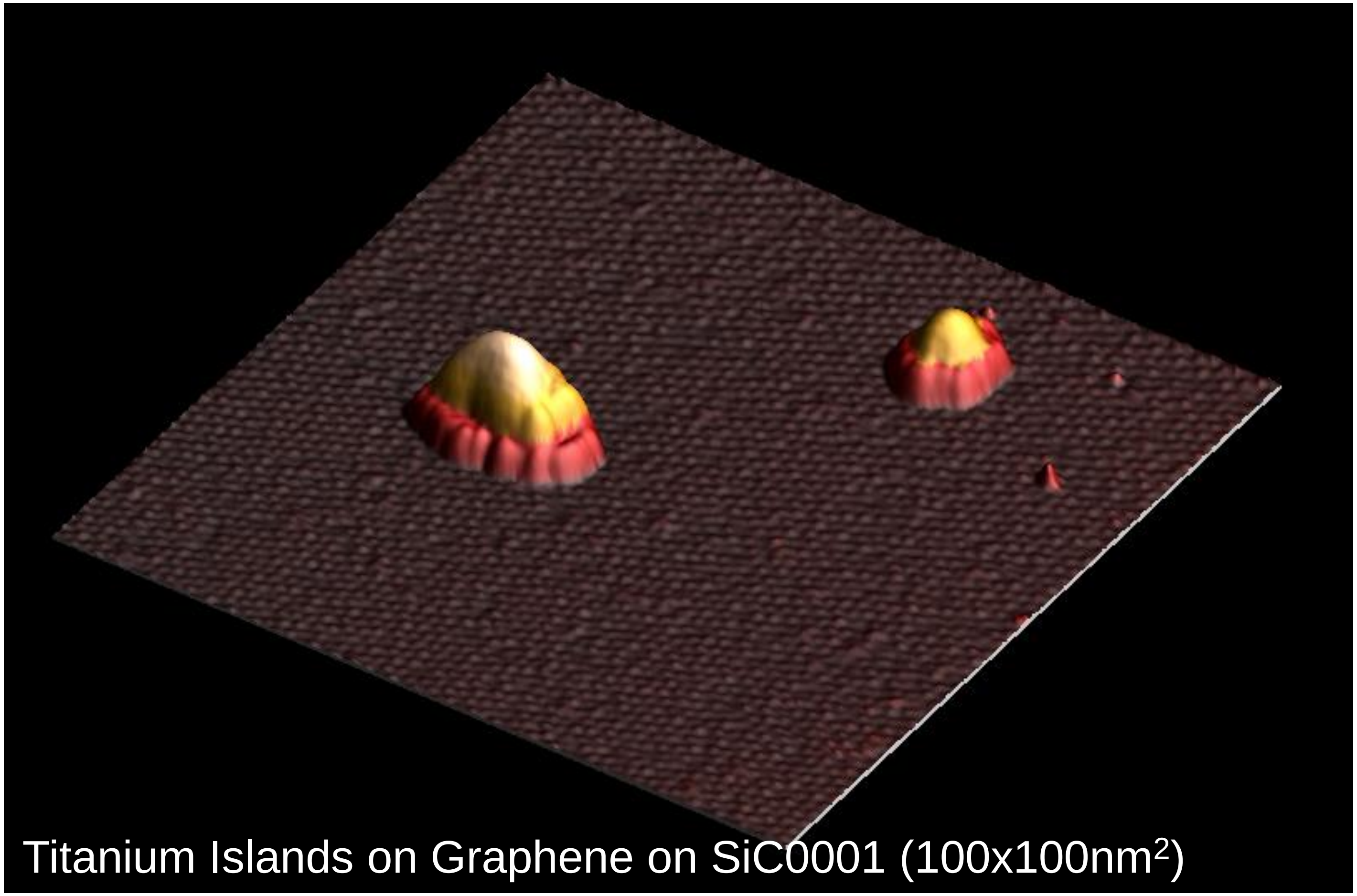
ML graphene on SiC(0001)
with reconstruction



After deposition of Ti at RT

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

Titanium on graphene



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

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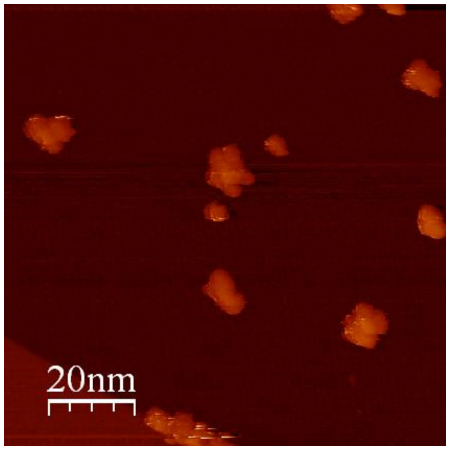
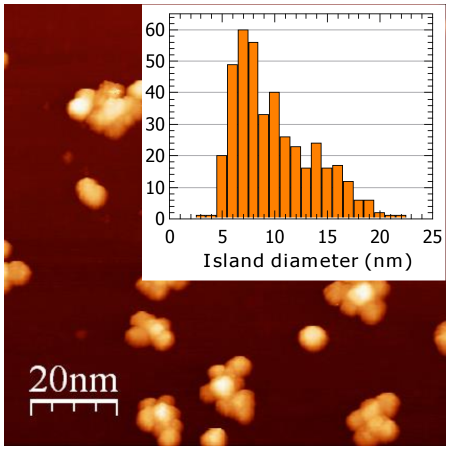
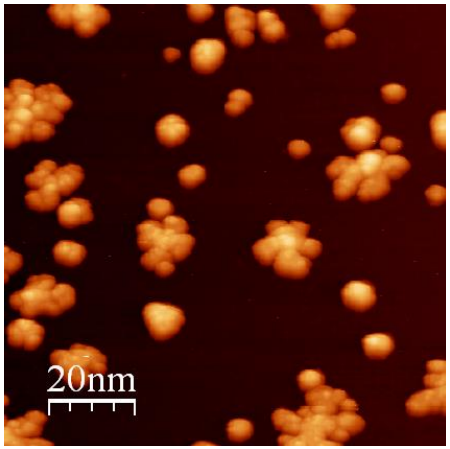
Titanium island growth



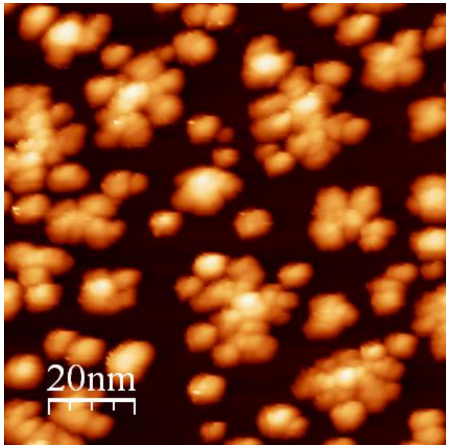
6% Coverage



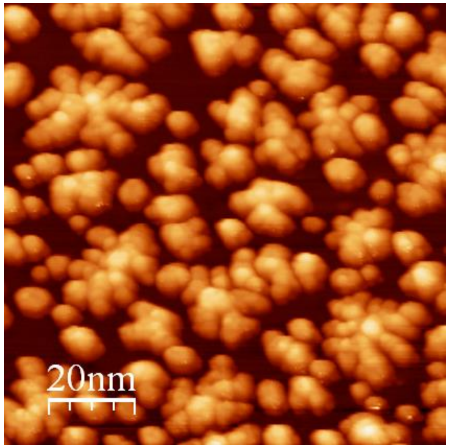
16% Coverage



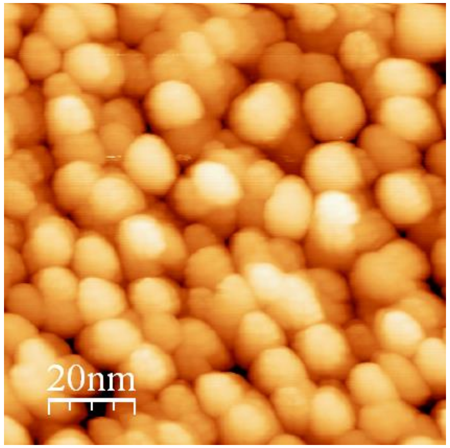
29% Coverage



53% Coverage



79% Coverage



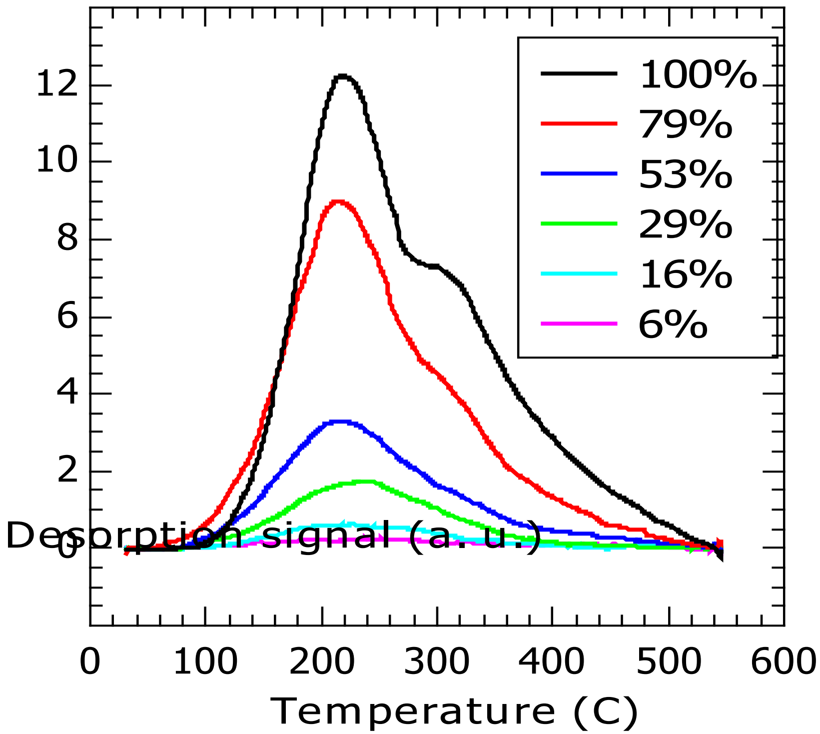
100% Coverage

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

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)

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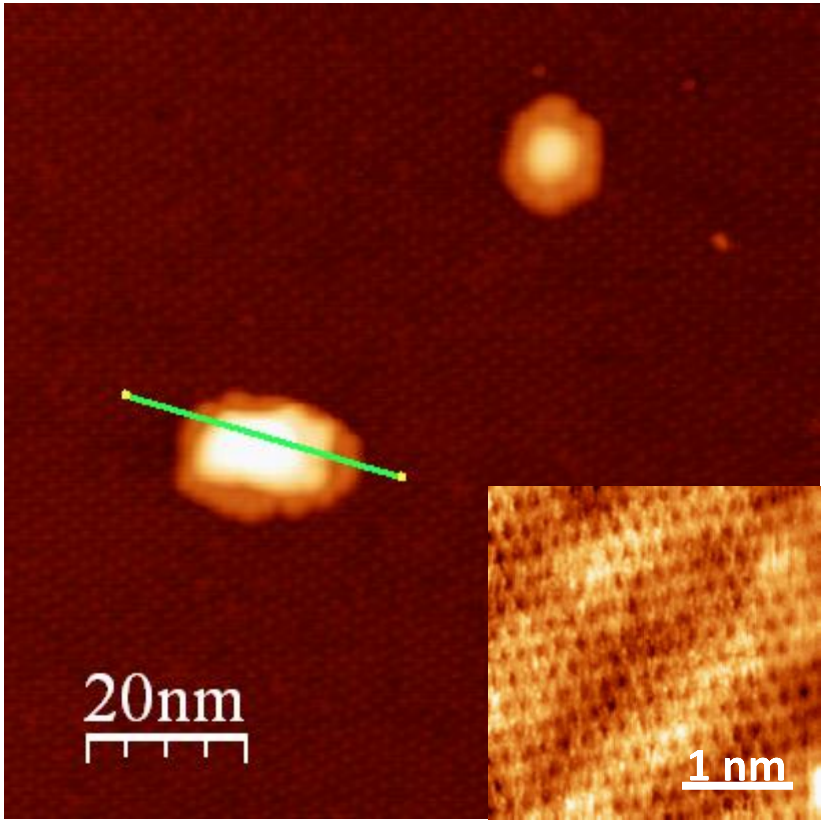
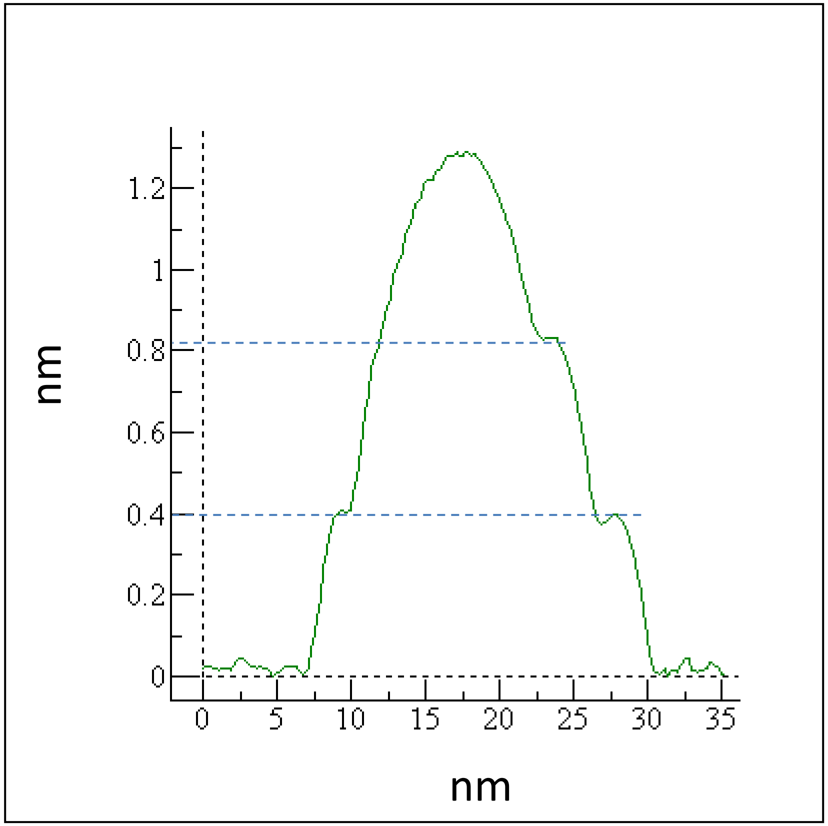
Forming of Islands



100 nm, 1 V, 82 pA



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

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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]

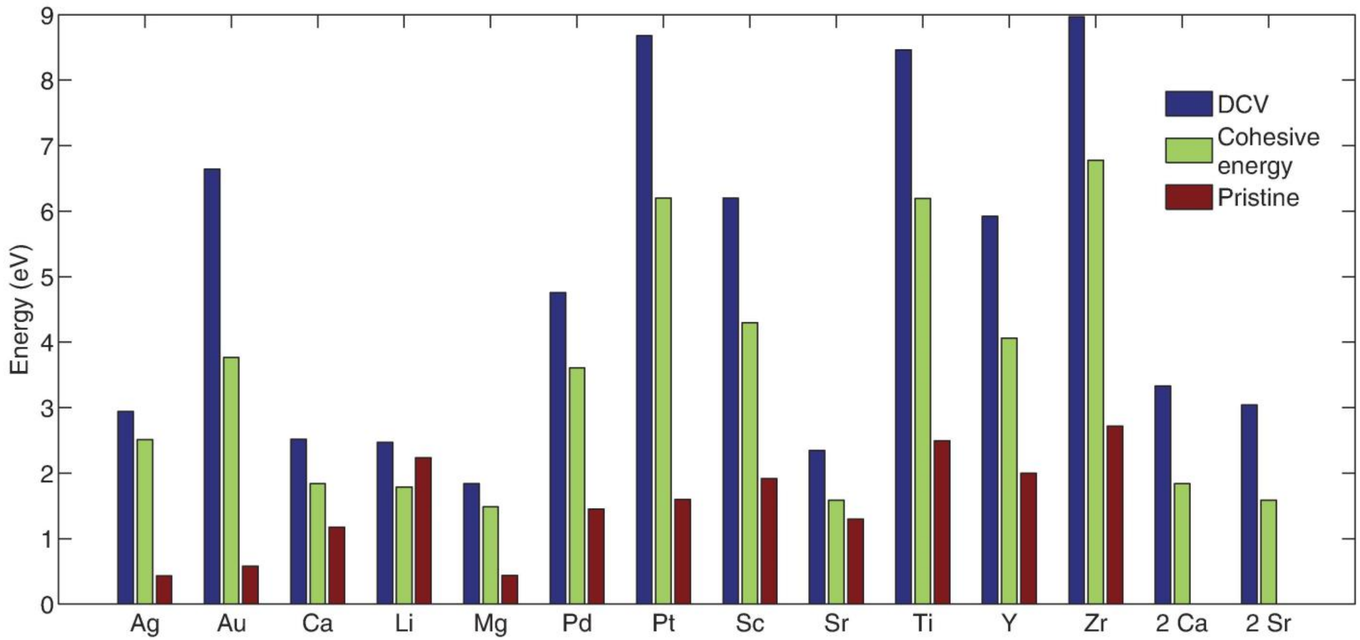
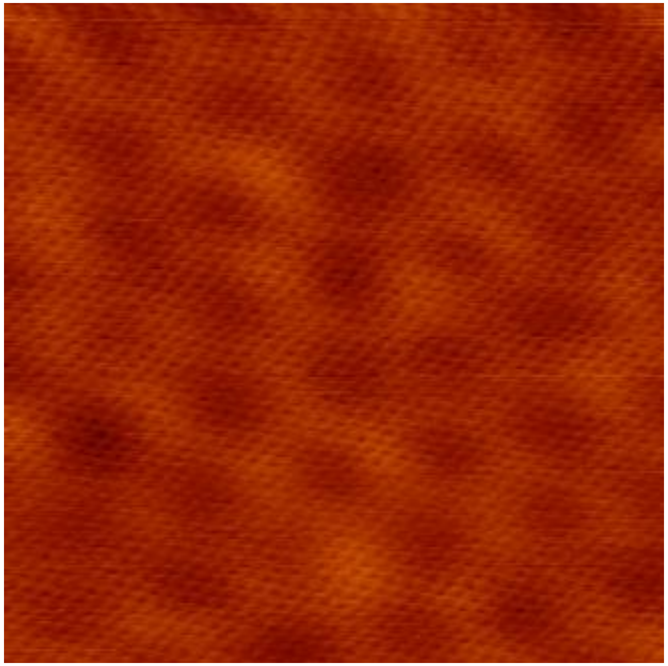
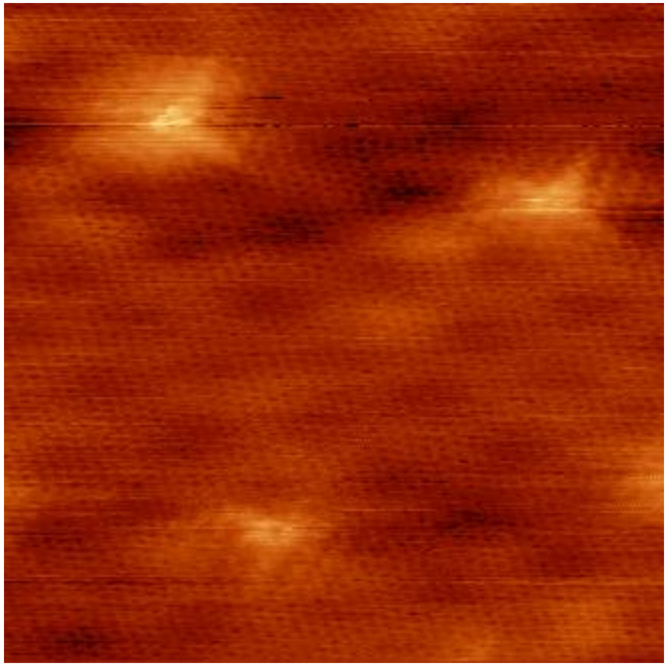


FIG. 1. (Color online) The binding energy of adatoms to graphene DCVs (blue), and pristine graphene (red), as well as the cohesive energy of the respective metal (green). Also included are the binding energies per adatom of two Ca and Sr ("2Ca" and "2Sr") adatoms with one on either side of the DCV.

DCV = Double Carbon Vacancy

N_2 - sputtering of the graphene surface

Clean graphene surface	Sputtered 150s @100eV
	
10x10 nm², 1V, 0.8nA	10x10 nm², 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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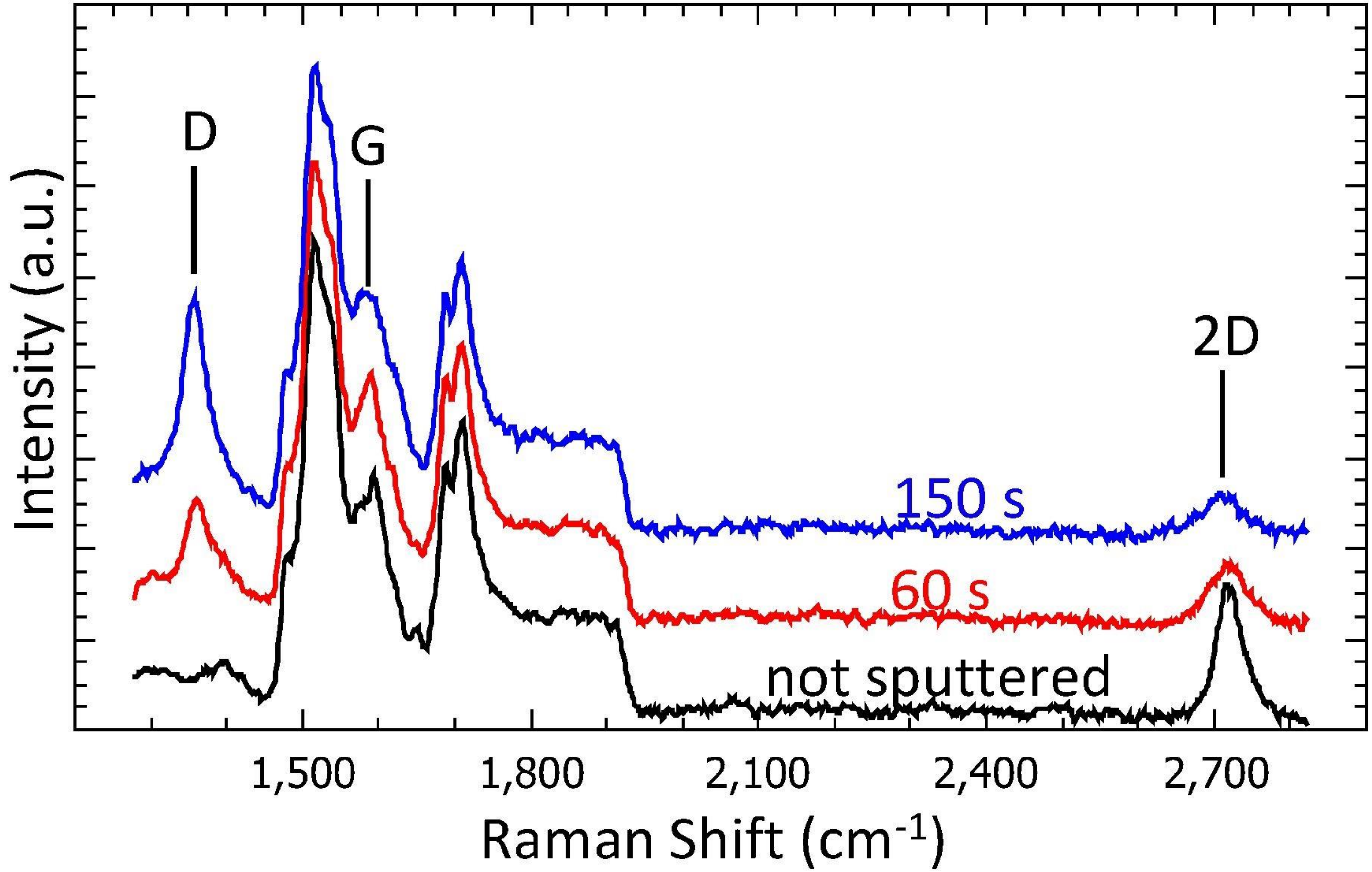
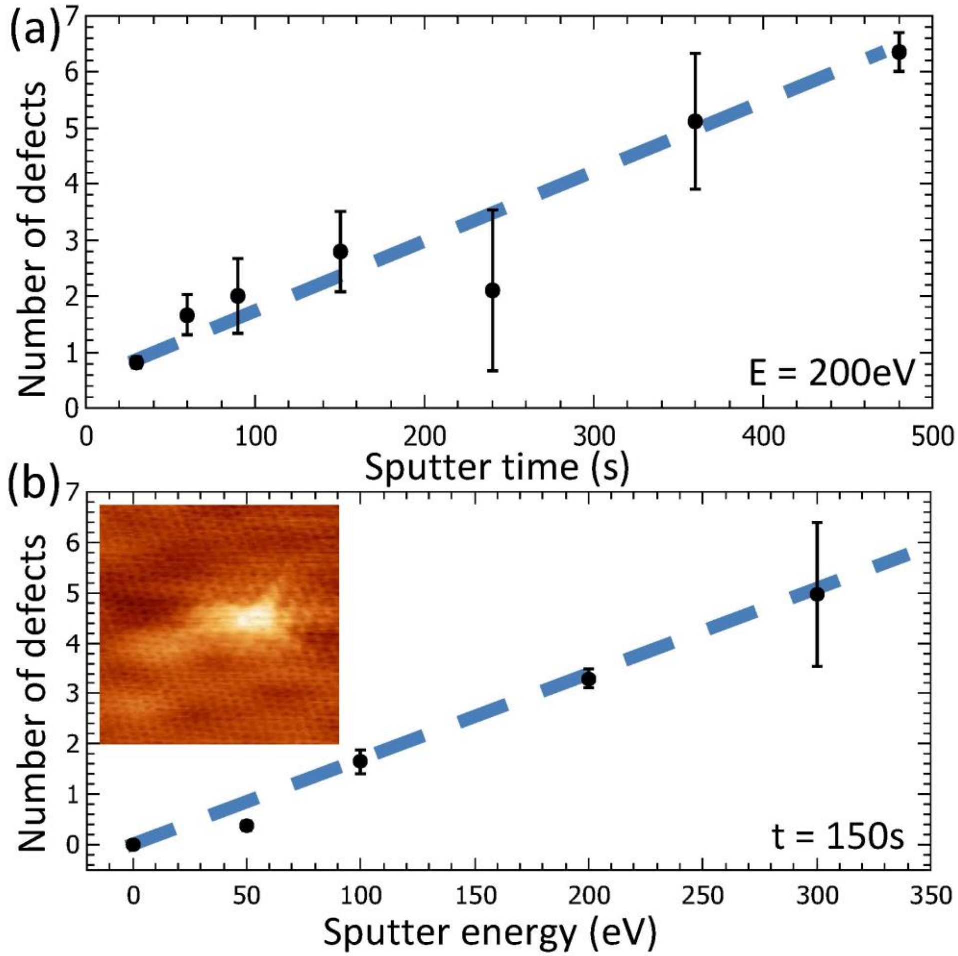
Raman



T. Mashoff *et al.*: Appl. Phys. Lett. **105**, 083901 (2015).

Distribution of defects



Average number of induced defects per 100nm^2

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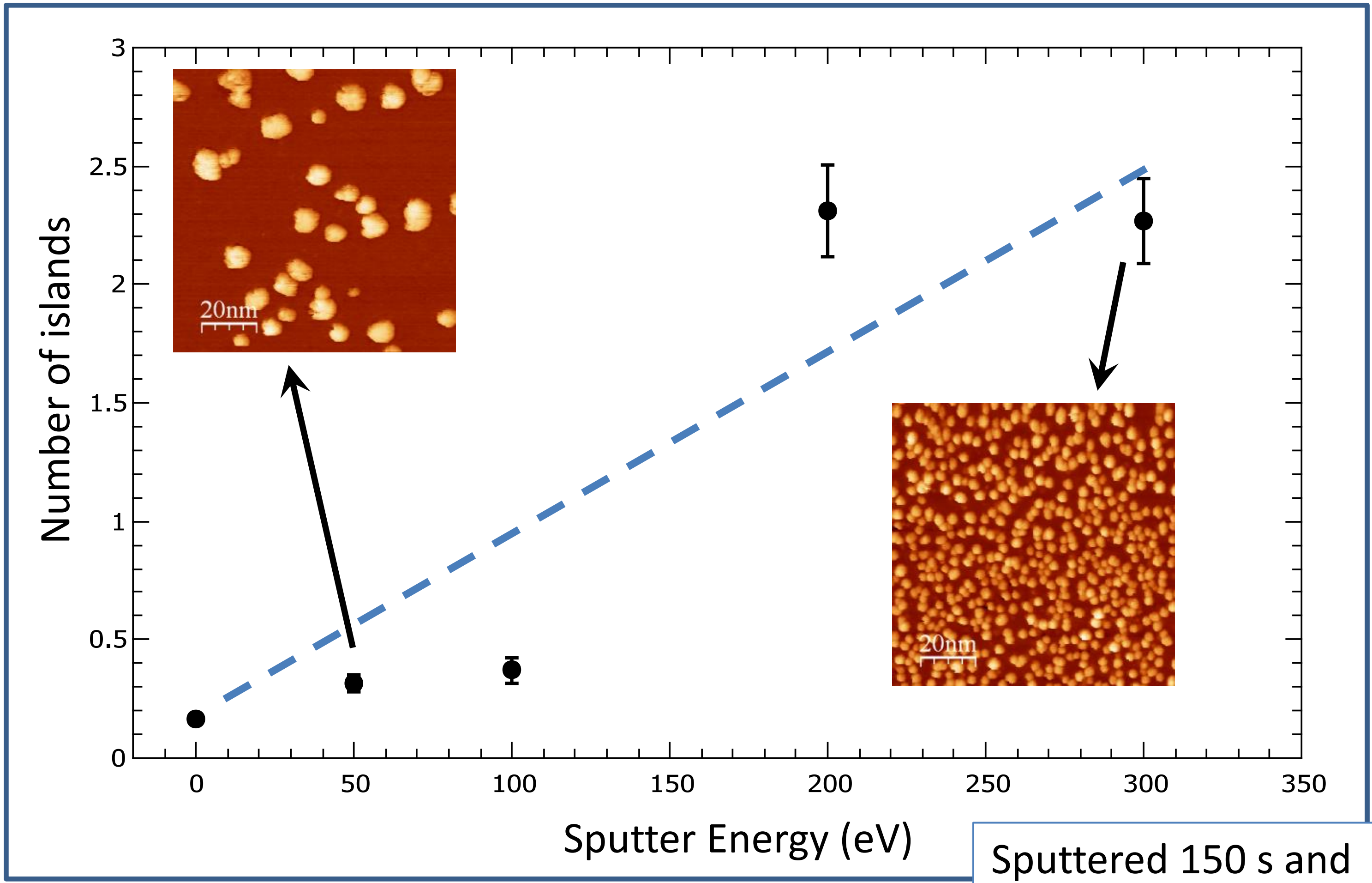
Average Number of Islands per 100 nm^2



Sputtered 150 s and
Deposition of 0.5 ML Titanium

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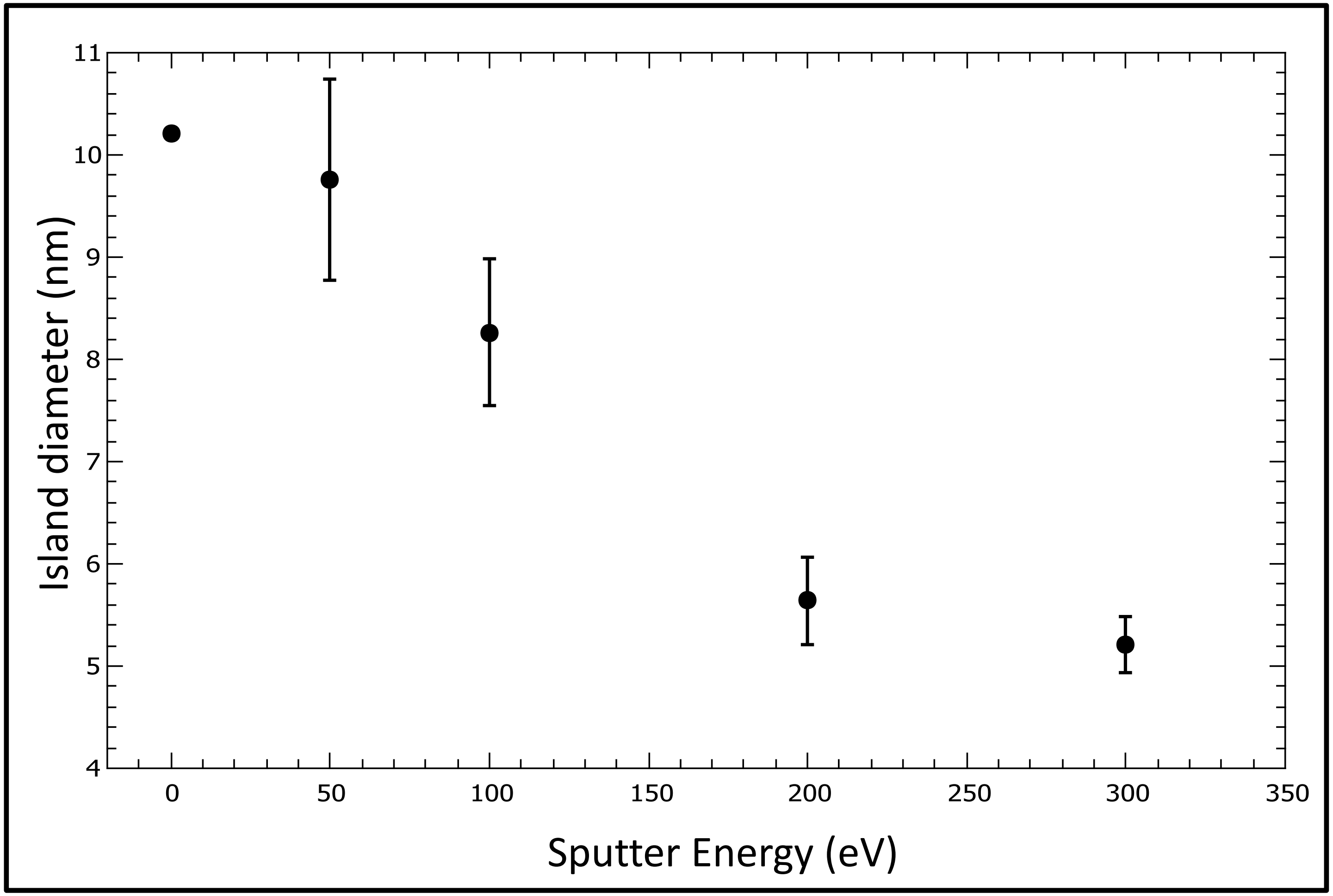
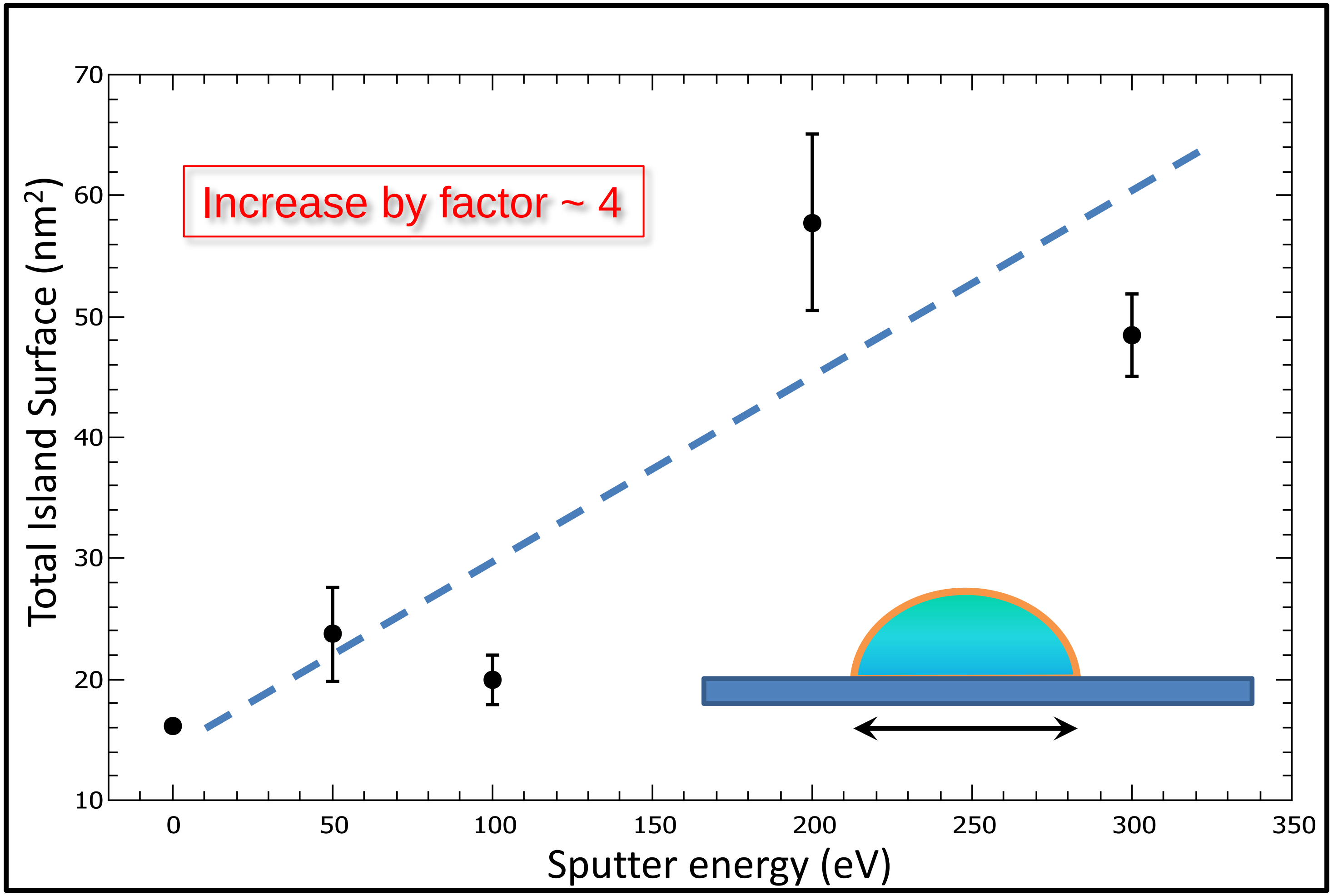
Average diameter of individual Ti-Islands



T. Mashoff *et al.*: Appl. Phys. Lett. **105**, 083901 (2015).

“Active” 3D-surface per 100nm^2



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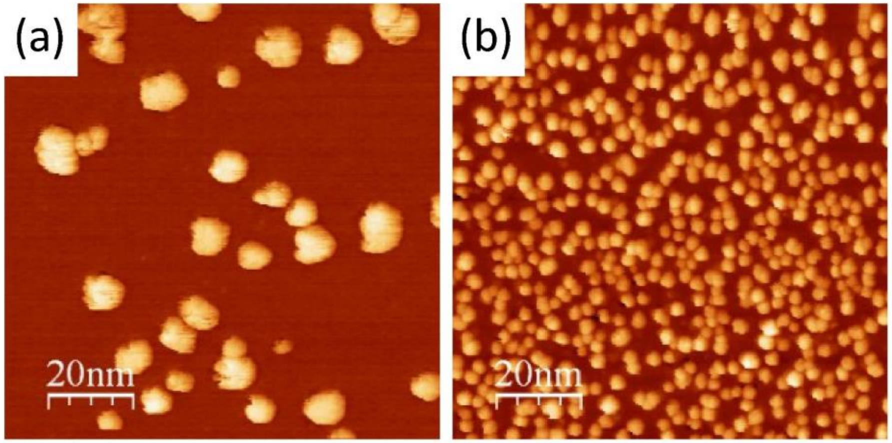
Increase in active surface

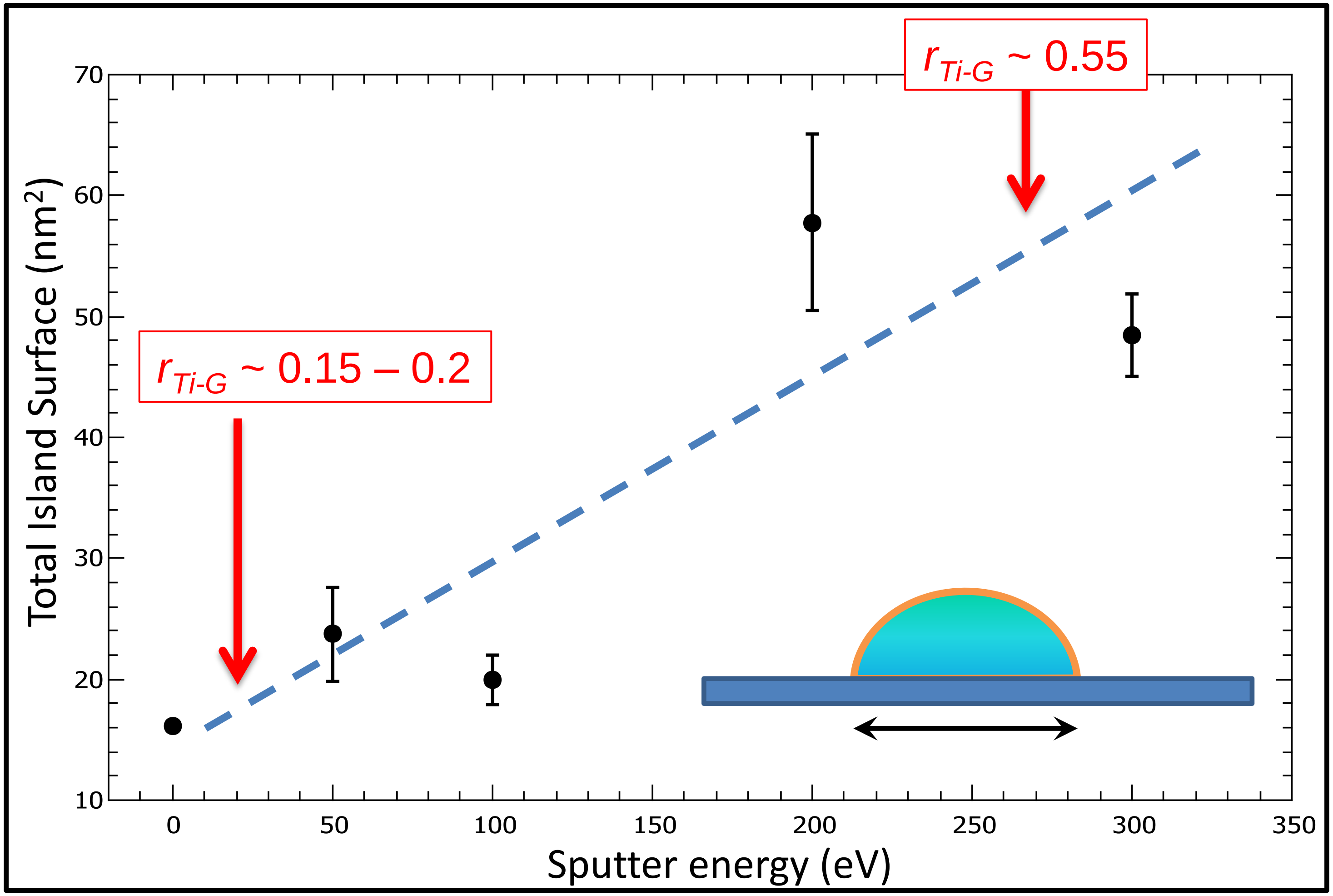
- The fraction *r* of surface Ti atoms to Ti atoms in the bulk increases.
- The ratio $r_{Ti\text{-}G}$ of Ti surface to graphene surface increases.



- Larger islands are 2 – 3 layers high: $r \sim 0.3 - 0.5$.
- Small islands are of monolayer height: $r = 1$.

T. Mashoff *et al.*: Appl. Phys. Lett. **105**, 083901 (2015).

“Active” 3D-surface per 100nm^2



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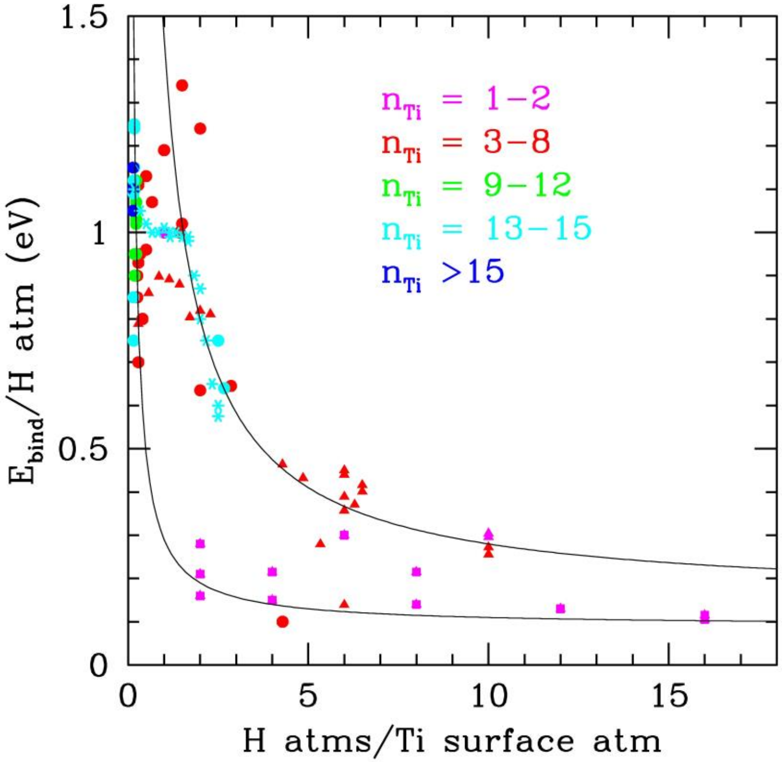
Hydrogen Uptake



- We assume n_{H2} = 1 H_2 molecule per Ti surface atom.
- Agrees within factor 2.5 with estimate from TDS experiment (n_{H2} = 0.4).

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Gravimetric Density

- $GD = M_H / (M_{Ti} + M_G + M_H)$
- Small islands (r = 1 and $r_{Ti\text{-}G}$ = 0.55): GD ~ 1.8%.
- With $r_{Ti\text{-}G}$ = 1: GD ~ 2.4%.
- Larger islands (r = 0.15 – 0.2 and $r_{Ti\text{-}G}$ = 0.3 – 0.5): GD ~ 0.5 – 0.75%.
- Reducing island size further (n_{H2} = 4), GD = 7% seems feasible.

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

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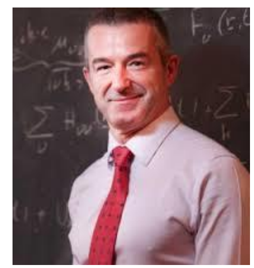
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