Metal-functionalized Graphene for Hydrogen Storage

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National Enterprise for nanoScience and nanoTechnology

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1. Quantum transport in superconductors
2. Physics of low-dimensional systems
3. Graphene

Advanced Photonics

1. Intersubband polaritonics
2. THz photonics
3. OptoMechanics

NanoBioScience

1. Visualizing brain function in the living mouse
2. Lab-on-a-chip technologies
3. Nanoscale single-molecule spectroscopy of soft matter

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Outline

- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Functionalization
  - Ti-functionalization
  - Li-functionalization

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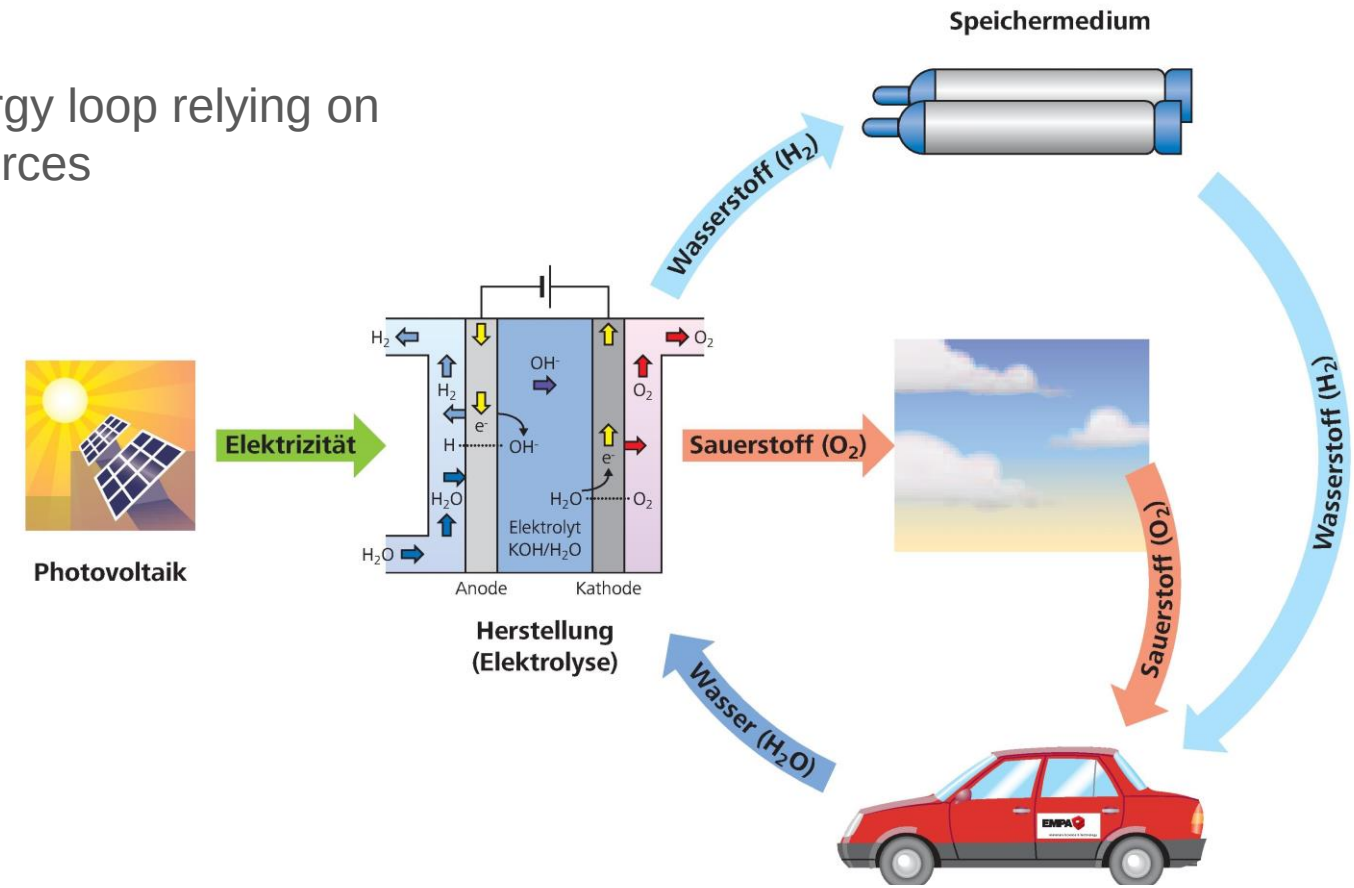
Hydrogen Life Cycle

Complete energy loop relying on renewable sources

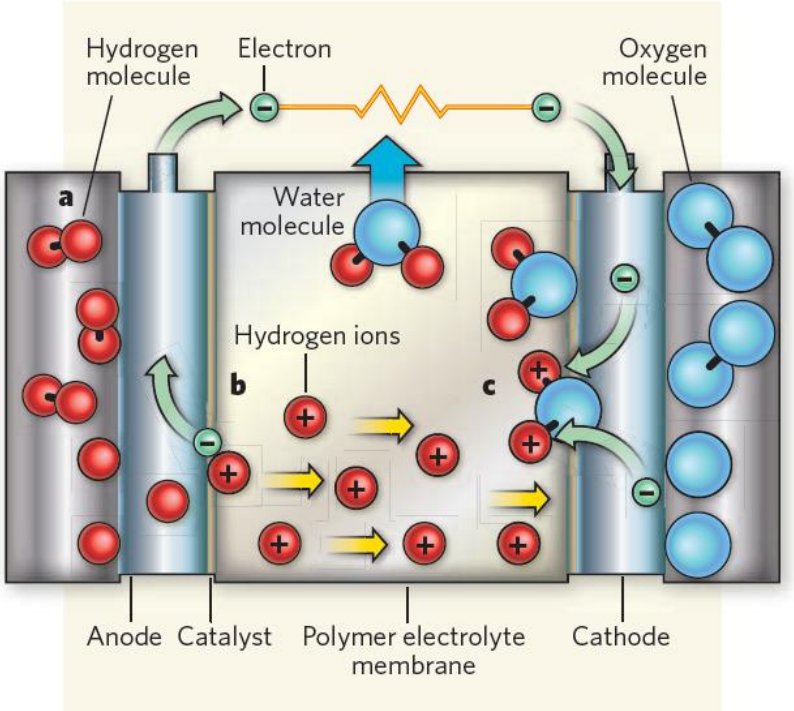


Hydrogen Storage in a safe and cheap way is **a critical issue**

Hydrogen & energy

As a fuel, hydrogen has advantages:

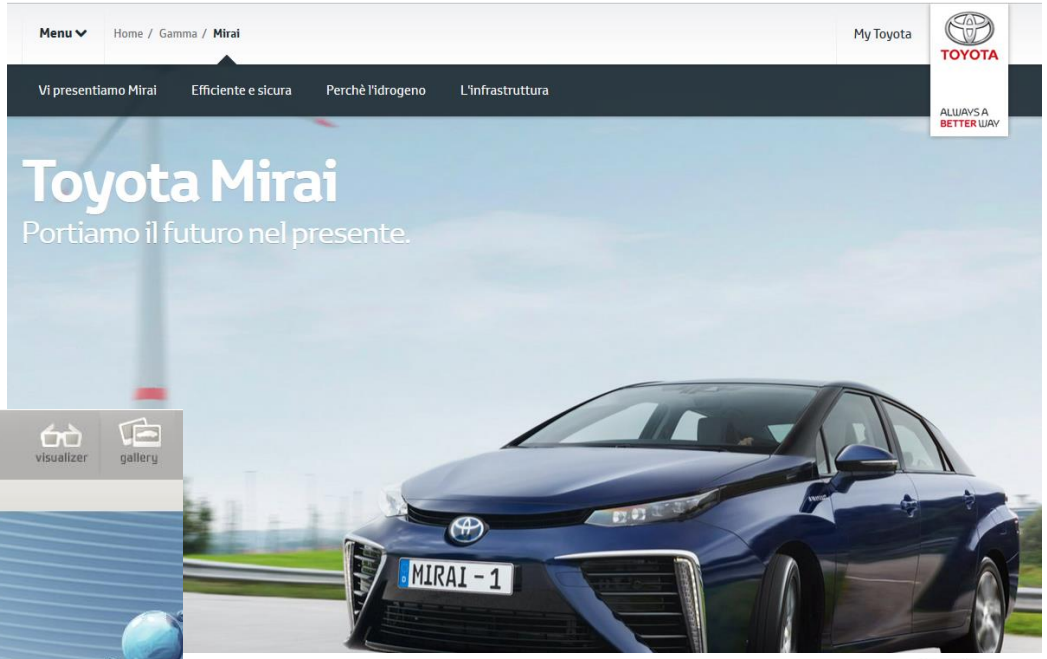
- Highest energy-to-mass ratio
- $H_2 + 1/2\ O_2 \rightarrow H_2O$ $\Delta H = -2.96eV$
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency



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-fuelled Vehicles



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Hydrogen-fuelled Train

ALSTOM

Coradia iLint regional train

Hydrogen-fuelled Airplane

Zero-emission air transport –
first flight of four-seat passenger aircraft HY4

29 September 2016

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Hydrogen-Storage

- Storing enough hydrogen on-board a vehicle to achieve a driving range of 400 km is a significant challenge.
- Needed: 4 kg of hydrogen for 400 km.
- At room temperature and atmospheric pressure, 4 kg of hydrogen occupies 45 m^3, which corresponds to a balloon of 5 m diameter.

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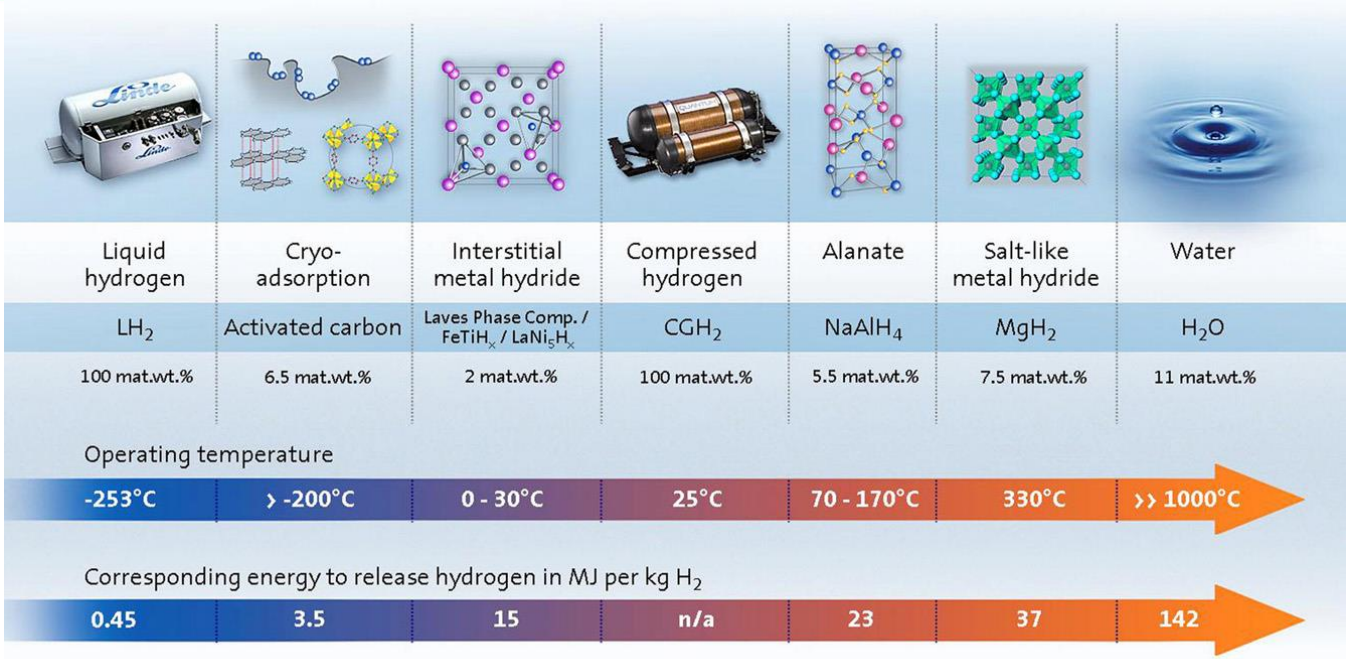
Hydrogen Storage



R. v. Helmolt, U. Eberle: J. Power Sources **165**, 833 (2007).

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

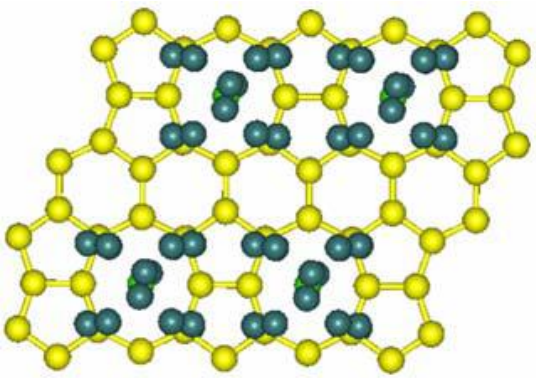
Solid State:
Physisorption
Chemisorption

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

… but it better be safe

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

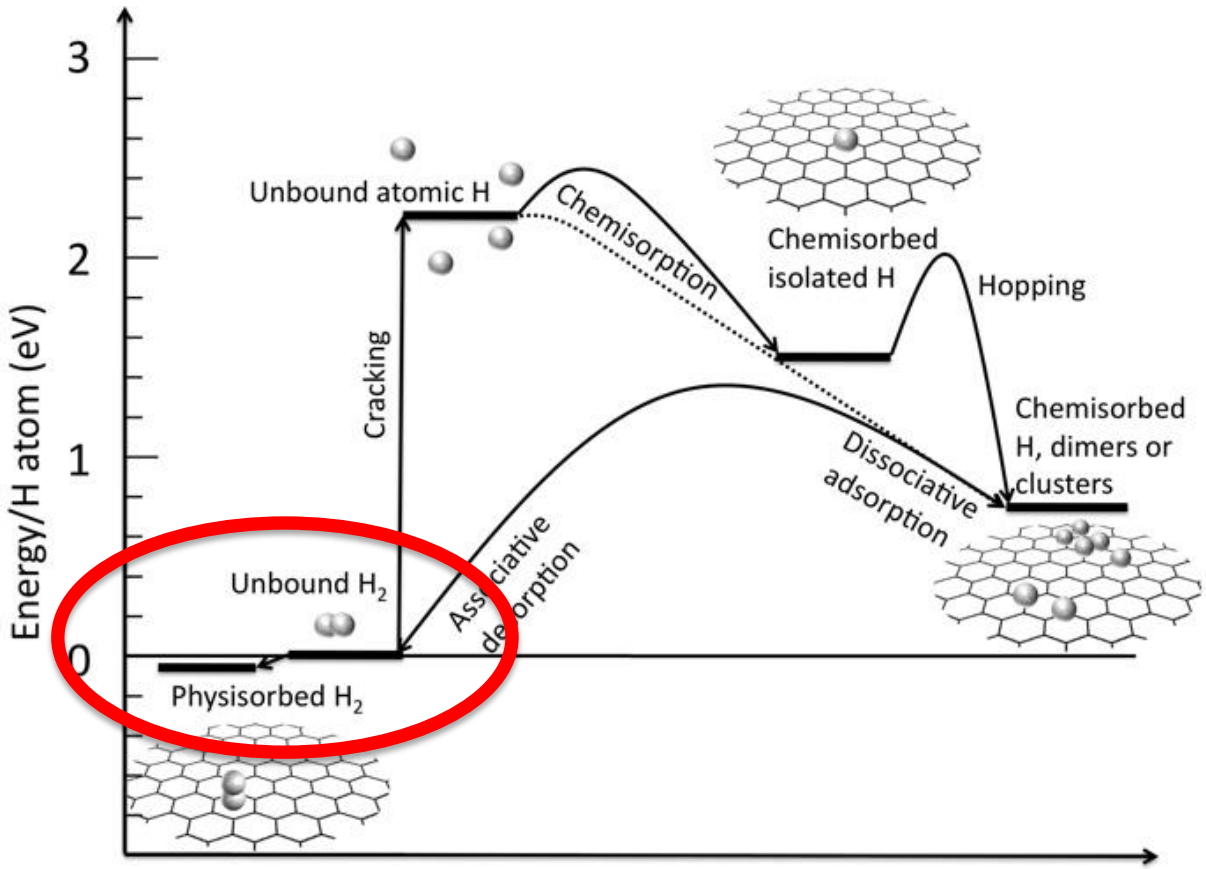


Yang et al., PRB 79 (2009) 075431

Graphene for hydrogen storage (2)

- To store 4 kg of H_2, assuming ρ_m = 10 wt%, we need 40 kg of graphene.
- Graphene surface area: ~ 2600 m^2/g.
- 40 kg of graphene cover ~10^8 m^2 or 10 km x 10 km.
- Assuming a layer distance of 1 nm, we can put 10^9 graphene layers in a stack of 1 m height.
- Then in 1 m^3 we have 10^9 m^2 graphene.
- Thus, 40 kg of graphene would fit into a 100 liter tank.

H storage in graphene



V. Tozzini and V. Pellegrini: Phys. Chem. Chem. Phys. **15** (2013) 80.

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  - Ti-functionalization
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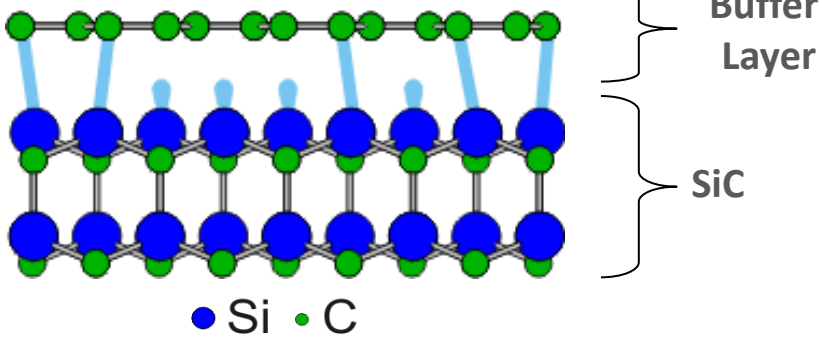
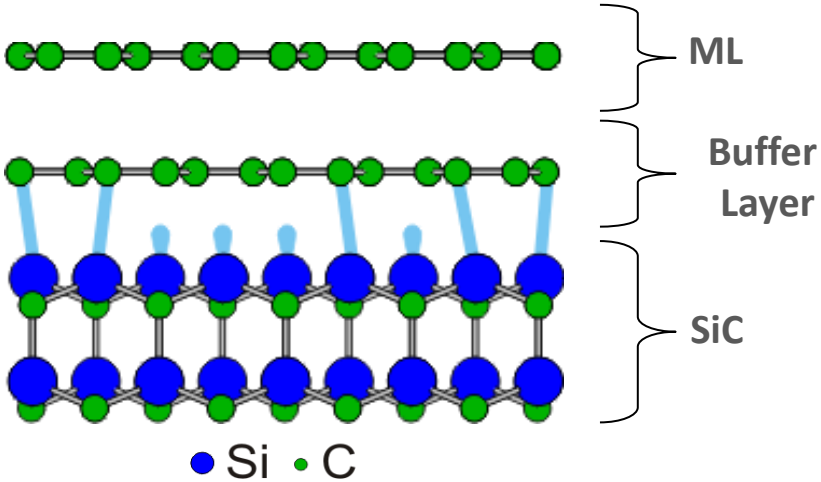
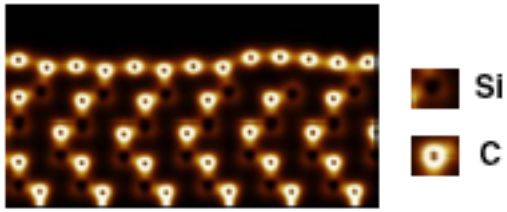
Graphene growth on SiC(0001)



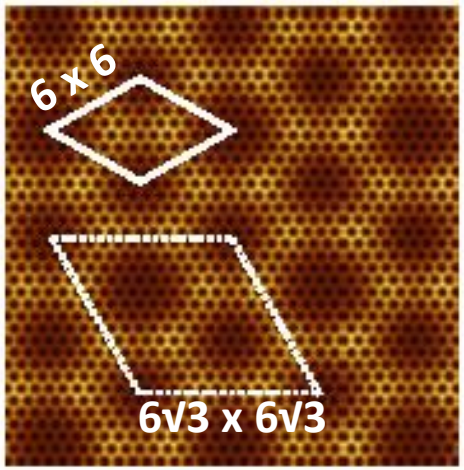


Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp^3 C-Si bonds.



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

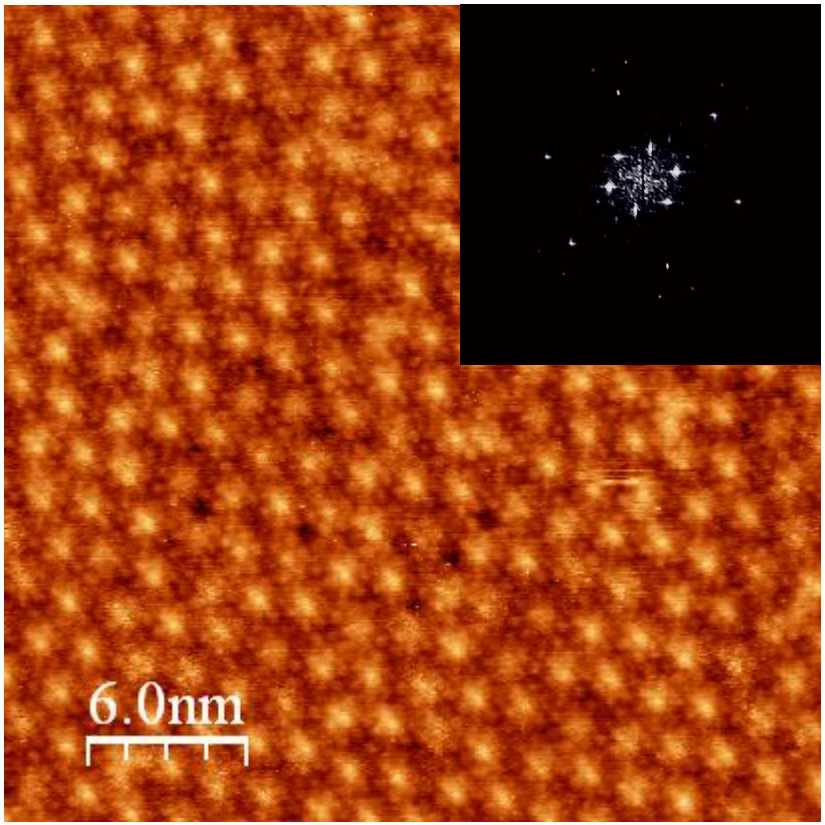
Theoretical Calculations



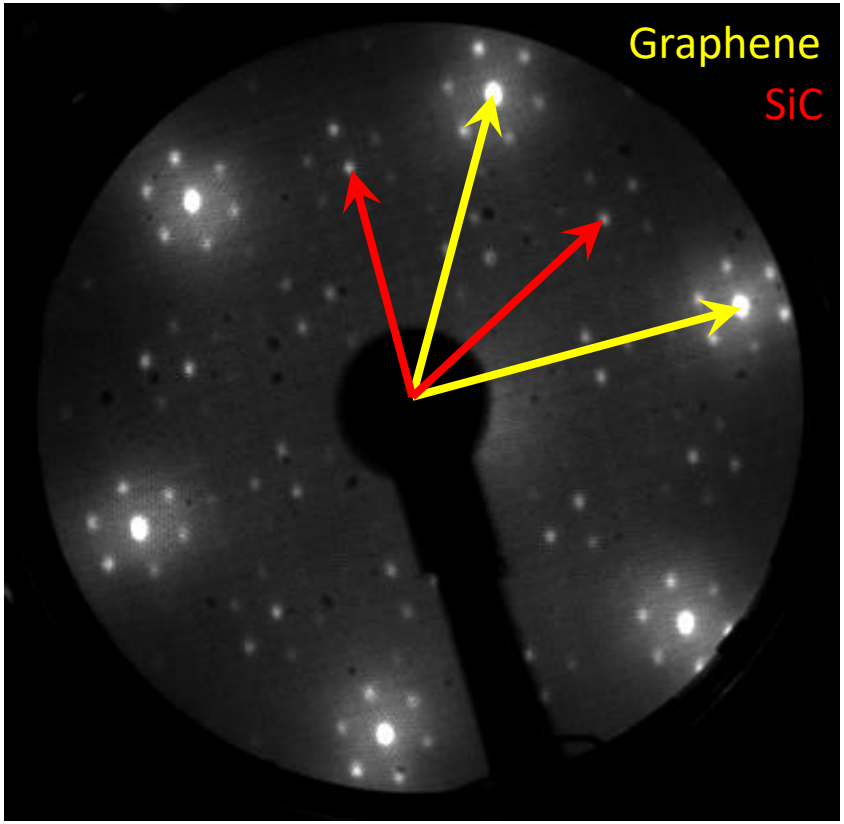
F. Varchon, et al., PRB 77, 235412 (2008).

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

6√3x6√3-Superstructure

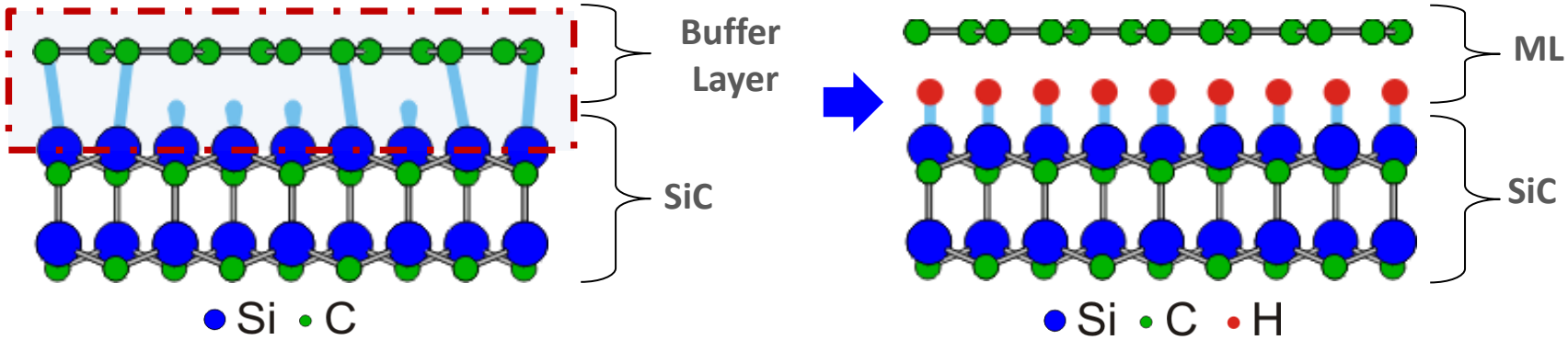


30 nm, 1V, 100 pA



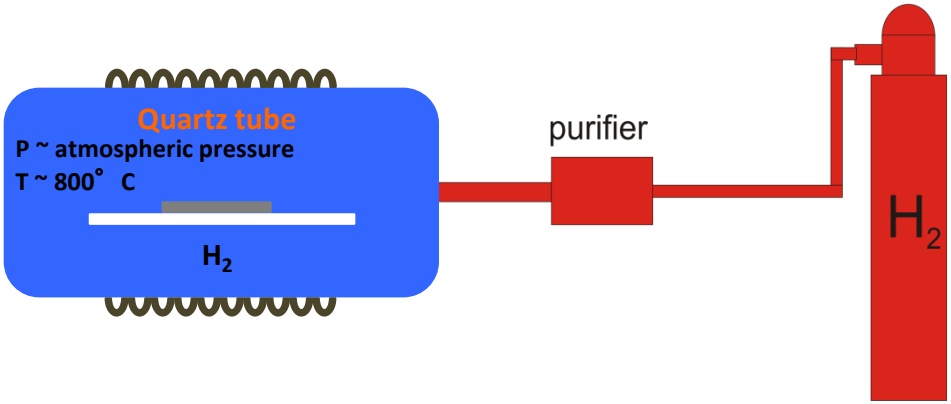
E= 75 eV

Hydrogen Intercalation



Buffer Layer (BL)

Quasi-free standing monolayer graphene (QFMLG)



C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009)

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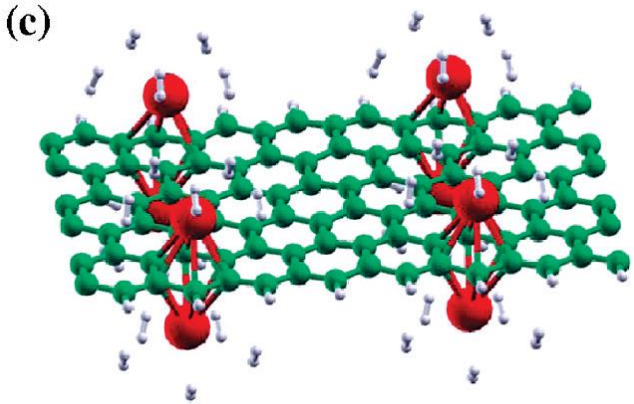
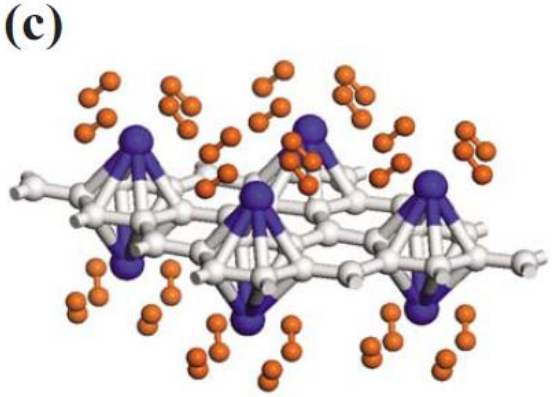
Functionalized Graphene

- 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)

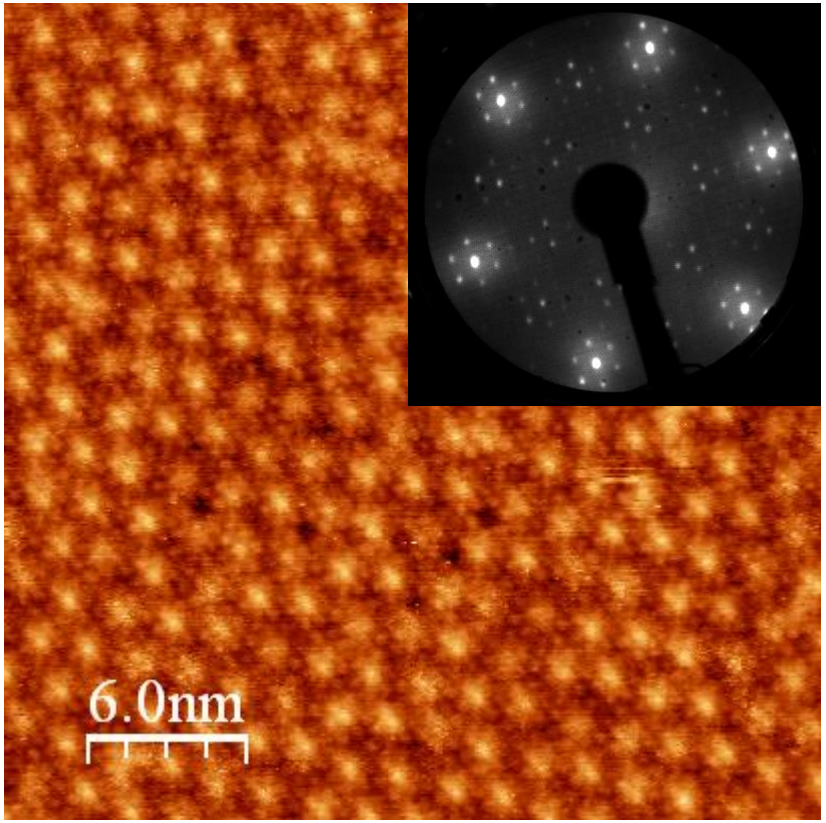


Lee et al., Nano Lett. 10 (2010) 793

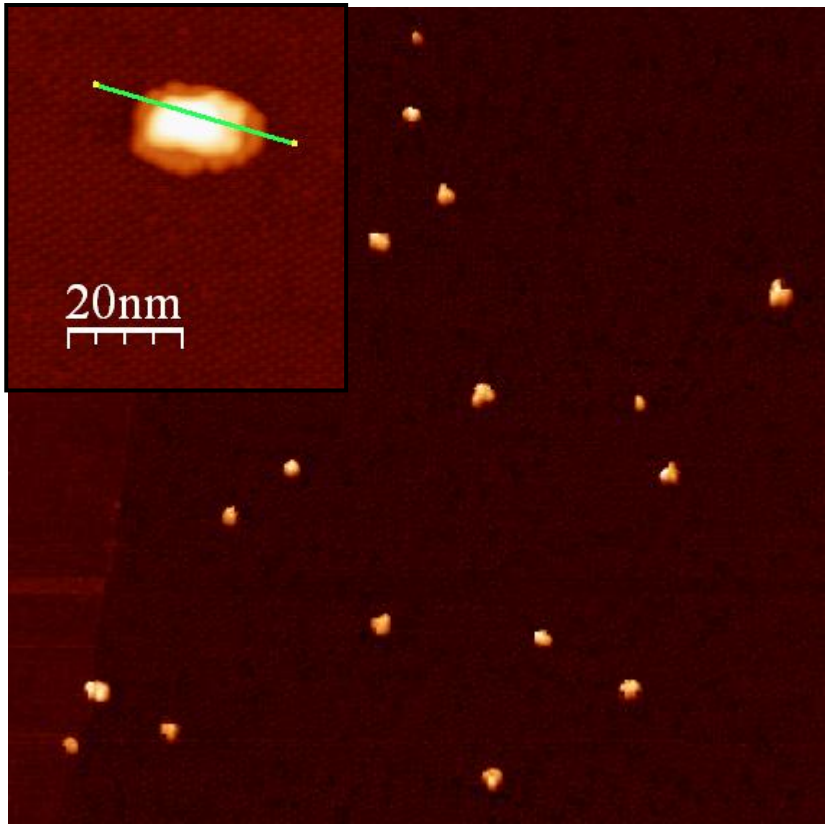


Durgen et al., PRB 77 (2007) 085405

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)

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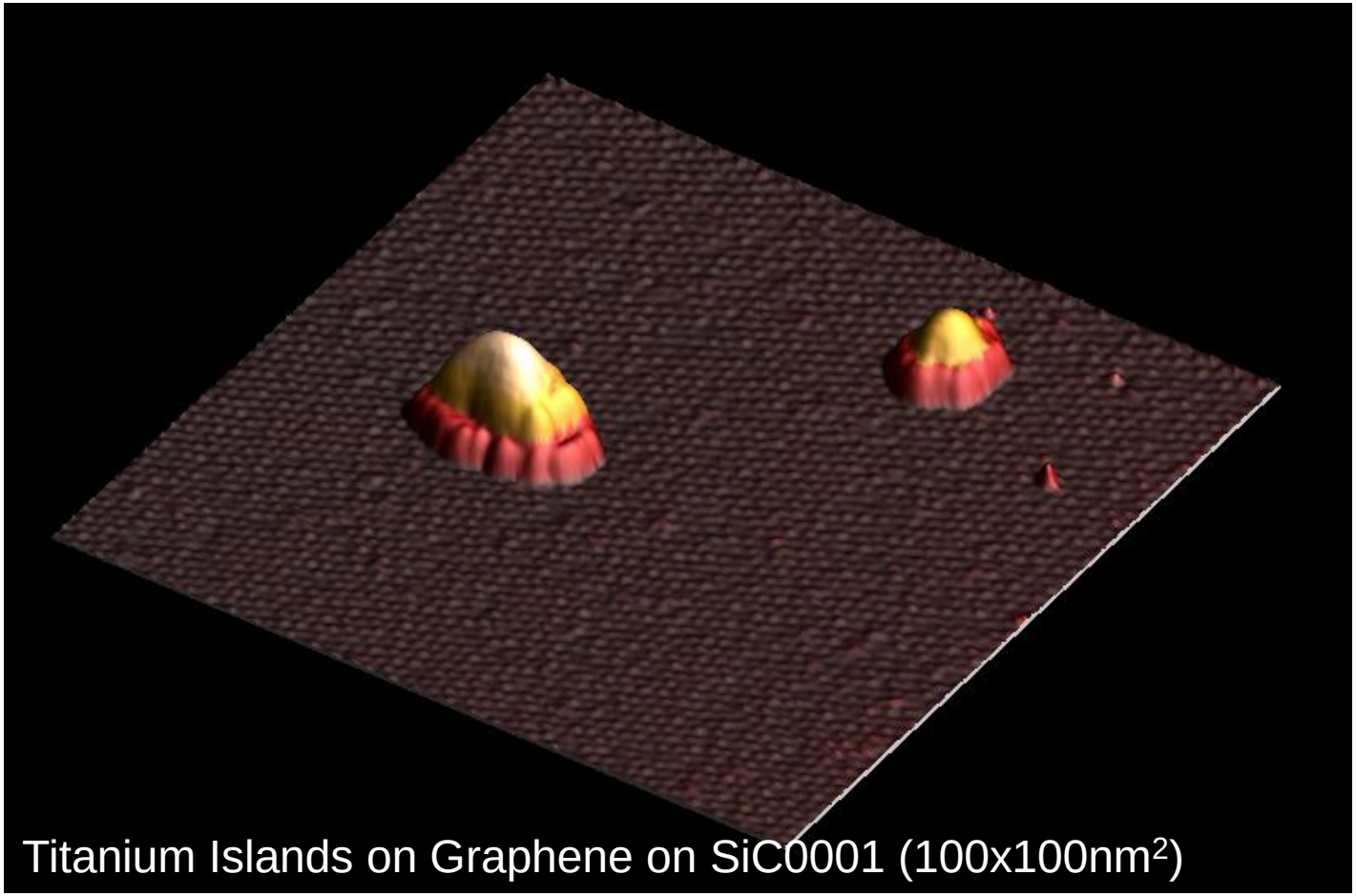
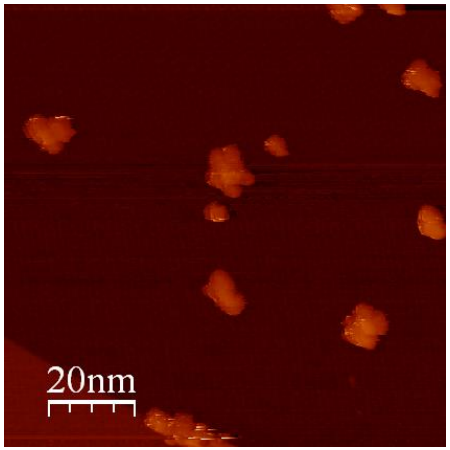
Titanium on graphene

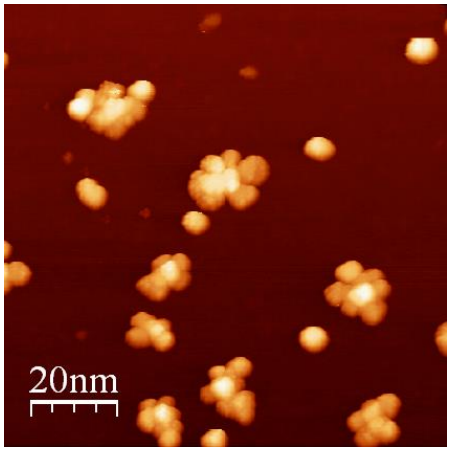


T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

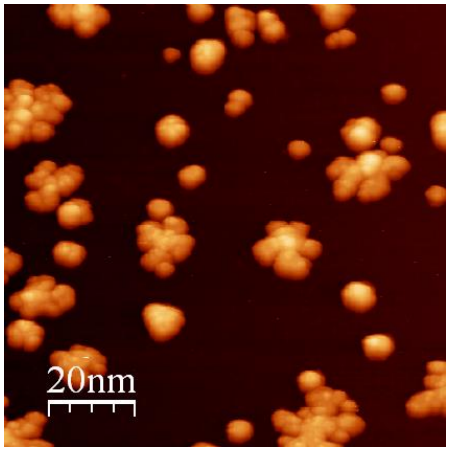
Titanium island growth



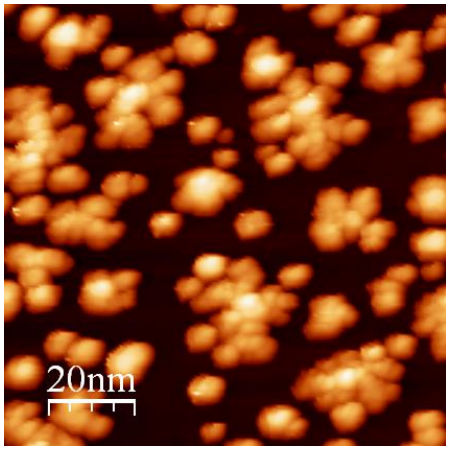
6% Coverage



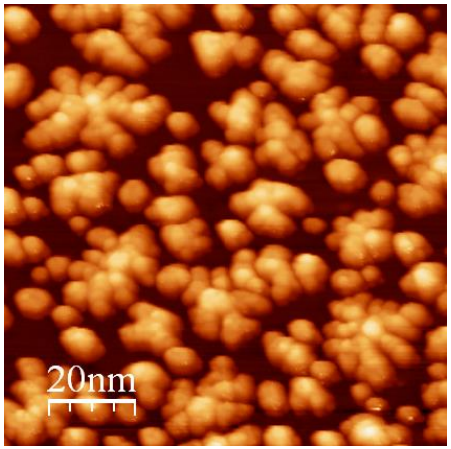
16% Coverage



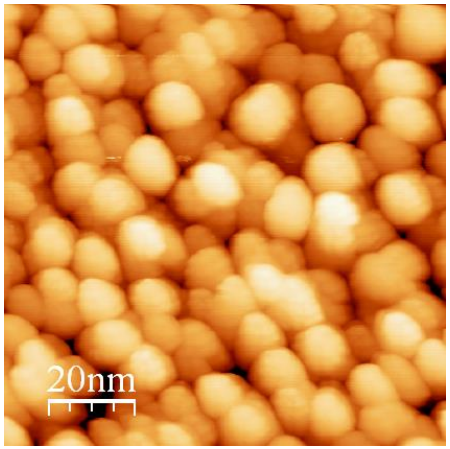
29% Coverage



53% Coverage



79% Coverage



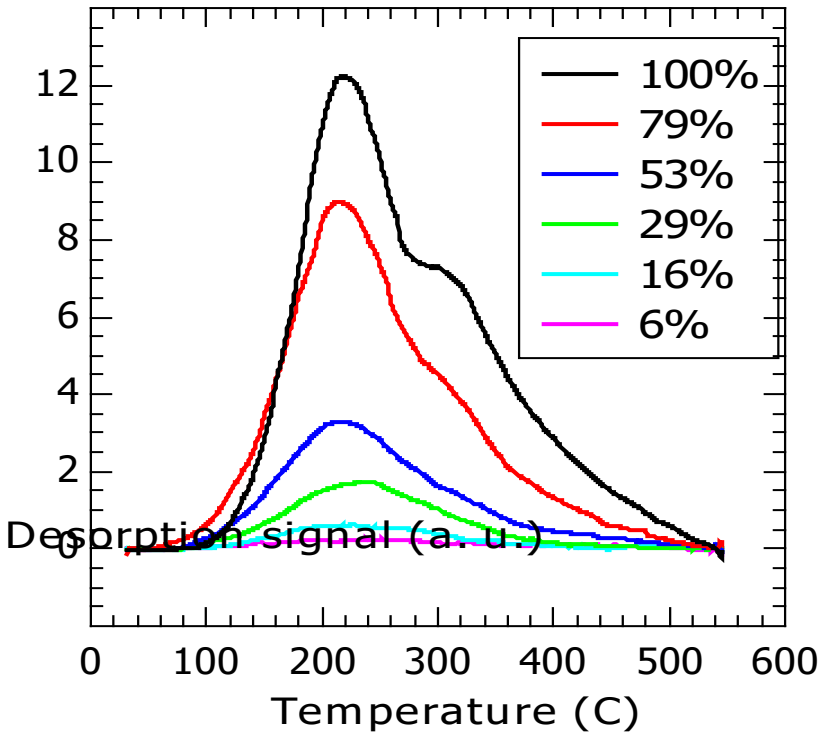
100% Coverage

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

Thermal desorption spectroscopy

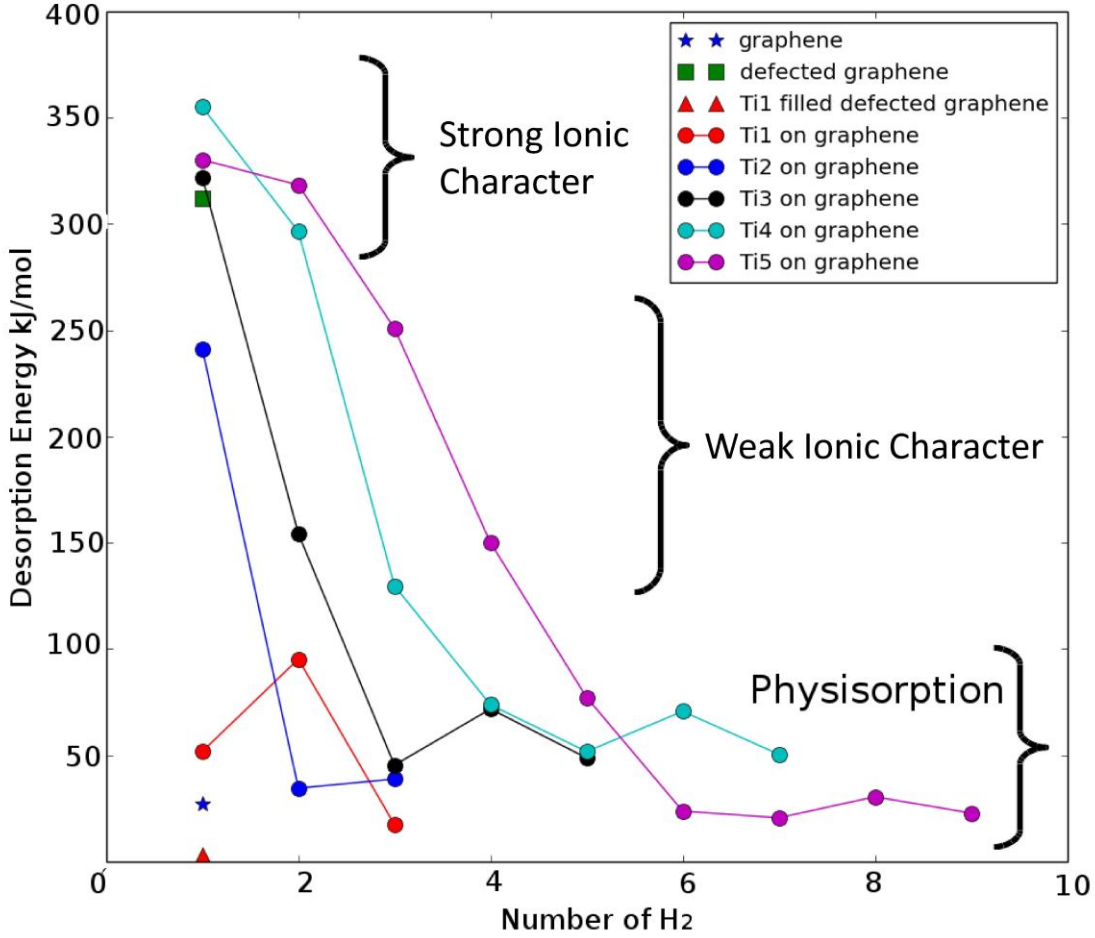
- Deposition of different amounts of Titanium
- Offering Hydrogen (D_2)
- ($1x10^{-7}$ mbar for 5 min)
- Heating sample with constant rate (10K/s) up to 550° C
- Measuring mass-sensitive desorption with a mass spectrometer

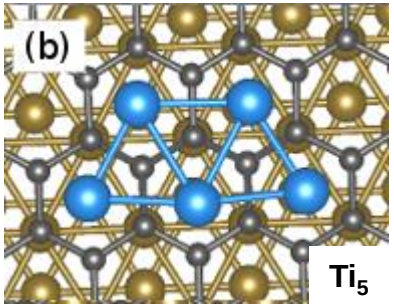
Spectra for different Ti-coverages

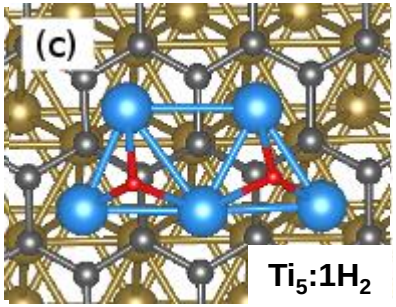


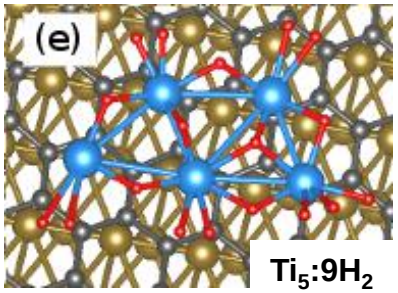
T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013)

Different bonding types



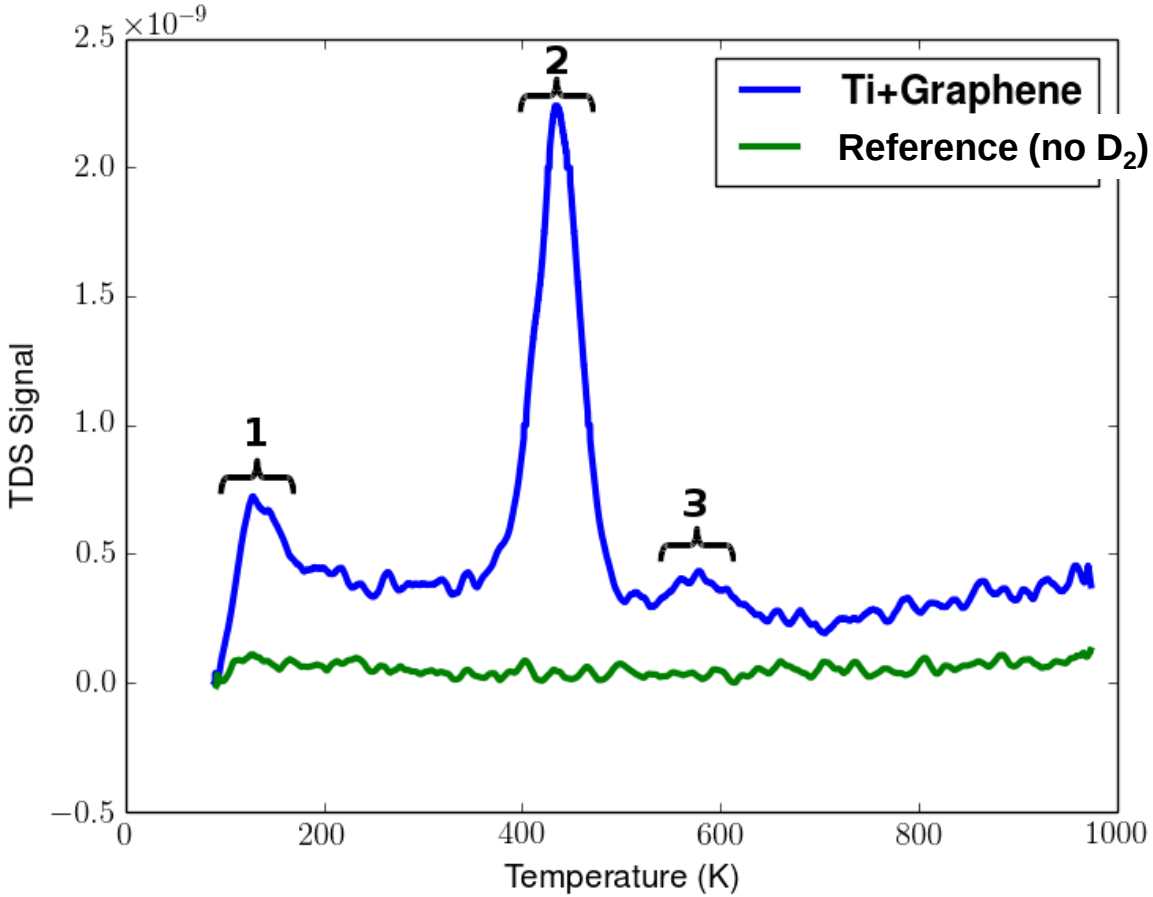






K. Takahashi *et al.*: J. Phys. Chem. C 120, 12974 (2016).

Thermal desorption spectroscopy



K. Takahashi *et al.*: J. Phys. Chem. C 120, 12974 (2016).

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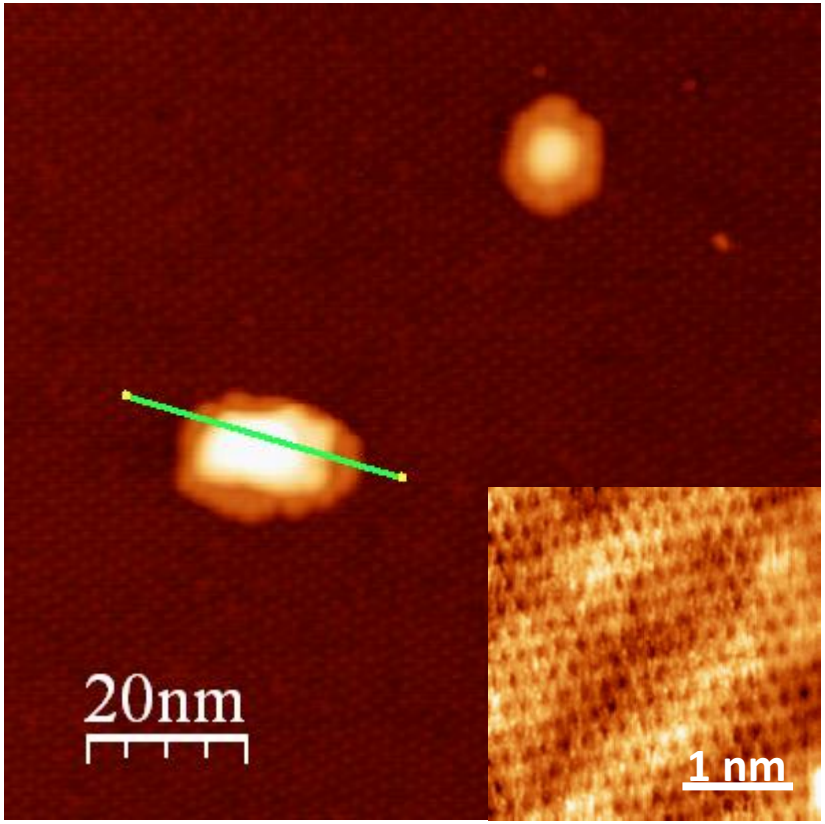
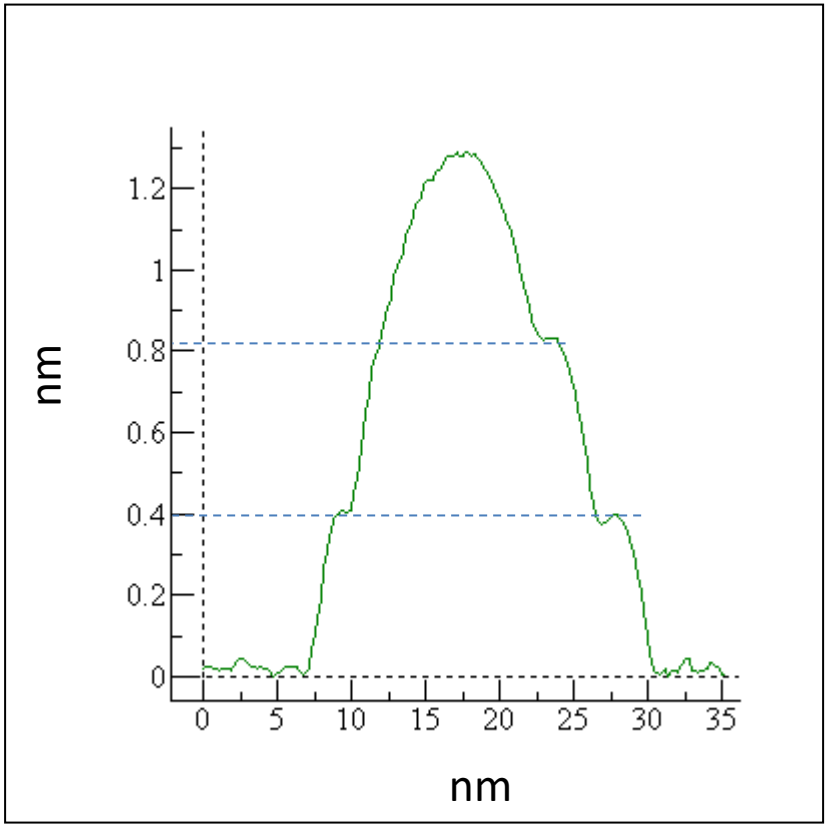
Forming of Islands



100 nm, 1 V, 82 pA



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

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]

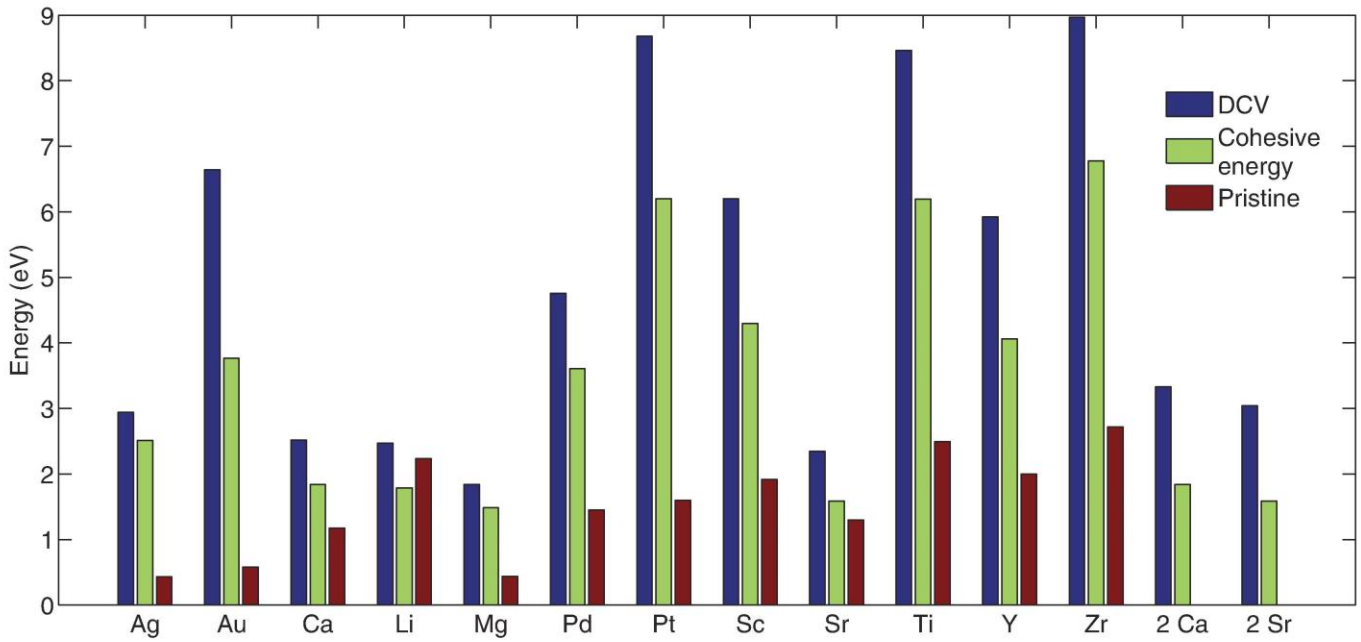
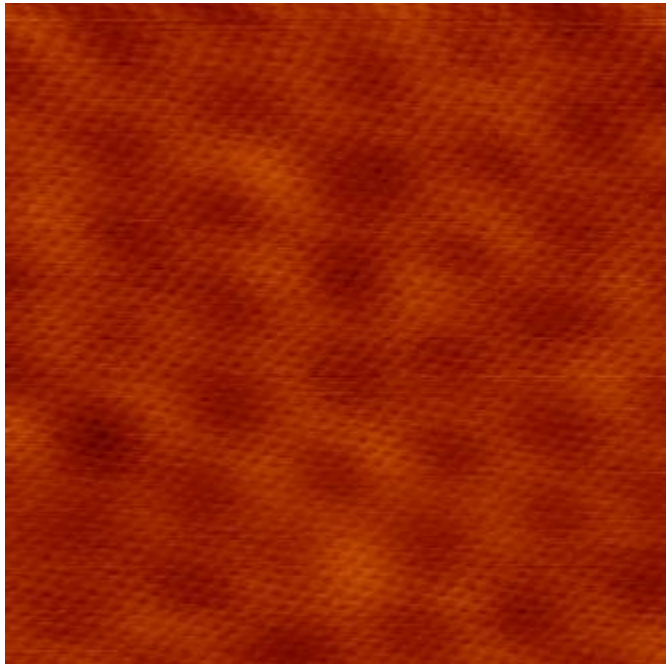


FIG. 1. (Color online) The binding energy of adatoms to graphene DCVs (blue), and pristine graphene (red), as well as the cohesive energy of the respective metal (green). Also included are the binding energies per adatom of two Ca and Sr ("2Ca" and "2Sr") adatoms with one on either side of the DCV.

DCV = Double Carbon Vacancy

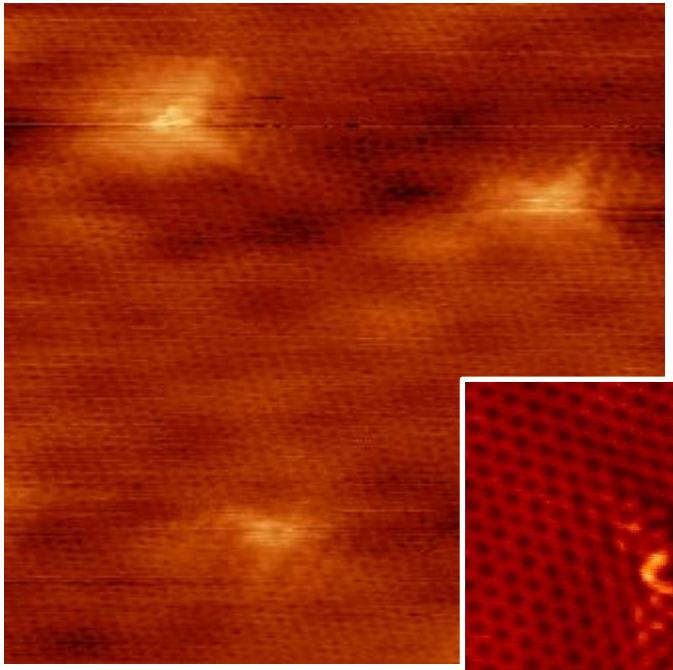
N_2 - sputtering of the graphene surface

Clean graphene surface



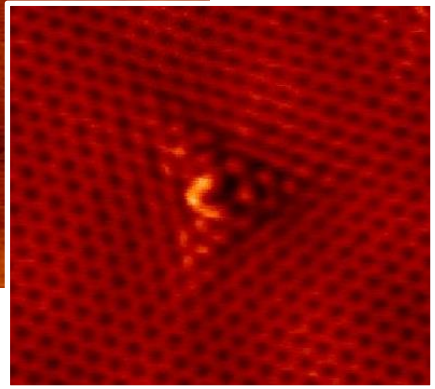
10x10 nm^2, 1V, 0.8nA

Sputtered 150s @100eV



10x10 nm^2, 1V, 0.8nA

200mV
200pA



Defects in the graphene film are expected to reduce the mobility of Ti-atoms and to lead to a larger number of smaller islands.

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

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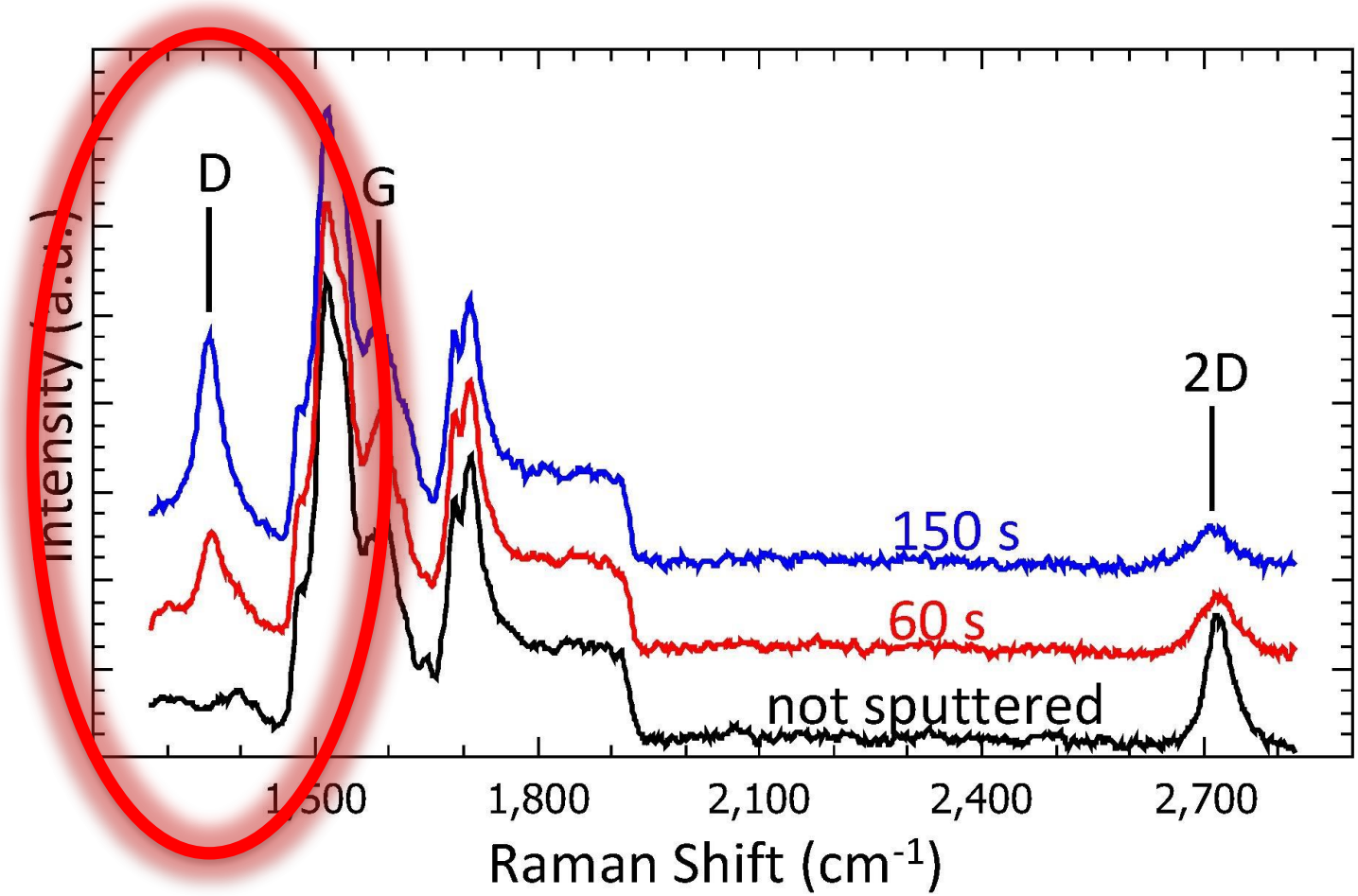
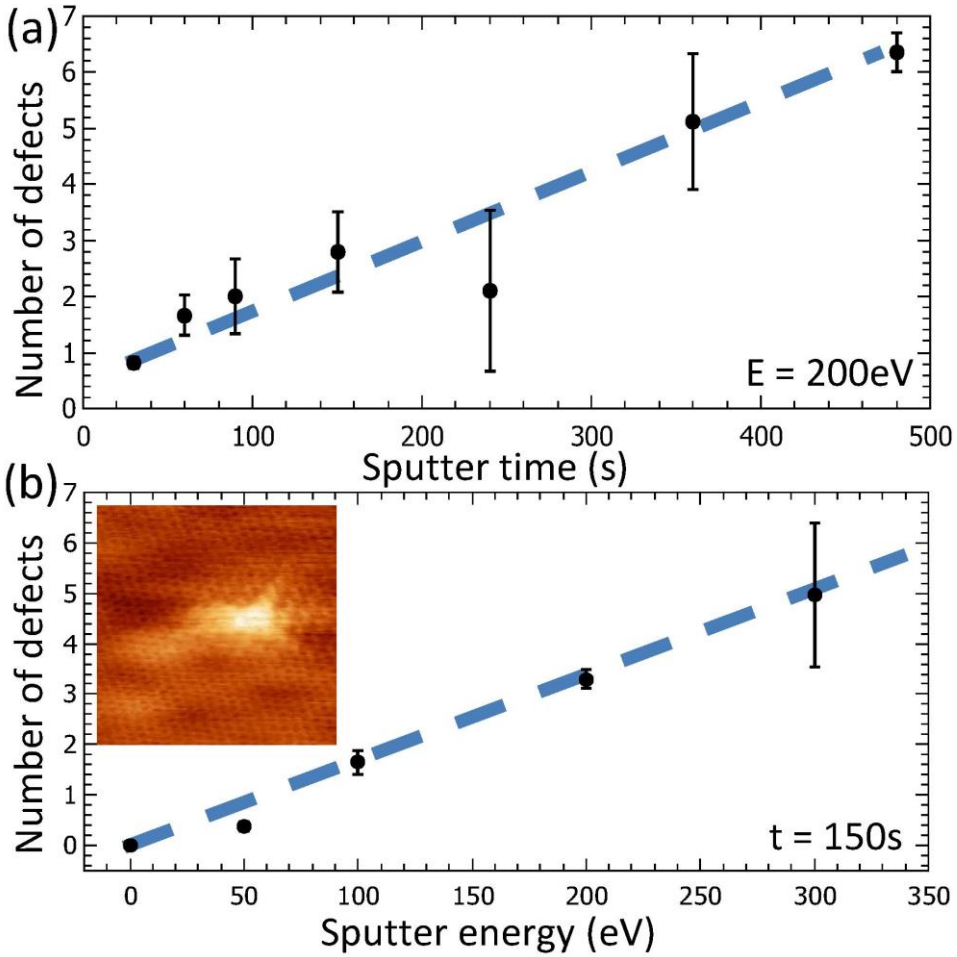
Raman



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

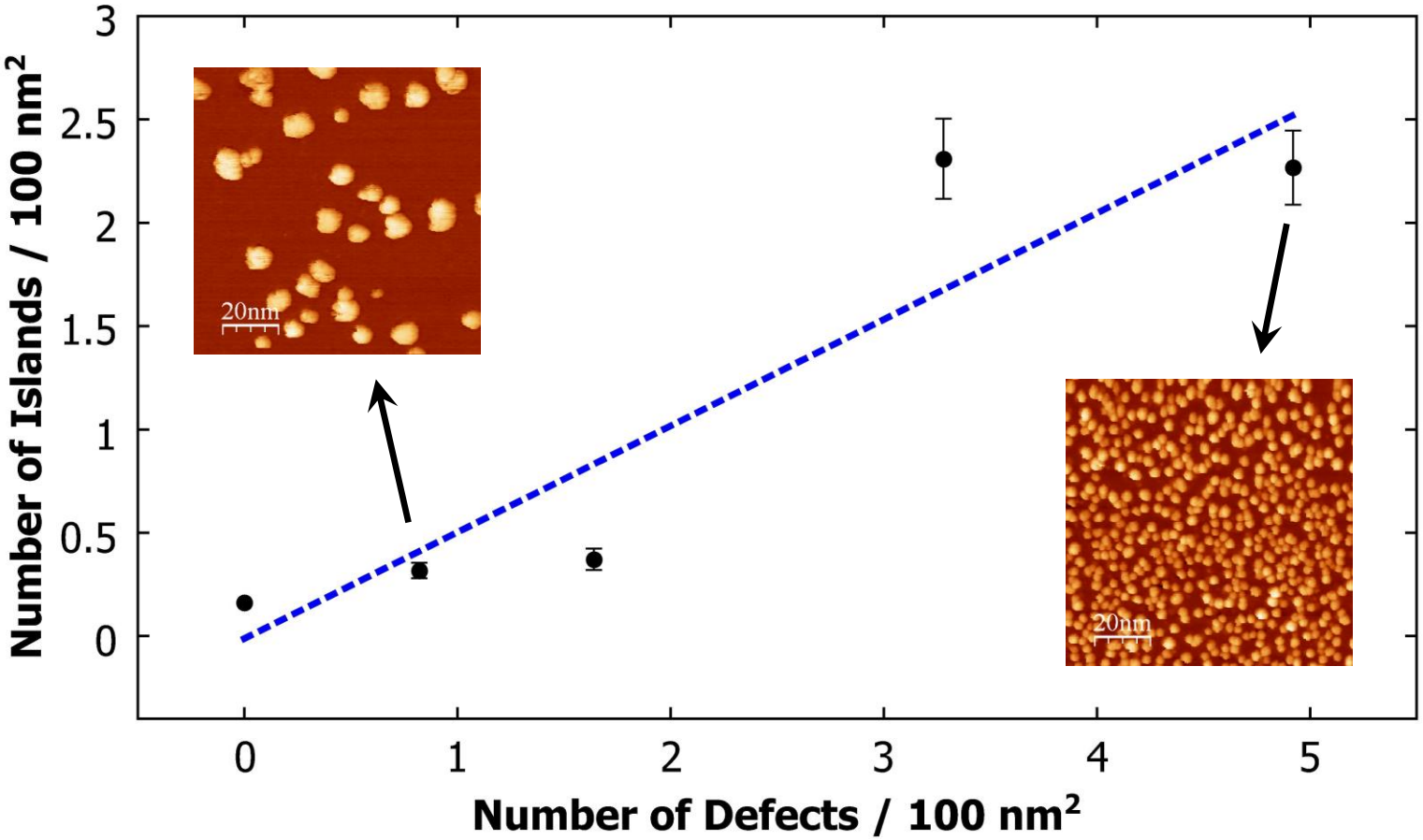
Distribution of defects



Average number of induced defects per 100nm^2

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

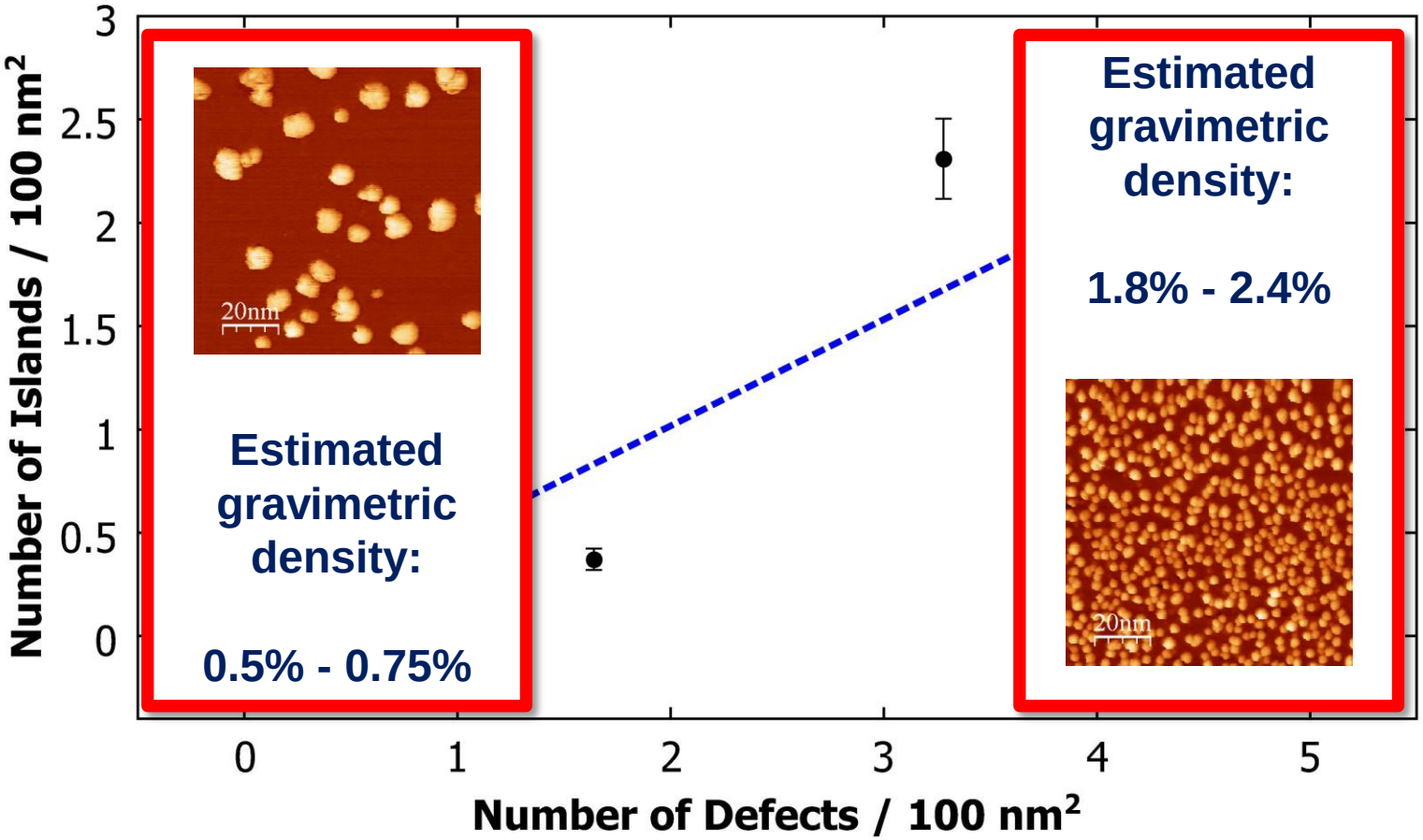
Average Number of Islands per 100 nm^2



Sputtered 150 s and
Deposition of 0.5 ML Titanium

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

Higher number of defects leads to smaller Ti islands

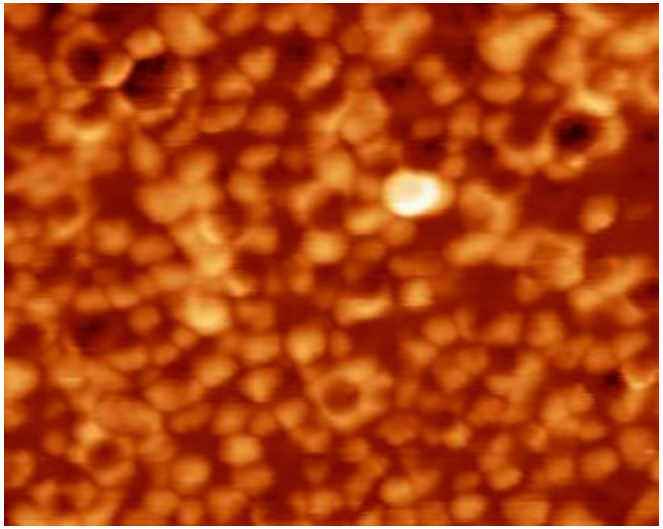


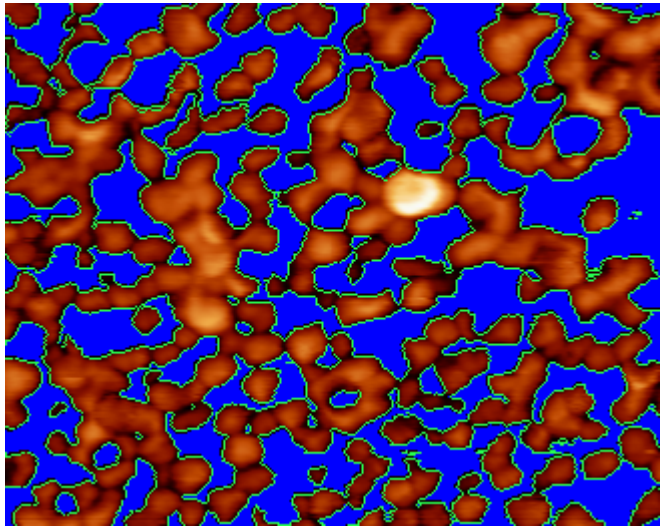
T. Mashoff *et al.*: Appl. Phys. Lett. **105**, 083901 (2015).

Amorphous Graphene

Ti deposition 0.55ML

51nm x 64nm total area 3259 nm^2

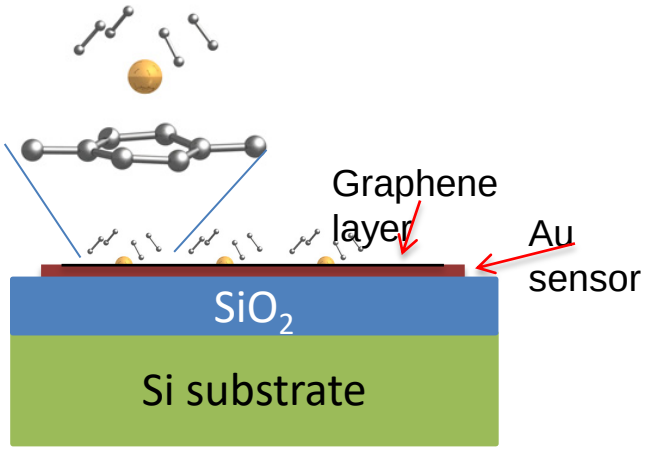




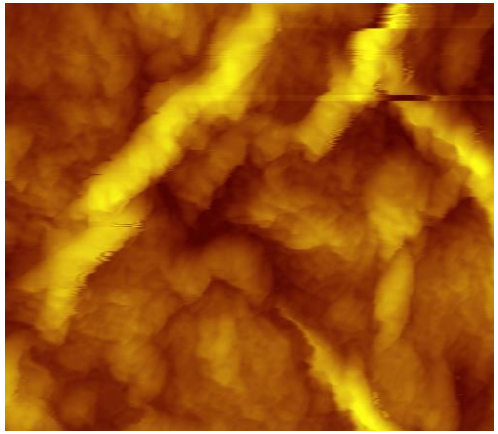
Ti grains
area; 2375 nm^2 (73.8%)
volume; 693 nm^3
average height: 0.29 nm
number of grains:
6.6 per 100nm^2
avg. diameter: 3.8 nm

Collaboration with Prof. Dongmok Whang
SKKU Advanced Institute of Nanotechnology

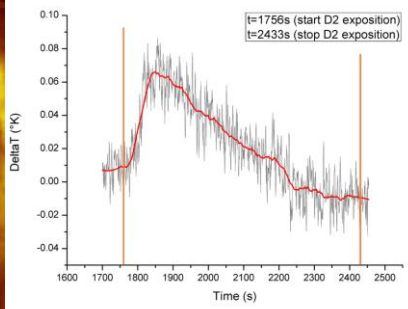
Calorimetry of Ti-functionalized SLG



- ✓ **Our system: Single Layer Graphene (SLG) functionalized with Ti**
- ✓ **Measurement idea: detect the heat release during deuterium loading with a gold film thermometer**
- ✓ **Methodology: tailored Wheatstone bridge with lock-in signal acquisition**
- ✓ **Sensitivity: $\Delta T \approx 0.01$ K**



STM image of SLG on gold



Thermal signal during Hydrogen loading.
Ti coverage 100%, $P(D_2) = 10^{-7}$ mbar

	Ti (ML)	E_d/molecule (eV)	H_r (μJ)	
		TDS	calorimetry	TDS
$G3_{(1)}$	12.4	1.32 ± 0.07	23.4 ± 4.7	21.8 ± 1.3
$G3_{(2)}$	16.6	1.24 ± 0.09	58 ± 12	53.8 ± 4.3

Calorimetric results summary

L. Basta: Master thesis, Università di Pisa (2017).

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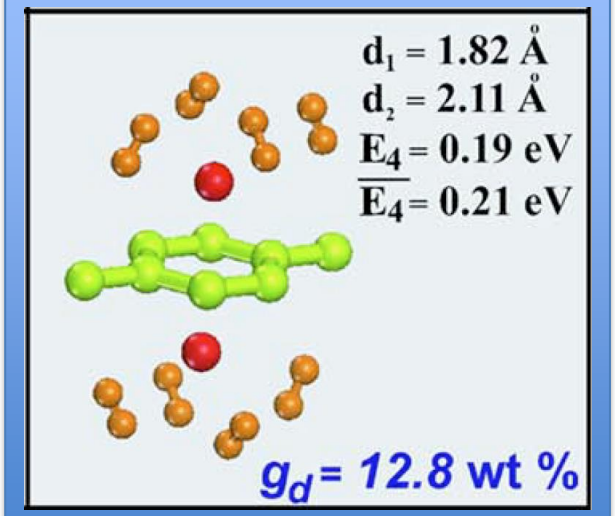
Outline

- Introduction to Hydrogen Storage
- Epitaxial Graphene
- Hydrogen Storage by Functionalization
  - Ti-functionalization
  - Li-functionalization

Li on Graphene: Motivation

Hydrogen Storage

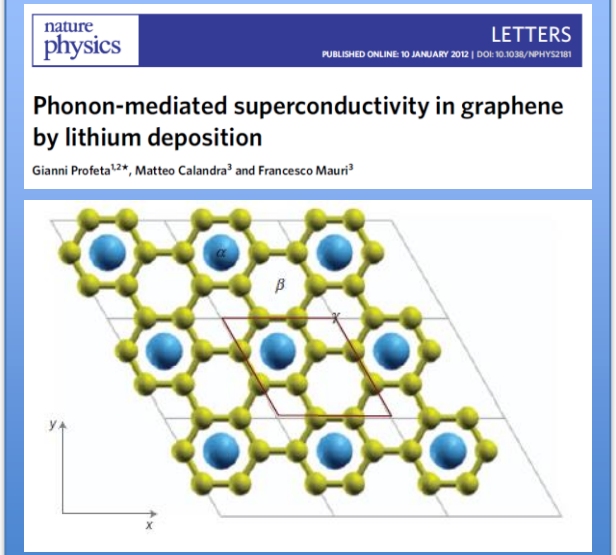


C. Ataca *et al.*,
Appl. Phys. Lett. 93 (2008) 043123.

Battery Technology

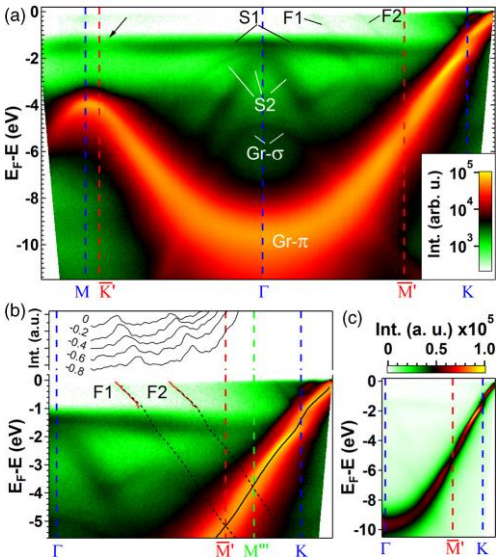
New Graphene
Lithium-Air Batteries

Superconductivity

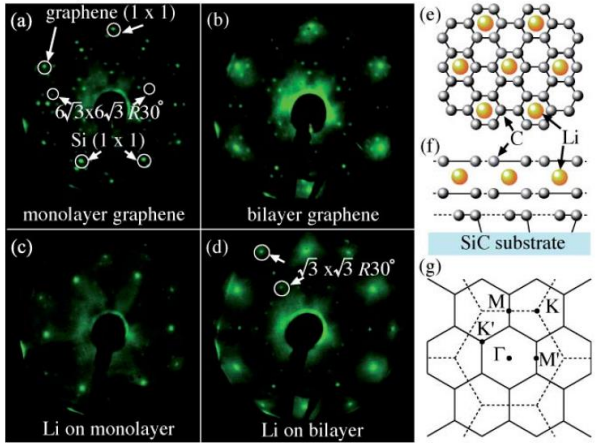


G. Profeta *et al.*,
Nat. Phys. 8 (2012) 131.

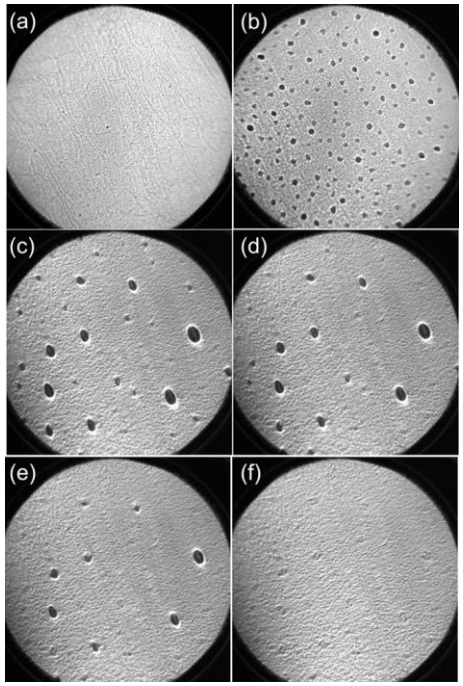
Li-intercalation



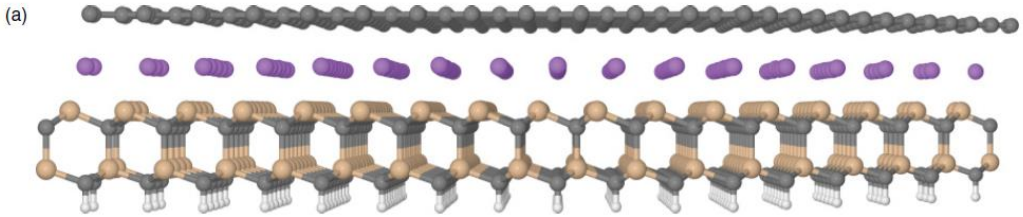
F. Bisti *et al.*,
PRB 91 (2015) 245411.



K. Sugawara *et al.*,
AIP Advances 1 (2011) 022103.

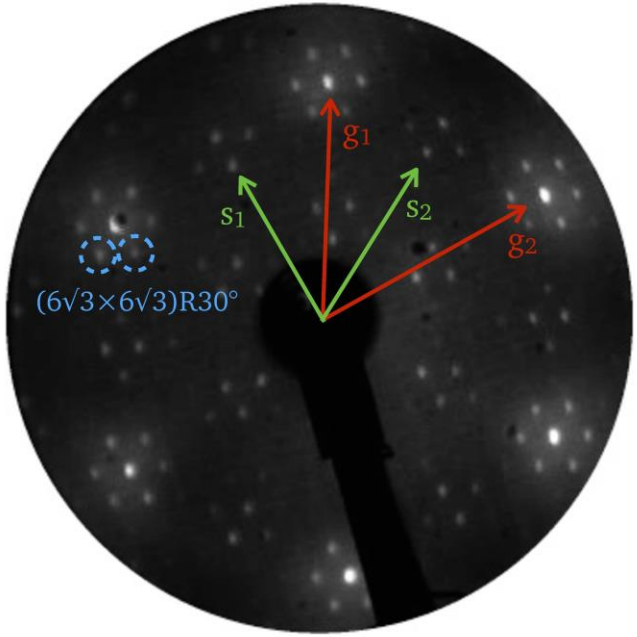


C. Virojanadara *et al.*,
PRB 82 (2010) 205402.



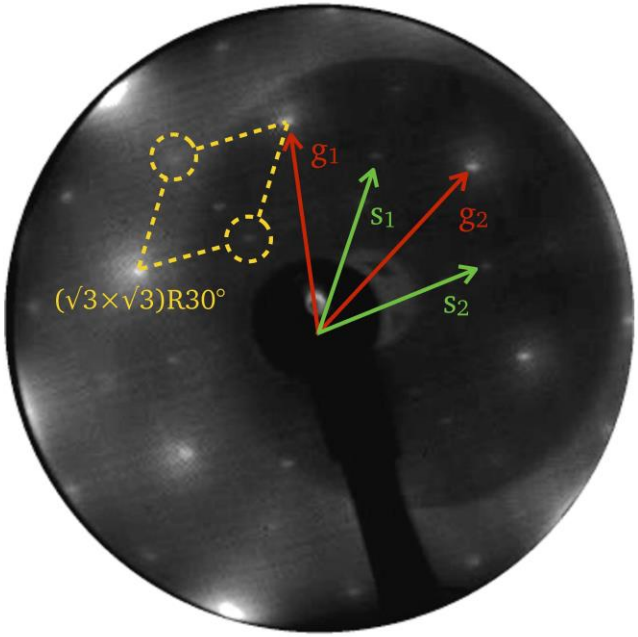
I. Deretzis *et al.*, PRB 84 (2011) 235426.

LEED



0 ML Li
$6\sqrt{3} \times 6\sqrt{3}\ R30°$

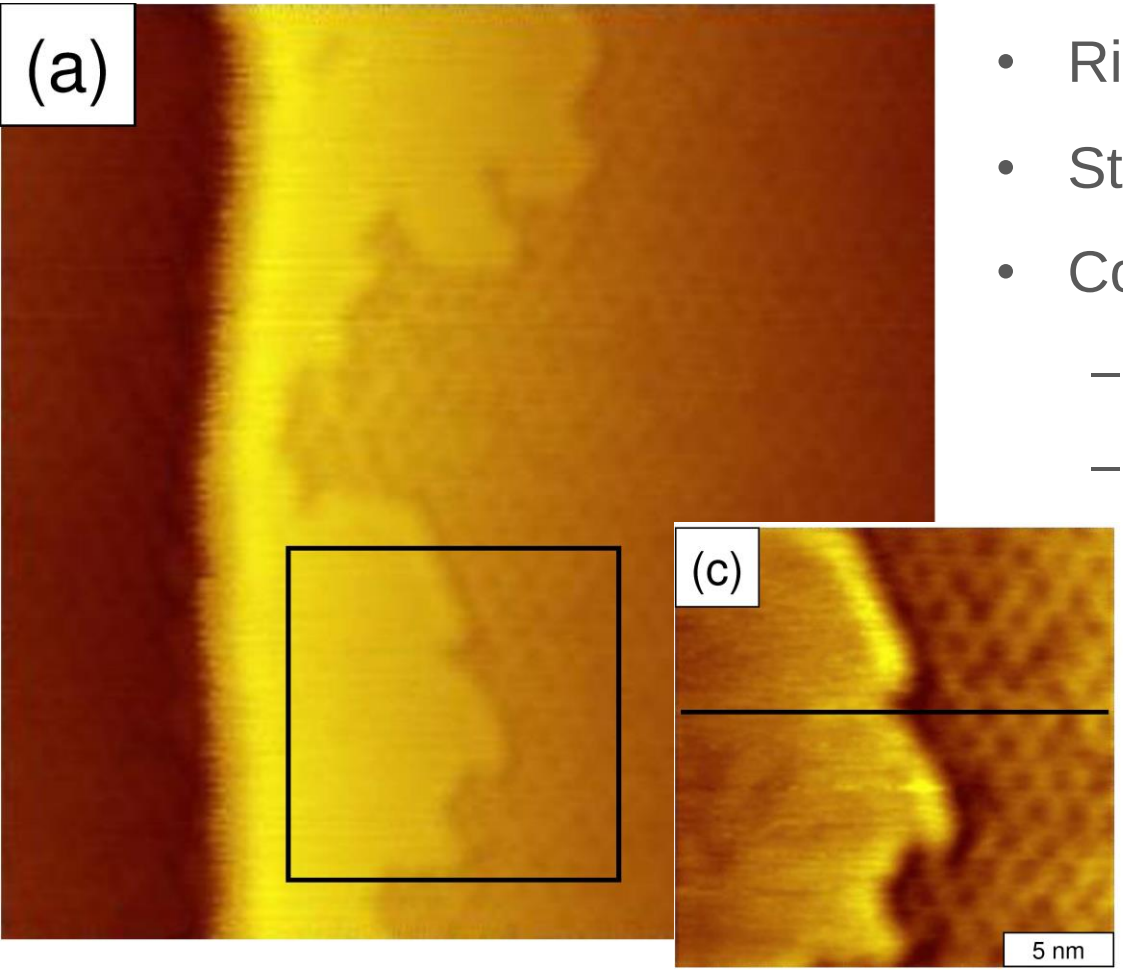
0.28 ML Li
1×1



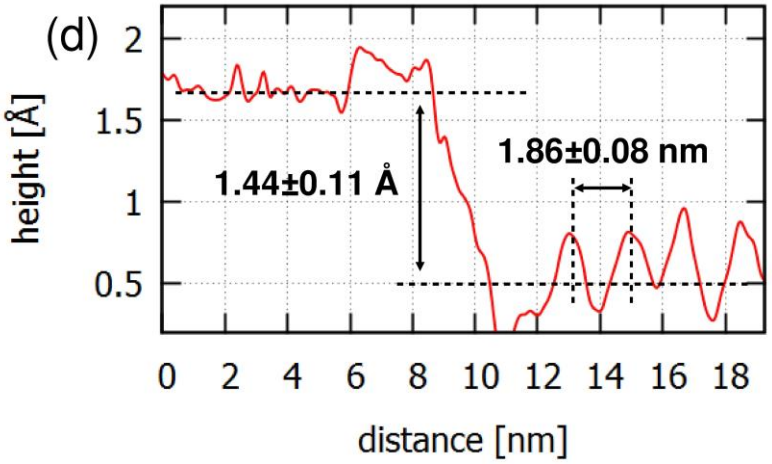
0.56 ML Li
$\sqrt{3} \times \sqrt{3}\ R30°$

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

0.031 ML Li on EMLG



- Right: $6\sqrt{3}$, left: not.
- Step height: 1.44 Å
- Corrugation:
  - Right: 0.45 Å (EMLG)
  - Left: 0.22 Å



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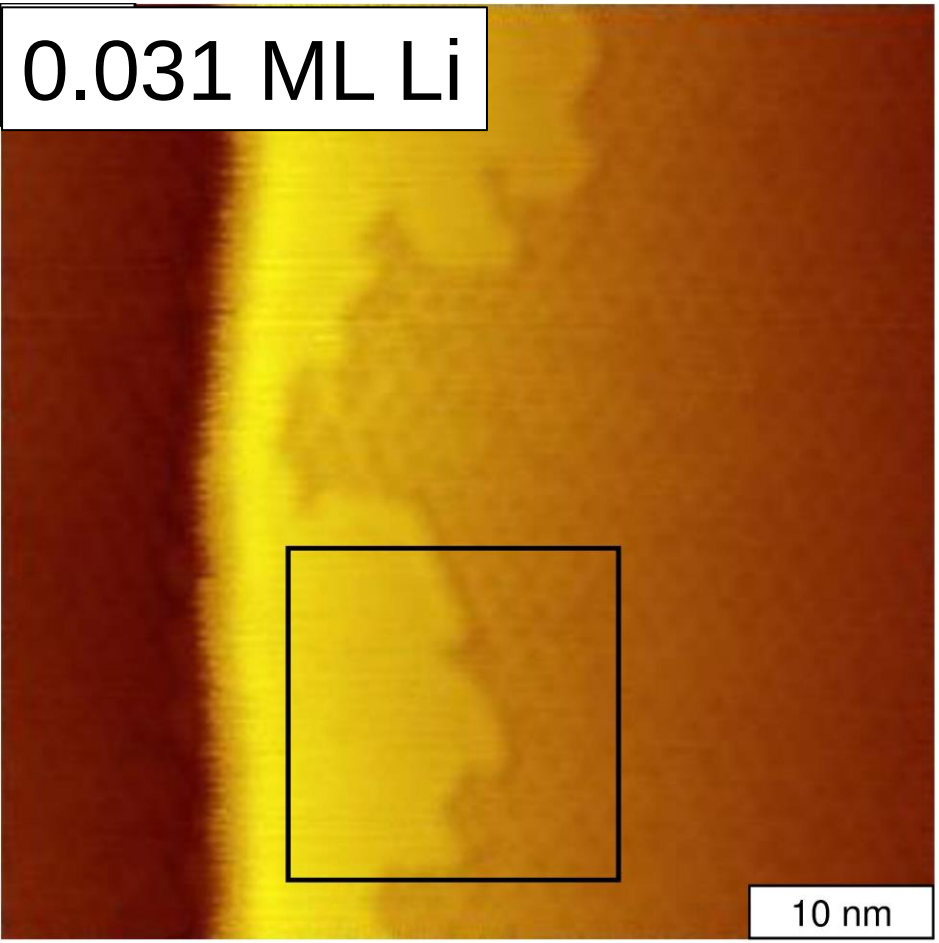
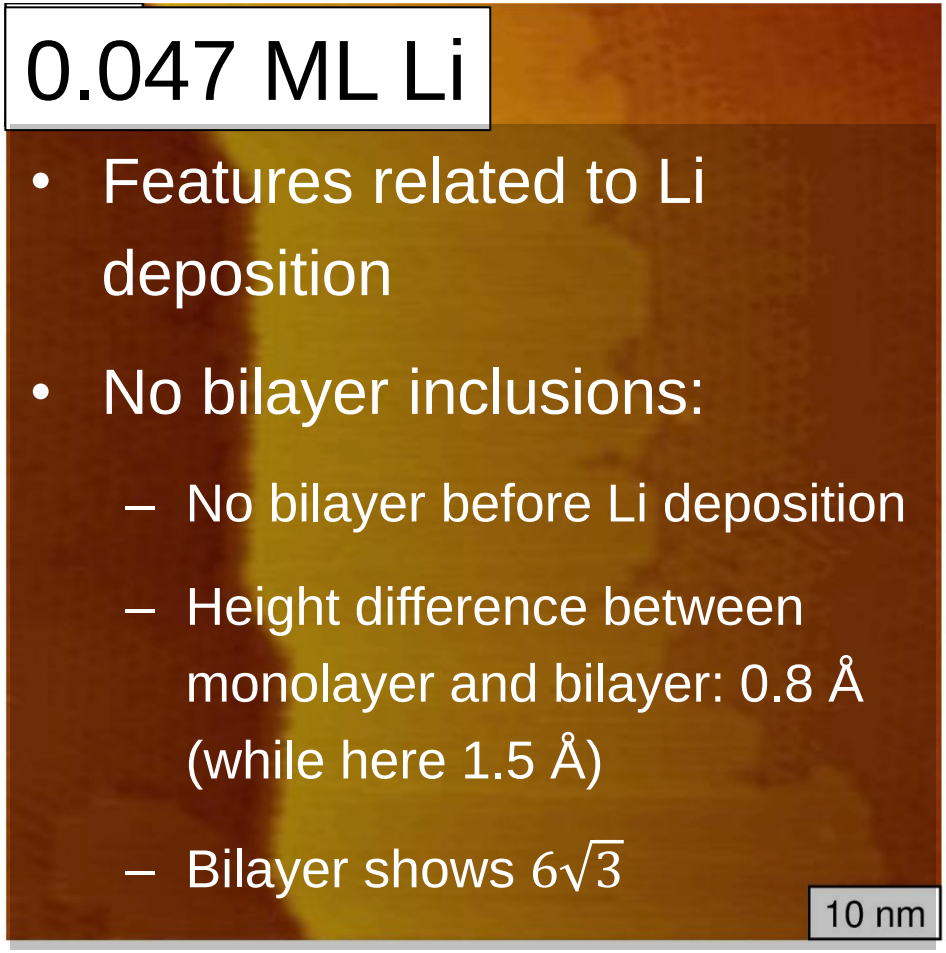
0.031 ML Li on EMLG

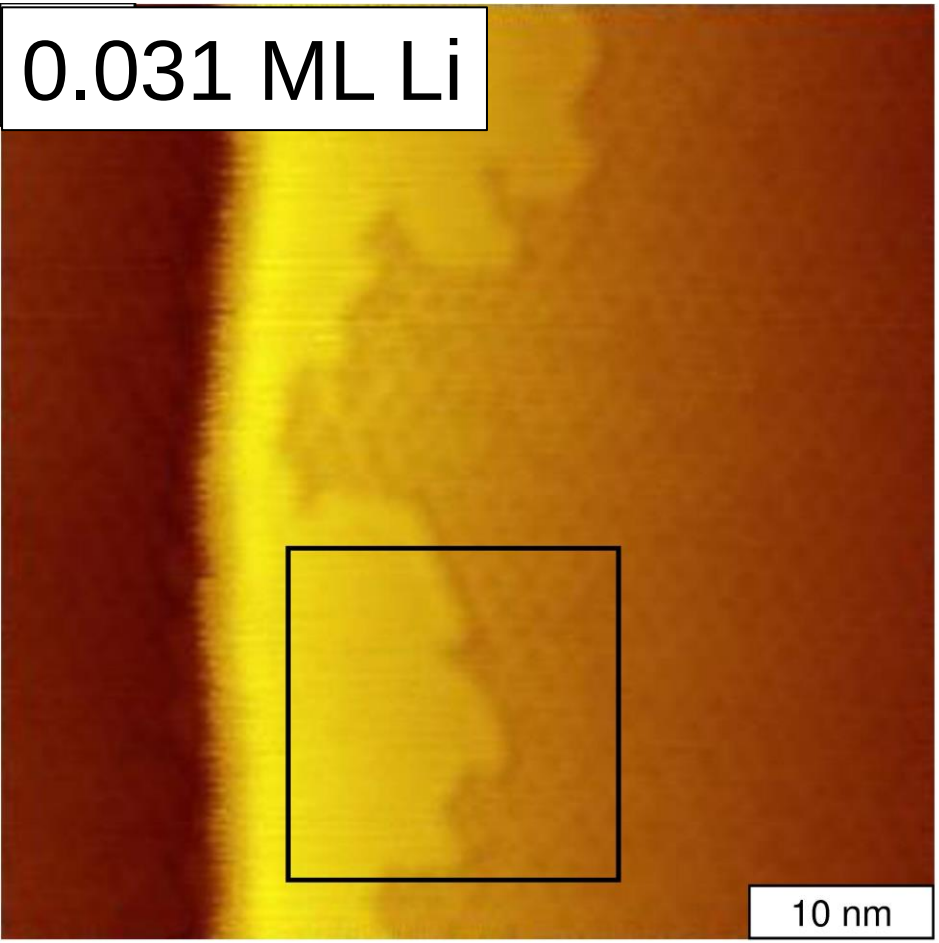


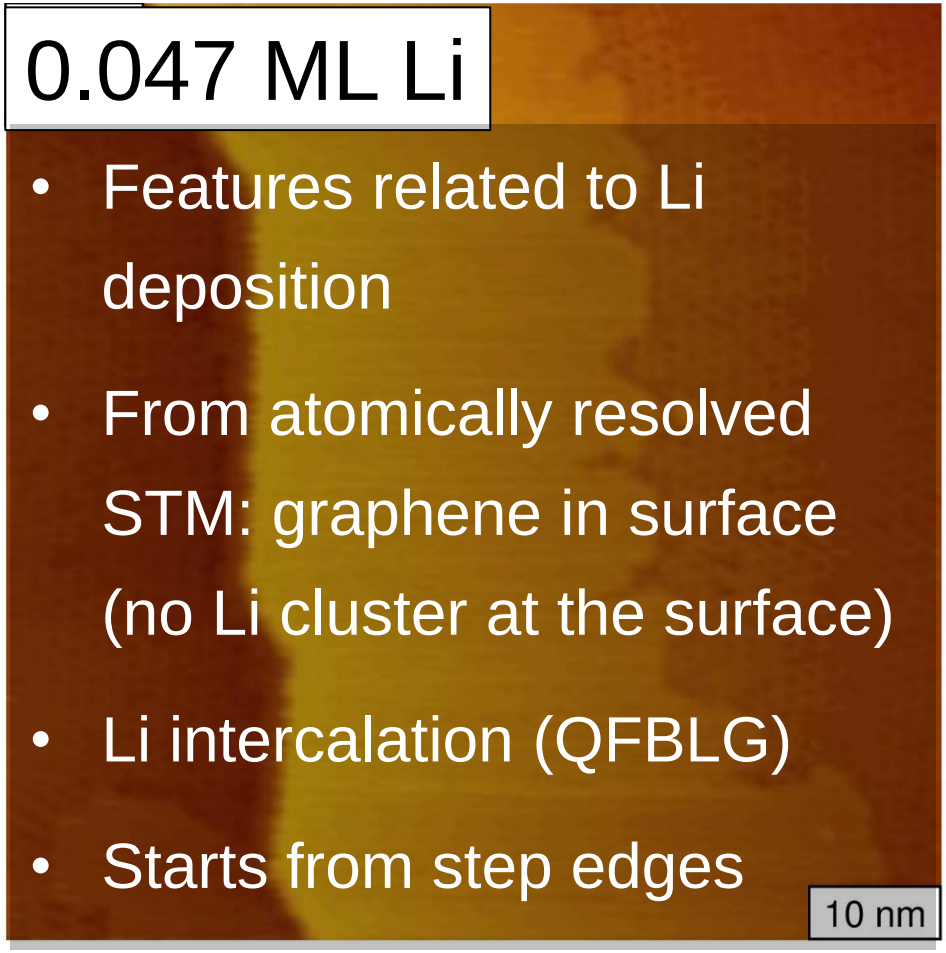


- Features related to Li deposition
- No bilayer inclusions:
  - No bilayer before Li deposition
  - Height difference between monolayer and bilayer: 0.8 Å (while here 1.5 Å)
  - Bilayer shows $6\sqrt{3}$

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

0.031 ML Li on EMLG

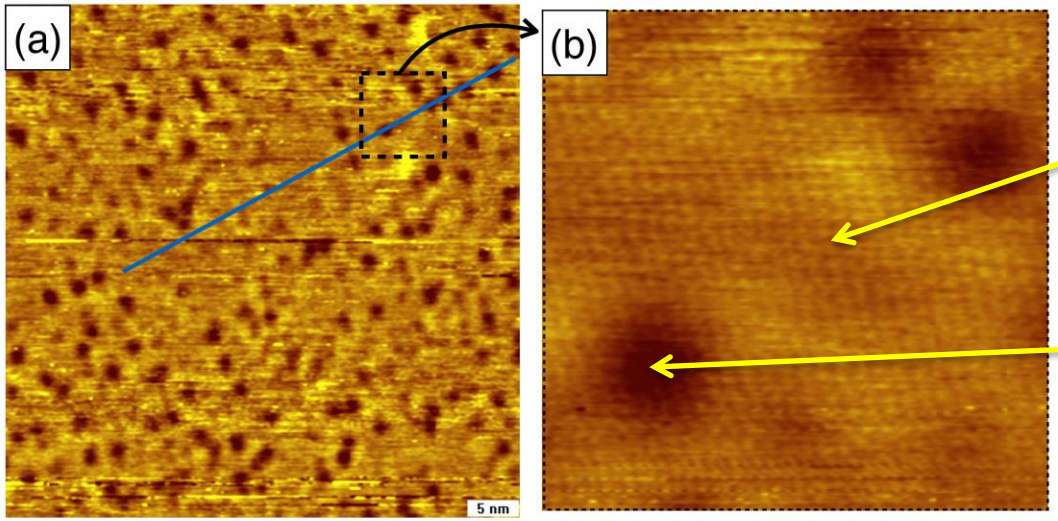


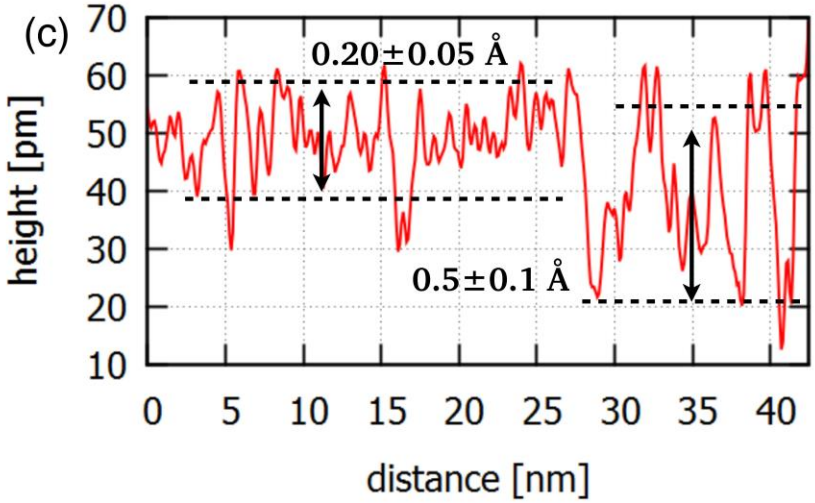


- Features related to Li deposition
- From atomically resolved STM: graphene in surface (no Li cluster at the surface)
- Li intercalation (QFBLG)
- Starts from step edges

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

0.28 ML Li on EMLG



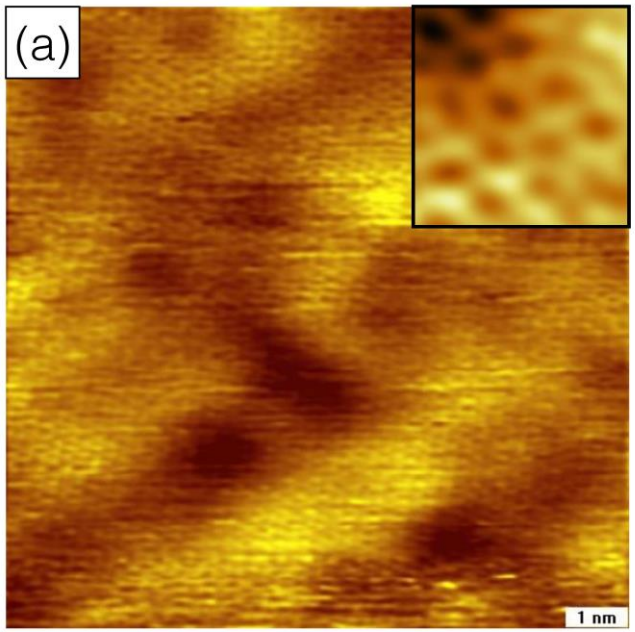


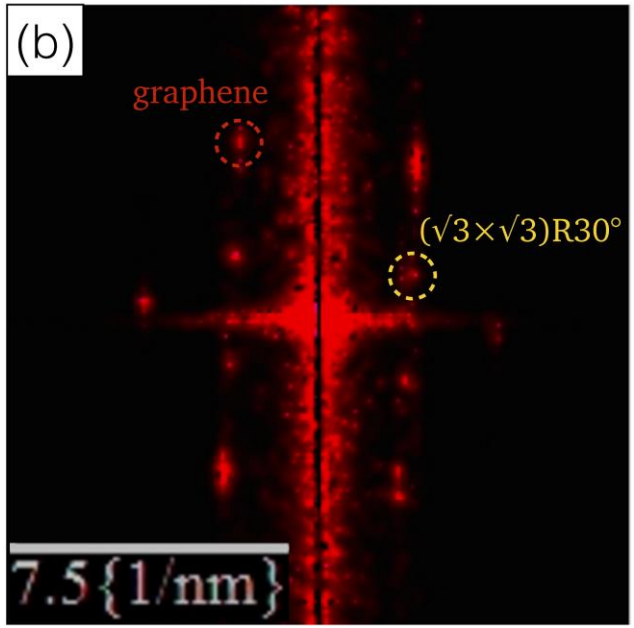
30% of C-atoms of the buffer layer form covalent bonds to Si atoms of the SiC substrate.

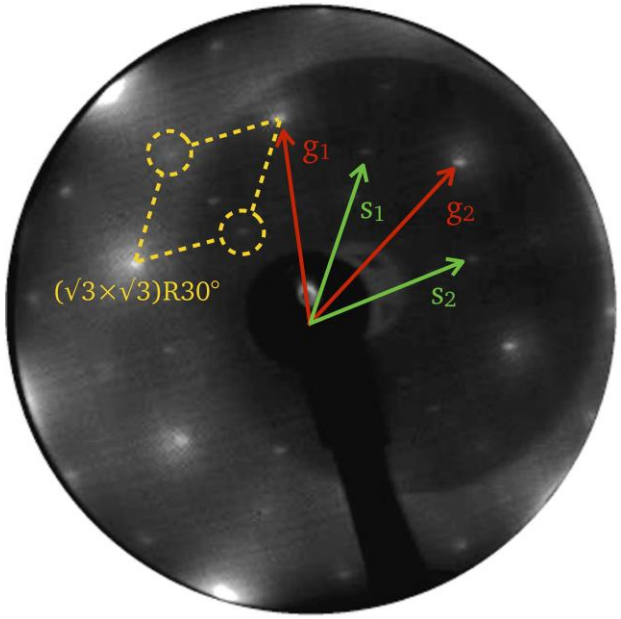
Excellent quantitative agreement!

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

0.56 ML Li on EMLG



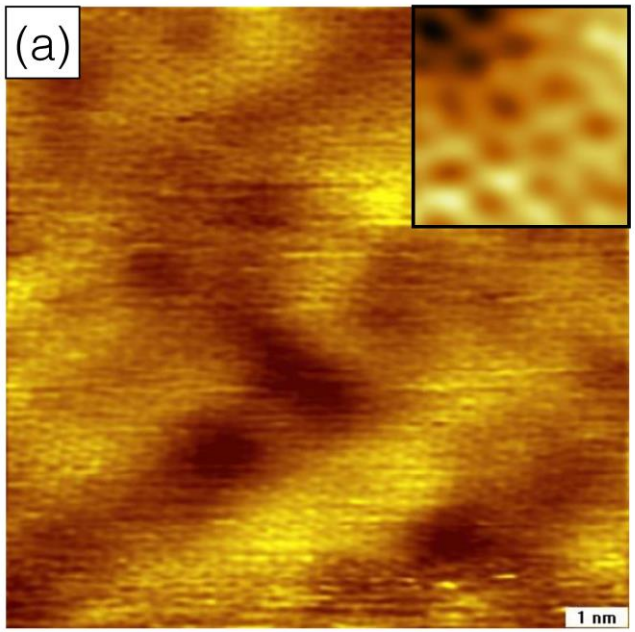


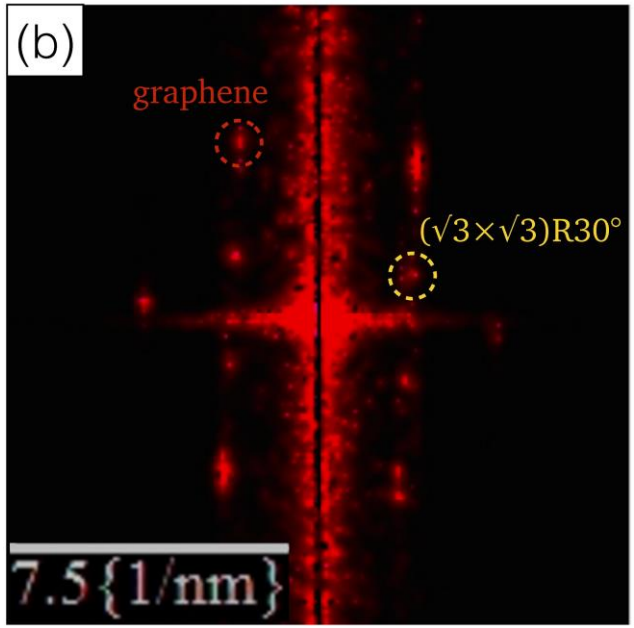


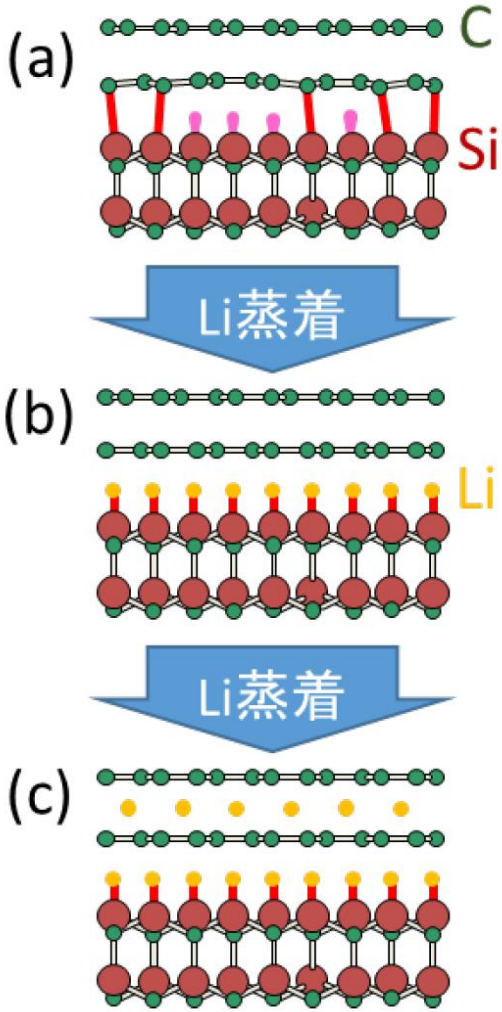
The $\sqrt{3}$ has been associated in literature to intercalation between the two graphene layers.

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

0.56 ML Li on EMLG







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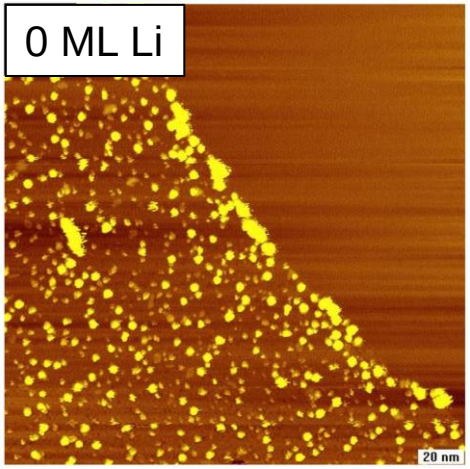
Li on Buffer Layer



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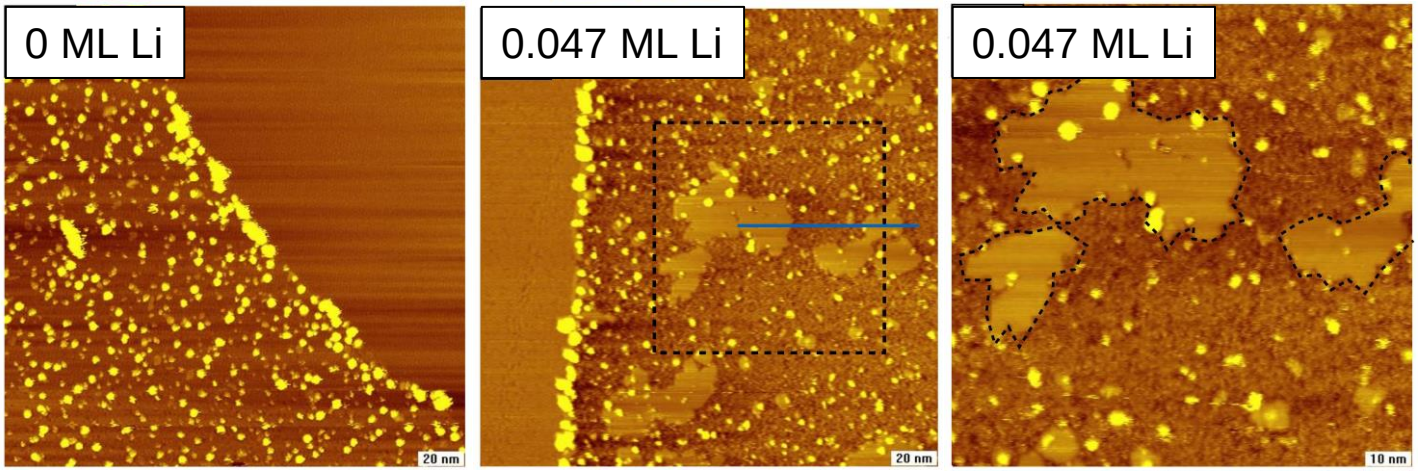
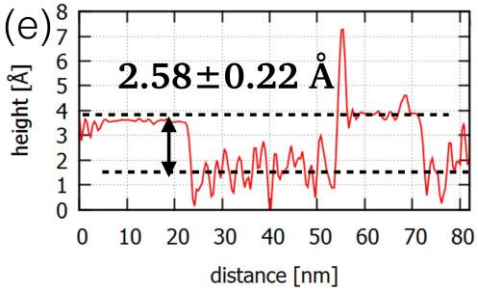
Li on Buffer Layer





- No $6\sqrt{3}$ on top of islands
- Islands are QFMLG
- Have same nature as stripes for EMLG

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

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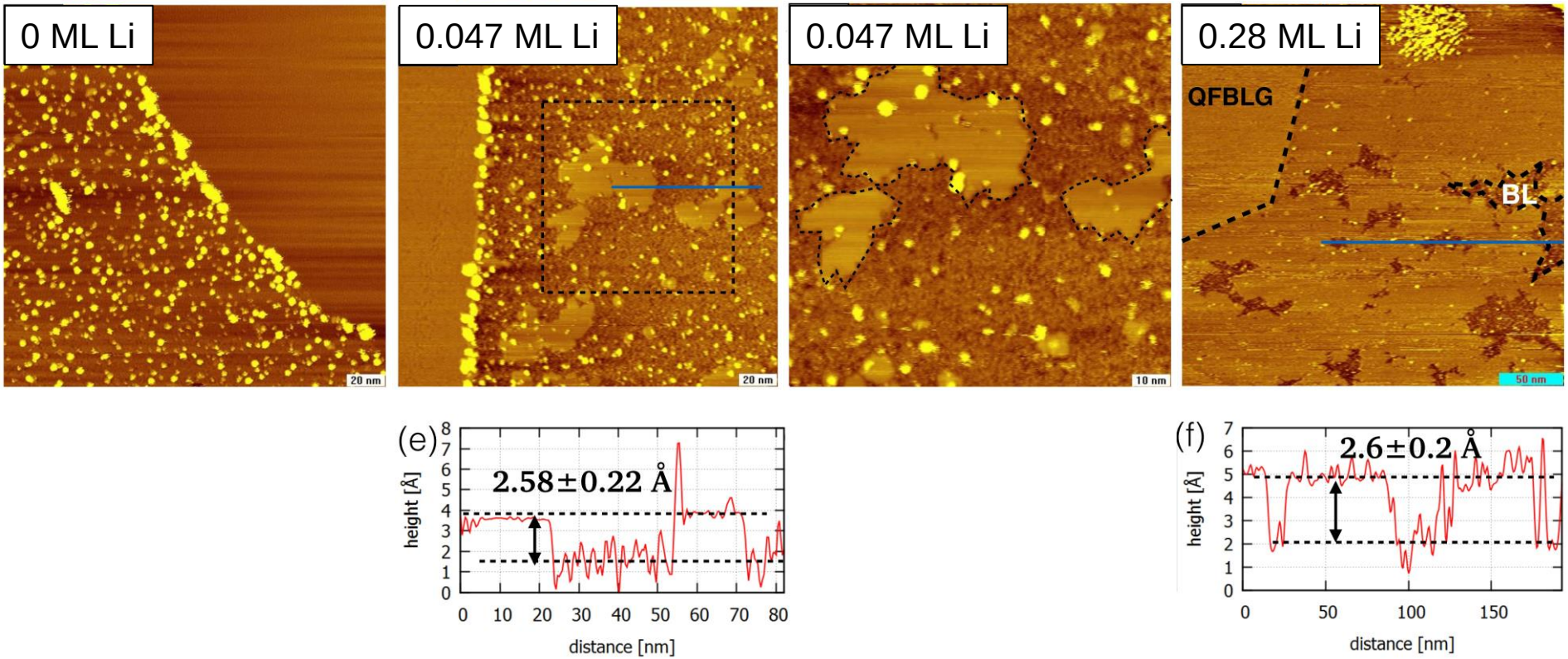
Li on Buffer Layer



S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

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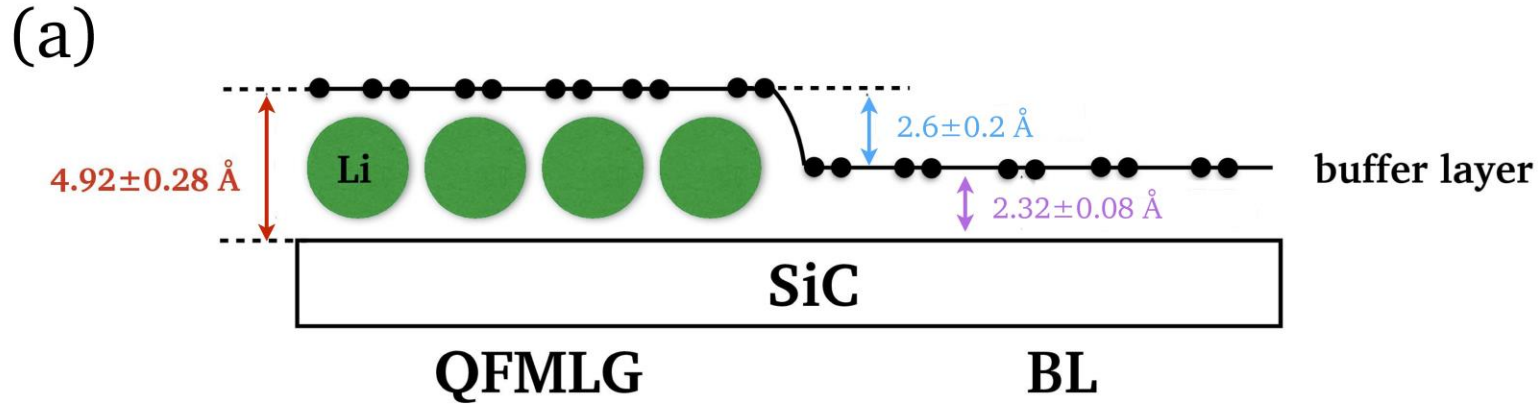
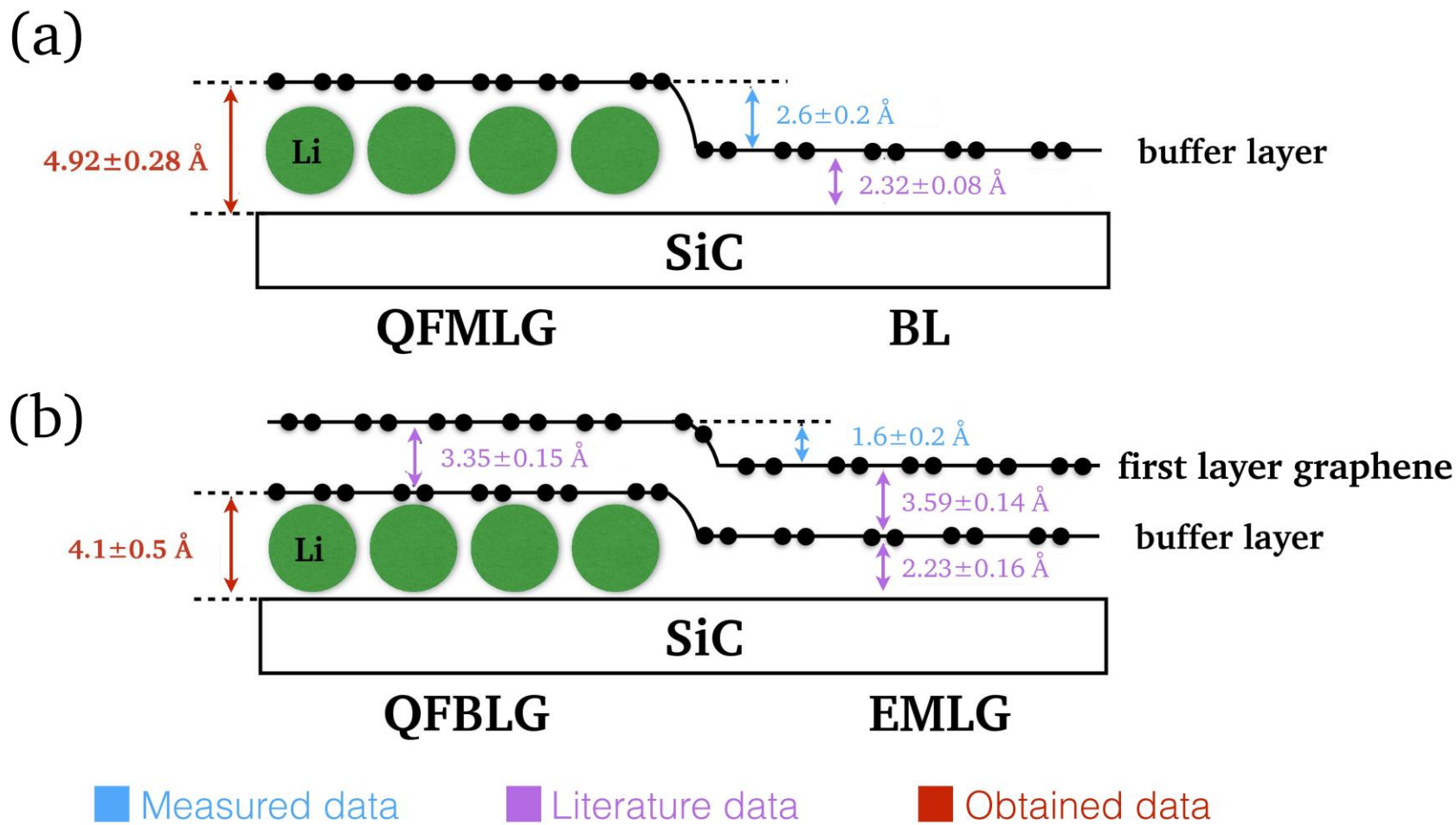
Model



Measured data Literature data Obtained data

S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

Model



S. Fiori et al., Phys. Rev. B, in press, arXiv:1706.01386

Conclusions

- Graphene is a promising material for hydrogen storage
- Graphene functionalized by Ti:
  - Stability of hydrogen binding at room temperature
  - Hydrogen desorbs at moderate temperatures
  - Modifying the size and distribution of Islands by sputtering and increasing the active surface
- Li-intercalated Graphene offers new and exciting possibilities for hydrogen storage.

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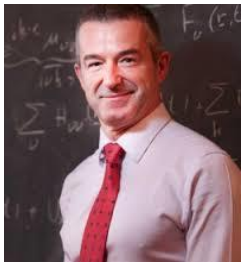
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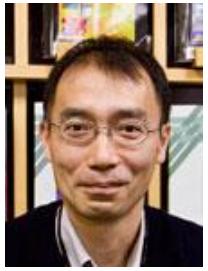
K. Omori


S. Isobe


M. Takamura


S. Tanabe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Thank you for your attention!

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