Li-functionalized Graphene on Silicon Carbide

Sara Fiori

Outline

- Introduction: Hydrogen Storage
- Graphene and its applications in hydrogen storage
- Experimental methods: LEED, STM
- Results and discussion of the experiment
    1. Calibrating the rate of Li on Si(111)
    2. Li deposition on G/SiC and annealing
- Conclusions

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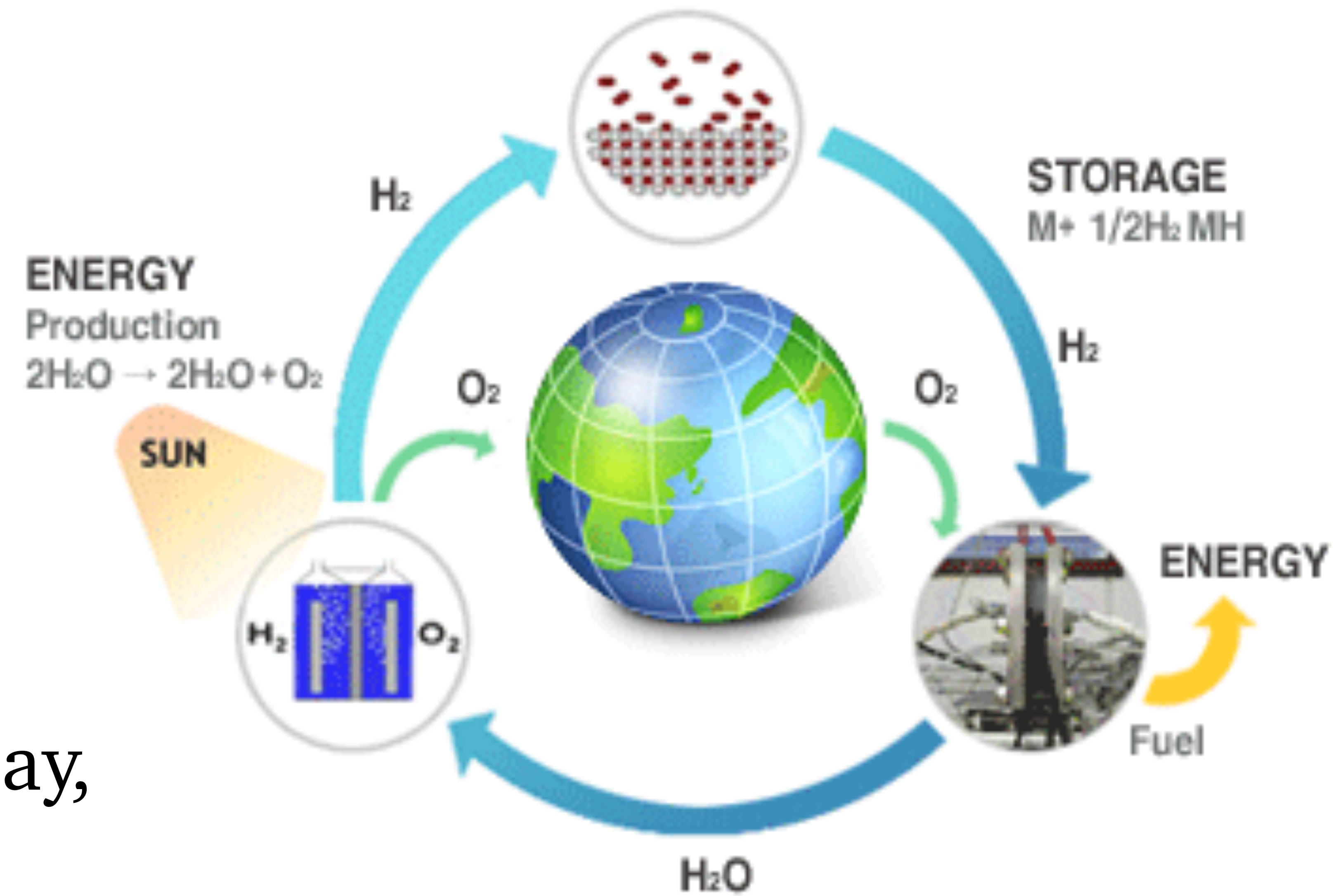
Oil is not an infinite resource
⇒ alternative energies
(wind, sun etc.)



Not available equally
during all time of the day,
and year

Hydrogen can be a promising
carrier for green energy

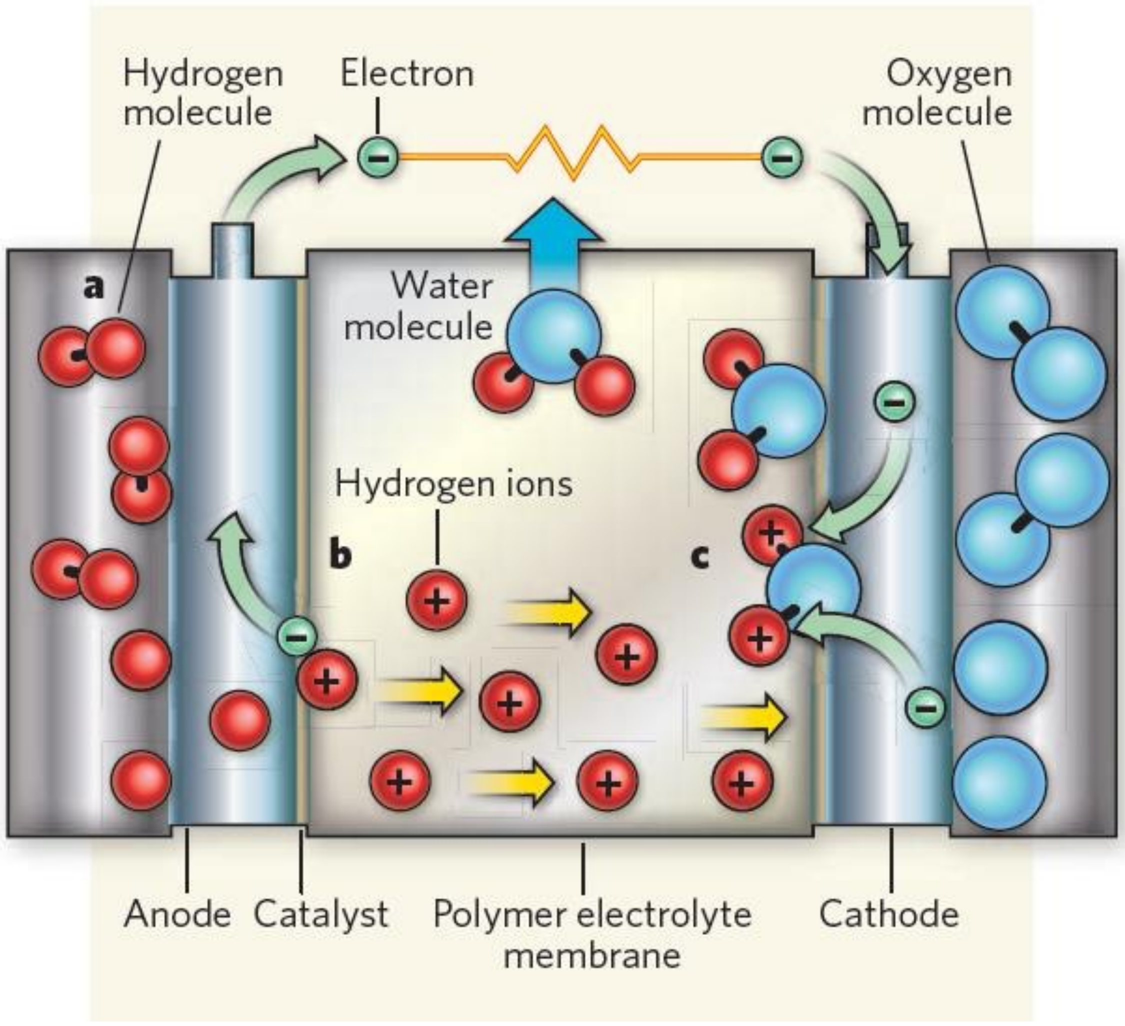
Hydrogen is not an energy source

$$H_2 + 1/2\ O_2 \Rightarrow H_2O \qquad \Delta H = -2.96\ eV$$

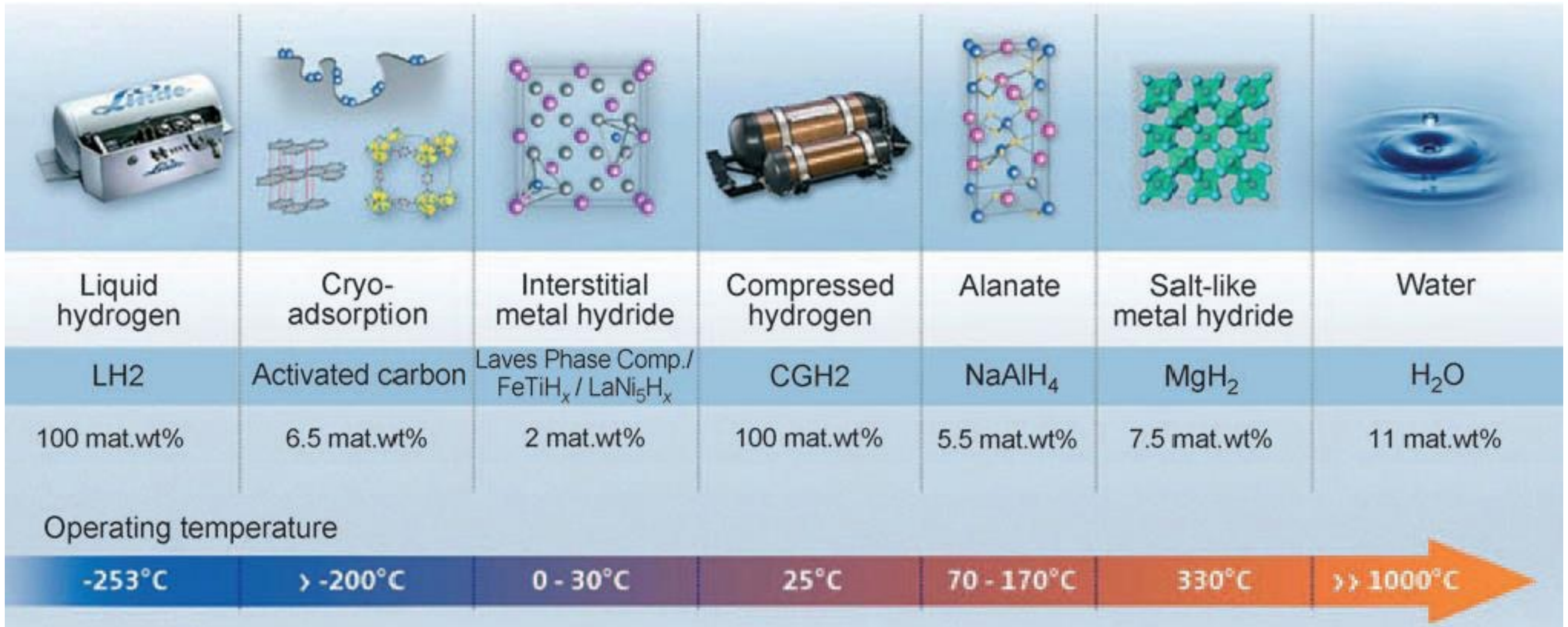
Supply $+2.96\ eV/H_2$, with zero balance with respect to energy production.

As a fuel, hydrogen has advantages:

- Highest energy-to-mass ratio
- Non toxic and "clean" (product=water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency



Nevertheless, hydrogen storage in a safe and cheap way is a critical issue.



- Compressed gas
- Liquid hydrogen
- Condensed state

Key issue

- Volumetric and gravimetric densities
- Kinetics
- Reversibility
- Operation temperature

Carbon materials such as **graphene** are considered promising candidates in hydrogen storage technology.

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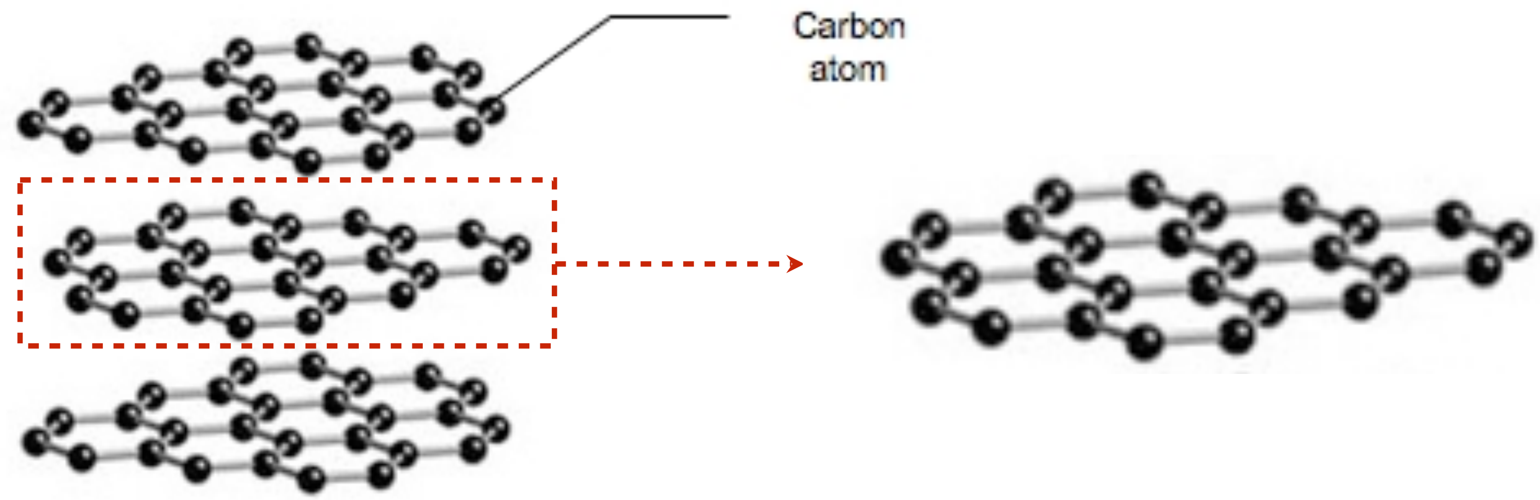
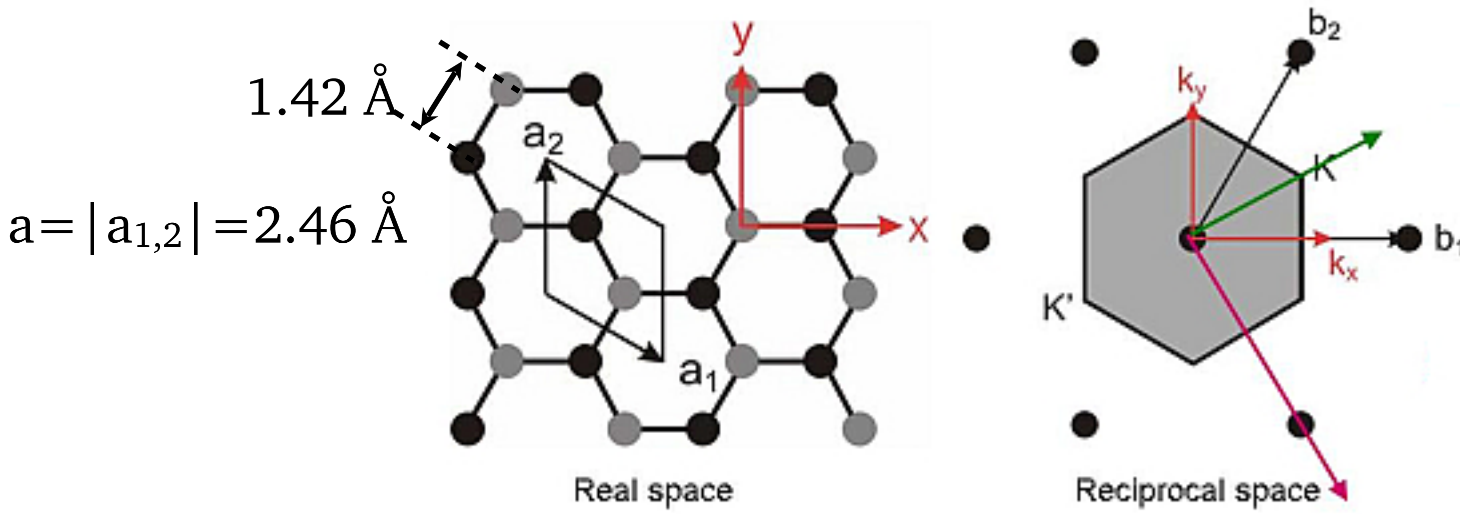
What is Graphene?

Structure of Graphite

Graphene

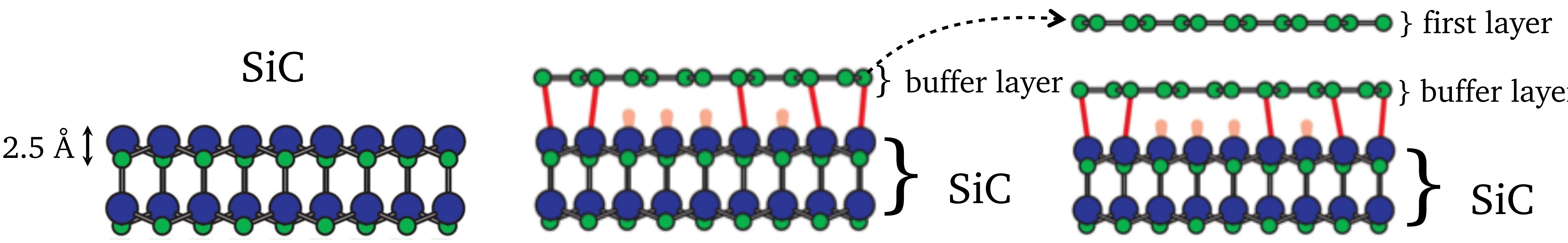




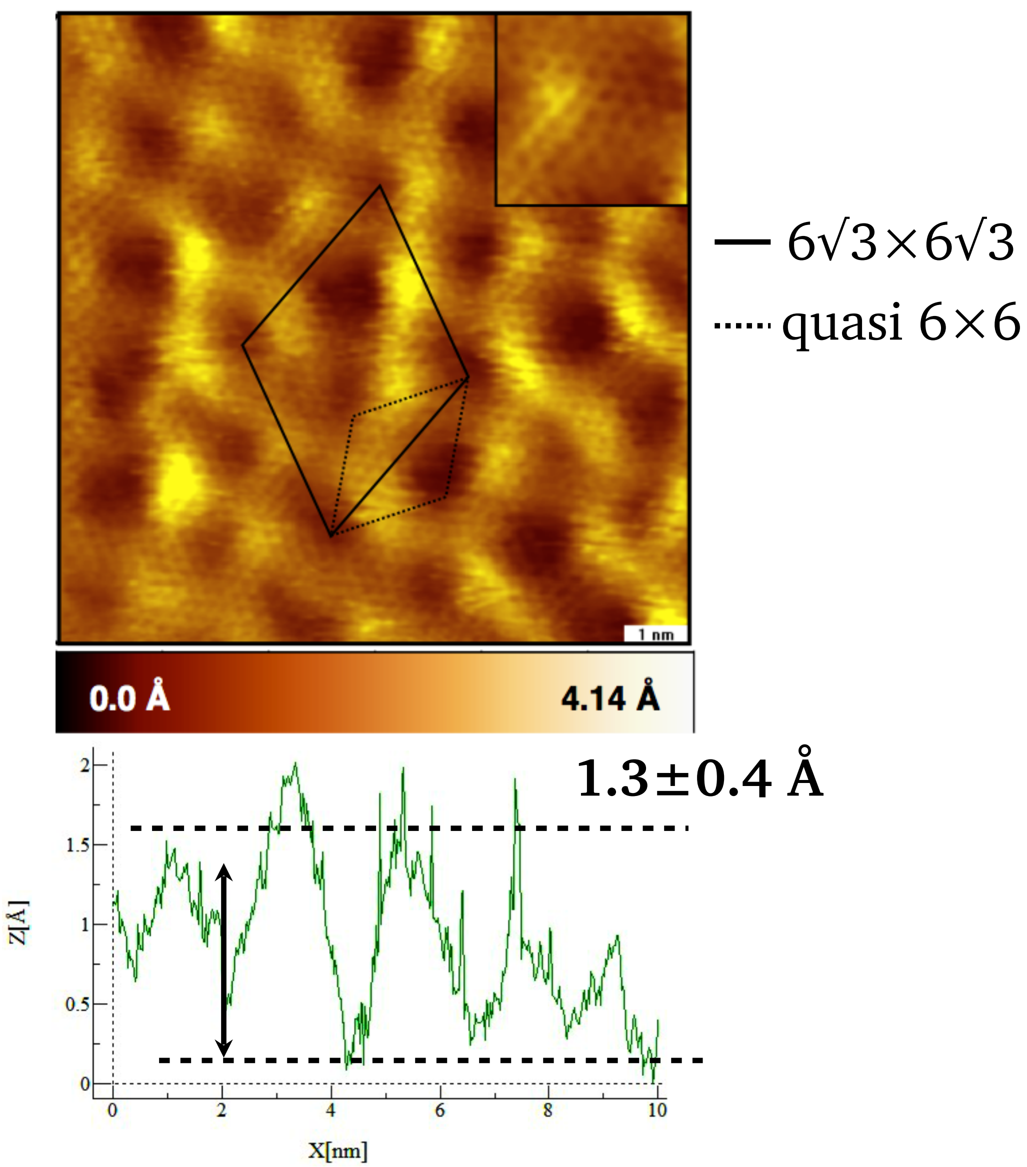
C atoms in graphene are arranged in a honeycomb lattice

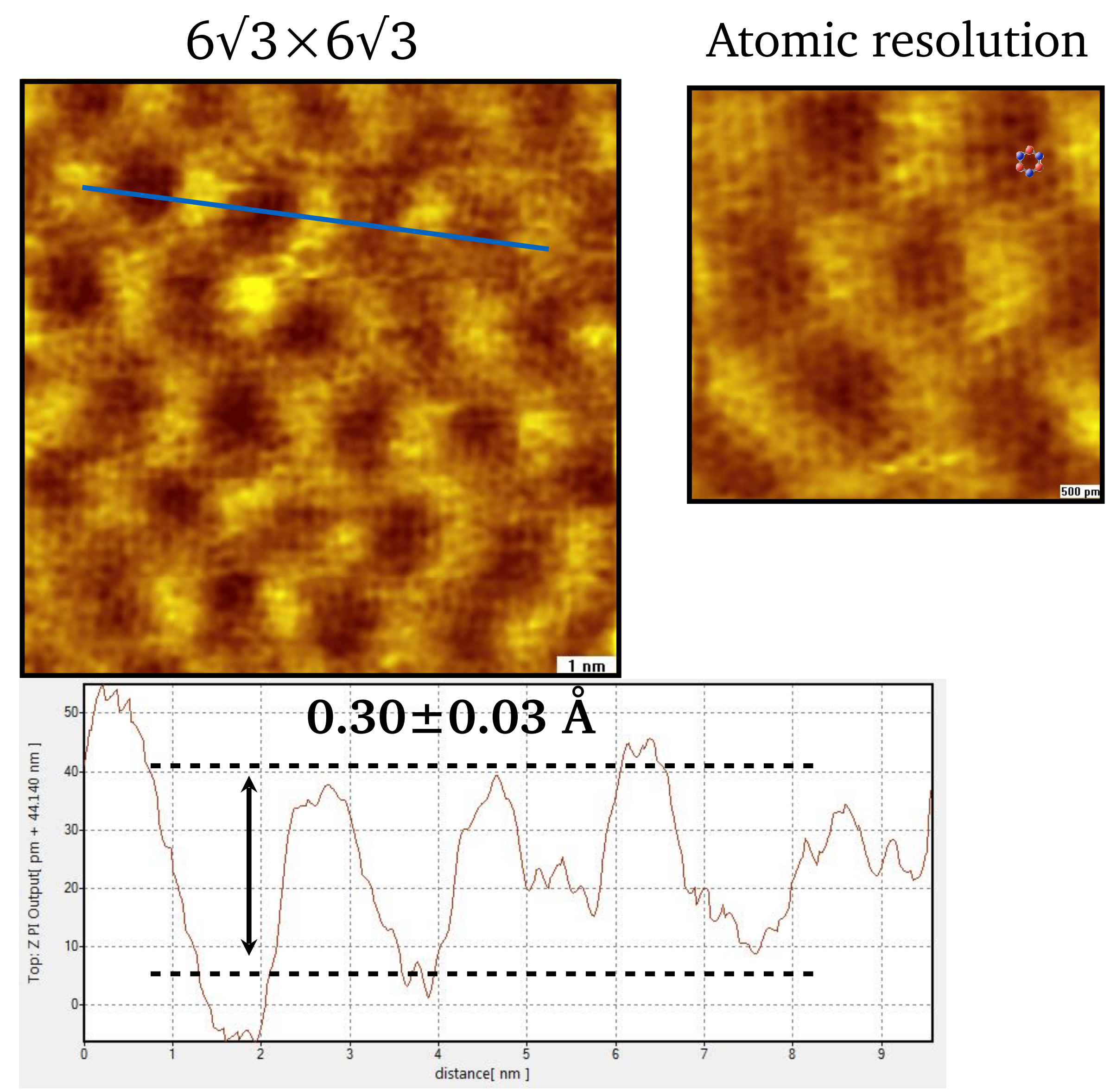
Nobel Prize in 2010 for graphene isolation in 2004

Epitaxial Graphene growth on SiC(0001)

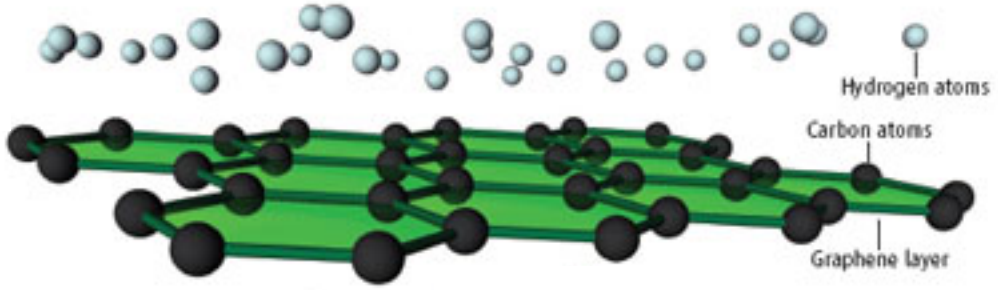


C Riedl et al., J. Phys. D: Appl. Phys. 43 (2010)





Graphene for Hydrogen Storage



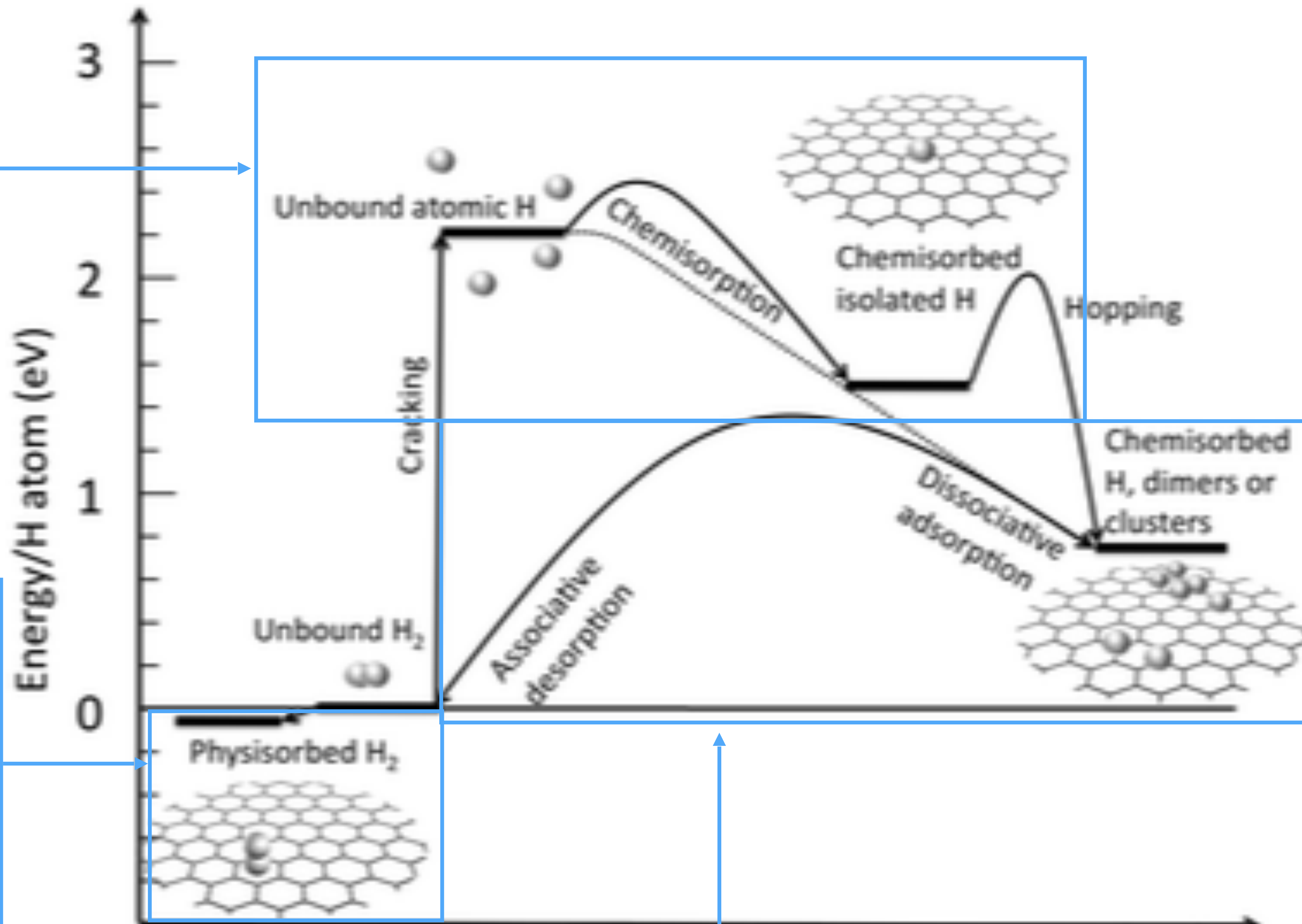
- Graphene is lightweight, robust, chemically stable
- Large surface area (2630 m^2/g)
- Functionalized graphene has been predicted to adsorb up to 9 wt.% of hydrogen (Yang et al., PRB 79 (2009) 075431)

Chemisorption vs. Physisorption

❖ Chemical bonds H-C atoms.

Chemisorption barriers: 0.3 eV, binding energy H-C: 0.7 eV

H_2 must be cracked



❖ Physisorption of molecular Hydrogen

Van der Waals forces - low barrier (~0.05 eV)

Low temperatures and/or high pressure

V. Tozzini and V. Pellegrini, Phys. Chem. Phys., 2013, 15, 80

❖ Chemisorption of molecular hydrogen

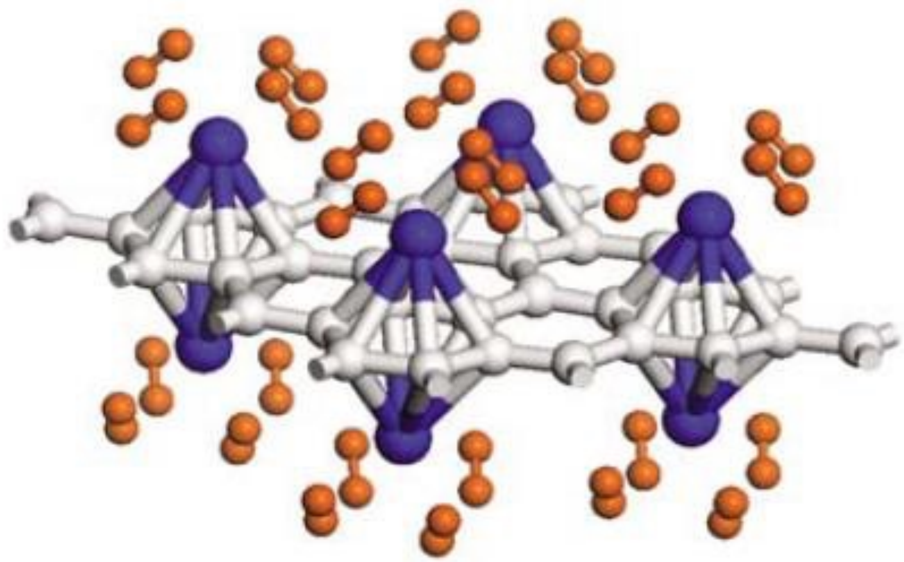
High barrier (~1.5 eV)

Catalytic mechanisms are necessary in the loading-release phases

Physisorption by functionalization

Transition metal (TM)-decorated graphene (Ti, Sc, and V):

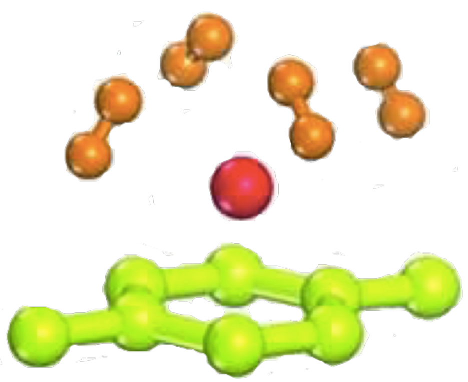
- Strong bonds with graphene
- Kubas interaction
- Issue: clusters



Durgen et al., PRB 77 (2007) 085405

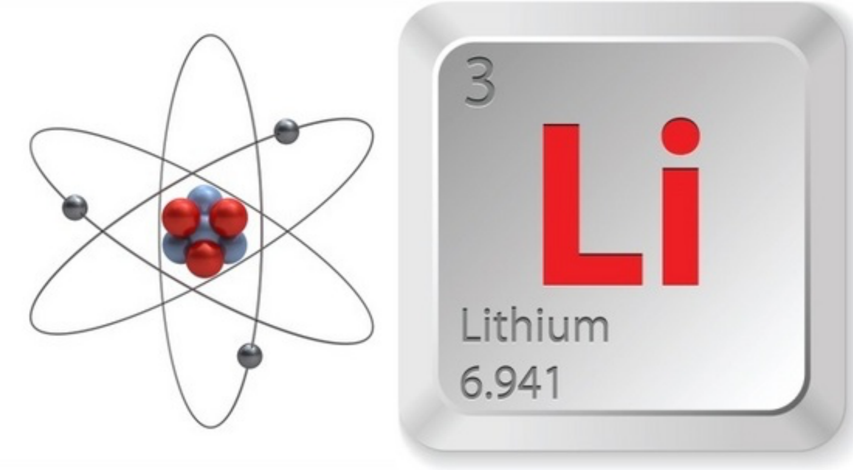
Alkali metal (AM)-decorated graphene (Li, Na, and K):

- Weaker bonds than TM with graphene
- Lower cohesive energy ⇒ higher hydrogen storage capacity.



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

Why Lithium?



Interesting:

➢ Theoretically: good hydrogen storage capacity ⇒ high predicted gravimetric density

➢ Experimentally: Li intercalates below epitaxial graphene ⇒ promising material for hydrogen storage

➢ Technologically: several application fields for Li intercalated devices (e.g. Li-ion batteries)

- Lithium, “Lìthos” from greek which means “stone” (discovered in 1817 by Arfvedson), is an alkali metal
- Symbol: **Li**
- Atomic number: **3**
- Electronic configuration: $\mathbf{1s^2 2s^1}$
- **Highly reactive**

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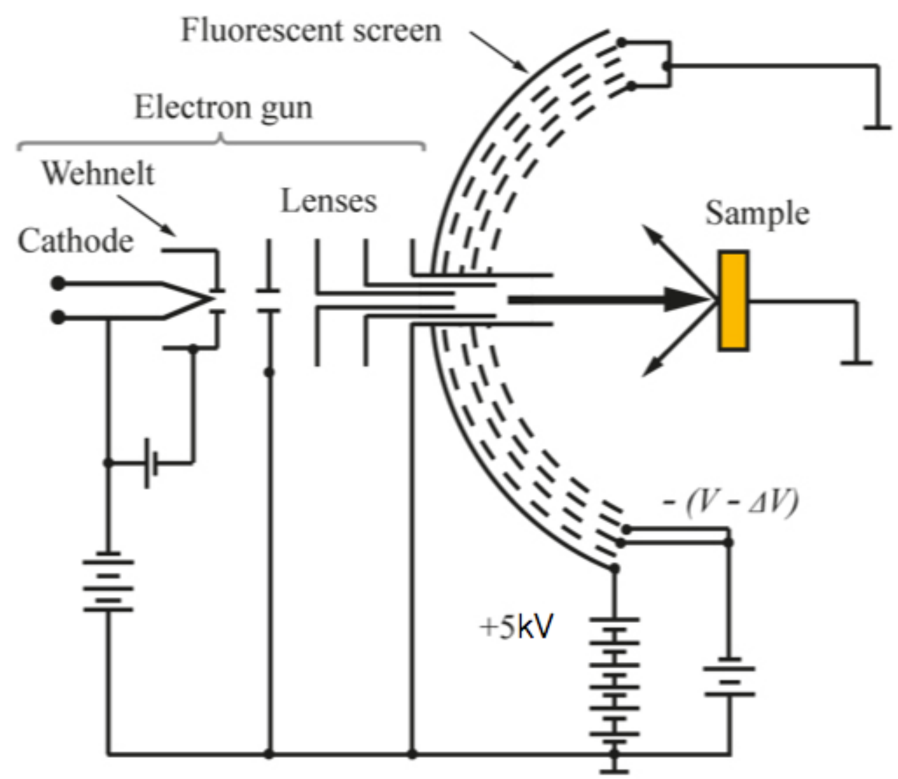
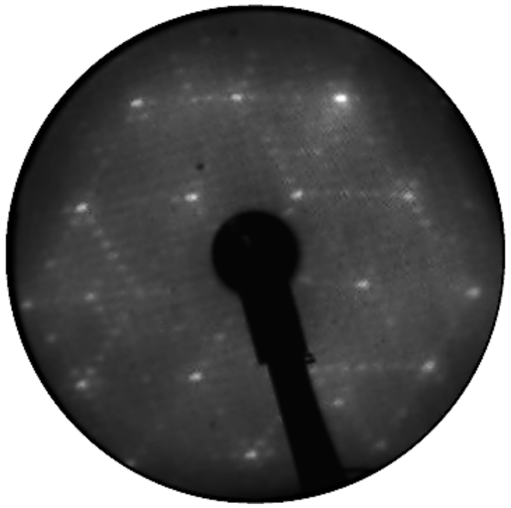
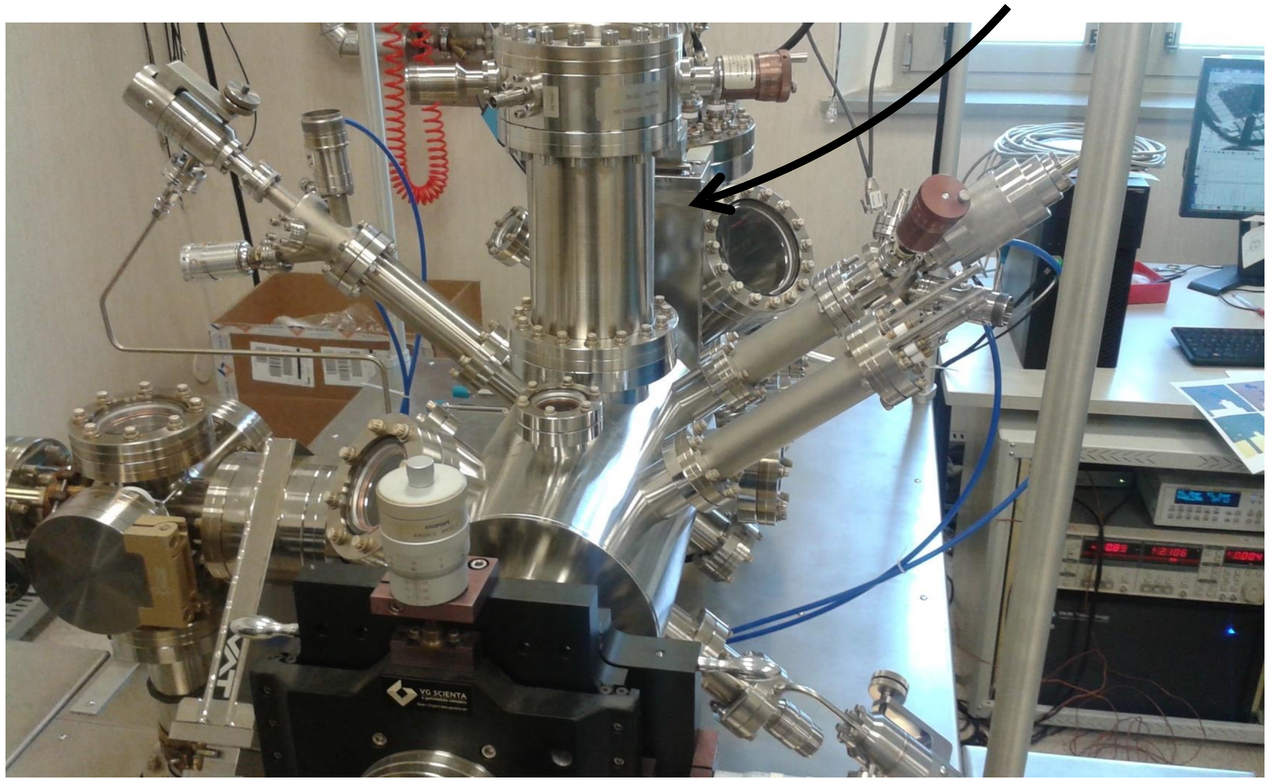
Low-Energy Electron Diffraction (LEED)

- Determination of surface structures
- Collimated electron beam of low energy (20-200 eV)
- Diffracted electron observed as spots on a fluorescent screen
- UHV (10^{-10}-10^{-11} mbar) $\Rightarrow$ avoid surface contamination

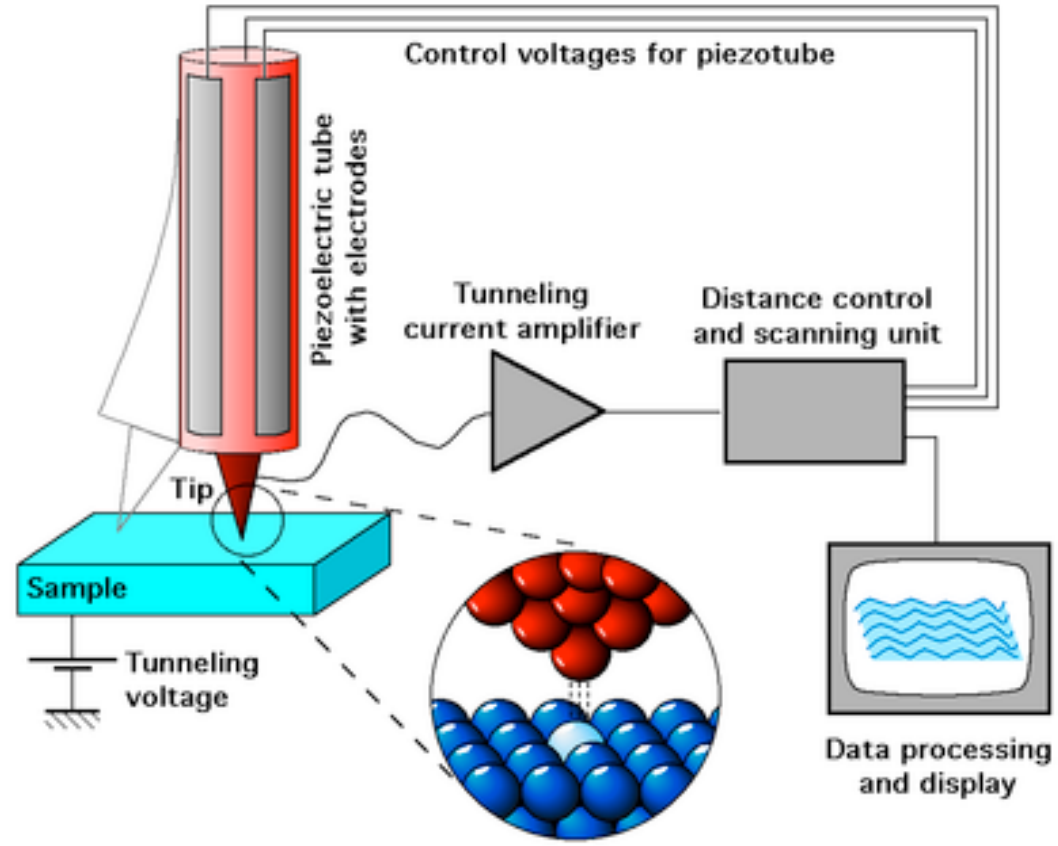




LEED



Scanning Tunneling Microscopy (STM)



- Binning and Rohrer in 1981 (Nobel in 1986)
- UHV (10^{-10}-10^{-11} mbar)
- Tunneling effect between the tip and the sample surface
- Analysis in x-y plane directions and in z direction

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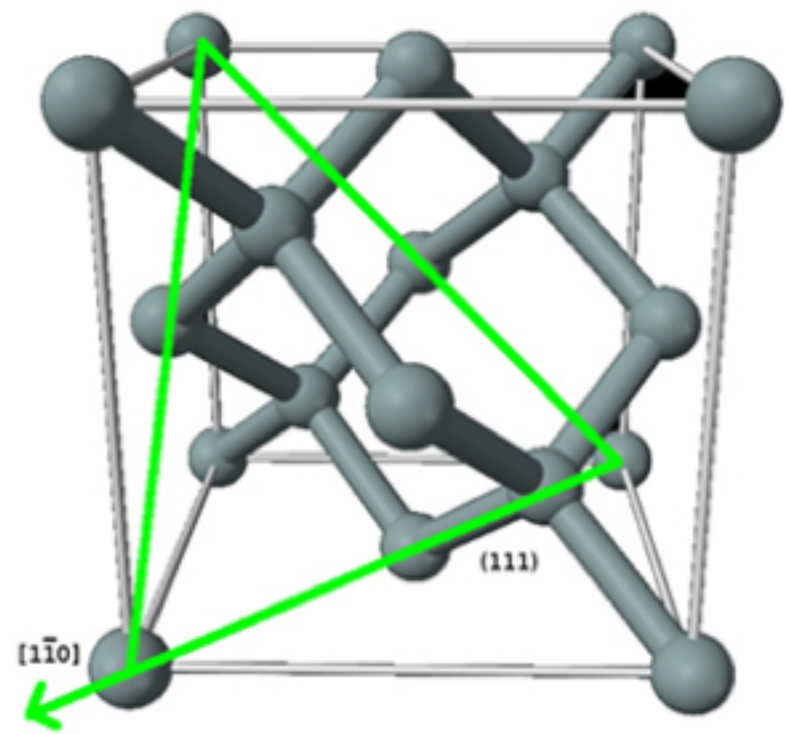
Si(111)

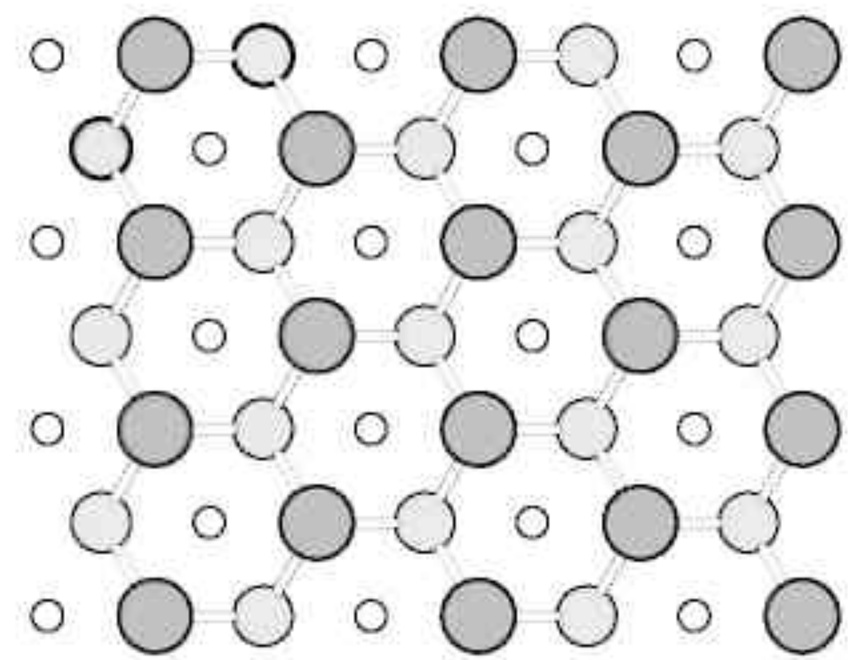
fcc unit cube



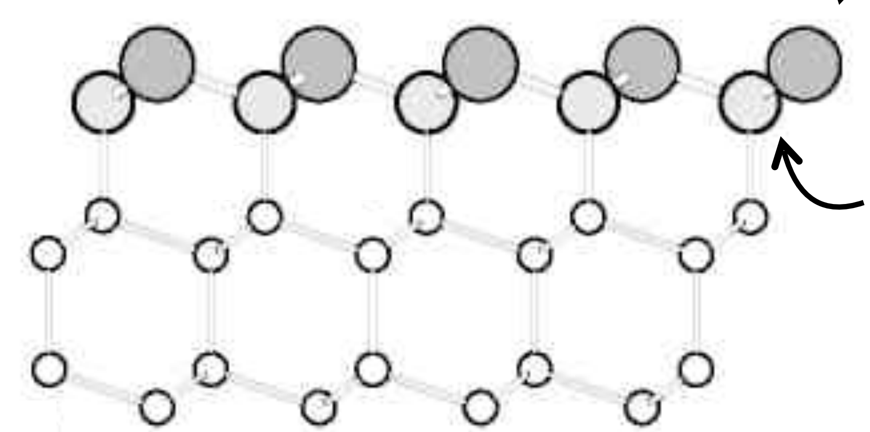
Two Si atoms in a unit cell:
(0,0,0) (1/4,1/4,1/4)

a_{Si} =5.43 Å

Top view

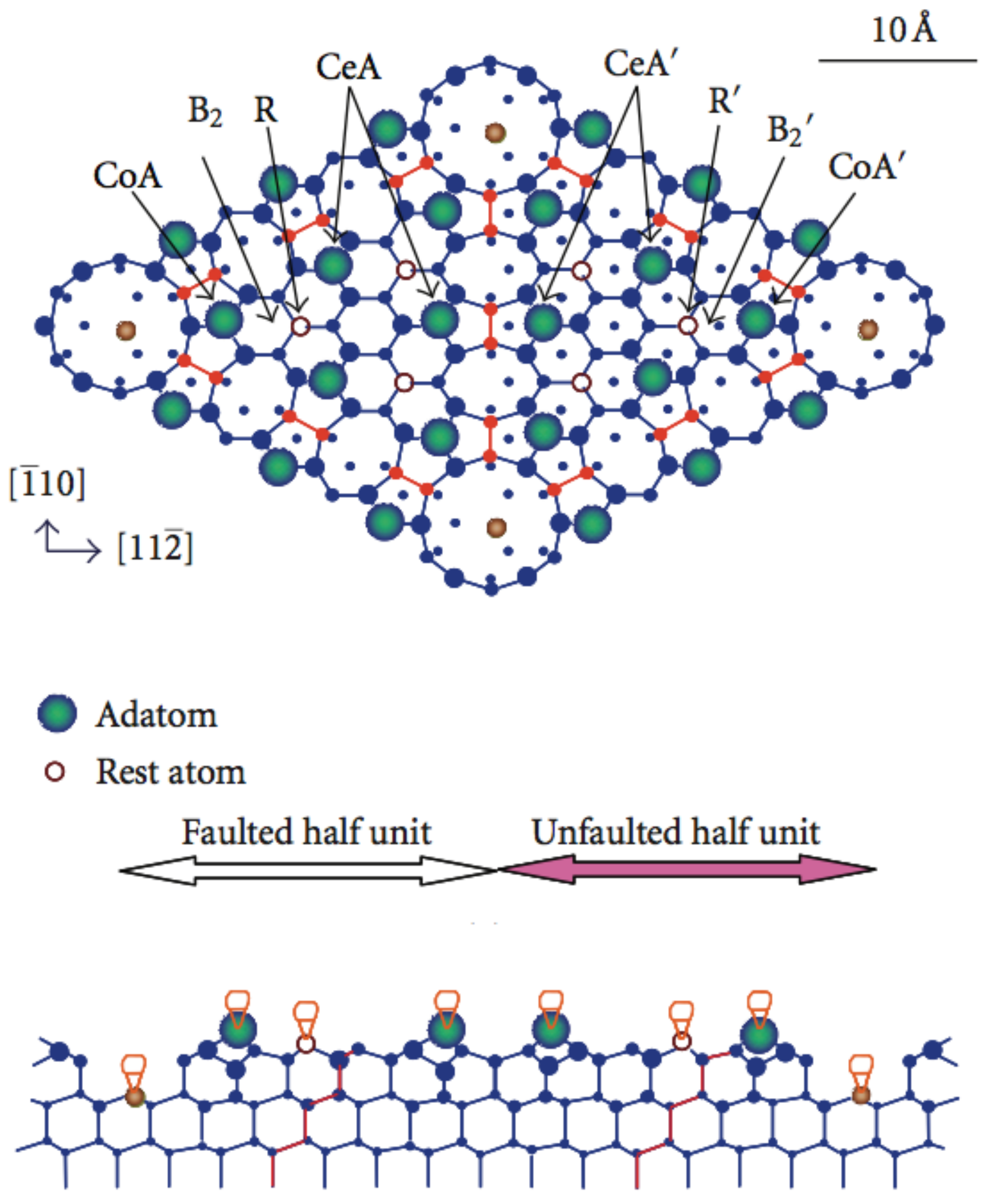


Side view



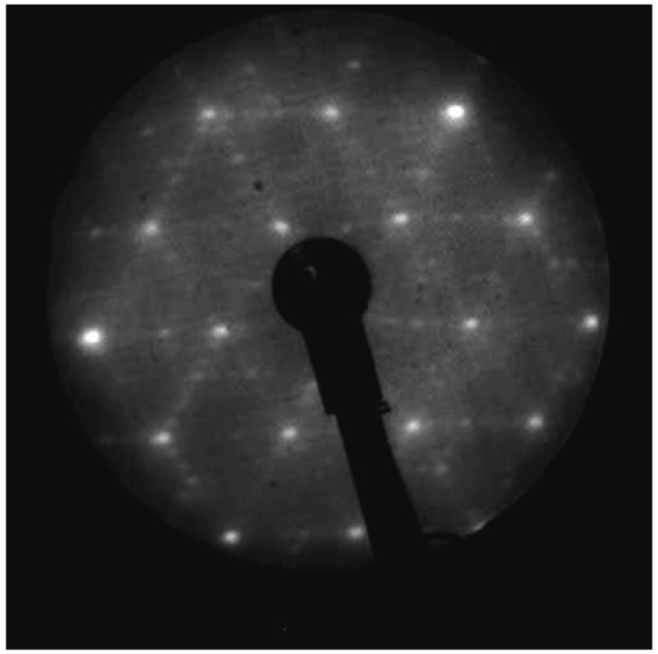
Si(111)-7×7

Theoretical model:
Dimer-Adatom-Stacking fault (DAS) model

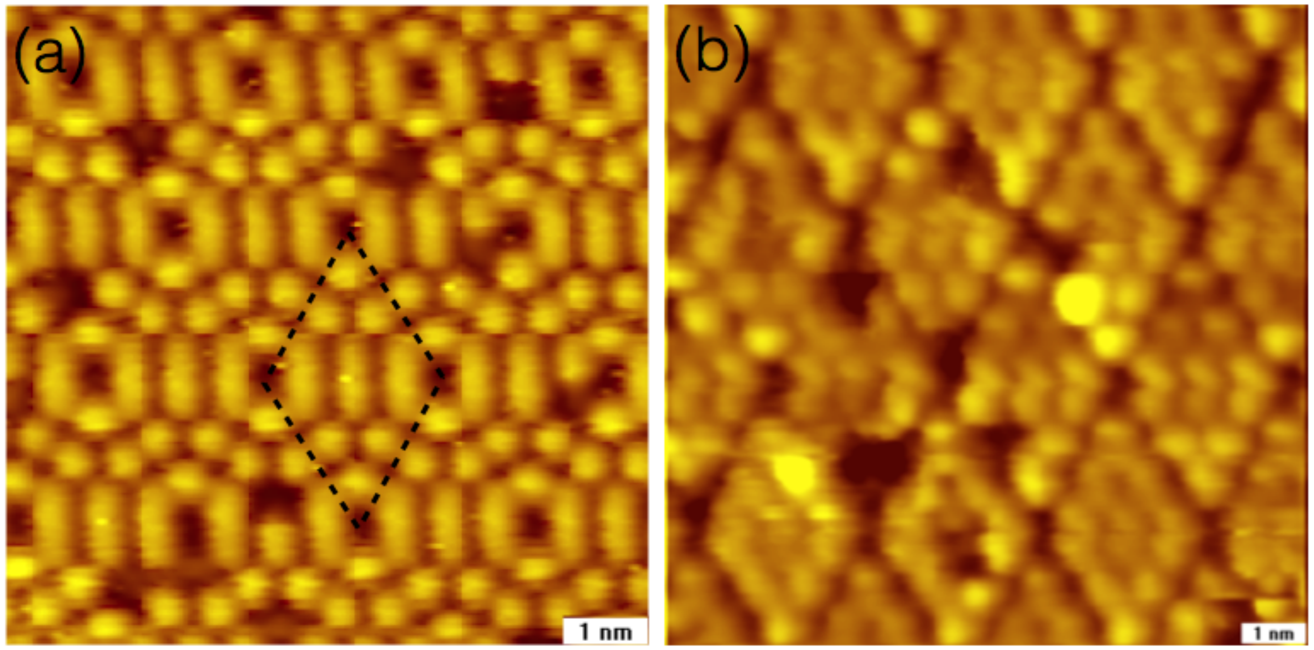


Y. L. Wang et al., Journal of Nanomaterials 2008 (2008): 40.

Experimental results



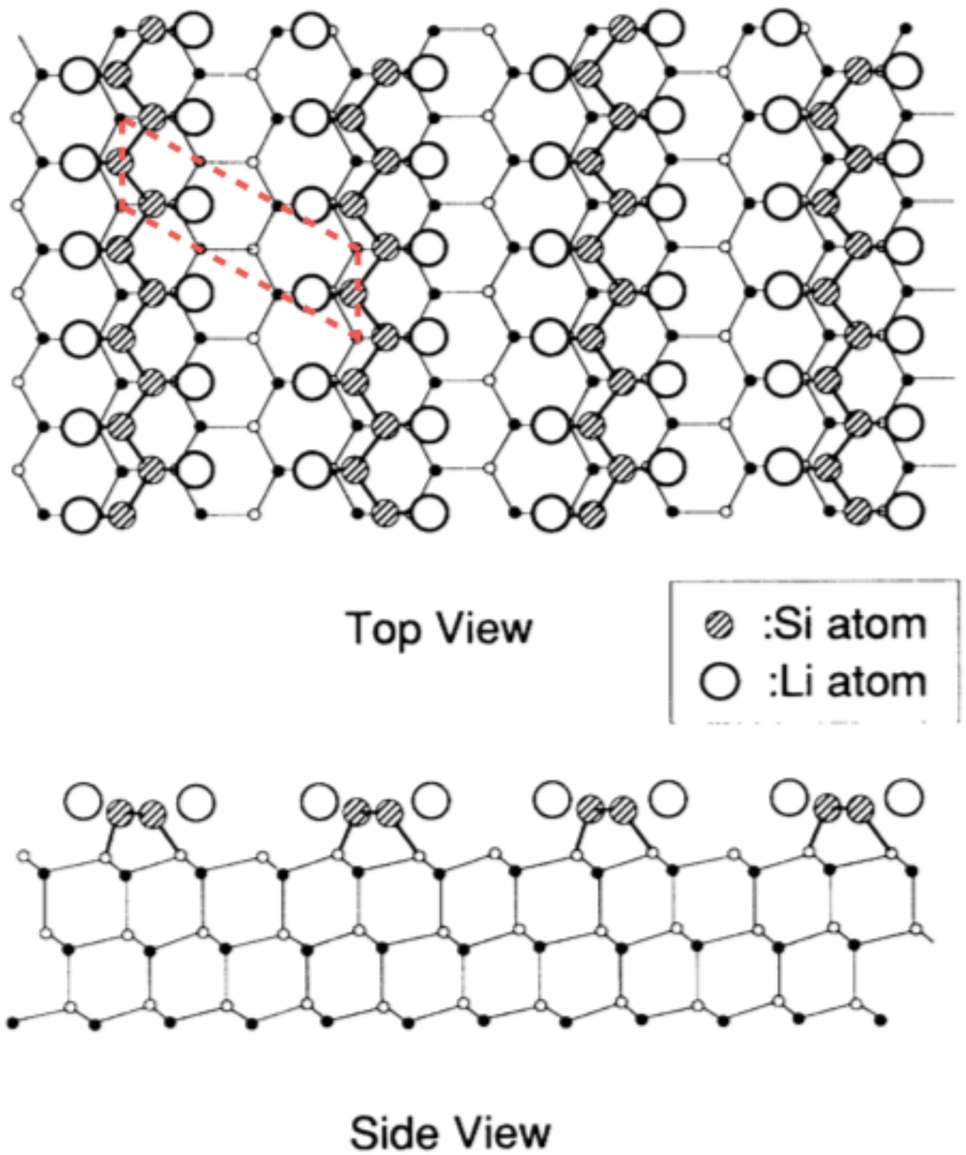
Electron energy: 97.5 eV



10×10 nm^2 scan area. (a) +1.4 V, 1 nA. (b) -1.4 V, -1 nA.

Li/Si(111)-3×1

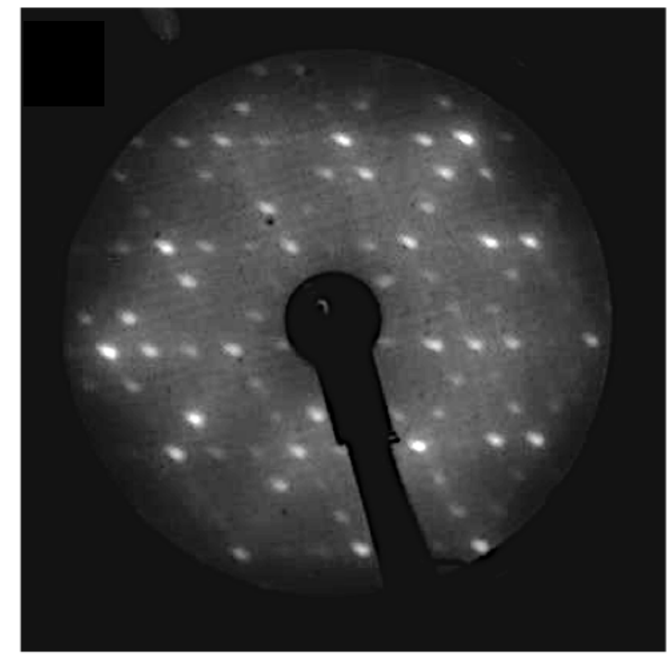
Theoretical model: Missing-Top-Layer (MTL) model



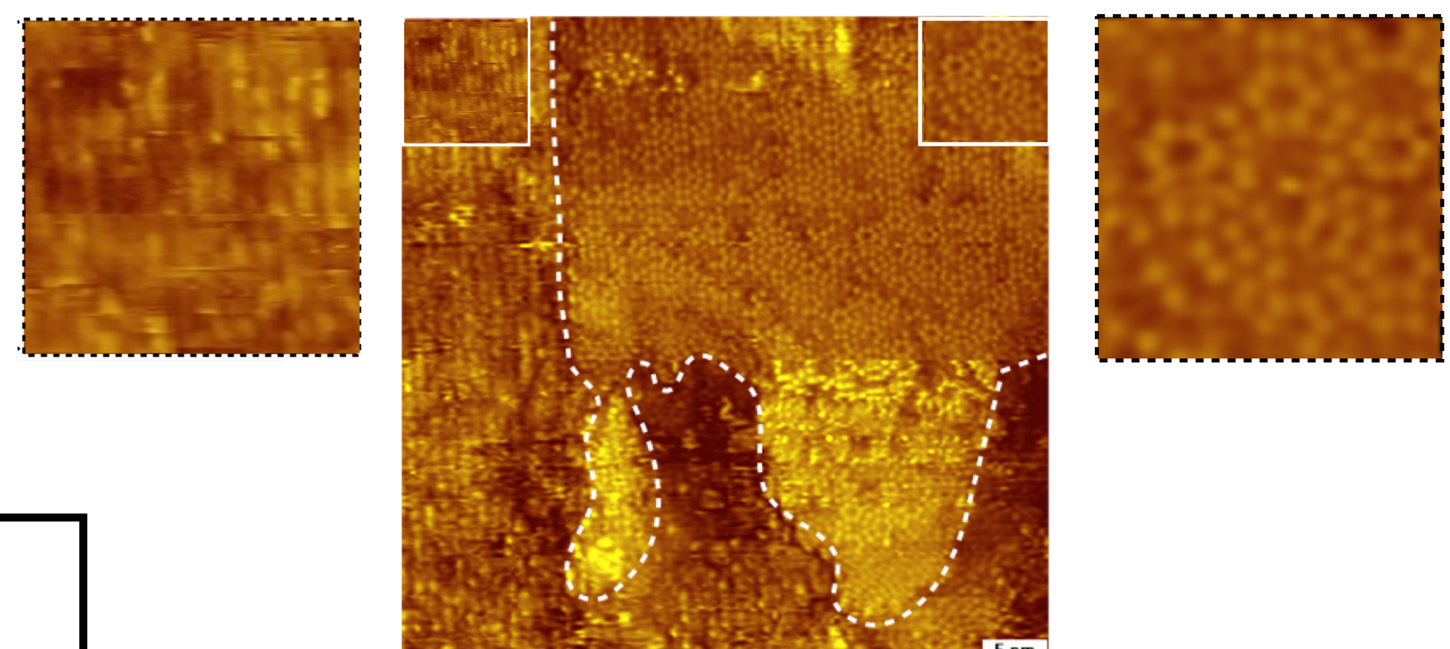
K.J.Wan et al., *Physical Review B* 46.20 (1992): 13635.

Calibration:
1.18×10^{14} Li atoms/cm^2/min

Experimental results



Electron energy: 122.5 eV



50×50 nm^2 scan area. 1.9 V, 0.9 nA

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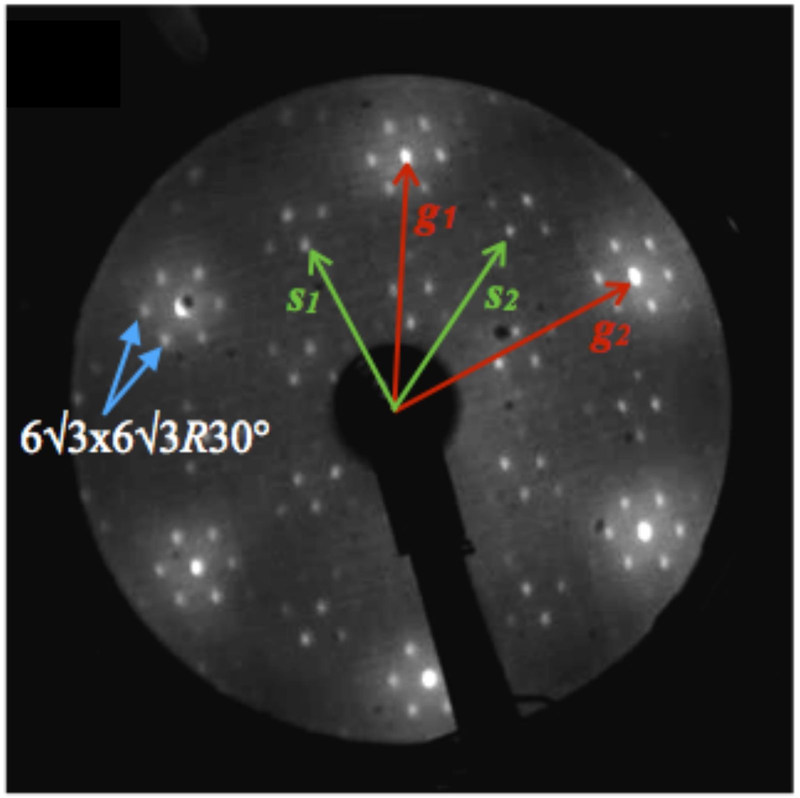
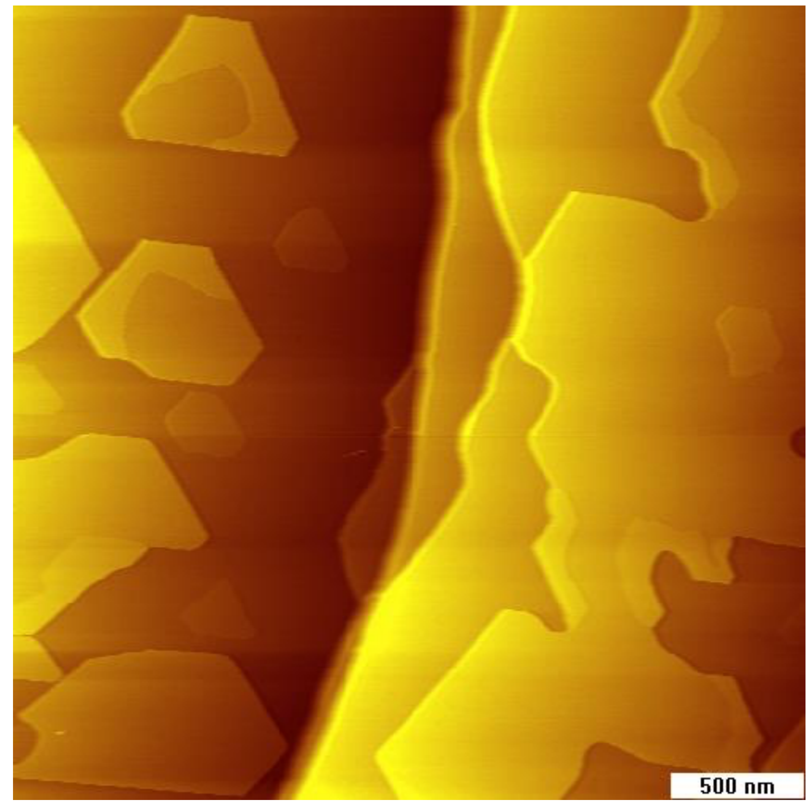
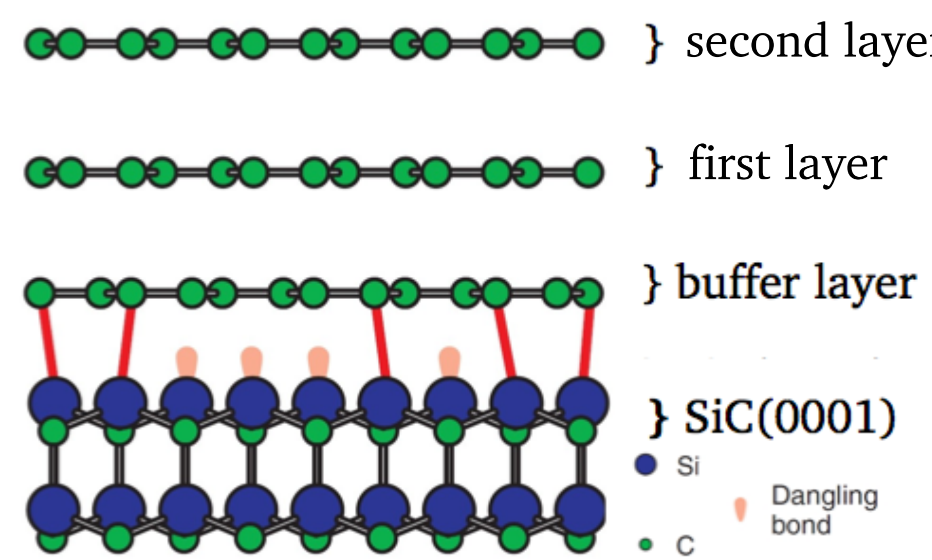
Pristine Graphene

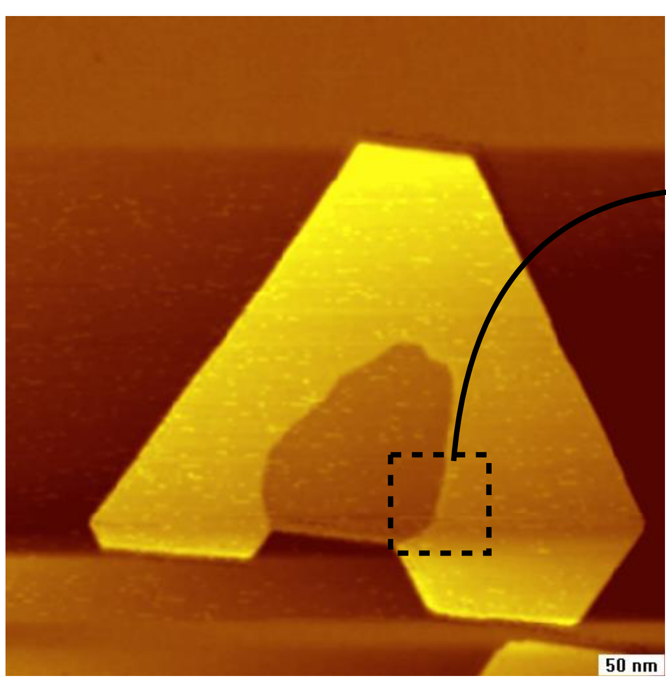


Electron energy: 92.5 eV

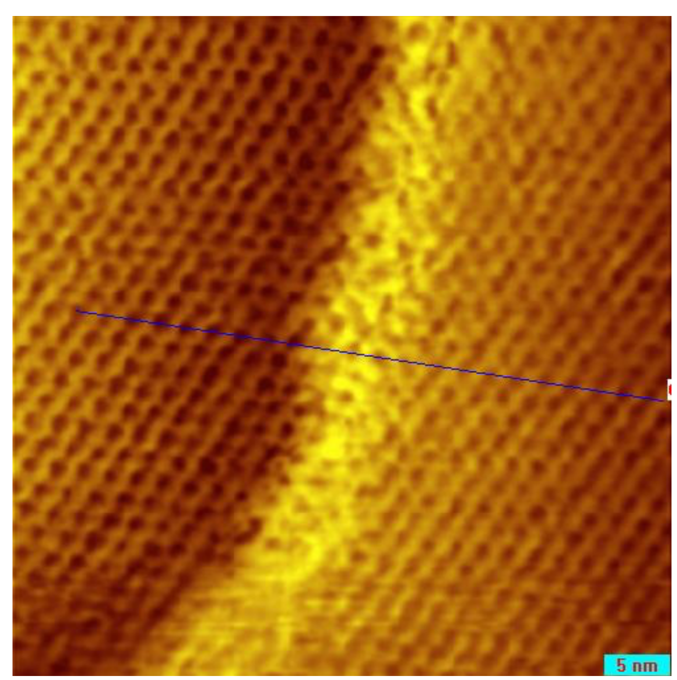


3×3 μm^2 scan area. 1 V, 1 nA

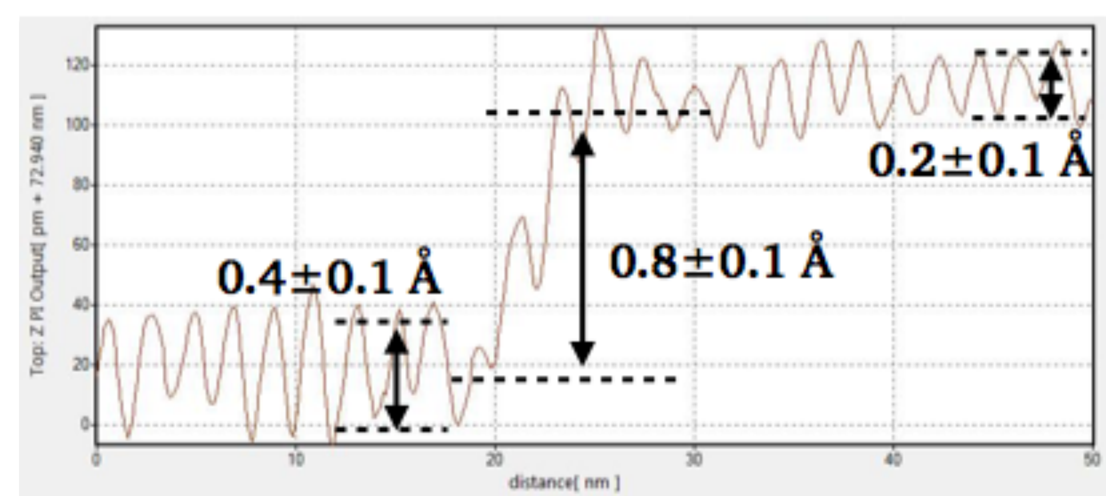




500×500 nm^2 scan area.
400 mV, 500 pA



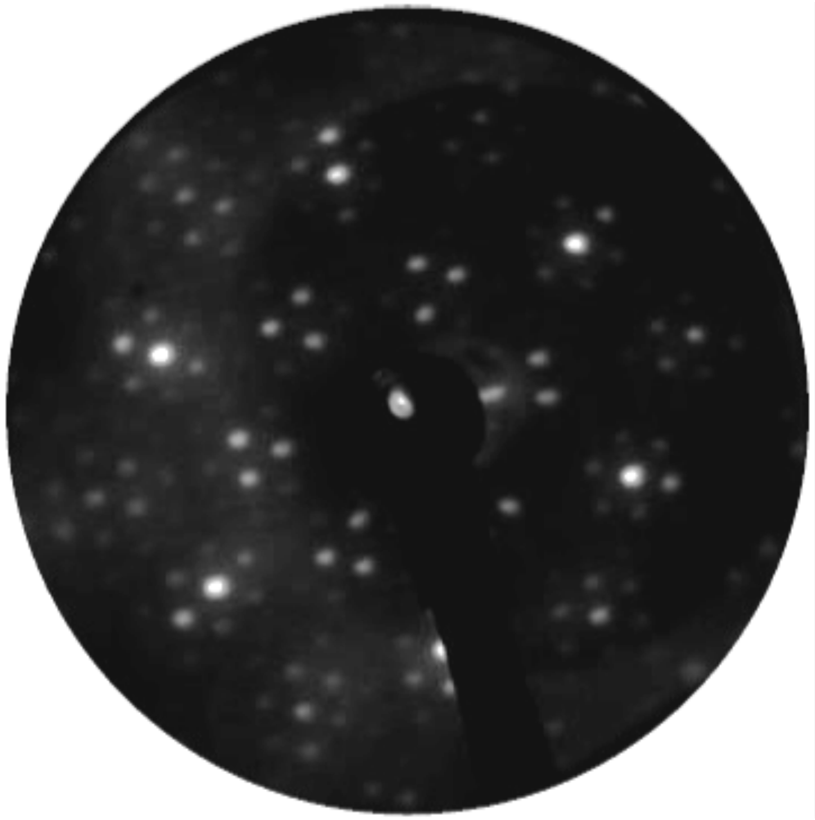
50×50 nm^2 scan area.
400 mV, 500 pA



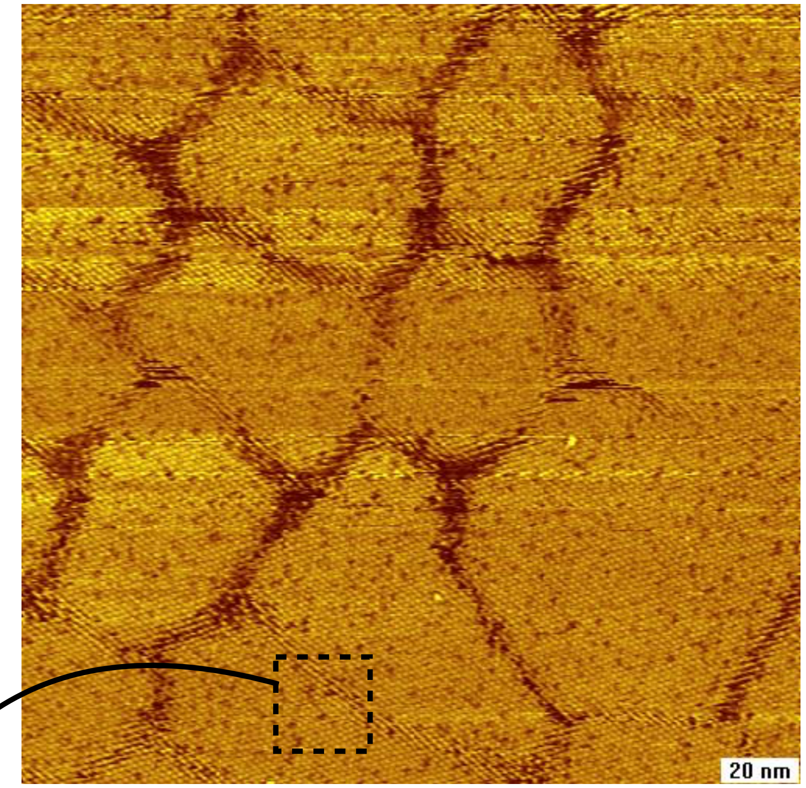
Monolayer Bilayer

Li deposition on epitaxial monolayer graphene

30 seconds of Li deposition (0.016 ± 0.001 ML)



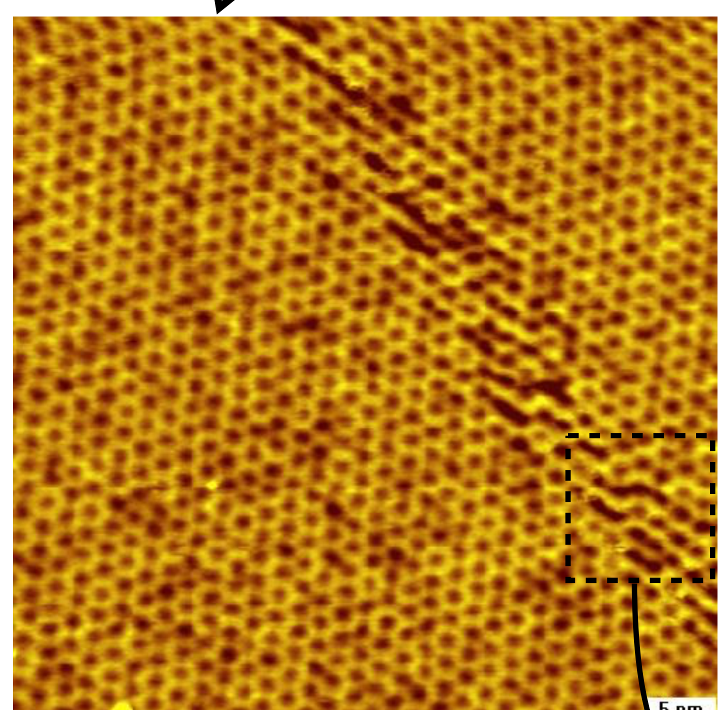
Electron energy: 95.5 eV



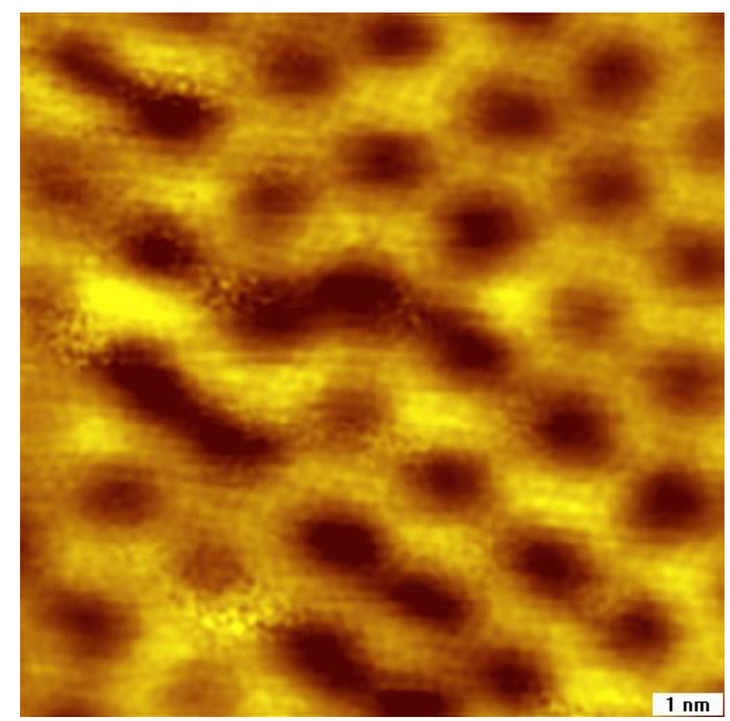
200×200 nm^2 scan area. 99 mV, 170 pA

Apparently, no change in LEED pattern…

…while in STM something is changing!



50×50 nm^2 scan area. 99 mV, 170 pA



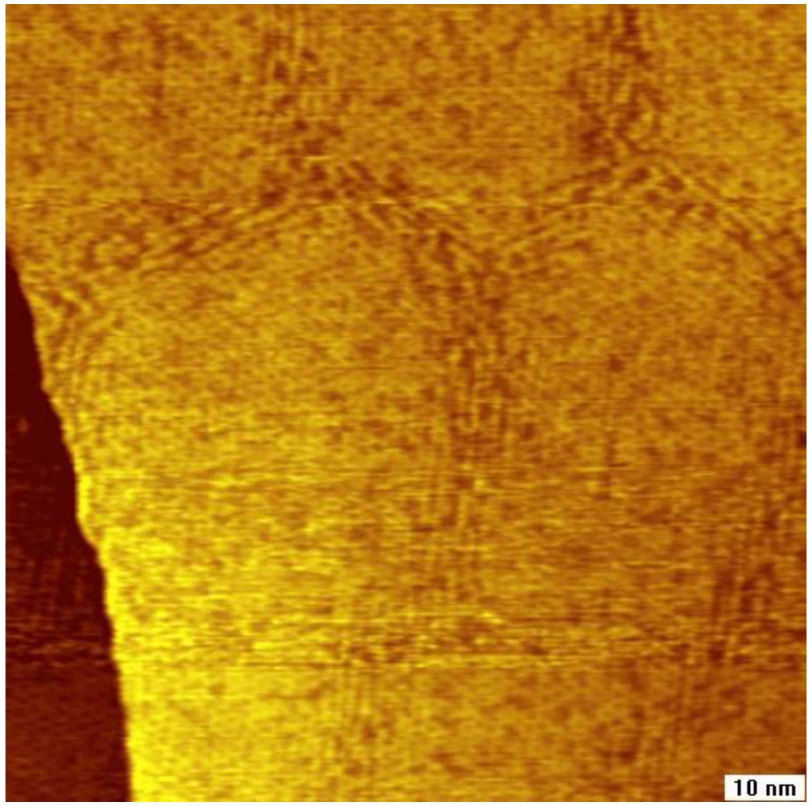
10×10 nm^2 scan area. 99 mV, 170 pA

1 minute of Li deposition (0.031 ± 0.002 ML)

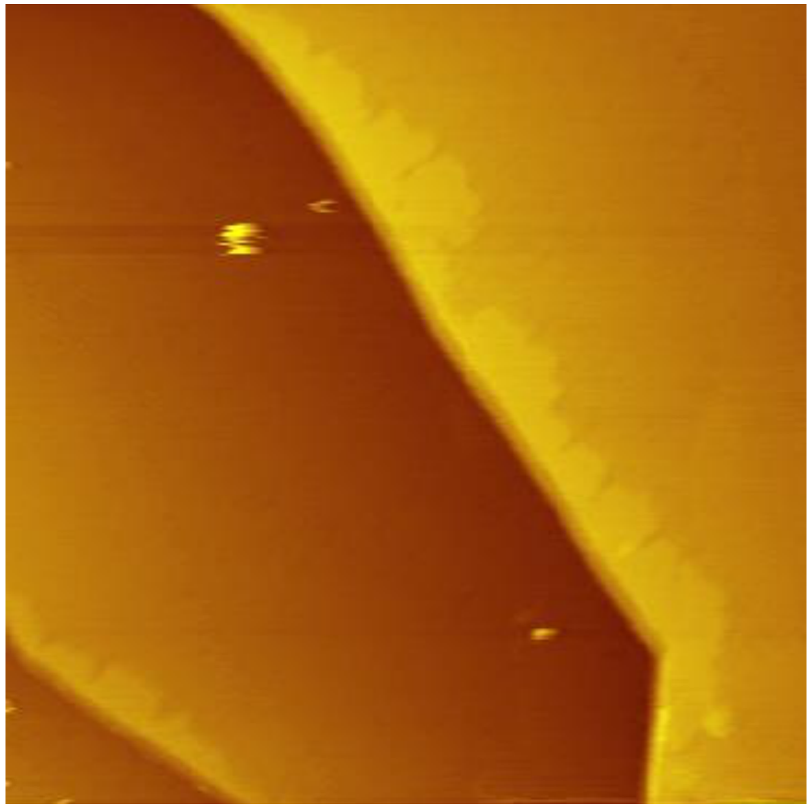
By LEED, a slow weakening of the Moiré spots is visible

Electron energy: 96.5 eV

By STM, the same as before and…



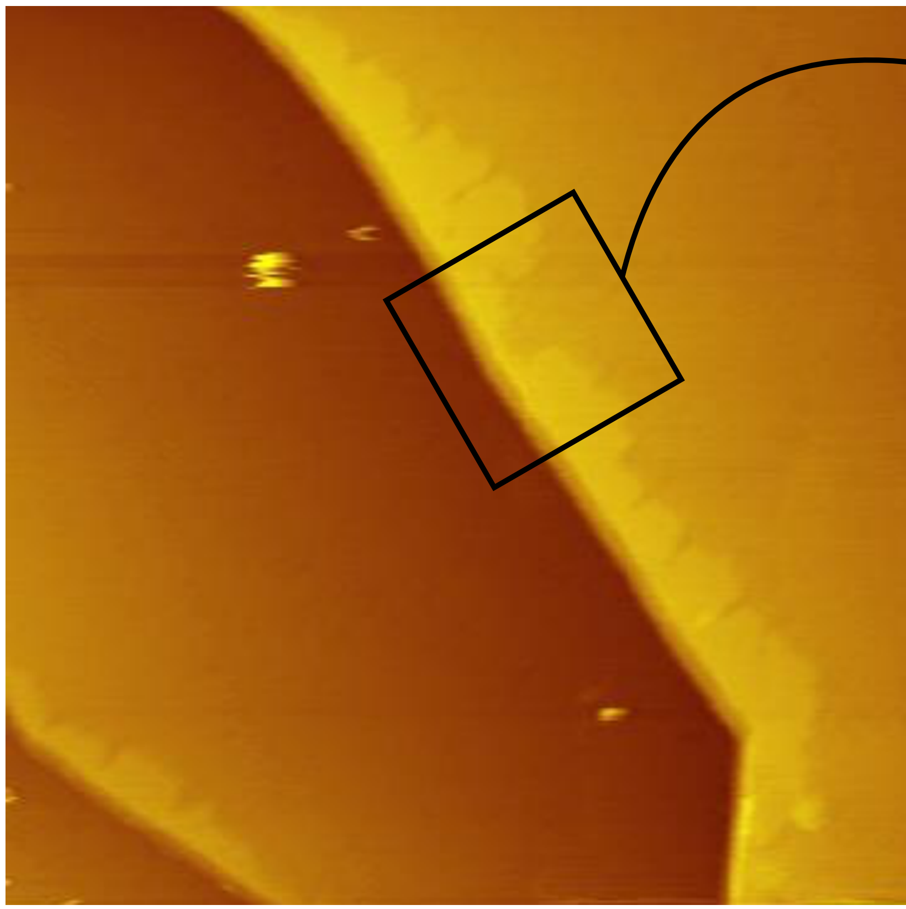
100×100 nm^2 scan area.
-500 mV, -170 pA



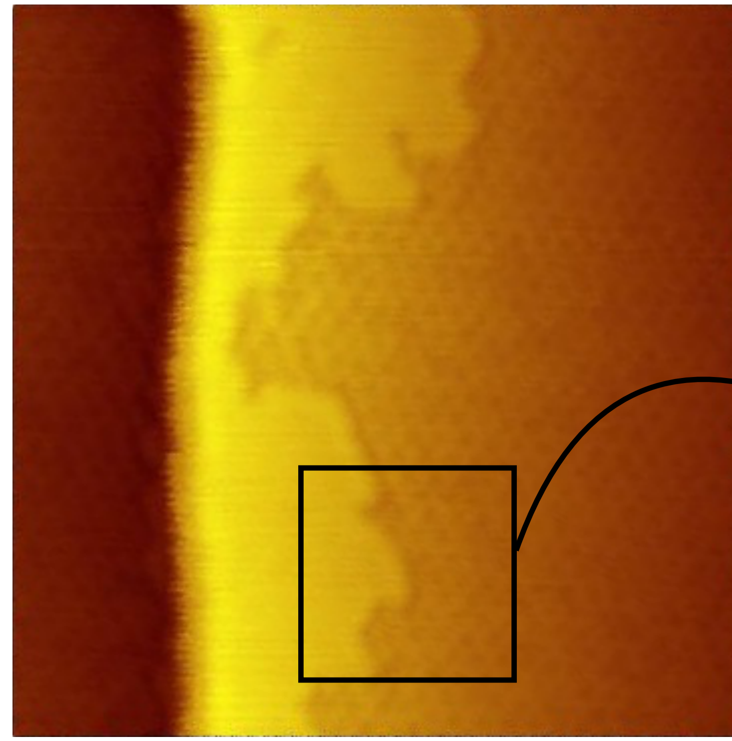
145×145 nm^2 scan area.
-500 mV, -170 pA

…something new!

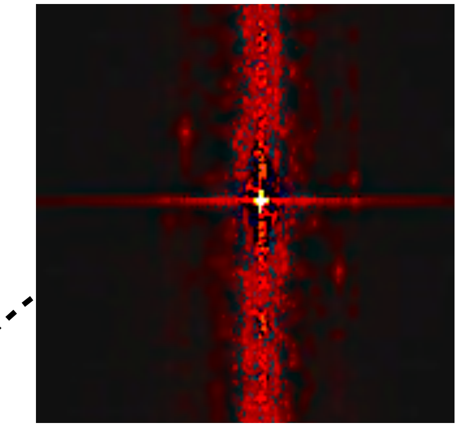
Zoom

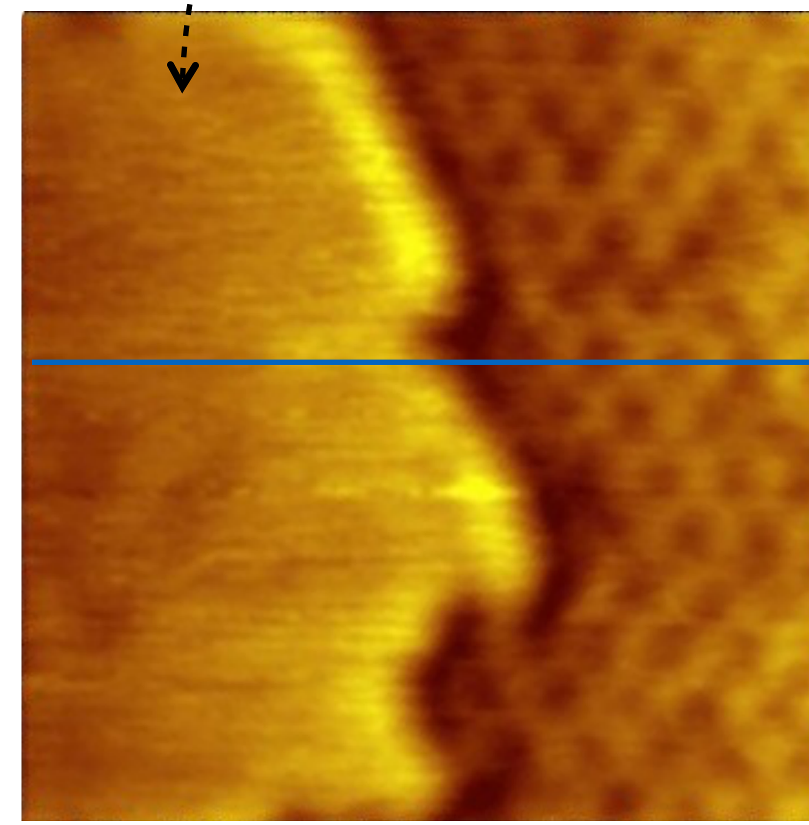


145×145 nm^2 scan area. -500 mV, -170 pA



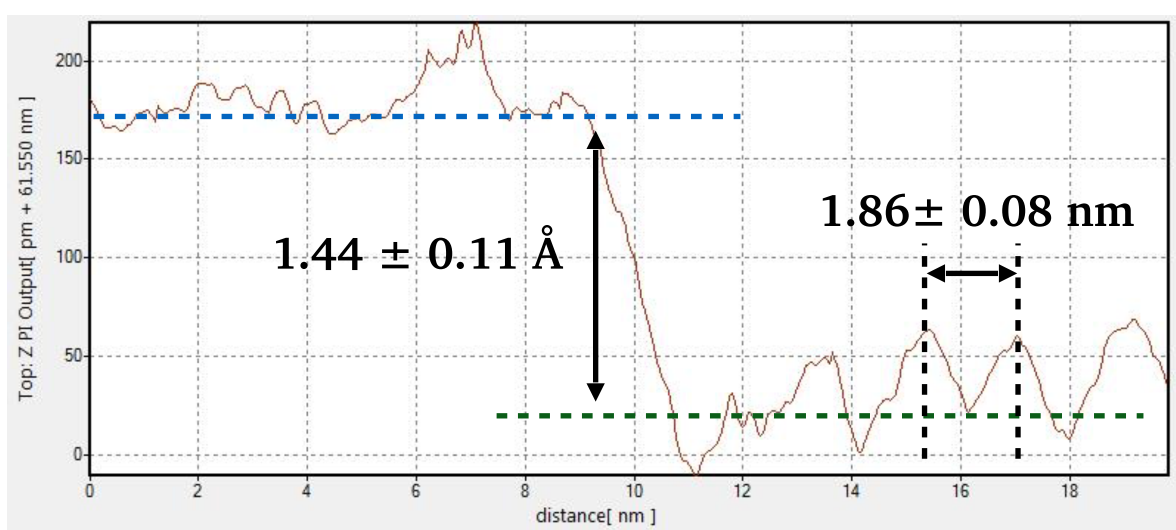
50×50 nm^2 scan area. -500 mV, -170 pA





20×20 nm^2 scan area. -500 mV, -170 pA

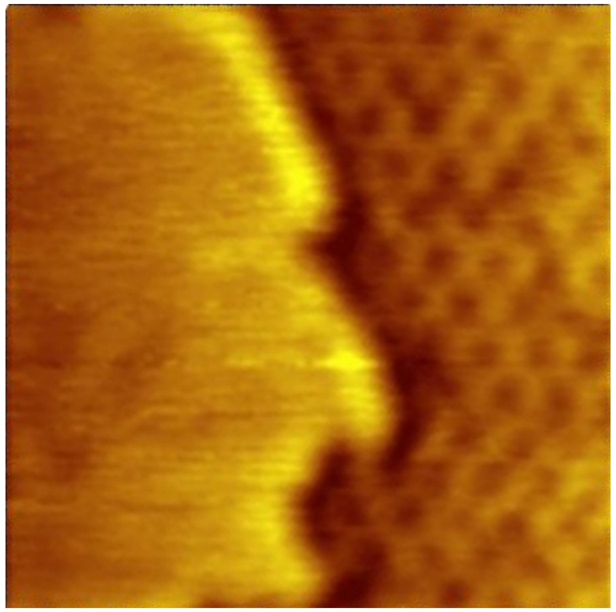
RMS corrugation:
0.22±0.06 Å

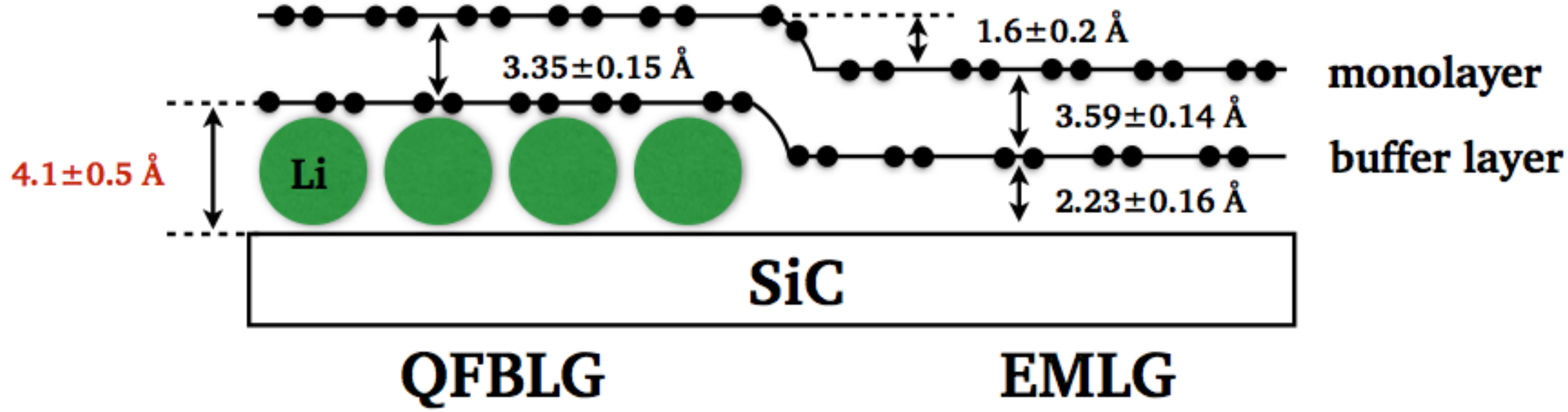


RMS corrugation:
0.35±0.05 Å

What can it be?

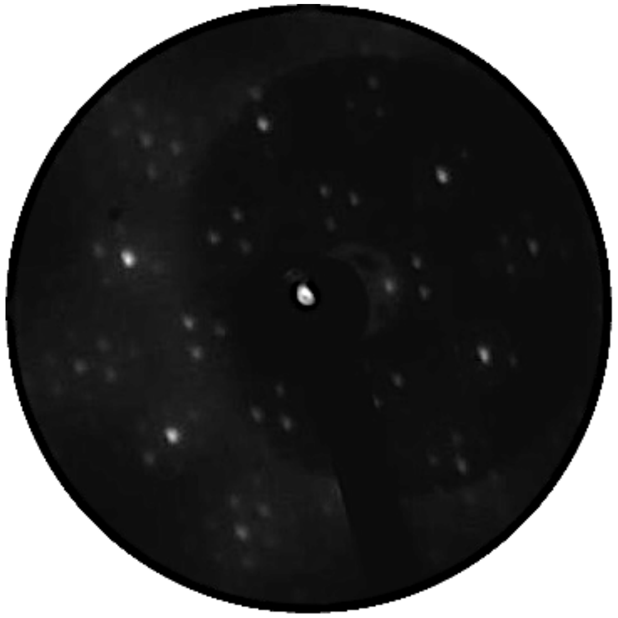
- Bilayer inclusions? No! No Moiré on the surface, difference height (0.8 Å vs. 1.4 Å)
- Li on? No! On the surface we see graphene lattice
- Li intercalated? Yes! Where? at the interface because the Moiré reconstruction is broken

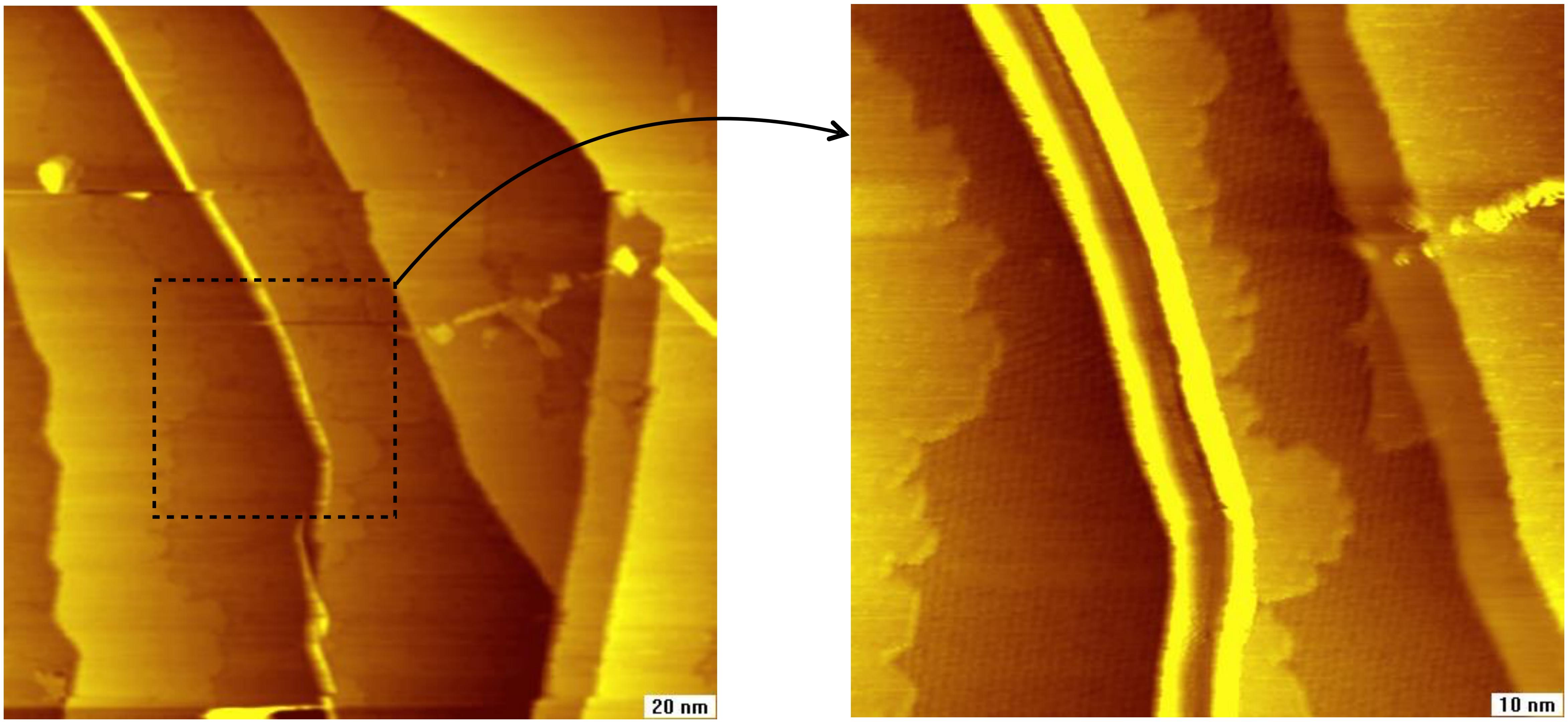




1 minute and half…

(0.047 ± 0.003 ML)





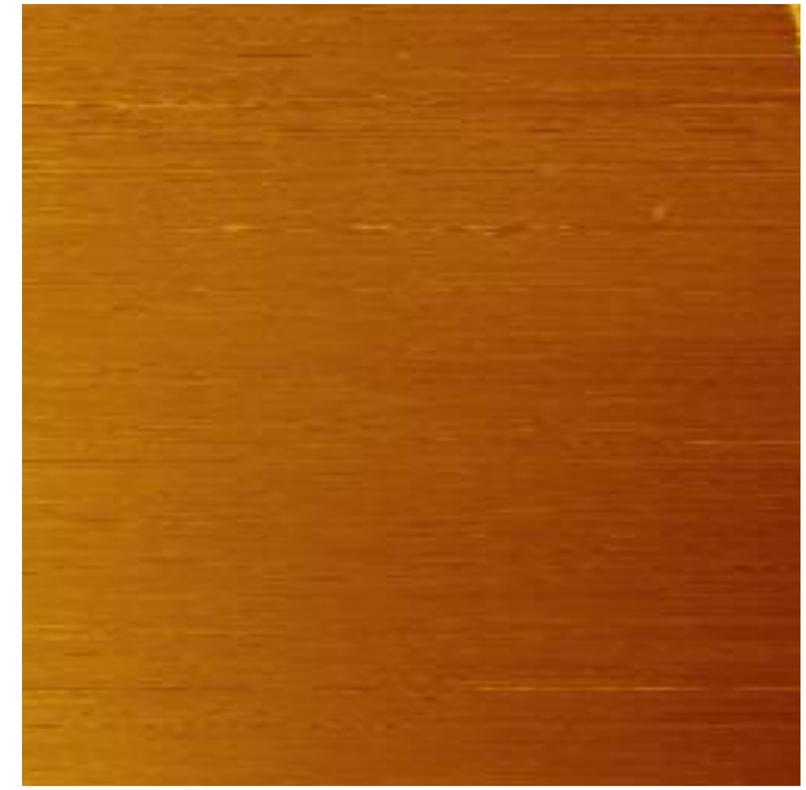
200×200 nm^2 scan area. 1 V, 1 nA 100×100 nm^2 scan area. 1 V, 1 nA

Li intercalated terraces extend inward the SiC steps

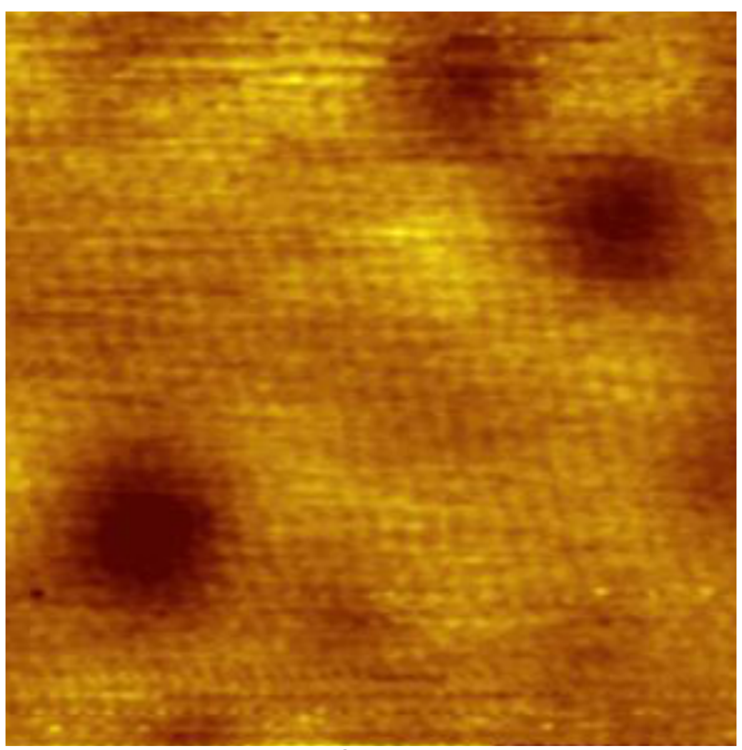
9 minutes of Li deposition (0.28 ± 0.02 ML)

Electron energy: 95.5 eV

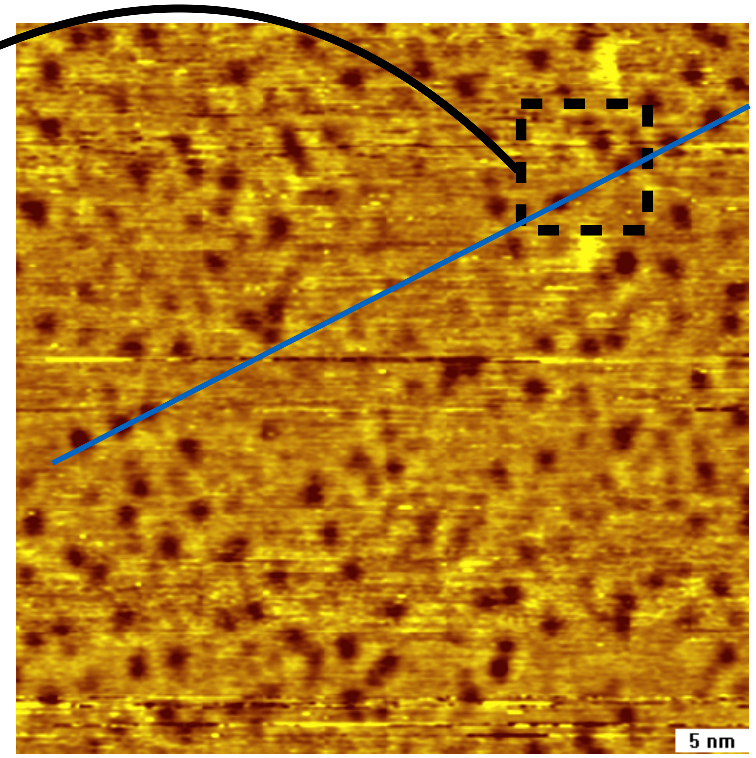
- LEED: graphene(1×1) and SiC(1×1) spots => no Moiré spots
- STM: uniform and homogeneous surface => no Moiré reconstruction



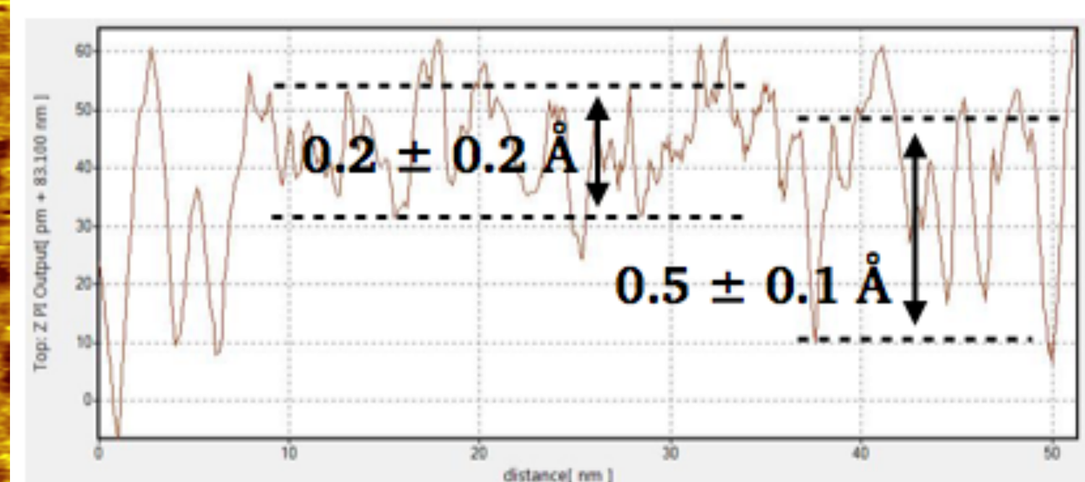
150×150 nm^2 scan area. 0.7 V, 300 pA



5×5 nm^2 scan area.
413 mV, 173 pA

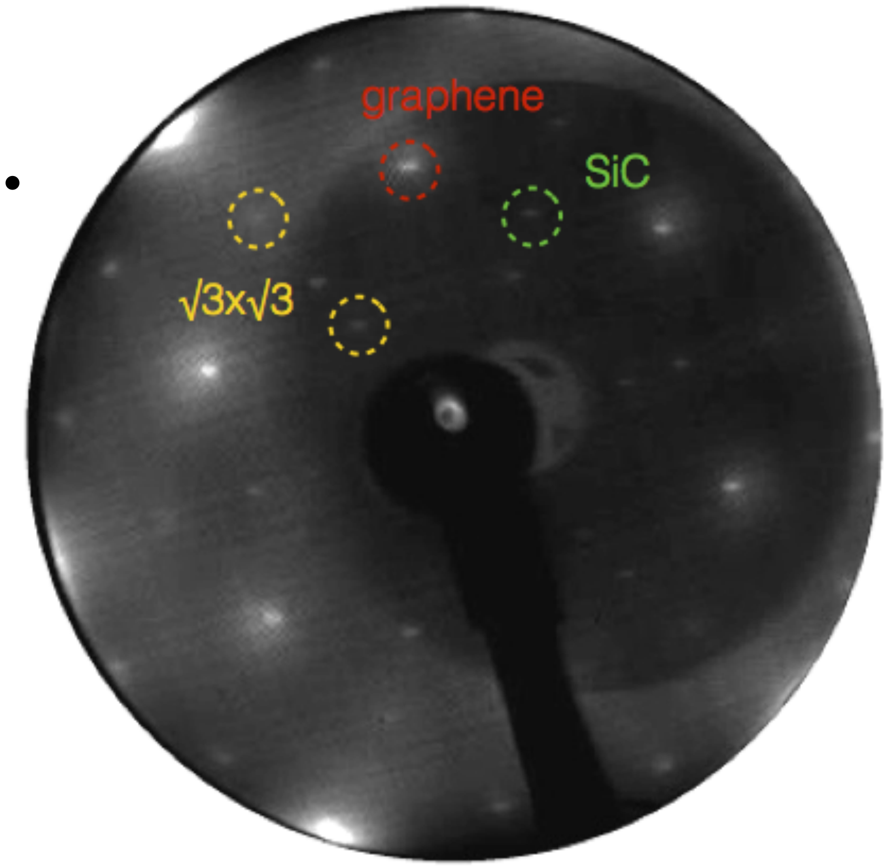


50×50 nm^2 scan area.
-500 mV, -0.51 nA



18 minutes of Li deposition (0.56 ± 0.04 ML)

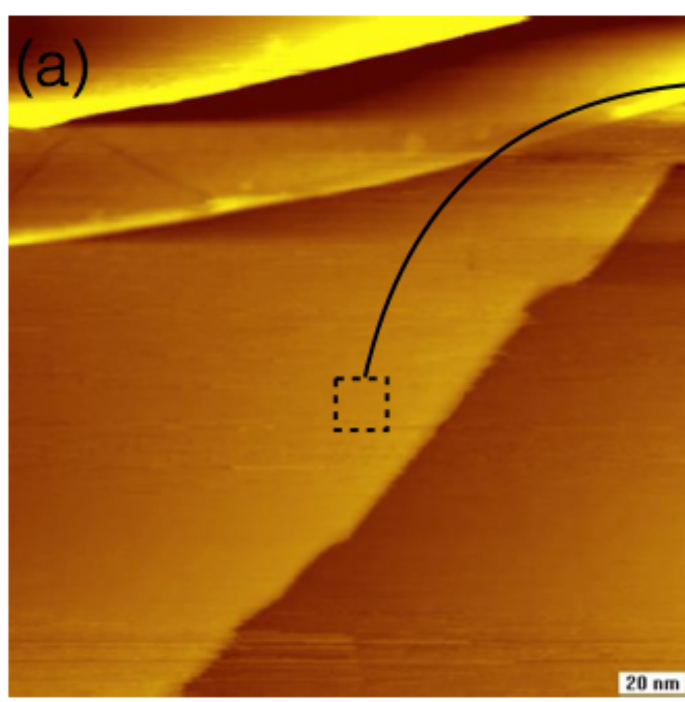
By LEED…



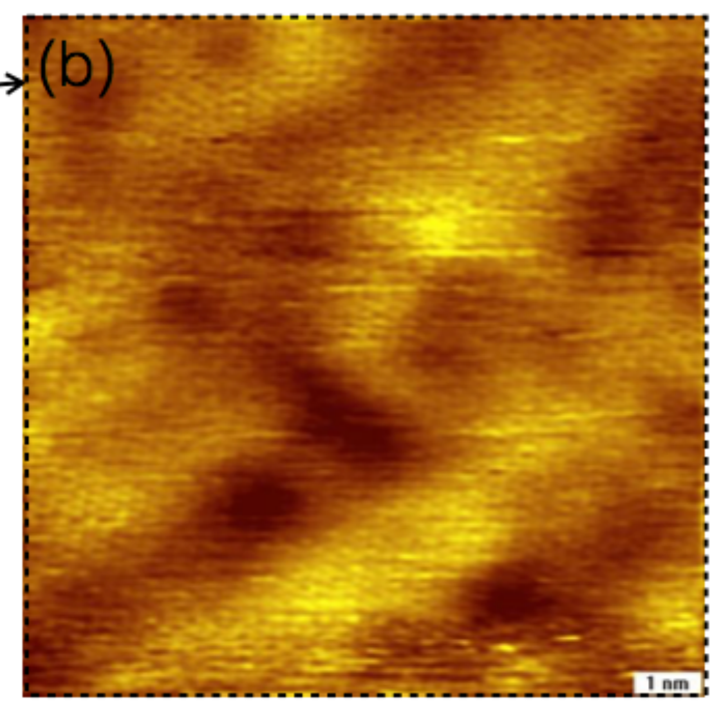
Electron energy: 135.6 eV

(√3×√3)R30° reconstruction!

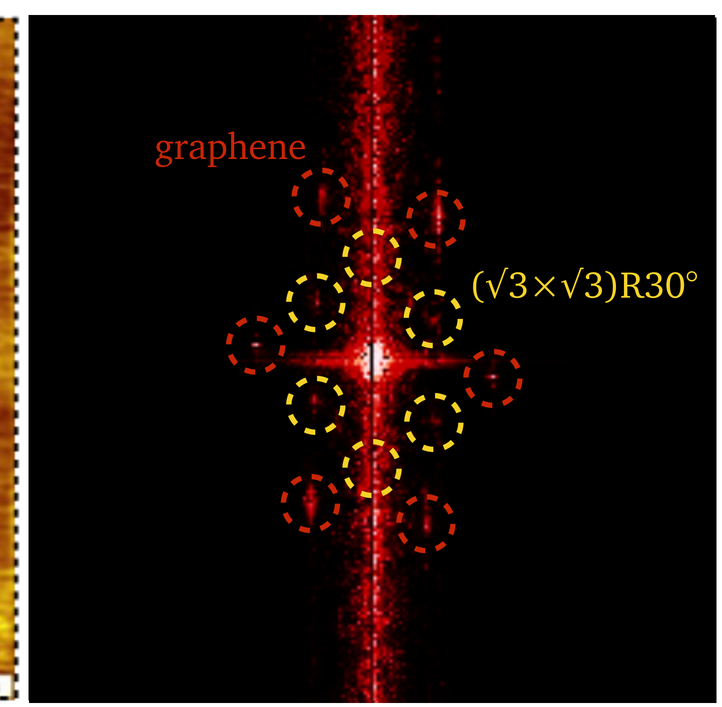
…which is visible also by STM!



200×200 nm^2 scan area.
30 mV, 90 pA



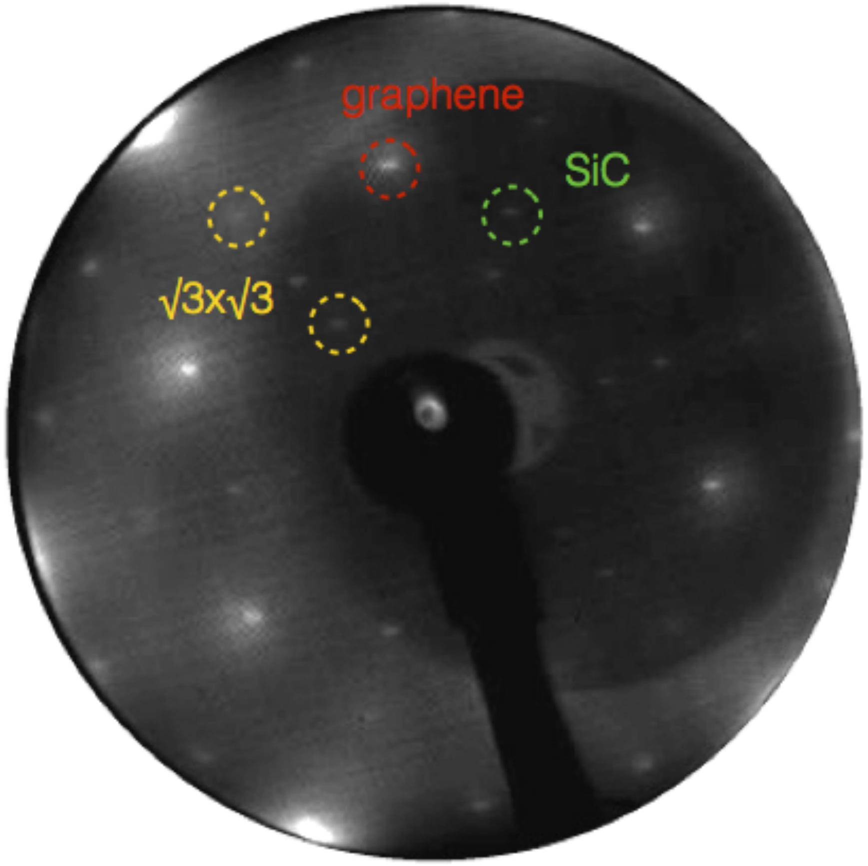
10×10 nm^2 scan area.
30 mV, 90 pA



2D-FFT

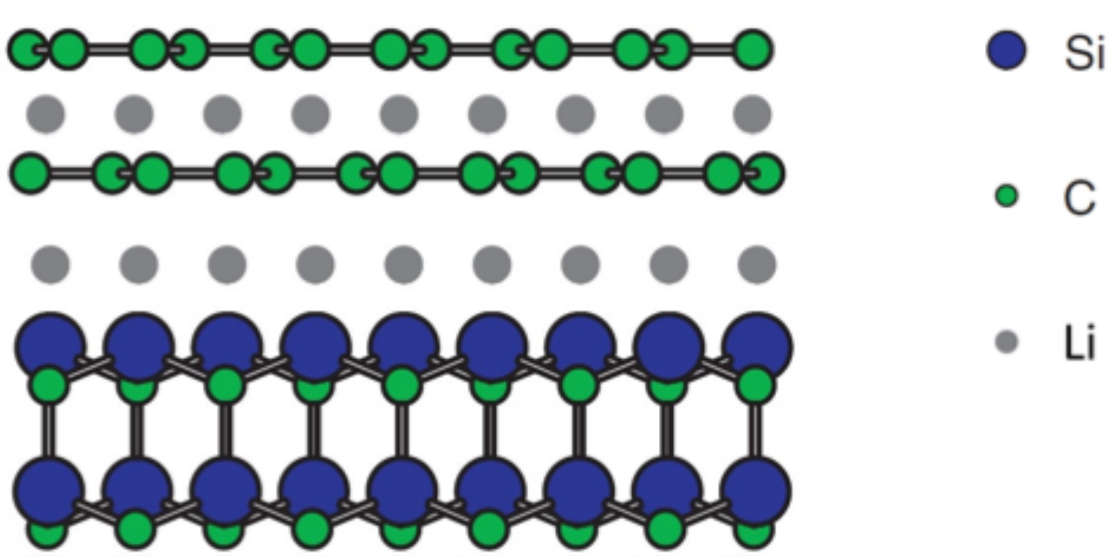
18 minutes of Li deposition (0.56 ± 0.04 ML)

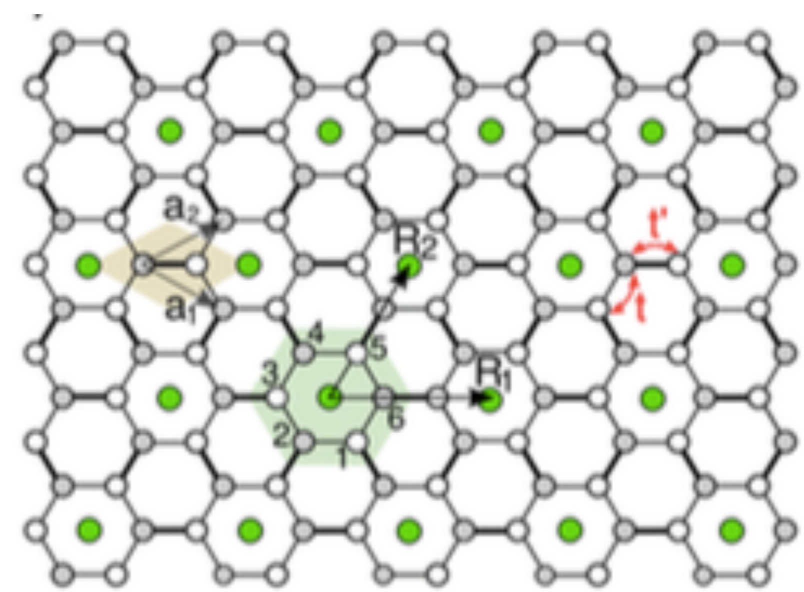
By LEED…



Electron energy: 135.6 eV

($\sqrt{3}\times\sqrt{3}$)R30° reconstruction!



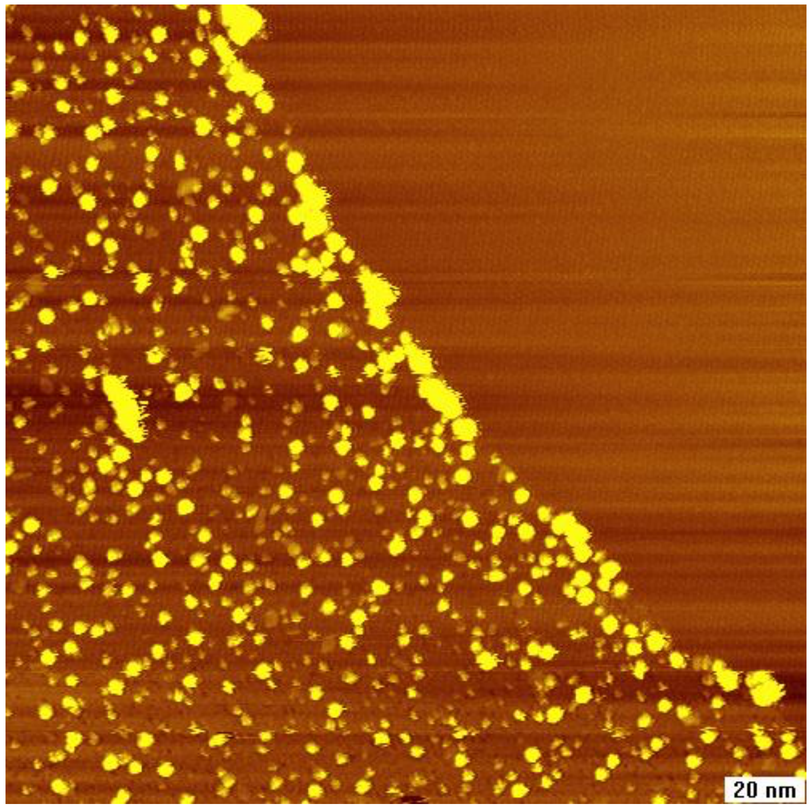


Nuala M. Caffrey et al., Phys. Rev. B **93**, 195421 (2016)

Li deposition on buffer layer

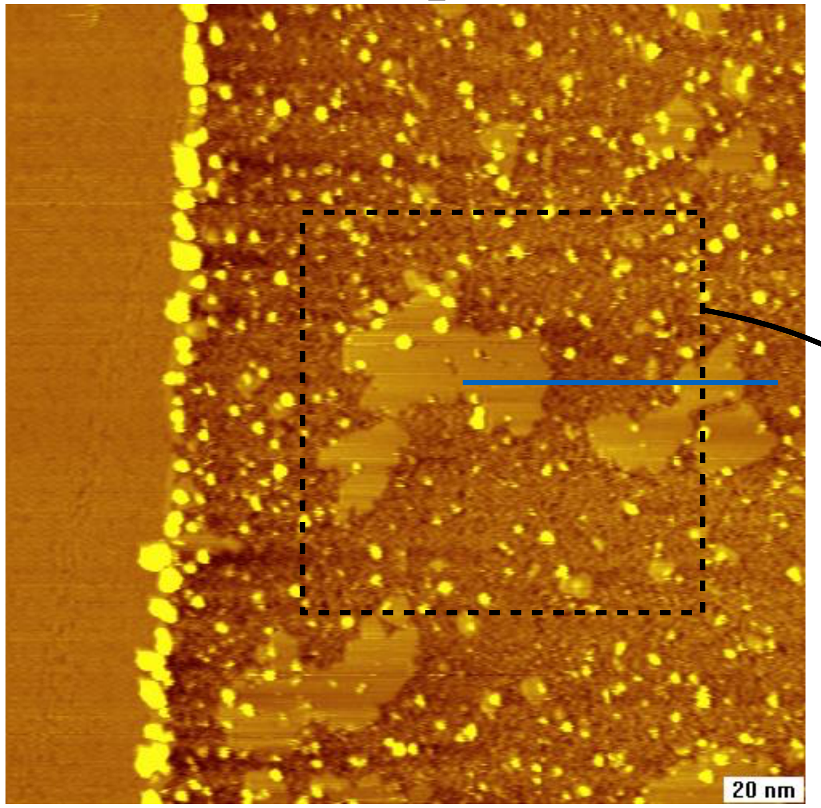
First significant changes after 0.047±0.003 ML of deposited Li (90 seconds)

Before Li deposition

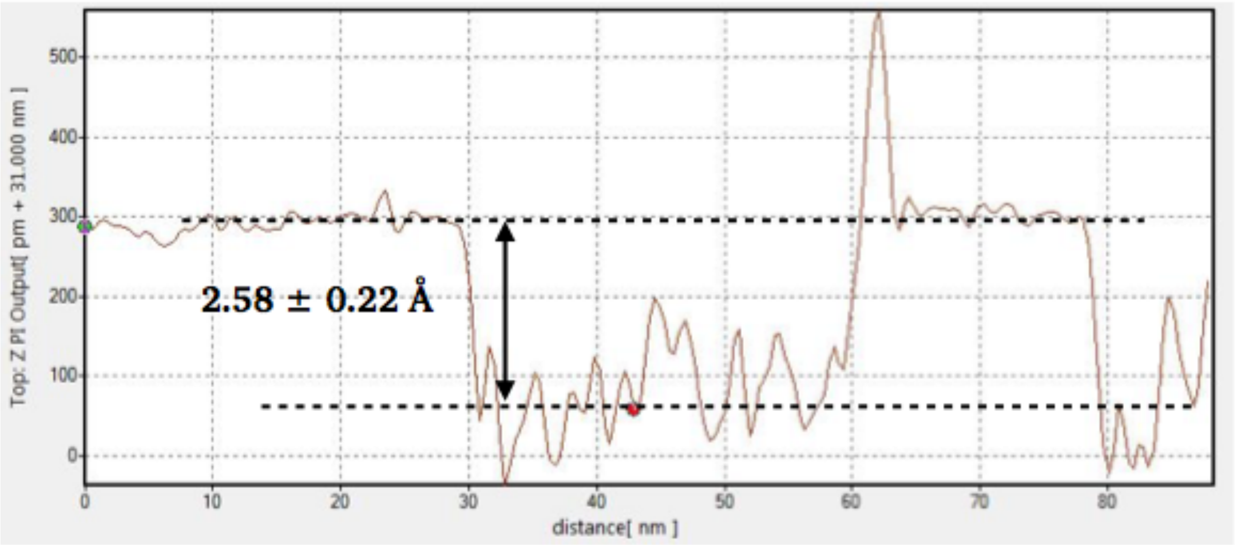


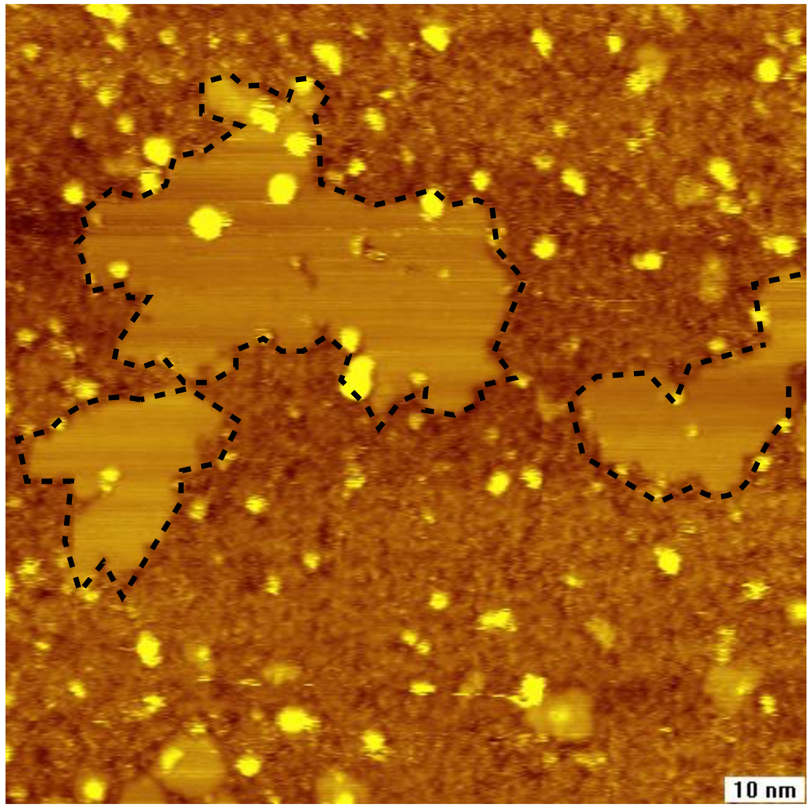
200×200 nm^2 scan area. 1 V, 1 nA

After Li deposition



200×200 nm^2 scan area. 1 V, 1 nA





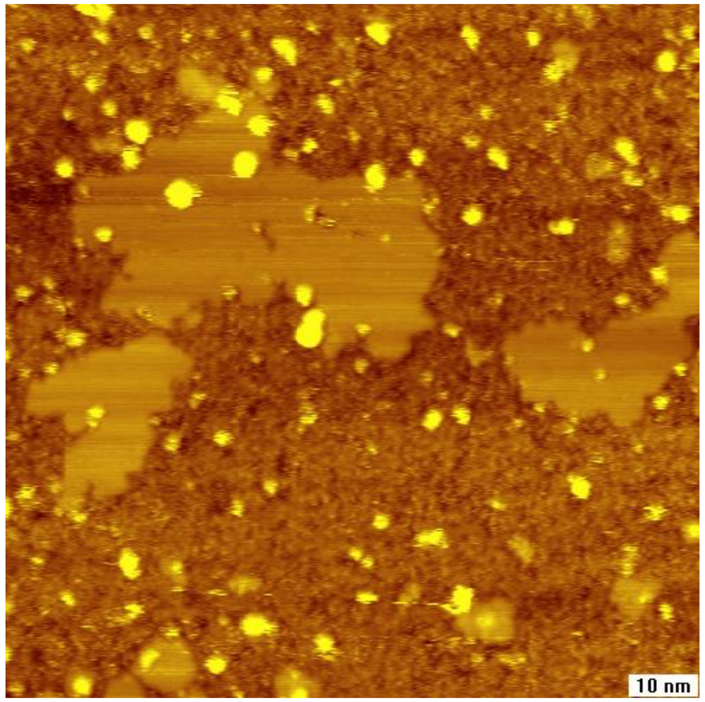
200×200 nm^2 scan area. 1 V, 1 nA

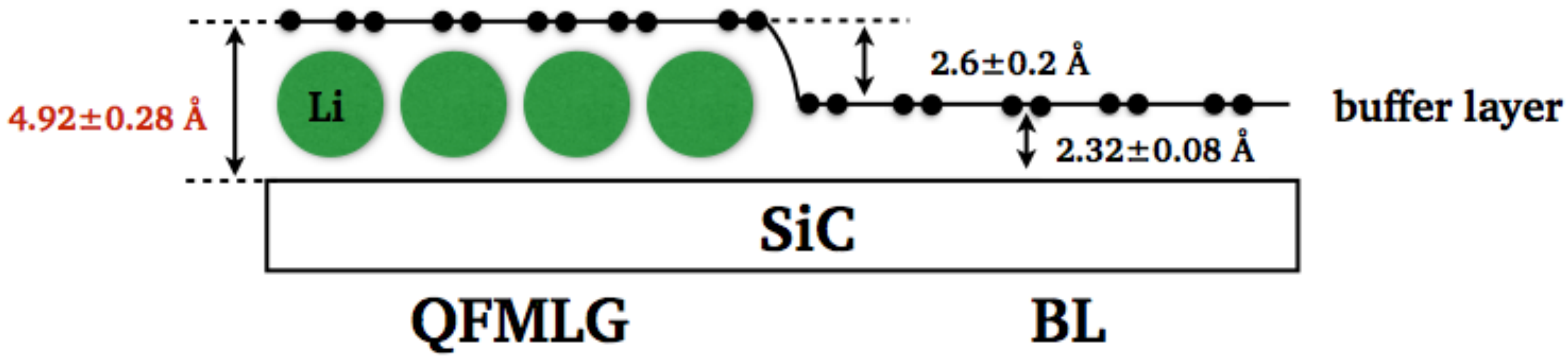
Also in this case…

Li intercalates below the buffer layer

⇒ transformation into a quasi-free-standing monolayer graphene

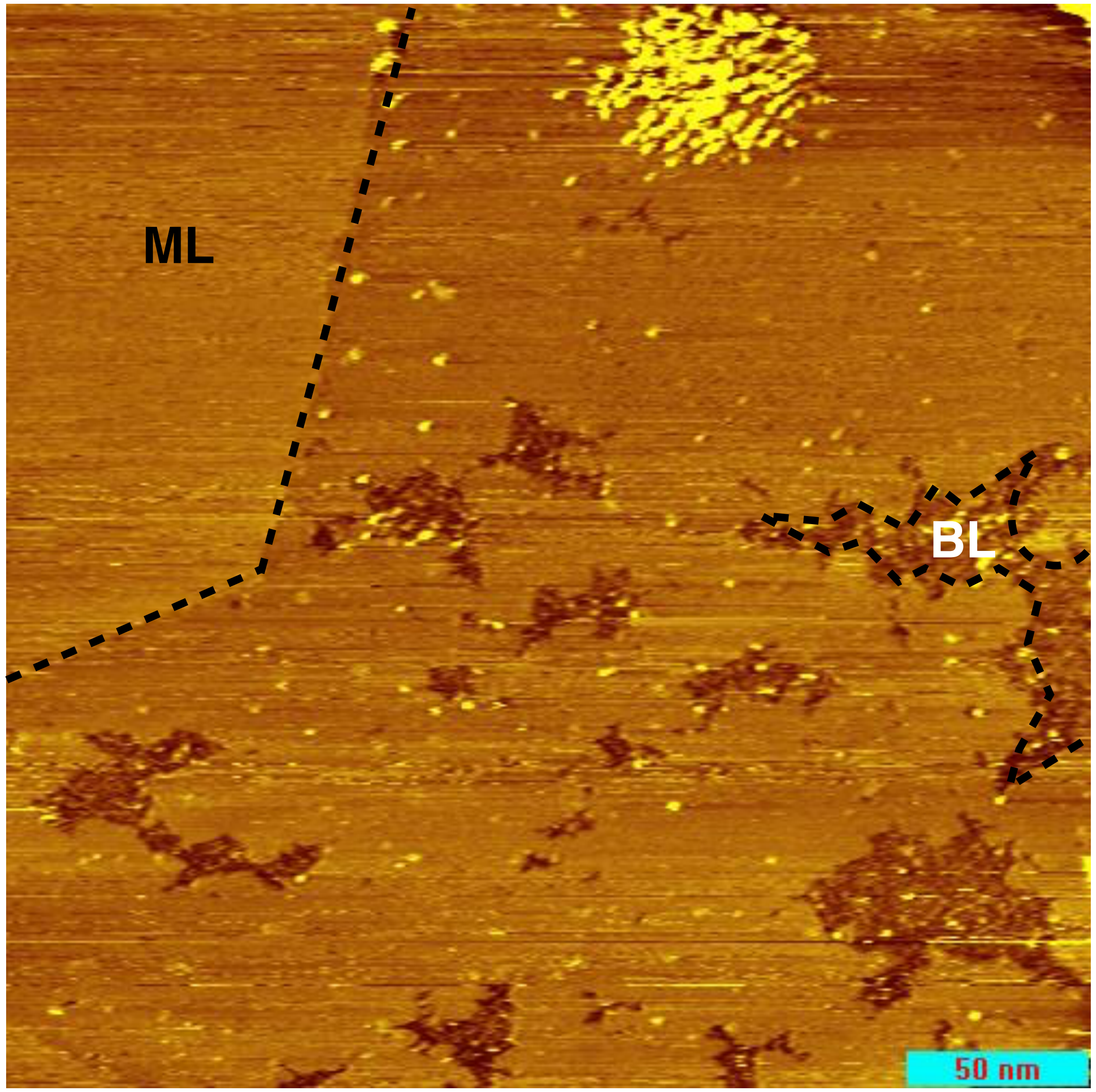
⇒ increase of the spacing between the substrate and the detached buffer layer.





9 minutes of Li deposition (0.28 ± 0.02 ML)

Electron energy: 95.5 eV



300×300 nm^2 scan area. 0.8 V, 1 nA

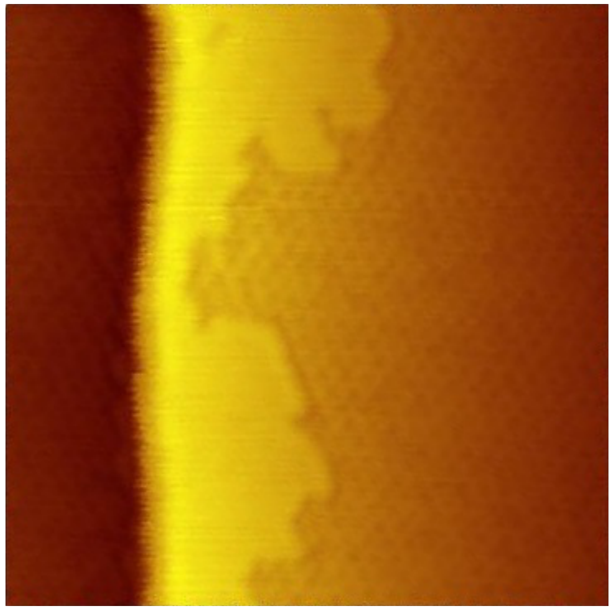
LEED: (1×1) reconstruction of graphene and SiC

STM: about complete intercalation of the total buffer layer area

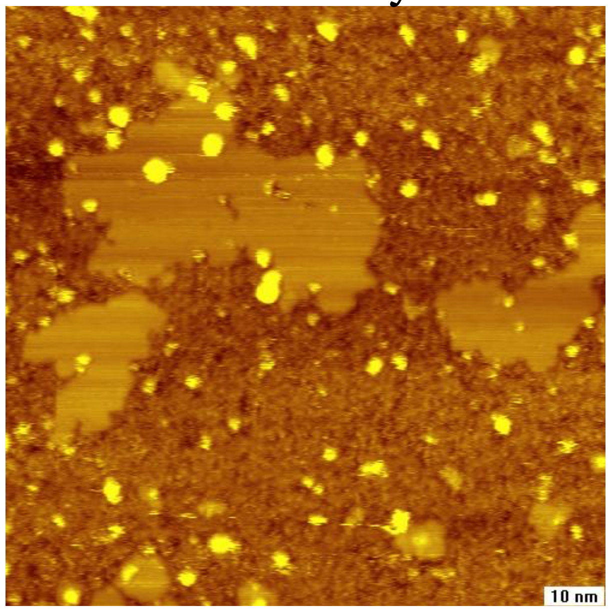
Li intercalation below EMLG
vs.
Li intercalation below buffer layer

1. Difference in shape: from where does Li intercalate?

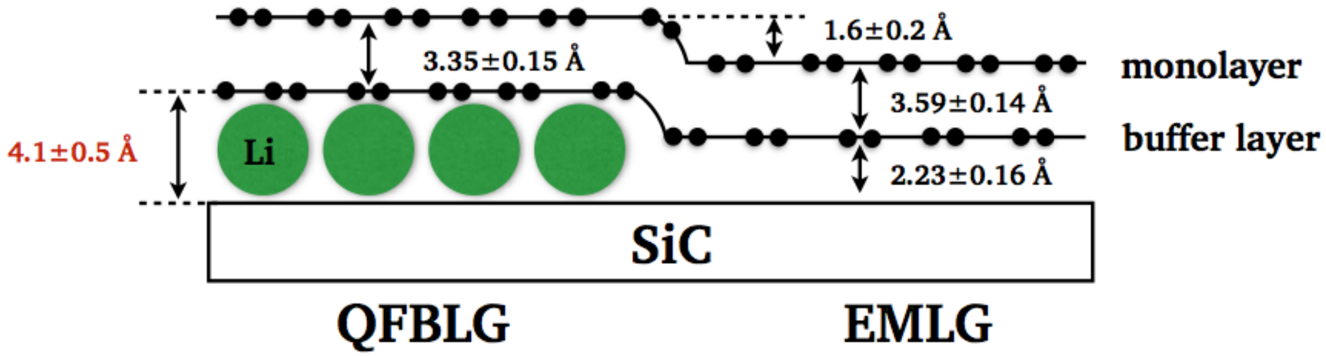
EMLG

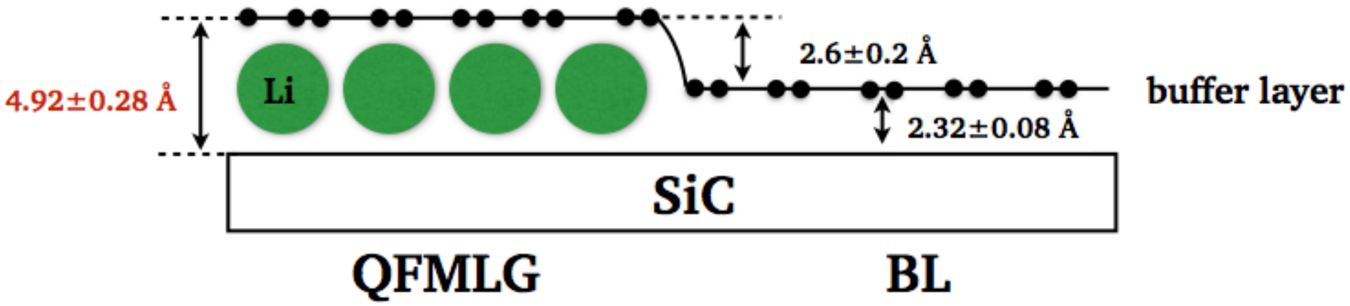


buffer layer



2. Difference in the interface spacing





Model

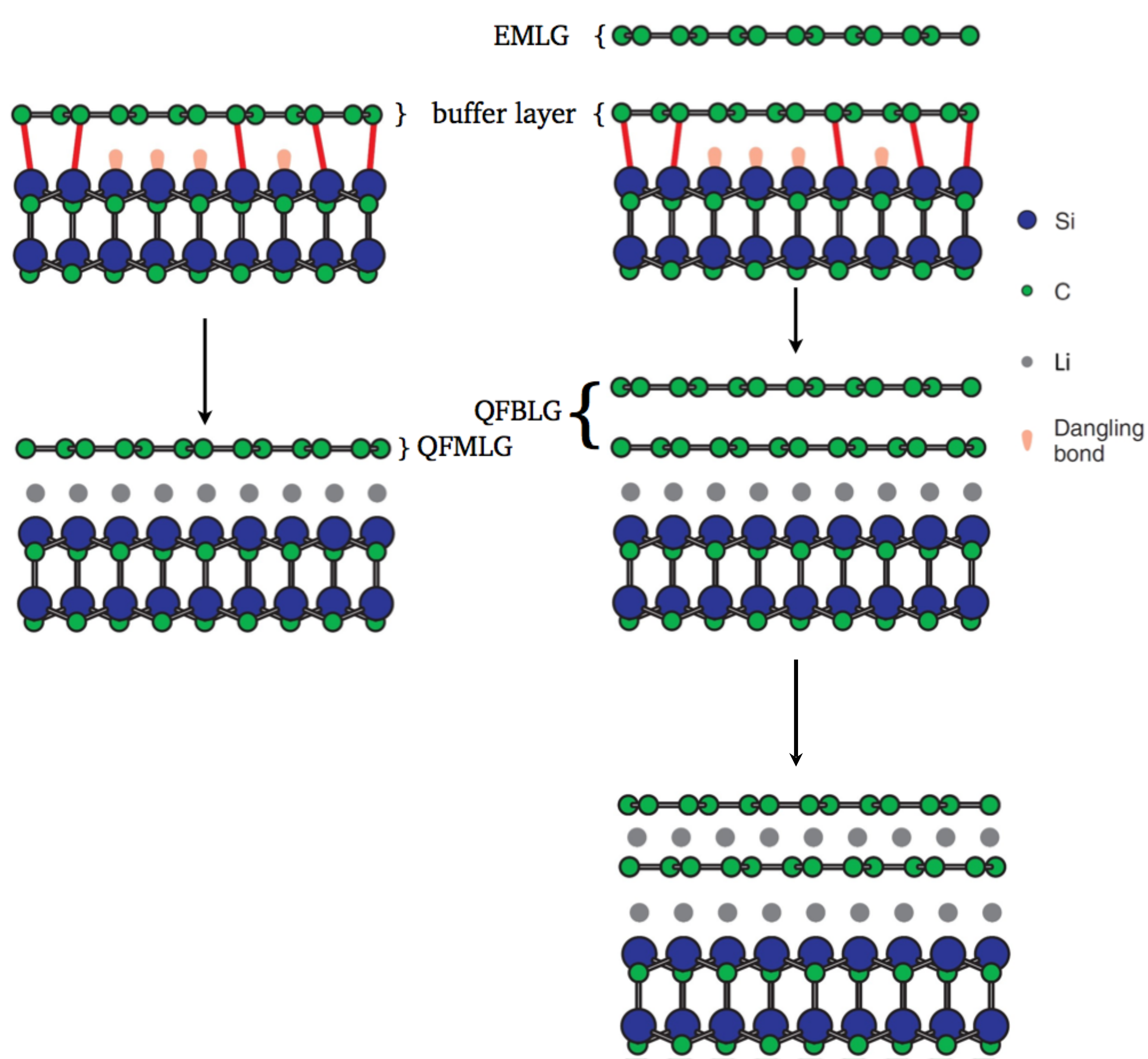
$6\sqrt{3}\times6\sqrt{3}$

$\Downarrow$

1×1

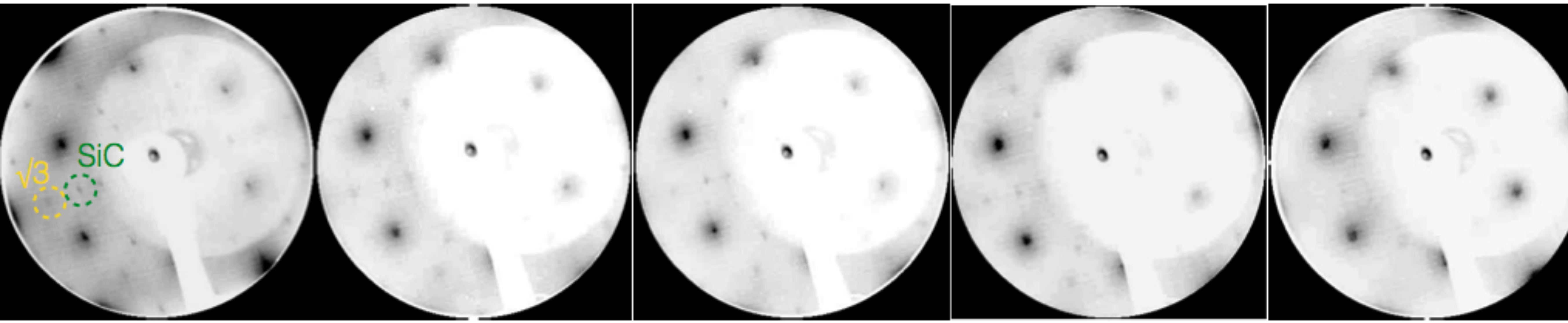
$\Downarrow$

$\sqrt{3}\times\sqrt{3}$



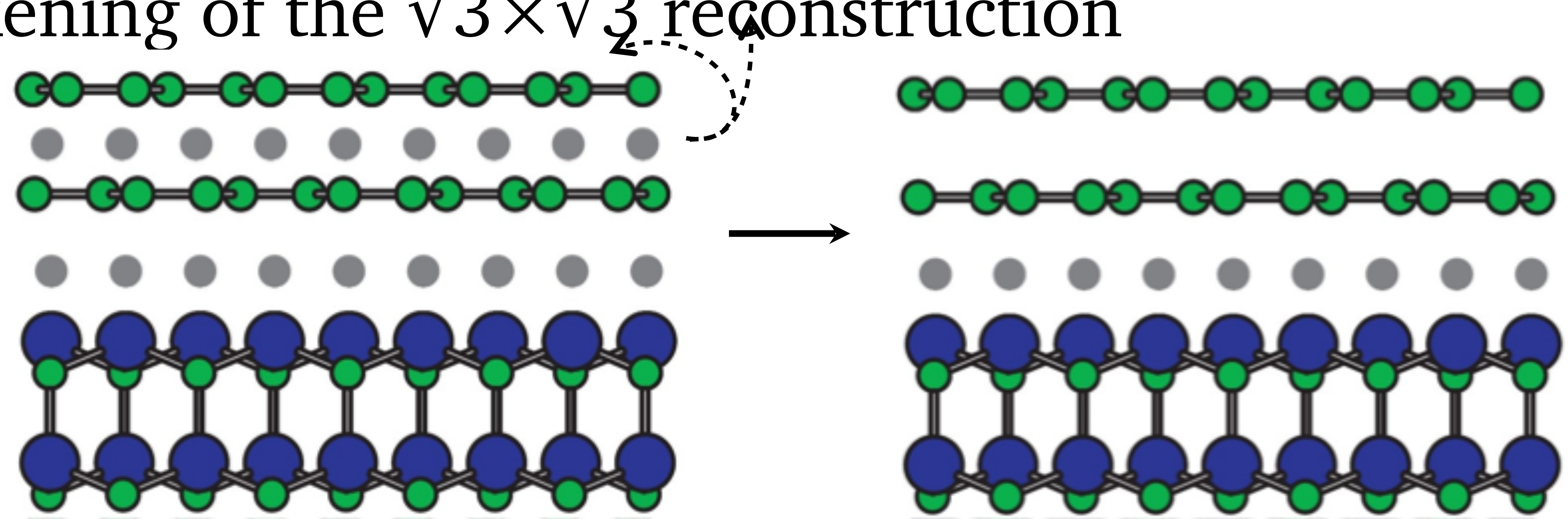
Annealing Experiments

LEED results

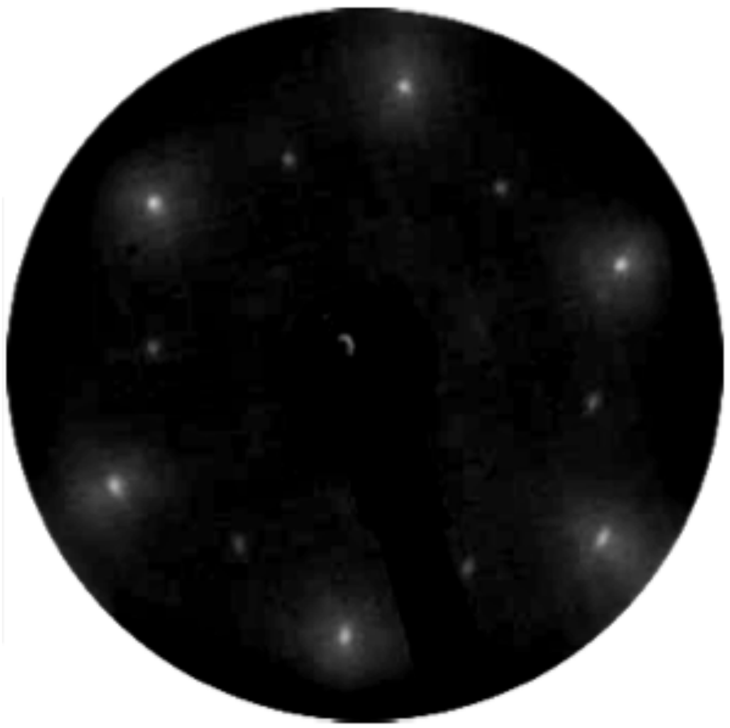


50 °C 80 °C 120 °C 150 °C 180 °C

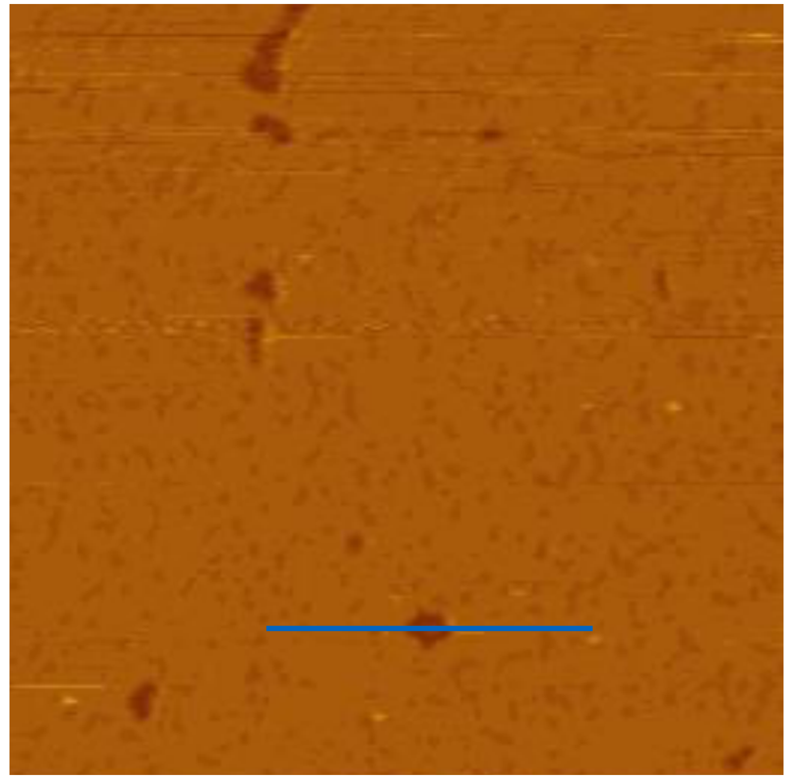
Weakening of the √3×√3 reconstruction → 1×1



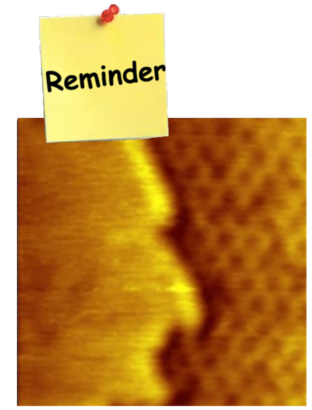
Annealing: 300 °C

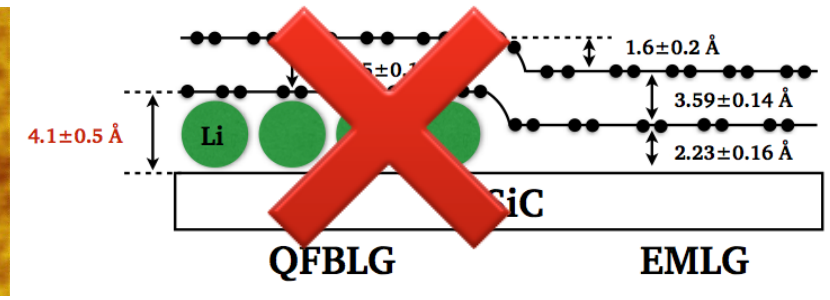


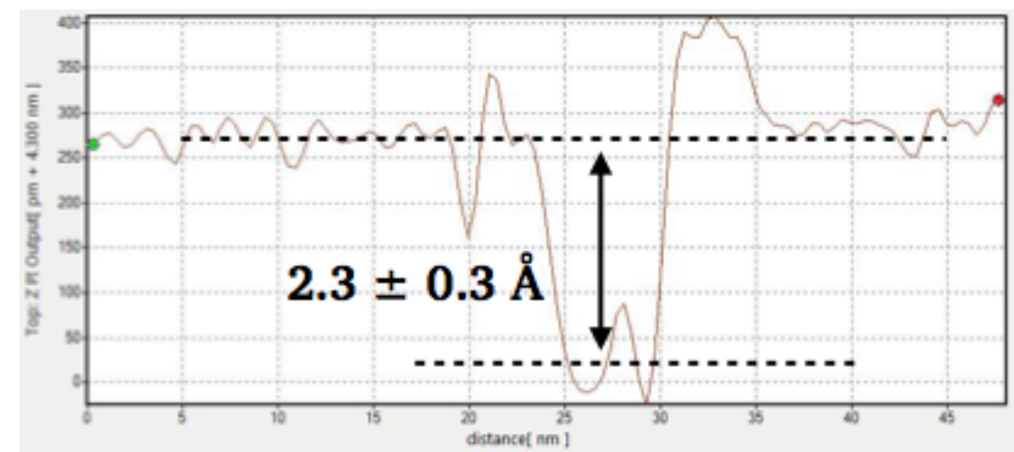
Electron energy: 95.5 eV



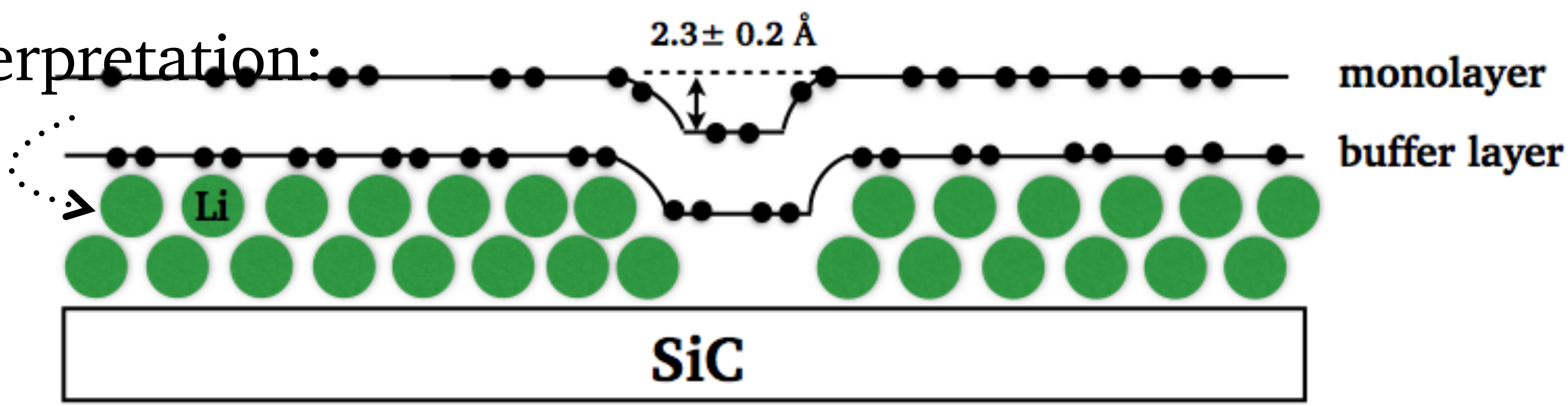
100×100 nm^2 scan area.
250 mV, 500 pA





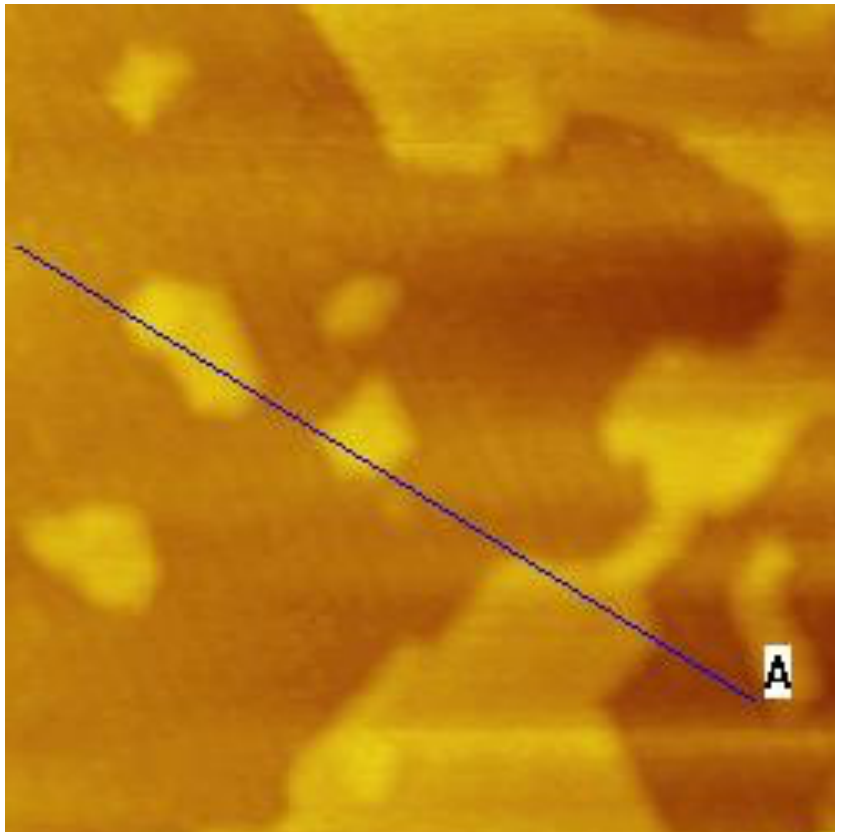


Our interpretation:

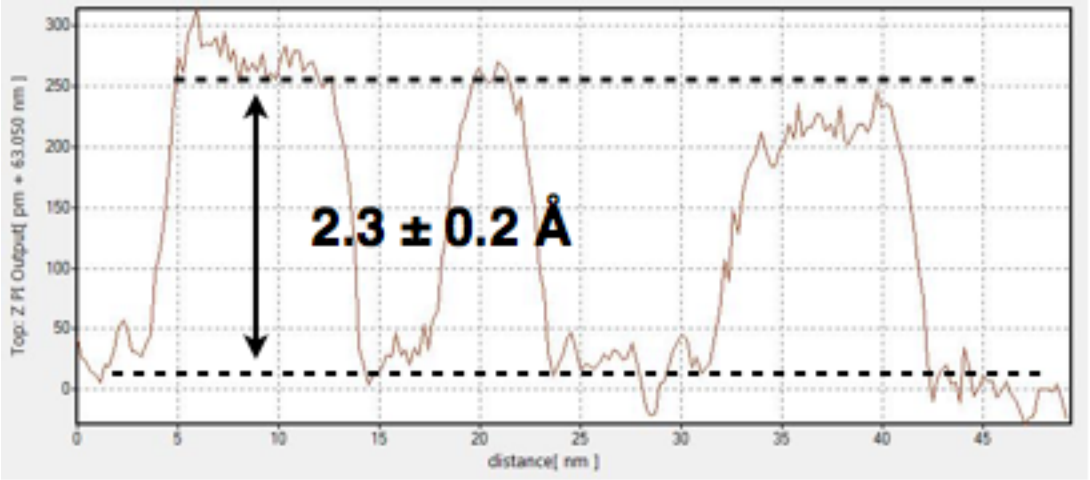


Annealing: 400 °C

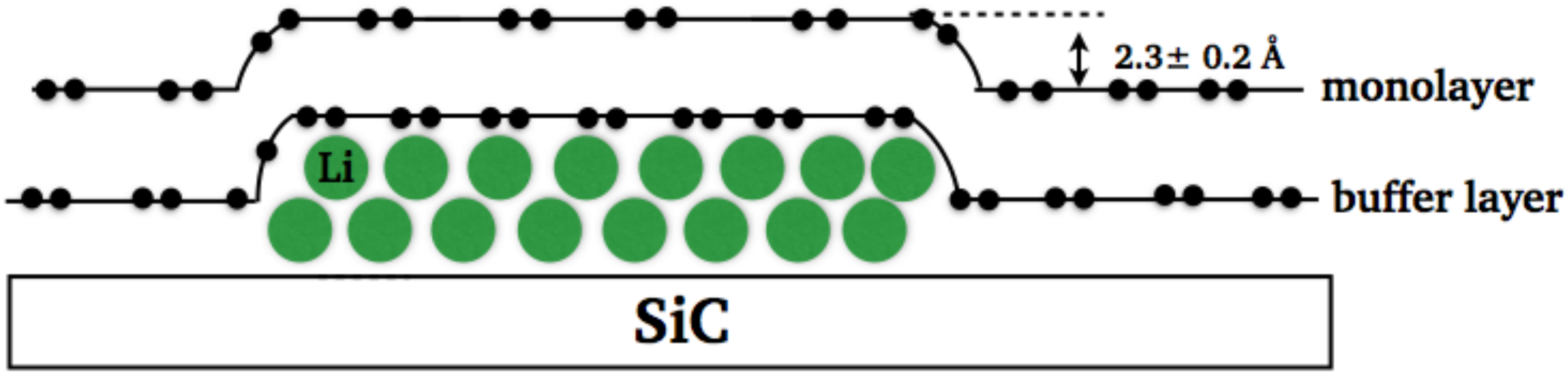
Electron energy: 95.5 eV



50×50 nm^2 scan area.
255 mV, 150 pA

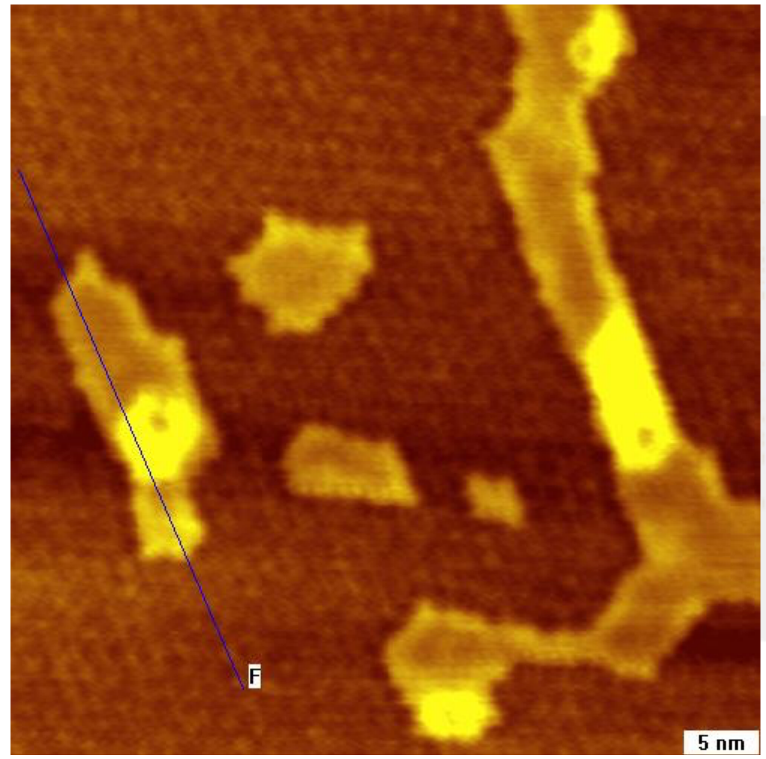


Moiré!!!

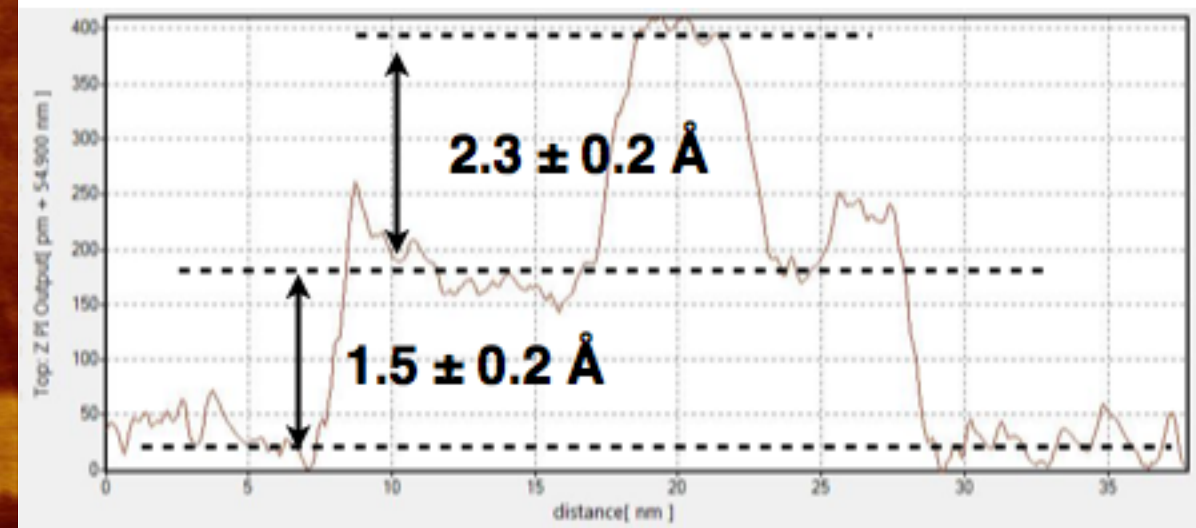


Annealing: 500 °C

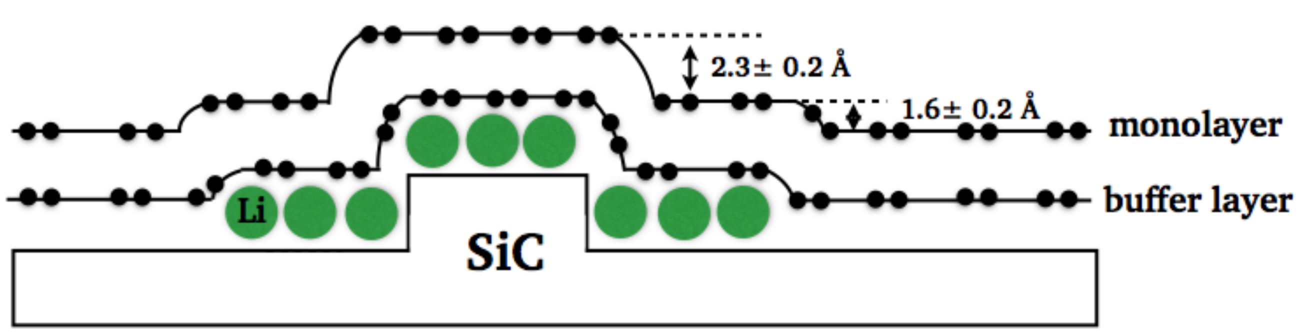
Electron energy: 95.5 eV



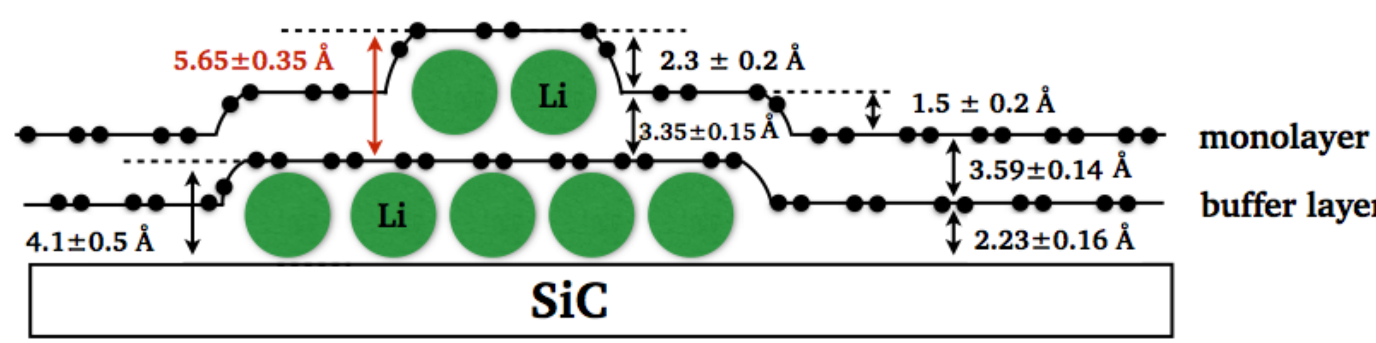
50×50 nm^2 scan area.
237 mV, 120 pA



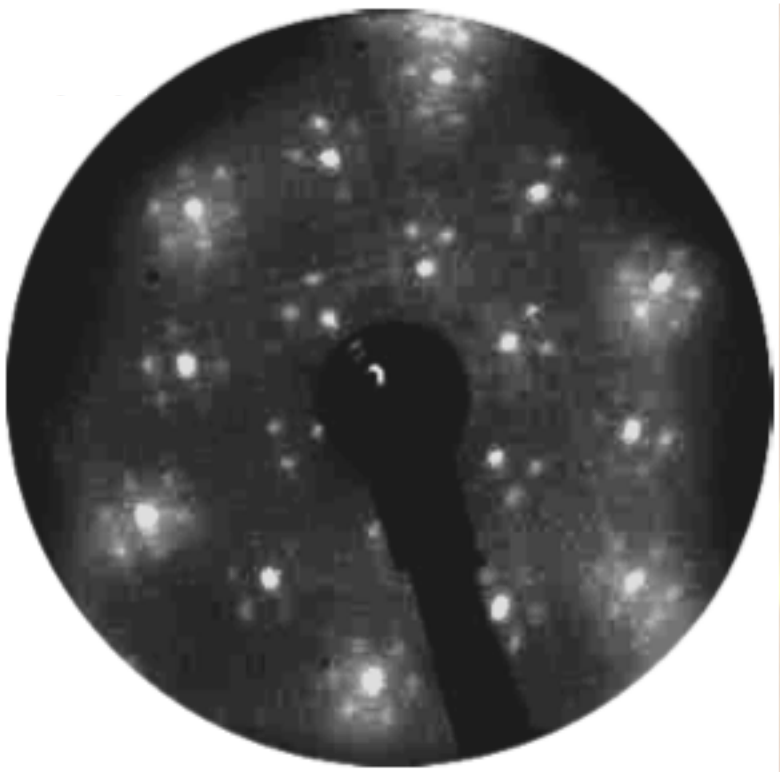
- SiC islands of monolayer height?



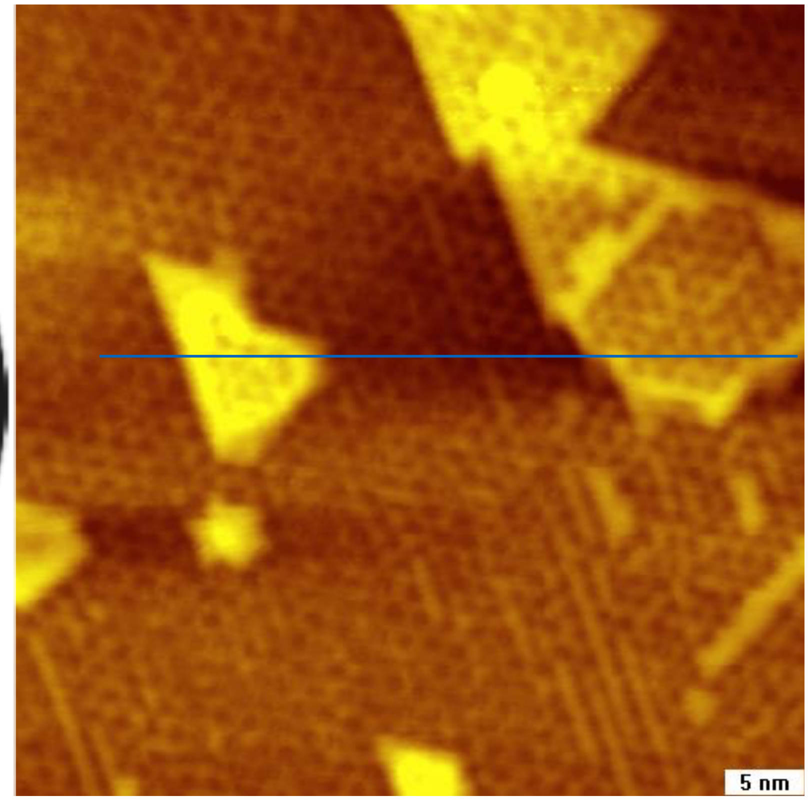
- Li moved to the spacing between the two graphene layers ad pinned to a defect in the buffer layer?



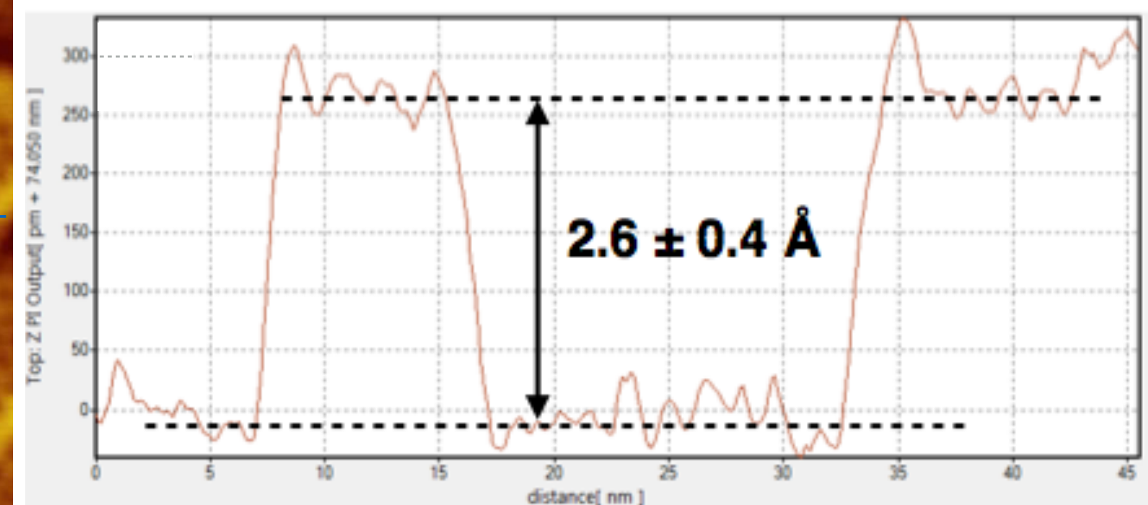
Annealing: 600 °C



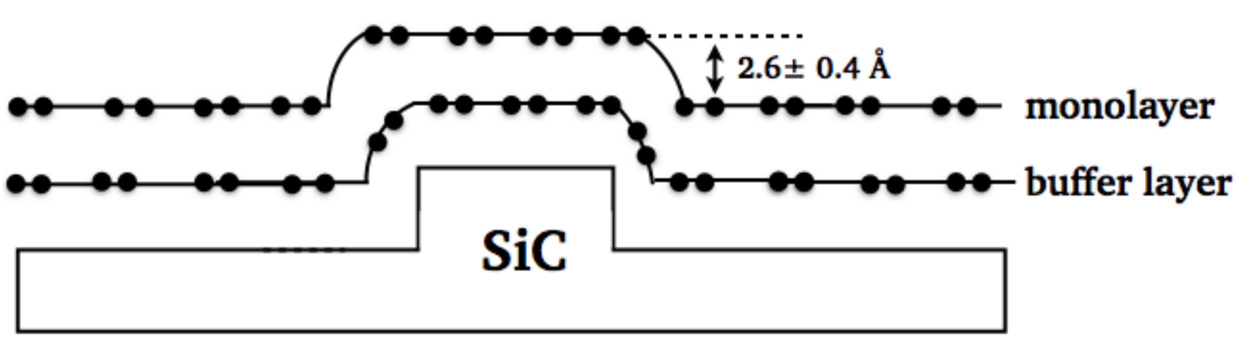
Electron energy: 95.5 eV



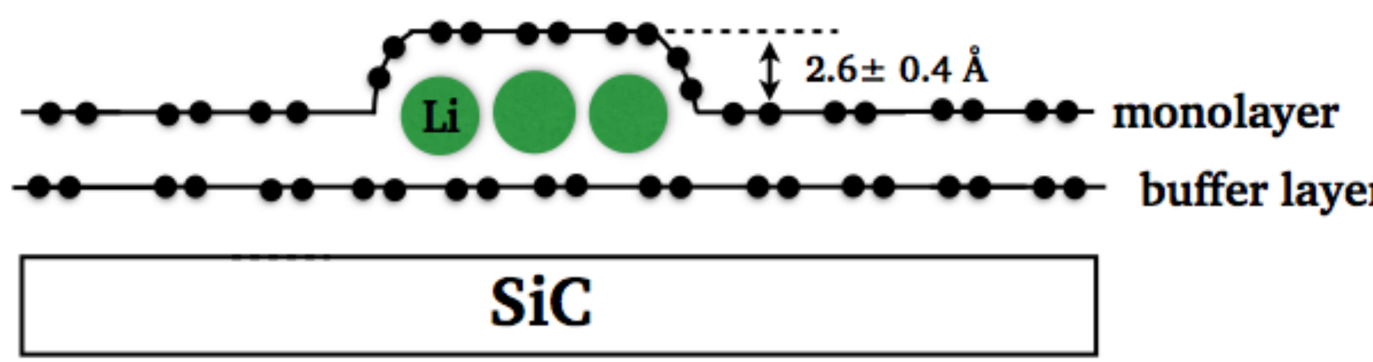
$50 \times 50\ nm^2$ scan area.
300 mV, 200 pA



- SiC islands of monolayer height?



- Li moved to the spacing between the two graphene layers ad pinned to a defect in the buffer layer?

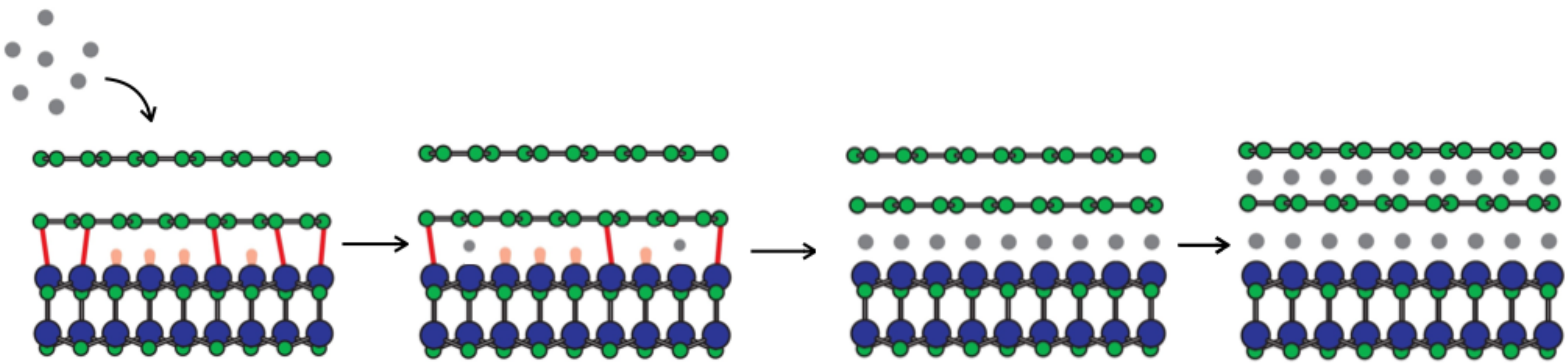


Outline

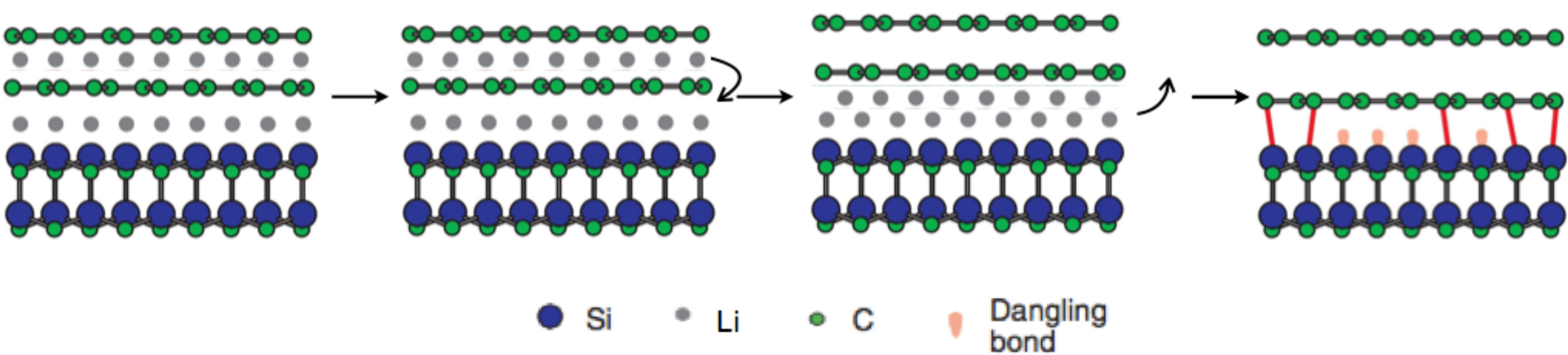
- Introduction: Hydrogen Storage
- Graphene and its applications in hydrogen storage
- Experimental methods: LEED, STM
- Results and discussion of the experiment
    1. Calibrating the rate of Li on Si(111)
    2. Li deposition on G/SiC and annealing
- Conclusions

Li deposition-intercalation-desorption process

- Depositing Li on G/SiC(0001)



- Supplying thermal energy



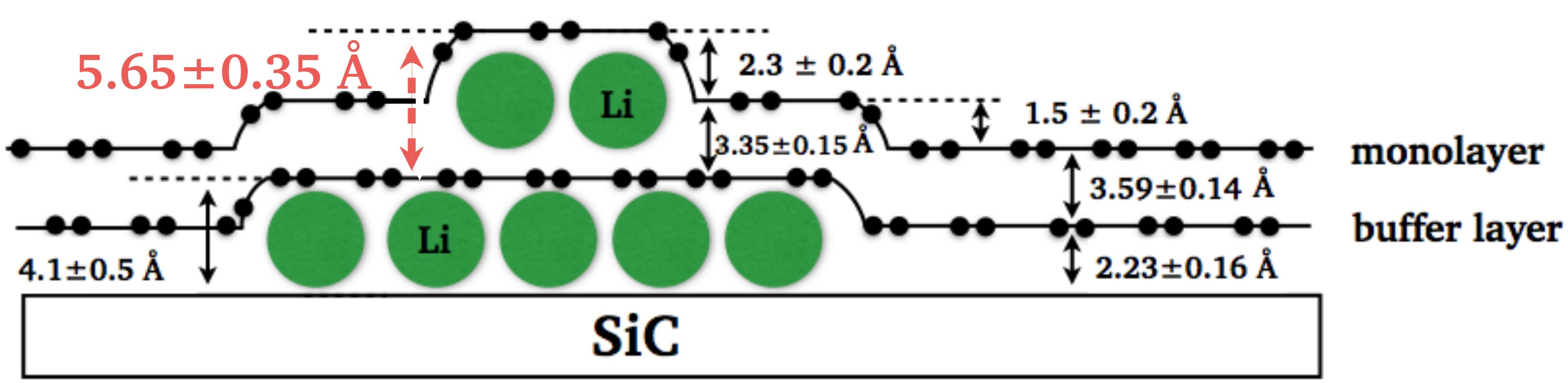
Summary

✓ LEED and STM studies of Li deposition/intercalation process

✓ LEED and STM studies of Li desorption process

✓ Measure of the interlayer spacing between substrate-buffer layer and detached buffer layer-monolayer

Li-functionalized graphene as an interesting material for hydrogen storage!



Thank you
for your attention!