The Abdus Salam International Centre for Theoretical Physics

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ICTP Conference Graphene Week 2008

25 - 29 August 2008

STM investigation of Few Layers Graphene (FLG) grown on the 6H-SiC(000-1) surface

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Outline:

- Epitaxial graphene, Si face (brief).
- Epitaxial graphene, C face:
  - *Motivation*
  - *Structure (atomic and electronic)*
  - *STM characterization of FLG*
  - *Interface layer.*

Coll.: D. Mayou (IN); W de Heer, C. Berger, E. Conrad (Gatech, Atlanta)
ANR GraphSiC,…

« Epitaxial graphene »: graphene layer(s) (FLG) formed by Si sublimation from SiC surfaces :

Van Bommel et al., Surf. Sci. 48, 463 (1975)

C. Berger et al., J. Phys. Chem. B 108, 19912 (2004) in the context of graphene physics.

- Good transport properties (mobility, …)

  W. de Heer et al. Solid State Comm. 143, 192 (2007) for a review.

- Mass (wafer size) production conceivable in principle,

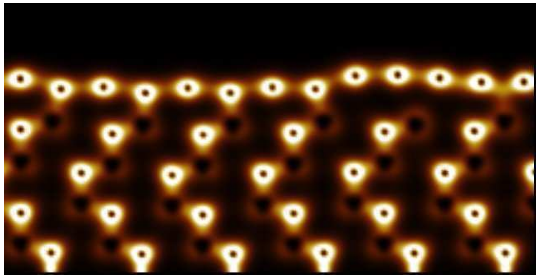
Allows the investigation of the detailed atomic and electronic structure of the sample by surface science techniques (XRD, ARPES, STM, …) and ab-initio calculations:

- Morphology: *domain size, défects,*
- Electronic structure: *band structure, doping, chirality*
- Interaction of single graphene layer with the substrate and with adjacent planes.
- 2 different substrate faces: -C (000-1) and –Si (0001).

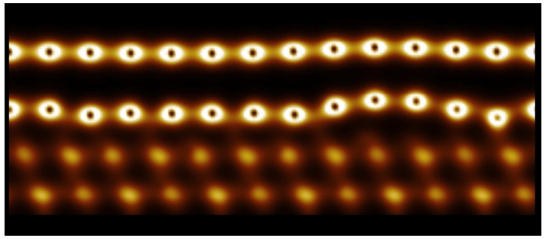
Example: atomic and electronic structure of FLG on Si face.

Varchon et al., PRB 77, 235412 (08)

1st C layer: “6R3”



2nd C layer: graphene.

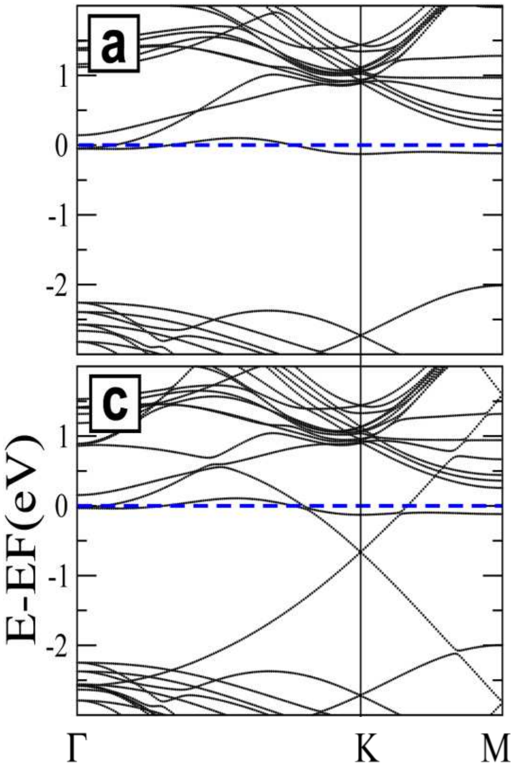


Ab-initio calculation.

Also: Kim et al., PRL 100, 176802 (08) (+ band structure calculation).

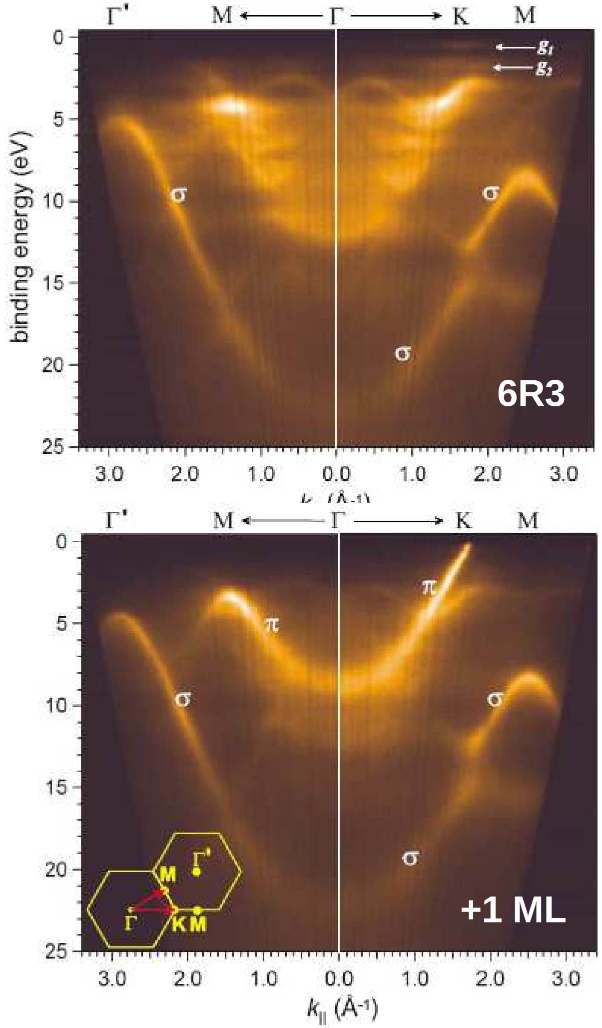
Poster by D. Mayou.

Varchon et al., PRL 99, 126805 (07)



Also: Mattausch et al., PRL 99, 076802 (07).

Emtsev et al., PRB 77, 155303 (08)



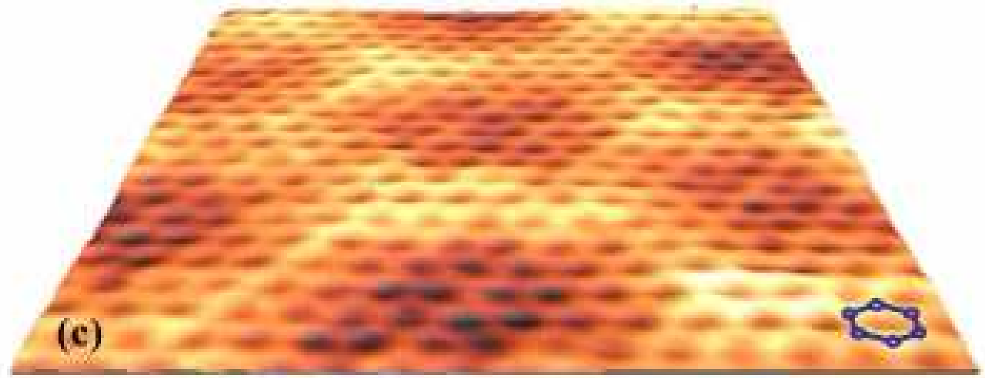
Strong interaction between the first graphitic layer and the substrate **on the Si face.**

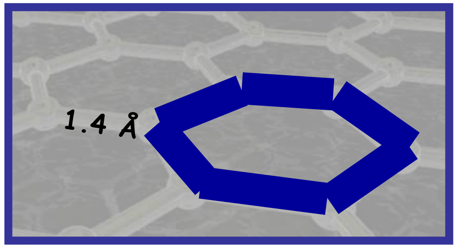
STM on ML and BL graphene (Si face): atomic contrast.

Mallet et al., PRB 76, 041403(R) (2007).

4 x 4 nm^2, sample bias +0.2V

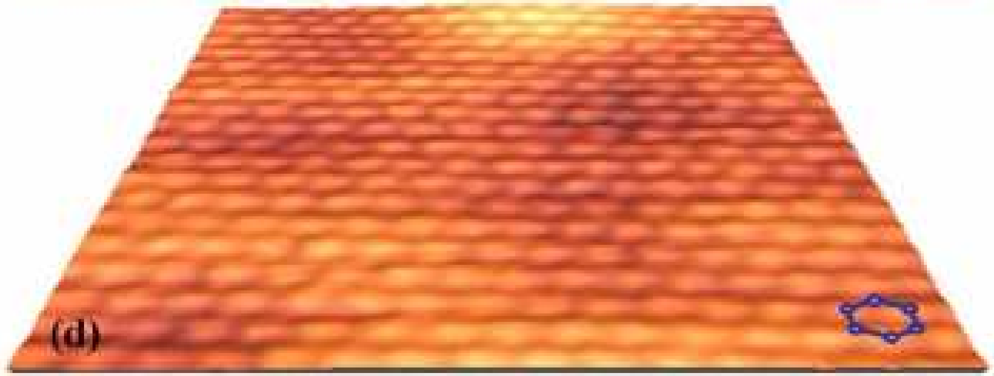
M terrace: **monolayer graphene.**

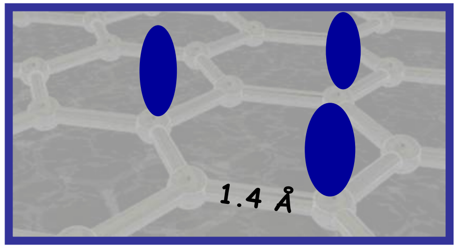




Honeycomb pattern

B terrace: **bilayer graphene.**





Triangular pattern (AB stacking)

Probing the chirality of electron states by STM: Poster by I. Brihuega + arXiv:0806.2616
Theory: C. Bena, PRL 100, 076601 (2008)

FLG on Si and C faces of SiC (4- or 6-H polytypes).

•"Surface science" experiments on the Si face on SL or BL graphene.

•Physical measurements (transport, optical spectroscopy…) are made on the C face (better transport characteristics) on FLG (5-10 L).

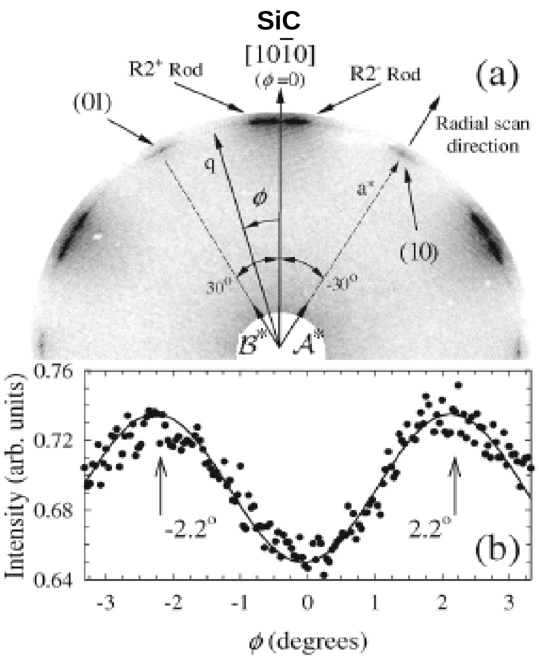
Single layer behaviour even for multilayer graphene on C face! (furnace grown samples)

- **Transport** (WAL: Wu et al., PRL 98, 136801 (07), "Berry phase": C. Berger et al., Science 312, 1191 (06)) : probe the interfacial (most) conducting layer.
- **Optical spectroscopy** (Raman: Faugeras et al., APL 92, 011914 (08), Magnetospectroscopy: Sadowski et al., PRL 97, 266405 (06), Solid State Comm. 143, 123 (07)): probe the whole layer thickness.

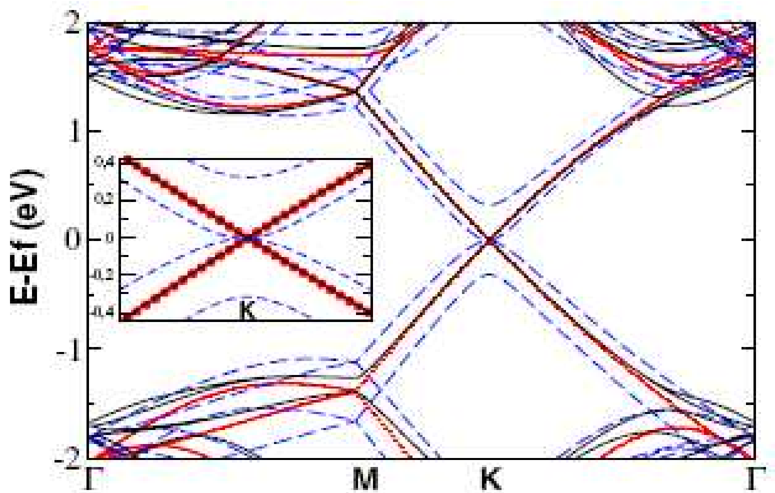
•Need for characterisation of the C face!

Electronic properties of FLG grown on the C face.

- Signature of single layer properties in multilayer graphene (C face).
- Origin (proposed): electronic decoupling of adjacent layers due to stacking faults (rotational disorder). J. Hass, F. Varchon et al., PRL100, 125504 (08)



10 L graphene (only Gr spots).



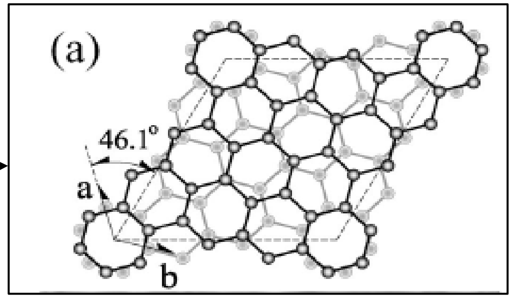
AB graphene bilayer, twisted AB bilayer and single layer graphene.

Also: Latil et al., PRB 76, 201402(R) 2007.

GXRD and STM: R30° and R2 ± are interleaved in the film ➔ stacking faults.

Common cell: √13x√13 R(46.1°) for R30°/R2° bilayer.

Ab-initio: drastic changes in band structure compared to an AB bilayer stacking.



STM investigations of FLG grown on the C face.

Previous investigations: furnace grown FLG (non UHV, high temperature: 1430℃).

- Relatively thick films: no access to the (conductive) interface layers.

We have undertaken the investigation of UHV grown samples, with control "in-situ" by LEED/Auger:

- Allows to probe the interface layer.
- Moreover: influence of the growth conditions (important).

I : structure of UHV grown multilayers.

II : interfacial single layer.

F. Varchon et al., PRB 77, 165415 (2008), F. Hiebel et al., submitted.

Multilayers: sample preparation

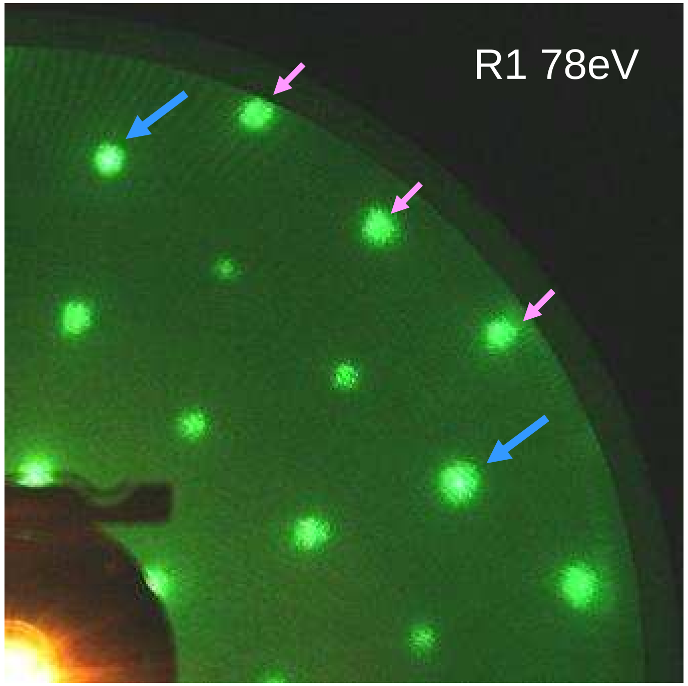
•Surface cleaning under Si flux. Further annealing: 3x3 SiC.

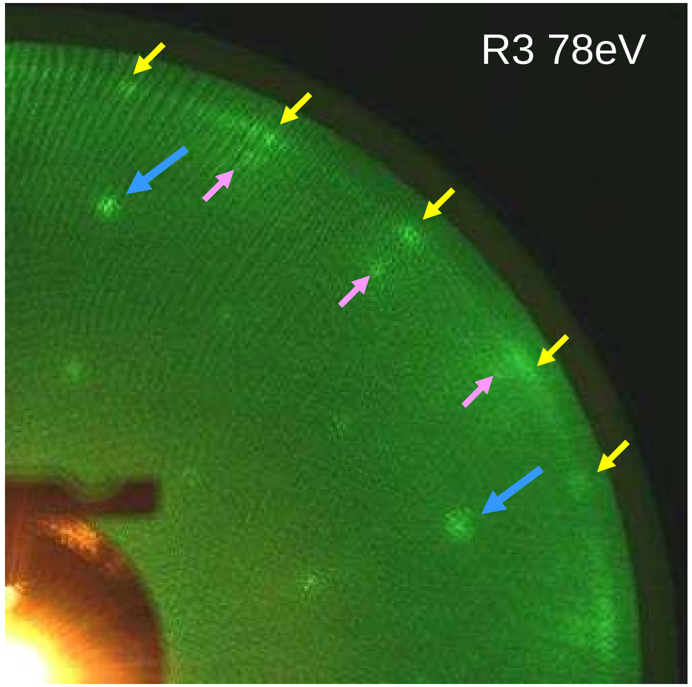
•Graphitisation by high temperature annealing, followed by LEED and AES.

•Estimated layer thickness for investigated samples: 3 and 5 ML graphene.

•Samples grown in this way show a significant amount of azimuthal (rotational) disorder.
Different from "epitaxial" growth on the Si face.
(well known, see e. g. I. Forbeaux et al., Appl. Surf. Sci. 162-163, 406 (2000)).

LEED patterns for increasing annealing temperatures. (up to ≅ 1150℃)

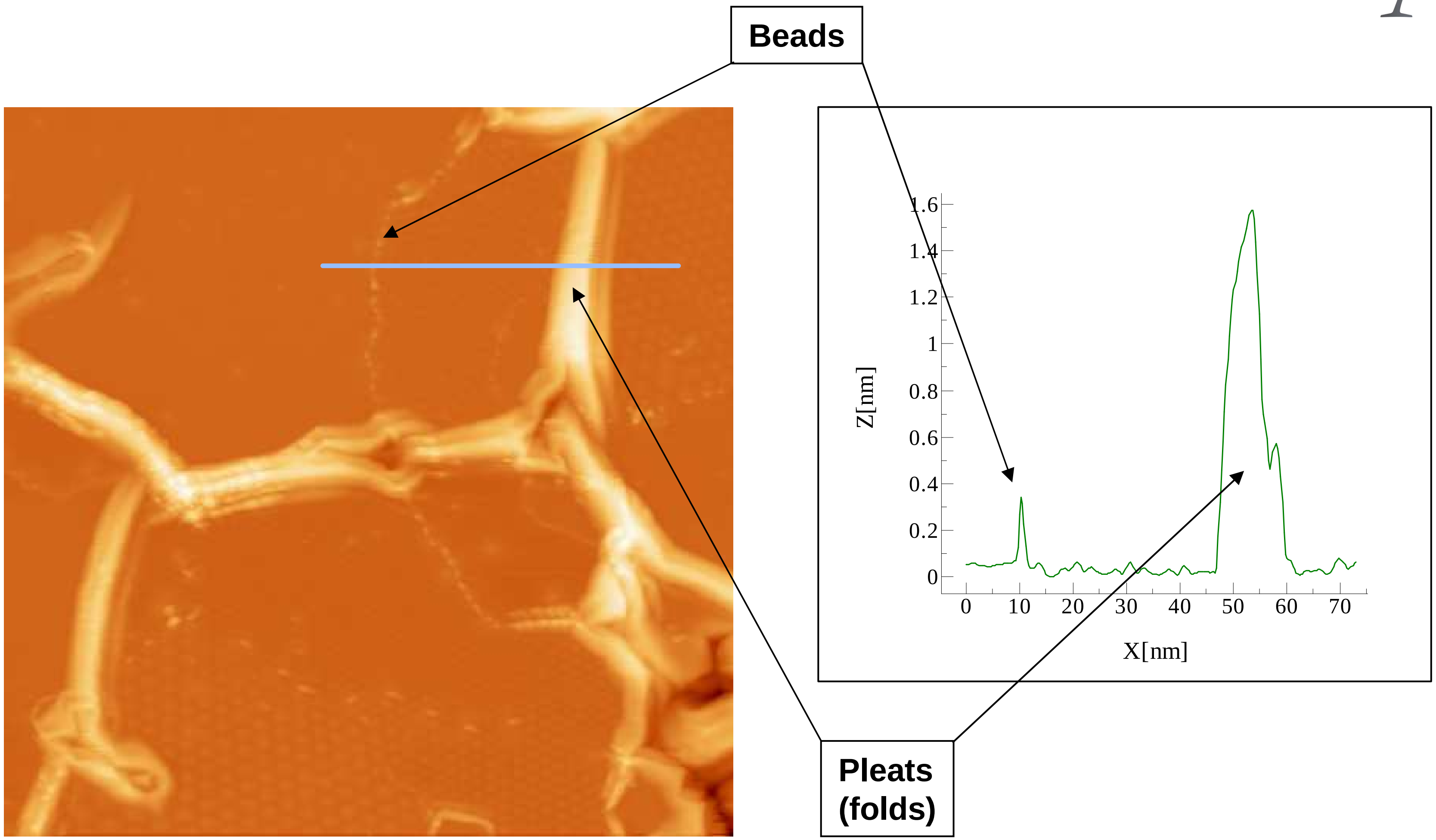




1x1 SiC:
3x3 SiC:
Graphite (1x1):

Orientation of UHV grown FLG is different from furnace grown samples!

Multilayers: large scale STM image.

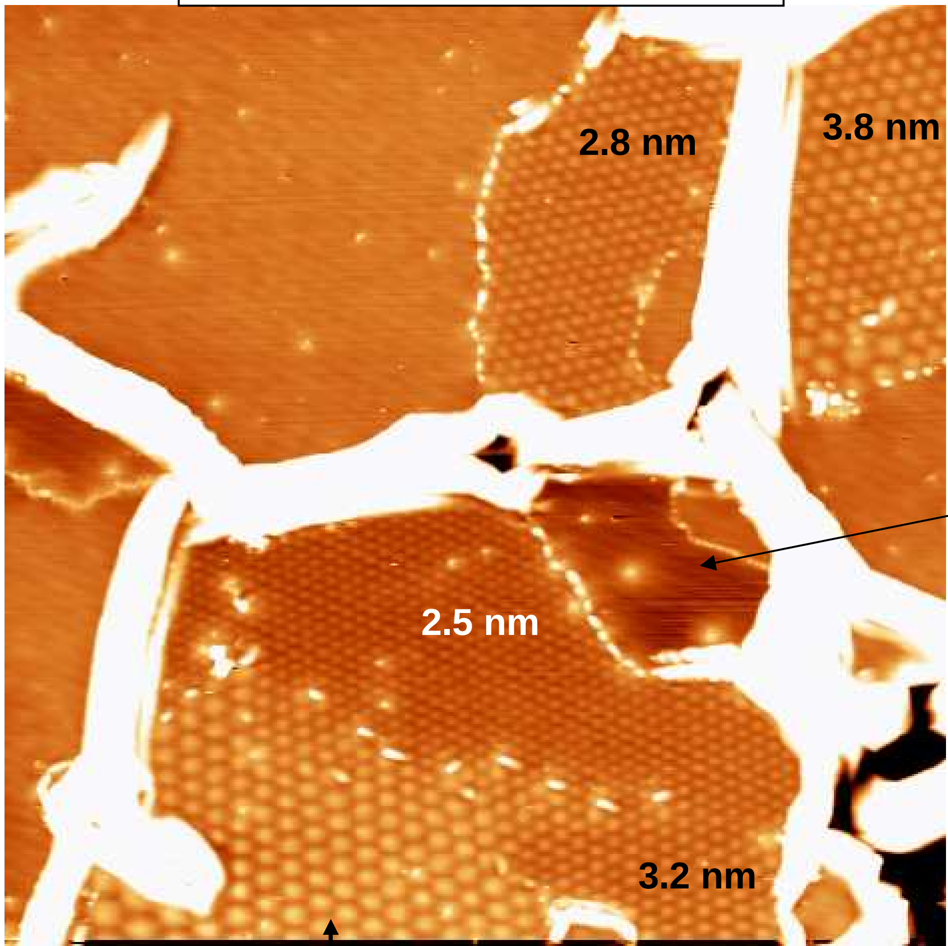


150x150 nm², +1.0 V, 0.1 nA.

- Single terrace (Δh<1.5 Å) cut by folds (pleats) with height ≅ 1-2 nm.
- Lines of beads with typical height ≅ 3 Å.
- Small domains compared to high temperature furnace growth (100-300 nm from XRD).

Multilayers, large scale image: enhanced contrast on the terrace.

150x150 nm², +1.0 V, 0.1 nA.



Superstructures with wavelength in the nanometer range.

Wavelength: 1.3 nm (hardly visible!)

Wavelength: 4.6 nm

Corrugation @ -500mV:
- 0.35 Å upper part (D=2.8 nm),
- 0.35-0.4 Å lower part (D≅3.0 nm).

Similar results: N. Naitoh et al., Surf. Rev. Lett. 10, 473 (2003).

Superlattices on graphite.

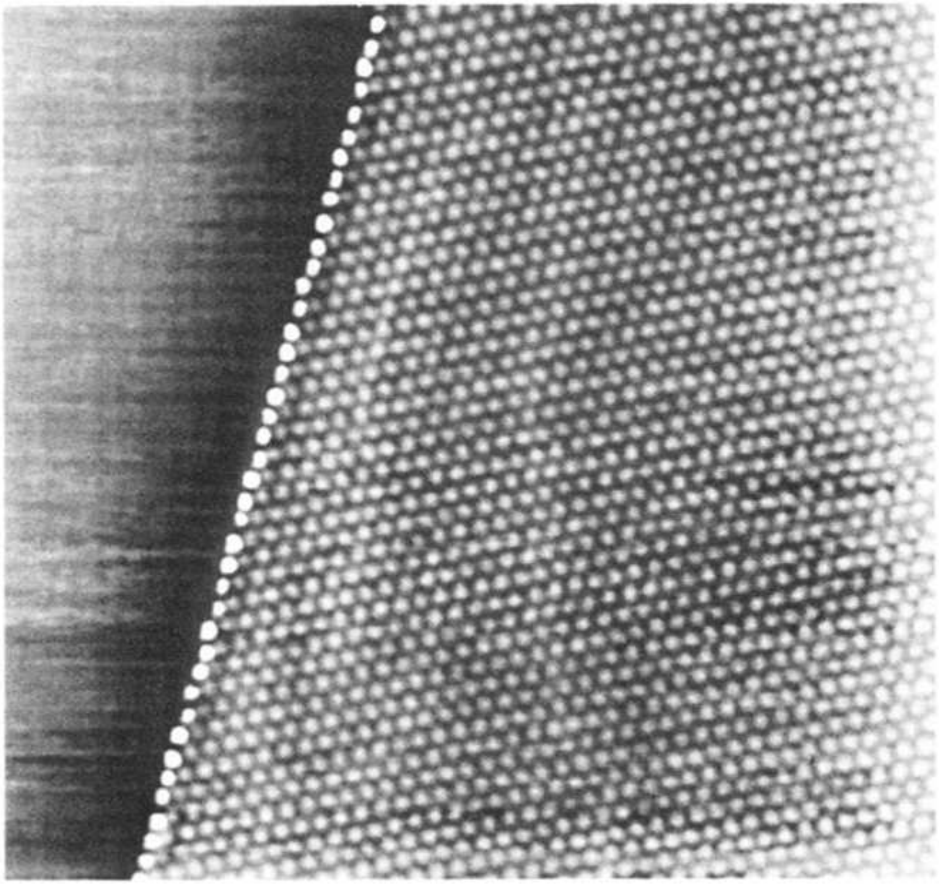


FIG. 1. A STM image (160×160 nm^2) showing a sharp boundary that separates the giant lattice from regular graphite. The giant lattice on the right-hand side of the boundary exhibits a hexagonal symmetry with a lattice constant of 3.8 nm.

160x160 nm^2.
D=3.8 nm, J. Xhié et al., PRB 47, 15835 (1993).
Corrugation: 1.5 Å @ |V|<0.5V. Notice the beads!

Commonly reported on graphite surfaces. Among others:

M. Kuwabara at al. et al., APL 56, 2396 (1990).
Z. Y. Rong and P. Kuiper, PRB 48, 17427 (1993).

Review:
W-T. Pong and C. Durkam, J. Phys.D.**38**, R329 (05).

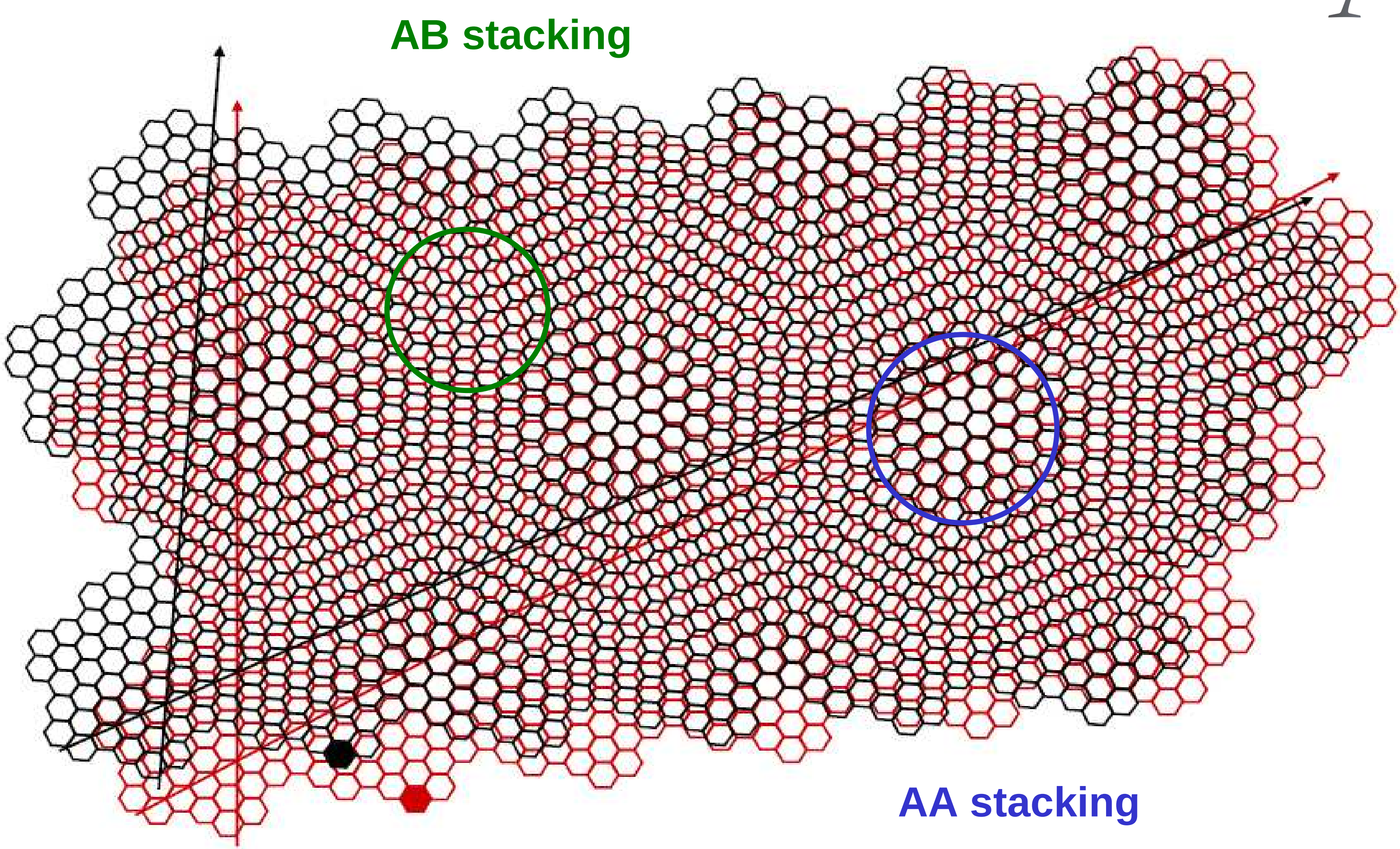
Origin: Moirés patterns
(rotation angle between the last two surface planes).

Exactly what we are looking for!

Electronic origin of the STM contrast.

Campanera et al., PRB 75, 235449 (2007)
McKinnon et al., PRB 54, 11777 (1996)

Moiré pattern: graphical.



For a **rotation angle** θ between two graphite layers:

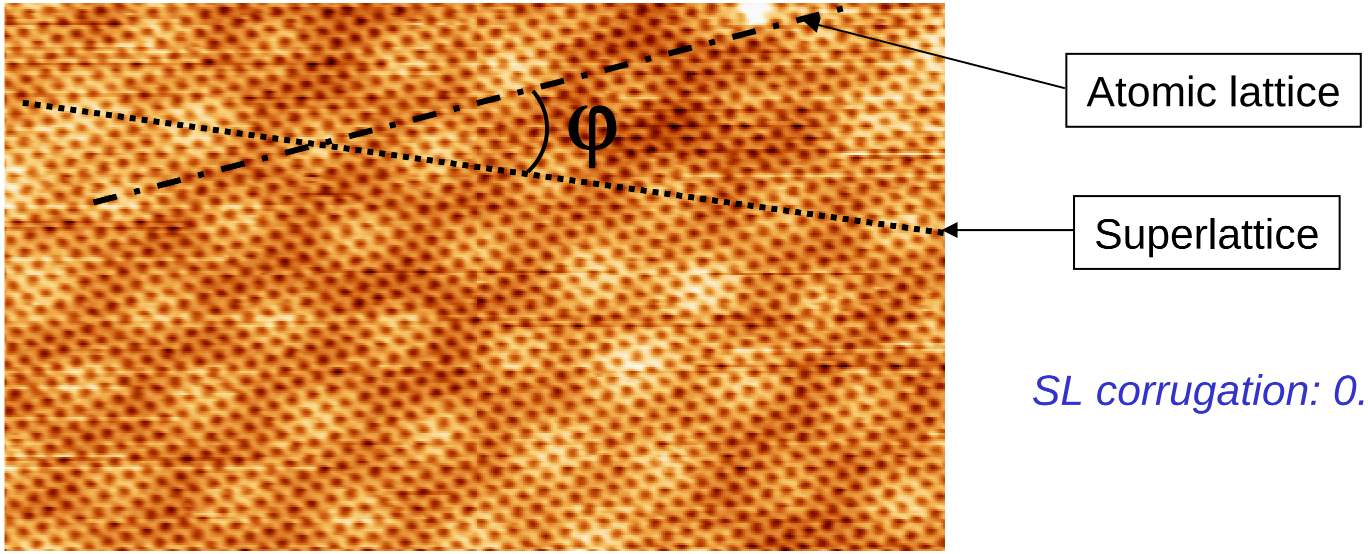
Period of the superlattice: **D(nm)=0.123/sin(θ/2)**

Angle φ between the SL and the atomic lattice: **φ=30°-(θ/2).**

Verified for graphite, to be checked for FLG.

Verification of the Moiré scenario for "epitaxial" graphene multilayers.

The simplest thing to do check the consitency between D and φ (θ computed).



12x7 nm², -500mV, 0.3nA

SL corrugation: 0.2 Å

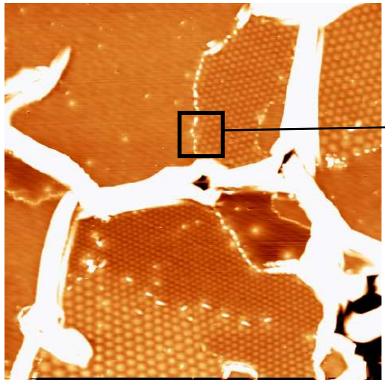
Small period superstructure: larger departure from 30° for φ.

•Here: **D=1.50 nm** (measured) ➔ θ=9.44° and φ=25.3° (calculated).

•Measured: **φ=25±2°** (different image, drift).

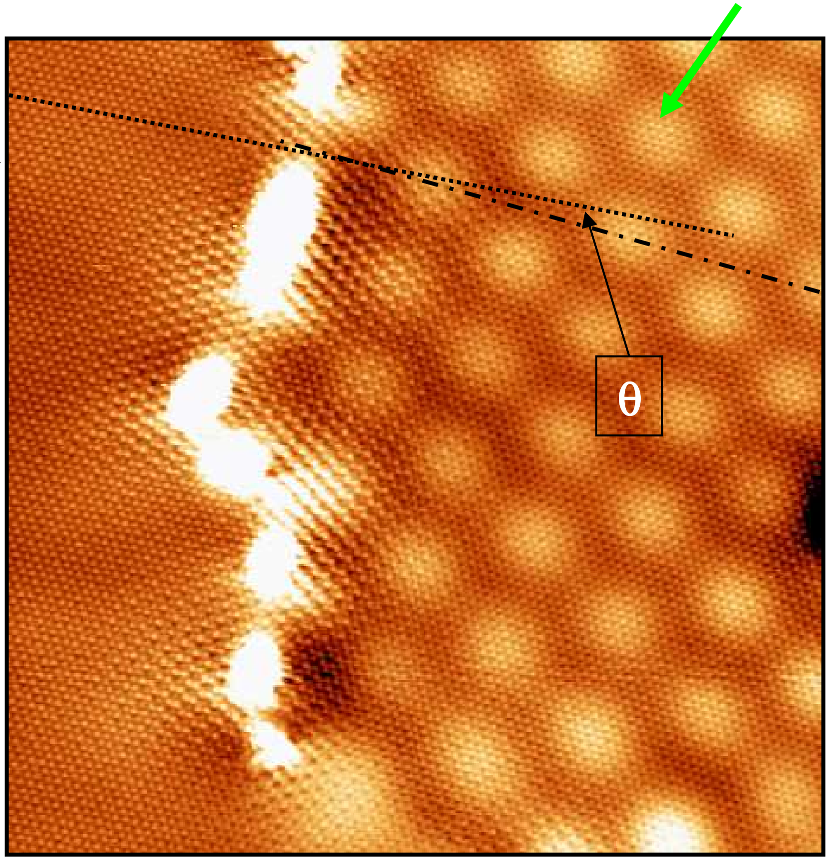
Consistent with superlattice = Moiré pattern.

Evidence for Moiré pattern on multilayers #2.

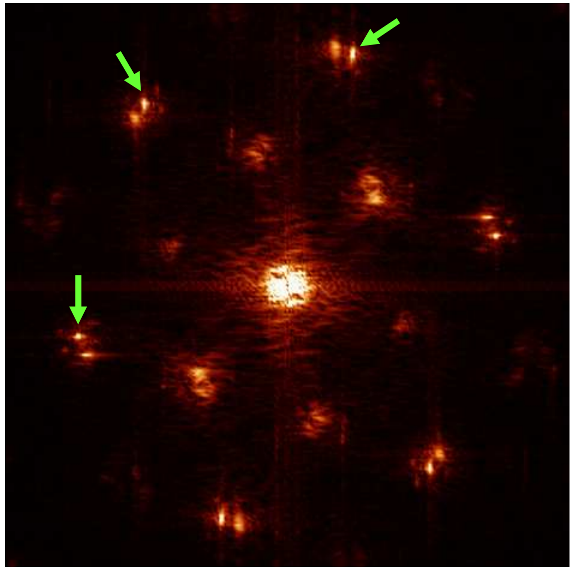


150x150 nm², +1.0 V, 0.1 nA.

SL corrugation ≅ 0.3 Å.



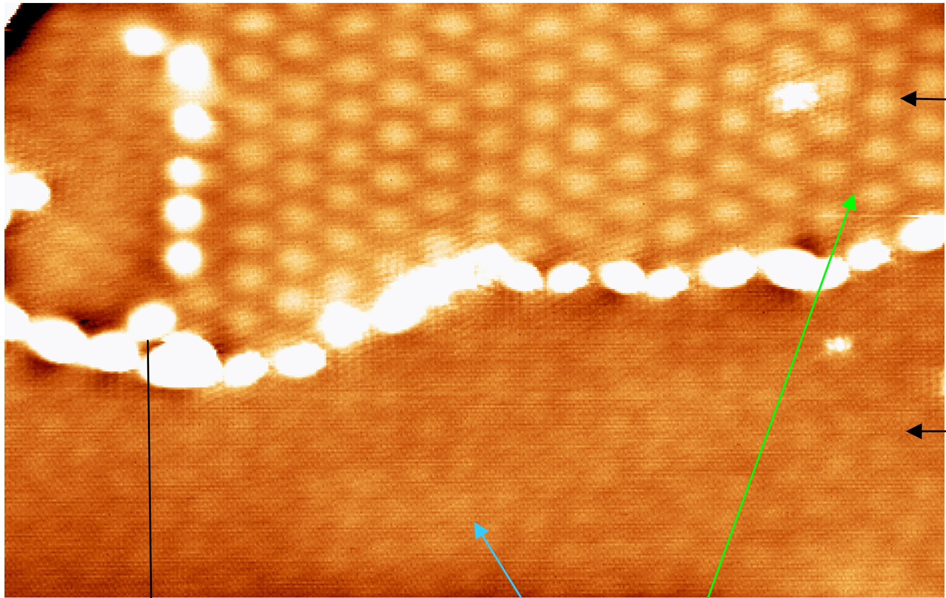
20x20 nm², -250mV, 0.1nA



Fourier transform

•Angle between graphite atomic lattice on the two sides: **θ ≅ 5°(TF and direct image).**
•**D=2.80 nm** (right) ➔ θ=5.0° and *φ =27.5°(calculated).*
•*Measured **φ ≅ 27.5°** (not far from 30°).*
Consistent with Moiré pattern.

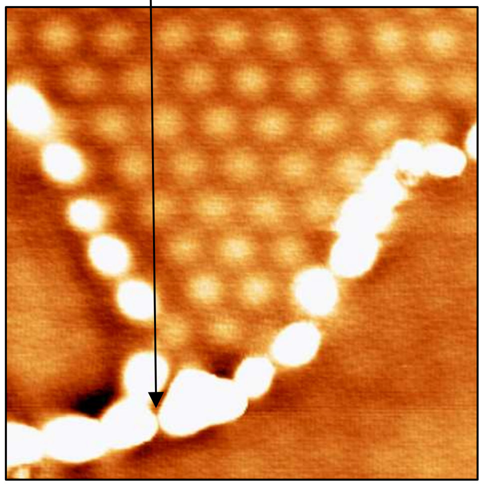
More on Moiré patterns for multilayers #2.



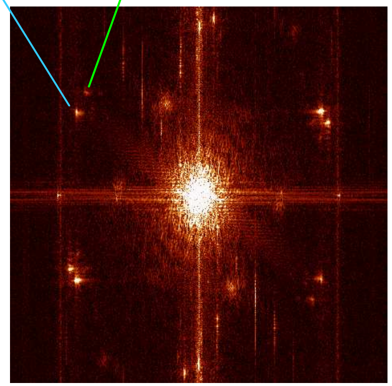
Superlattice with period 2.1-2.2 nm and corrugation 0.15-0.2 Å.

Superlattice with the essentially the same period but rotated by 15-20° and with reduced corrugation 0.04 Å.
(same effect at -500mV)

40x25 nm², +500mV, 0.4nA



Rotation by 30° and zoom.
20x20 nm², -500mV.



Subsurface stacking fault in the lower part (2 overlayers from AF of 5?).

Pong and Durkam, J. Phys.D.**38**, R329 (05).

Rotation is not limited to the top layer!
Also from double modulation (stack of 3 rotated layers):
Rotational disorder extends below the top layer.

Structure of UHV grown FLG (multilayers).

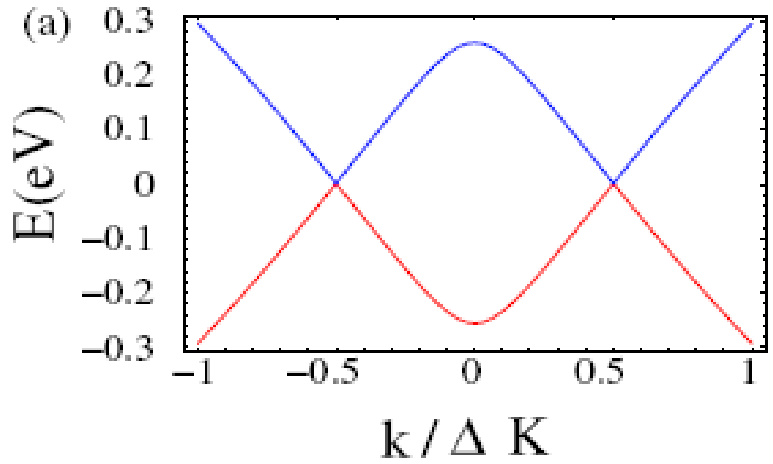
•**Rotated layers (stacking faults), with variable rotation angles. (from measured D values: 1.5°≤θ≤19°).**

•**Stacking faults in subsurface layers.**

Many "small" rotation angles: does it lead to electronic decoupling of adjacent layers?

Analytical computations for small rotation angles suggests it is indeed the case.
Lopez dos Santos, PRL 99, 256802 (07).

The linear dispersion (Dirac cones) is preserved at low energy for a twisted bilayer.



"However, the cones present in the bilayer with a twist are essentially the Dirac cones of each layer perturbed by the admixture of states of the opposing layer, which are distant in energy". Lopez dos Santos et al.

Observation of single layer behaviour (graphene -like) by STM?

Dispersion of the two states with smaller energy for θ=3.9° (D=3.6 nm).

Recent calculations for wide range of angles:
S. Shallcross et al., PRL 101, 056803 (08).

Simulation of STM images for rotated layers (large angle).

S. Latil et al., PRB 76, 201402(R) 2007.

Band structure for rotated trilayers: massless fermions

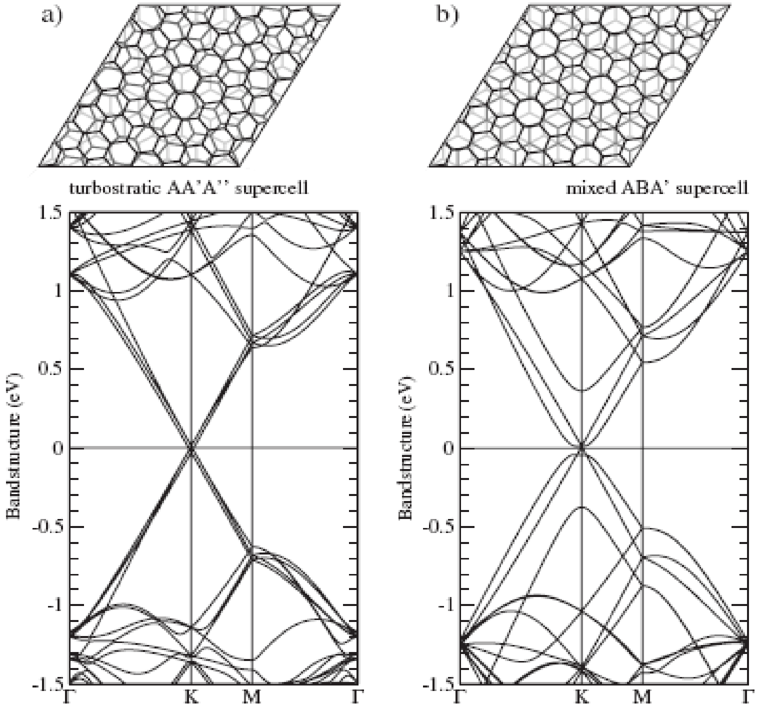
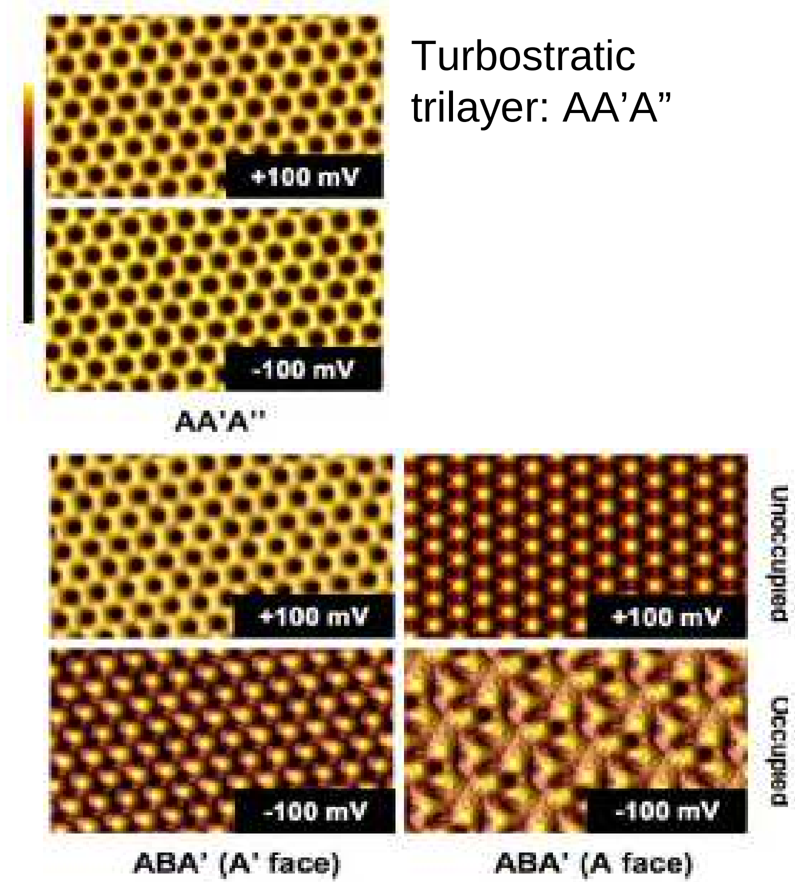


FIG. 3. Representation of the supercells and the corresponding electronic band structure for trilayer graphites. The turbostratic $AA'A''$ system (43.57° and 38.21° misorientation angles) is shown in (a), and the mixed ABA' structure is shown in (b).

Rotation θ: 16.3 and 21.8°, D=0.86 nm.

Computed STM images: graphene-like contrast.



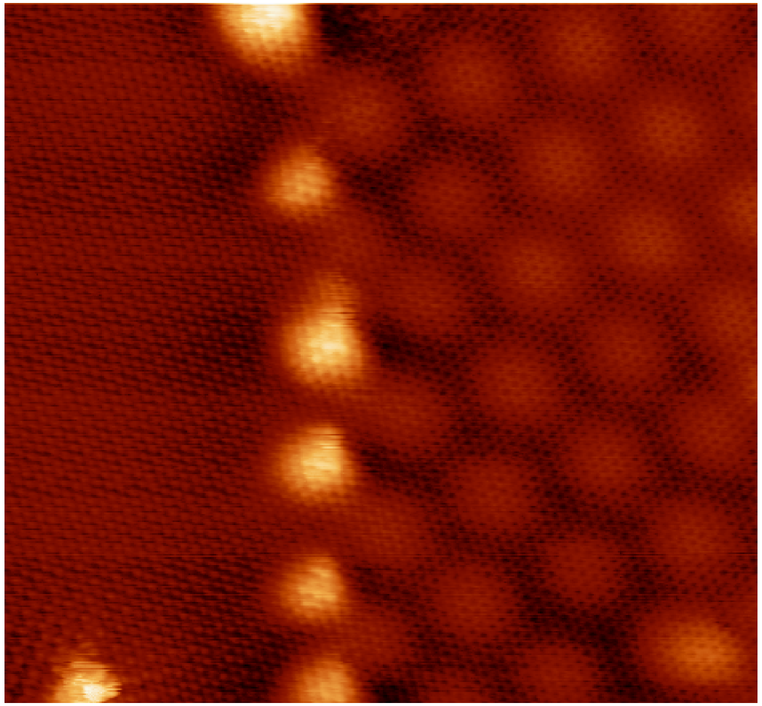
Turbostratic trilayer: AA'A"

Mixed trilayer: ABA'

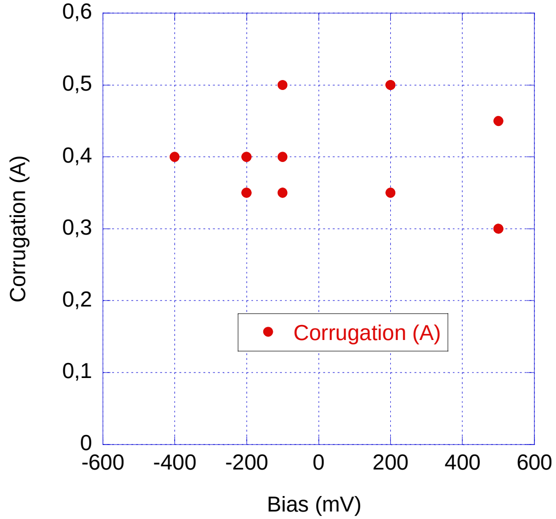
Dependence on stacking sequence and polarity beyond 2 ML!

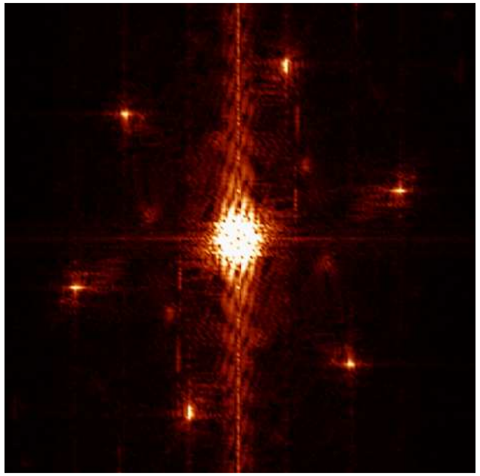
Atomic contrast on flat and corrugated area (multilayers).

In general: reduced A/B asymmetry on SR (expected), but in some cases very low….



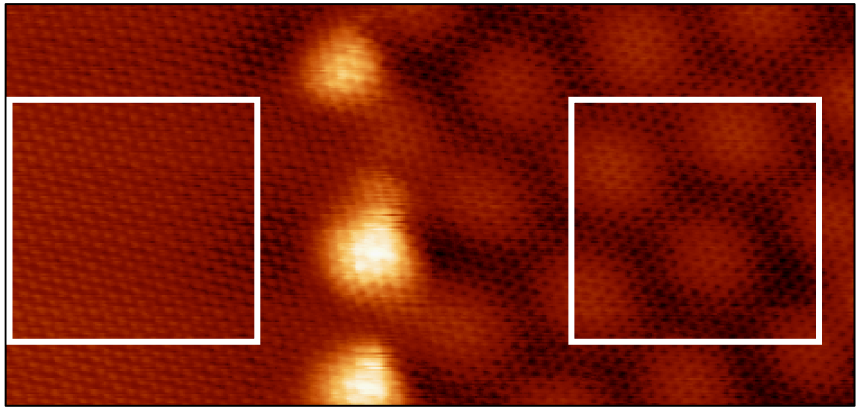
15x14 nm², +500 mV.



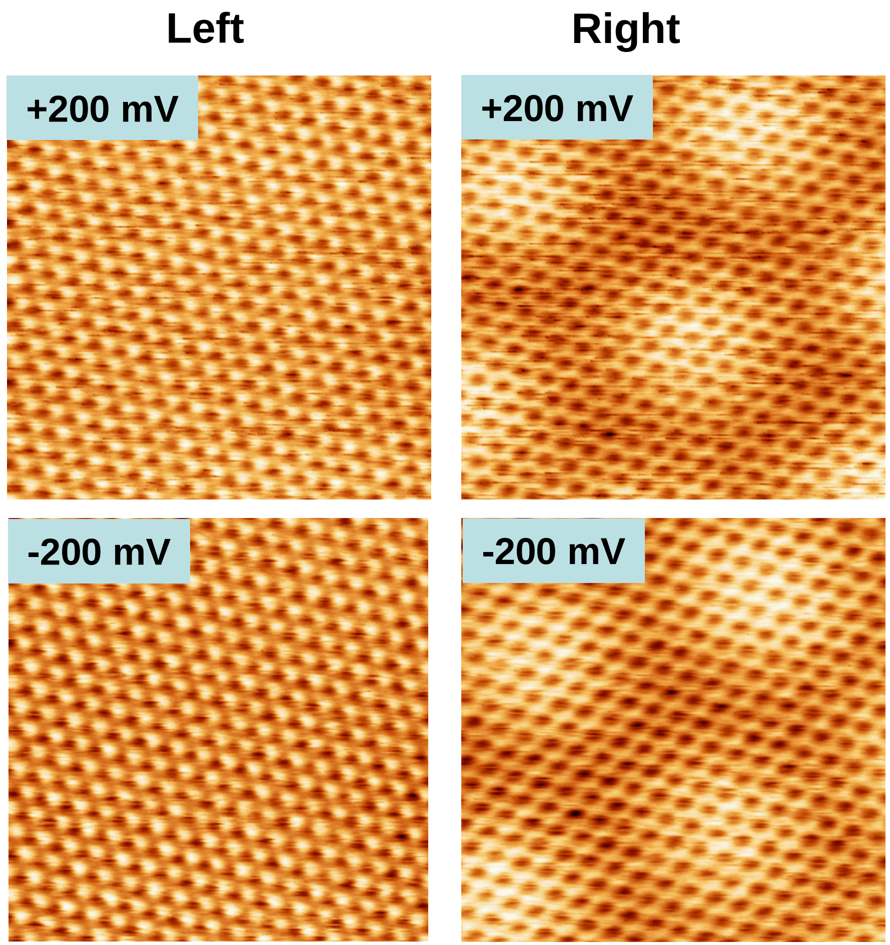


- Period: 2.27 nm (θ=6.2°)
- Scanning both corrugated and flat area with the same tip.
- Single orientation of the surface atomic plane (subsurface rotation).

Atomic contrast on flat and corrugated area.



15x7 nm^2, +500 mV, 0.4 nA.

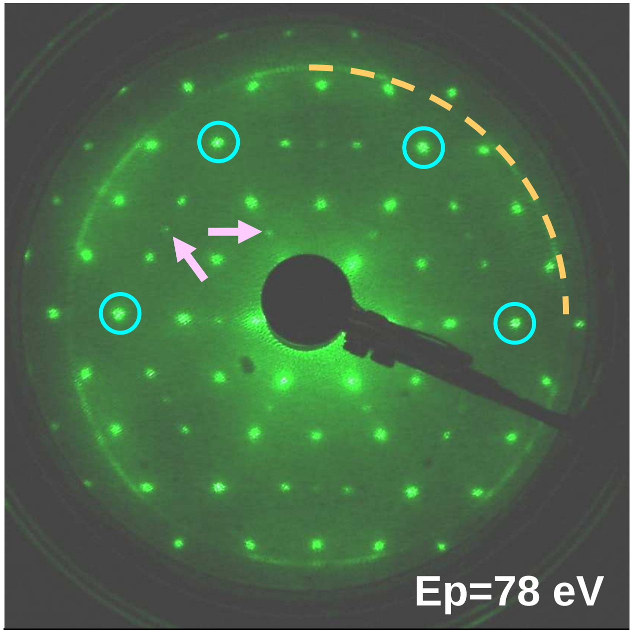


Zooms, 4x4 nm^2.

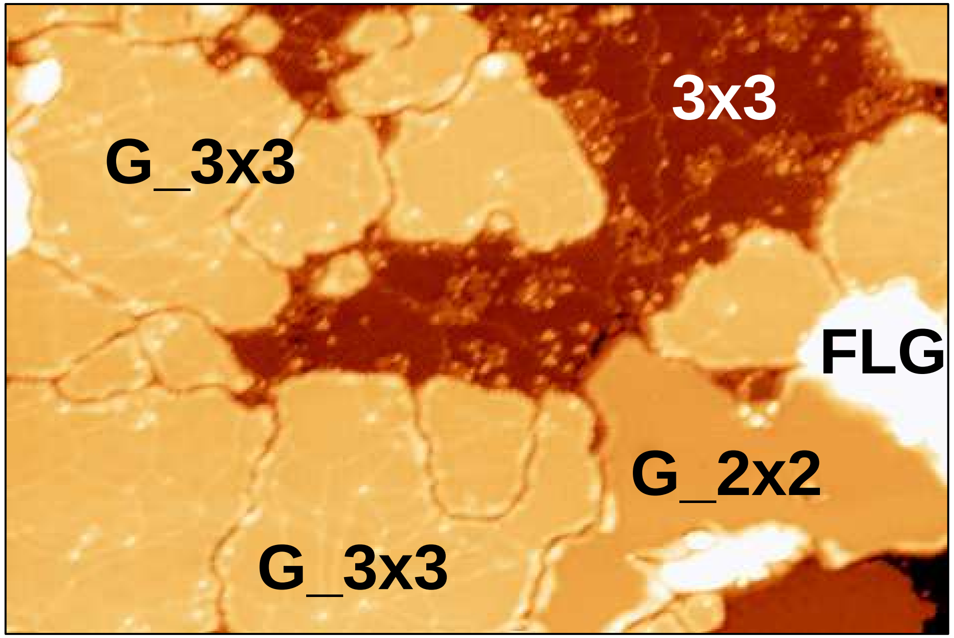
•**Contrast:** **rather Honeycomb on SR (Moiré, right) and triangular (graphite-like) on the flat area (left): more graphene-like when rotated?**

Interfacial layer, sample preparation.

•Same as before except lower annealing T (stopped when graphene signal in LEED).



3x3 SiC, 2x2 SiC, Gr.



Morphology: 120x80 nm², +2.5V, 0.5nA.

LEED:

Spots: 3x3 and 2x2 SiC, incomplete circle: graphene (rotationally disordered).

Forbeaux et al, Surf. Sci. 442, 9 (98); Emtsev et al, PRB 77, 155303 (08).

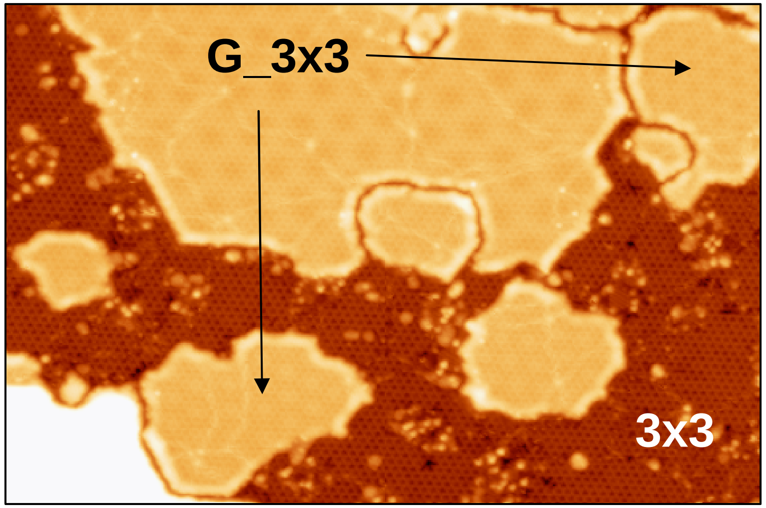
STM:

- « **3x3** » corresponds to the bare SiC surface with the 3x3 reconstruction.

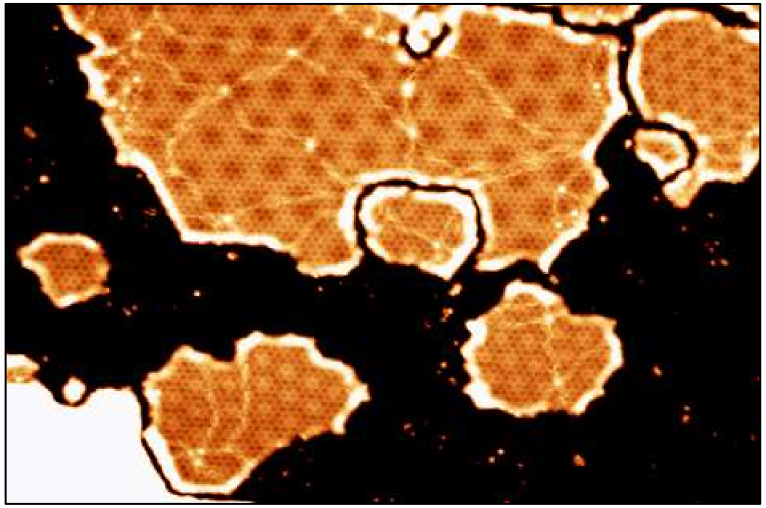
  Hoster et al., Surf. Sci 382, L658 (97); Bernhardt et al., Mat. Sci. Eng. B61, 207 (99).

- **G_2x2 and G_3x3**: small islands (lateral size ~ few tenths of nm) of height 2.6 Å (G_2x2) or 3.1 Å (G_3x3) : consistent with a single graphene layer (also from AES).

Superstructures on the G_3x3 and G_2x2 islands

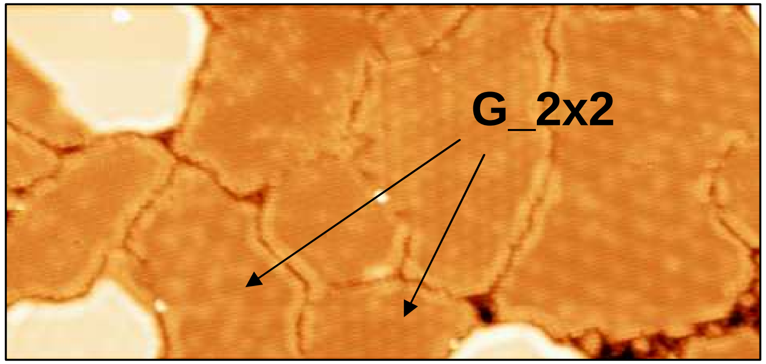


77x51 nm², -2.5 V, 0.2 nA.

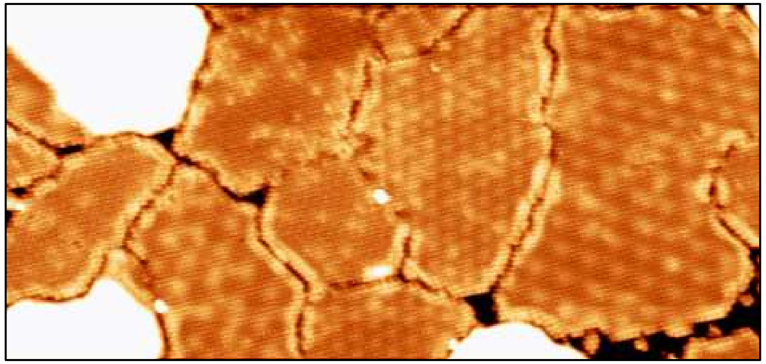


Enhanced contrast on islands

G_3x3



80x38 nm², +2.5 V, 0.2 nA.



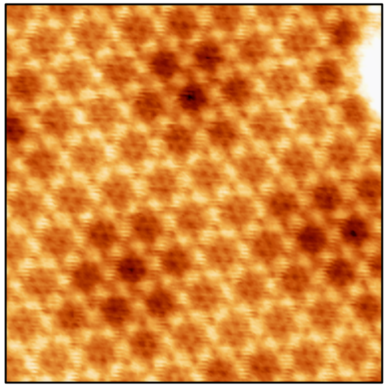
Enhanced contrast on islands

G_2x2

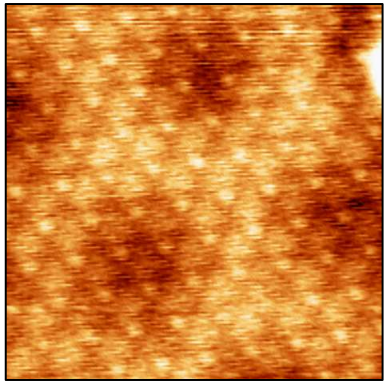
- Superstructures with different periods and orientations on both G_3x3 and G_2x2 islands : orientationnal disorder of the graphitic (graphene) layer on the surface (verified with atomic resolution images : rotation by 9° (6°)-30°, consistent with LEED).

Atomic resolution images on G_3x3 and G_2x2 : high bias.

G_3x3: 7.5x7.5 nm^2



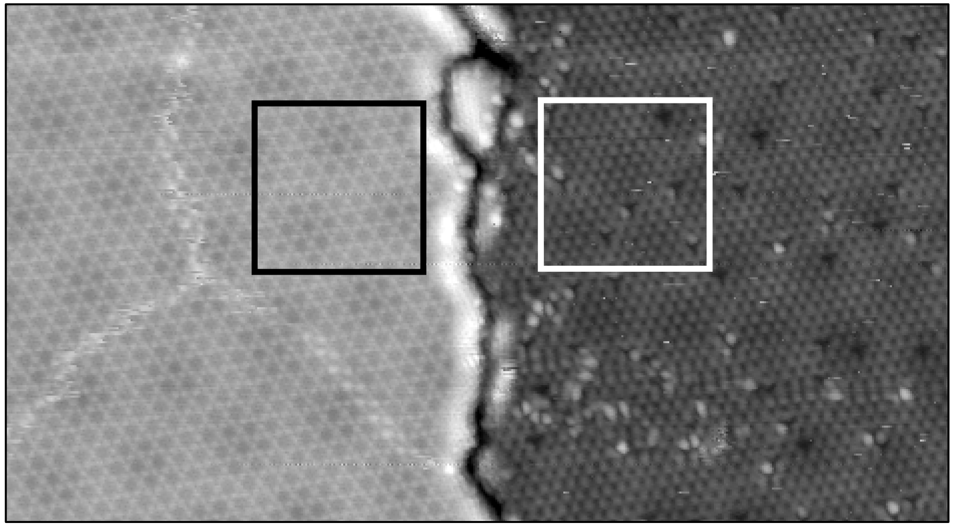
-2.0 V



+2.5 V

G_3x3
4.1 nm, 16°

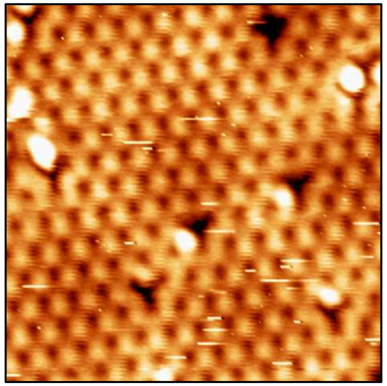
G_2x2
3.5 nm, -22°



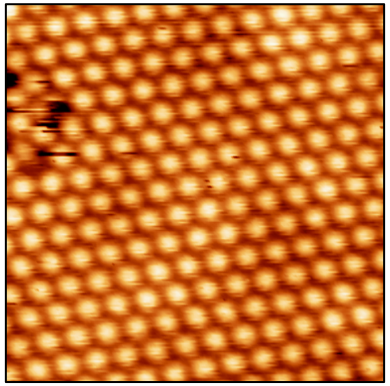
40x22 nm^2, -2.0 V, 0.2 nA

Images taken simultaneously with the same tip.

G_2x2: 7.5x7.5 nm^2



-2.0 V



+2.5 V

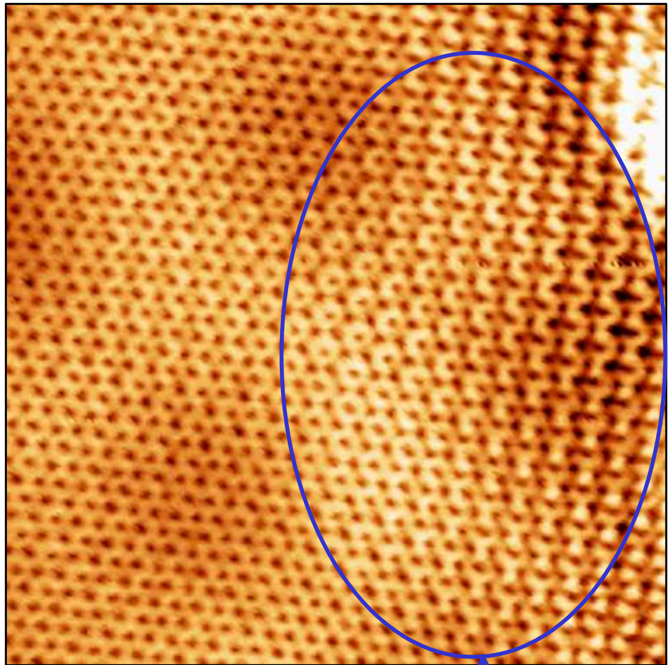
- $\pm$V contrast similar to the one of the bare SiC 3x3 and SiC 2x2 surfaces.
  Hoster et al. Surf. Sci. 382, L658 (97), Seubert et al. Surf. Sci. 454-456, 45 (00).
  $\Rightarrow$ Genuine SiC surface reconstructions preserved below the graphene layer ($\neq$ Si).
- Graphene is essentially transparent at high bias. (Rutter et al. PRB 76, 235416 (08))

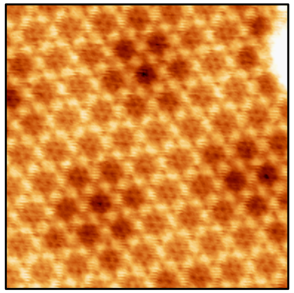
Atomic resolution images on G_3x3 and G_2x2 : low bias.

G_3x3

7.5x7.5 nm², -50 mV, common z range 1.17 Å

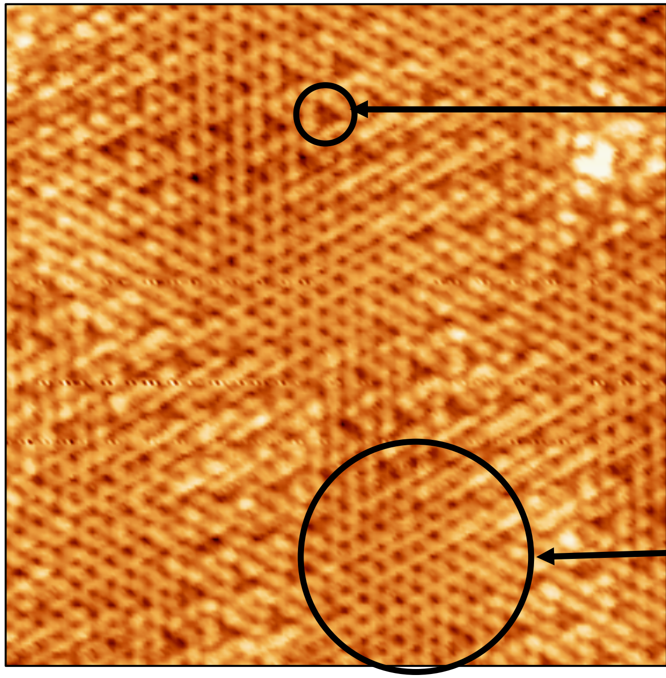
G_2x2





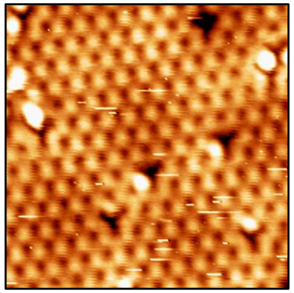
« R3 » : SW patterns

Graphene everywhere!



« Missing » atoms with SiC 2x2 period on boundaries

Graphene -like in basins



- Almost **ideal graphene on G_3x3.**
- Graphene with **significant interaction with the substrate on G_2x2.**

Graphene-SiC interface, C face.

Graphene-like contrat at low bias (p_z states close to E_F) for the first graphitic C layer.

- Different from the Si face (no graphitic signal for the buffer layer).
- Weaker graphene-substrate interaction on the C face than on the Si face. (no true « buffer layer).

  Id. Emtsev et al, PRB 77, 155303 (08). from photoemission data.

  <u>Additional indications</u>: rotational disorder, conservation of SiC surface reconstructions, weak sensitivity to substrate phase boundaries.

- Difference with previous studies which indicate strong interaction:

  Hass et al., PRB 75, 214109 (07) : difference in sample preparation (High T°, low vacuum)

  Forbeaux et al, Surf. Sci. 442, 9 (98) : high lying states, only on (2x2).

Reconstruction dependent interaction between graphene on SiC surface (C face):

- Weak on the (3x3) reconstruction, larger on the (2x2).

Conclusions

STM on FLG on 6H-SiC(000-1) (C face):

Multilayers

•Rotational stacking faults in FLG grown on the C face (UHV or not).

•They may be responsible for the SL electronic behaviour of FLG.

Gr_substrate Interface:

•Rotational disorder present already in the first interface layer.

•Interaction of the first graphitic plane with the substrate smaller than for the case of the Si face.

•Reconstruction (substrate structure) dependent interaction.