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Growth and structure of epitaxial graphene on Iridium

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Growth and structure of epitaxial graphene on Iridium

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[†] II. Physikalisches Institut, Universität zu Köln
[‡] Institut Néel, Grenoble, from Oct. 2008

Alexander von Humboldt Stiftung/Foundation

Deutsche Forschungsgemeinschaft DFG

Graphene on metal: why ?

Chemical + mechanical

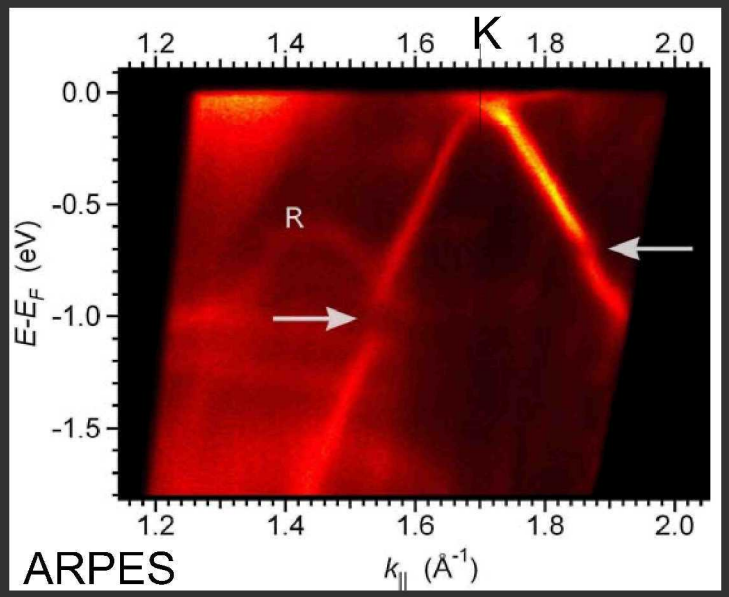
- Towards practical realisations ?

Tailor in a reproducible way the morphology
of high quality and large scale graphene

Geim *et al.*, Nature Mat. 2007

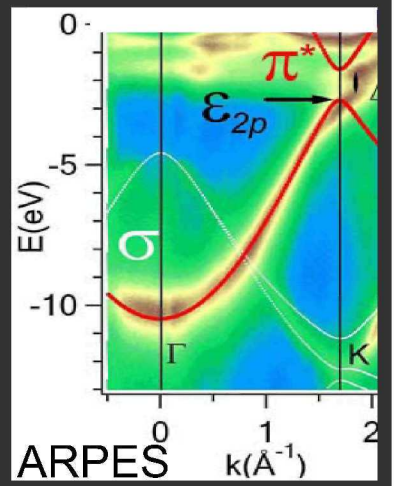
Yu *et al.*, arXiv

- The electrode issue: the C/metal interface



C/Ir(111):
almost intact Dirac cone !!!
Pletikosić, Kralj, Pervan, Brako, Coraux,
N'Diaye, Busse, Michely
arXiv:0807.2770v1

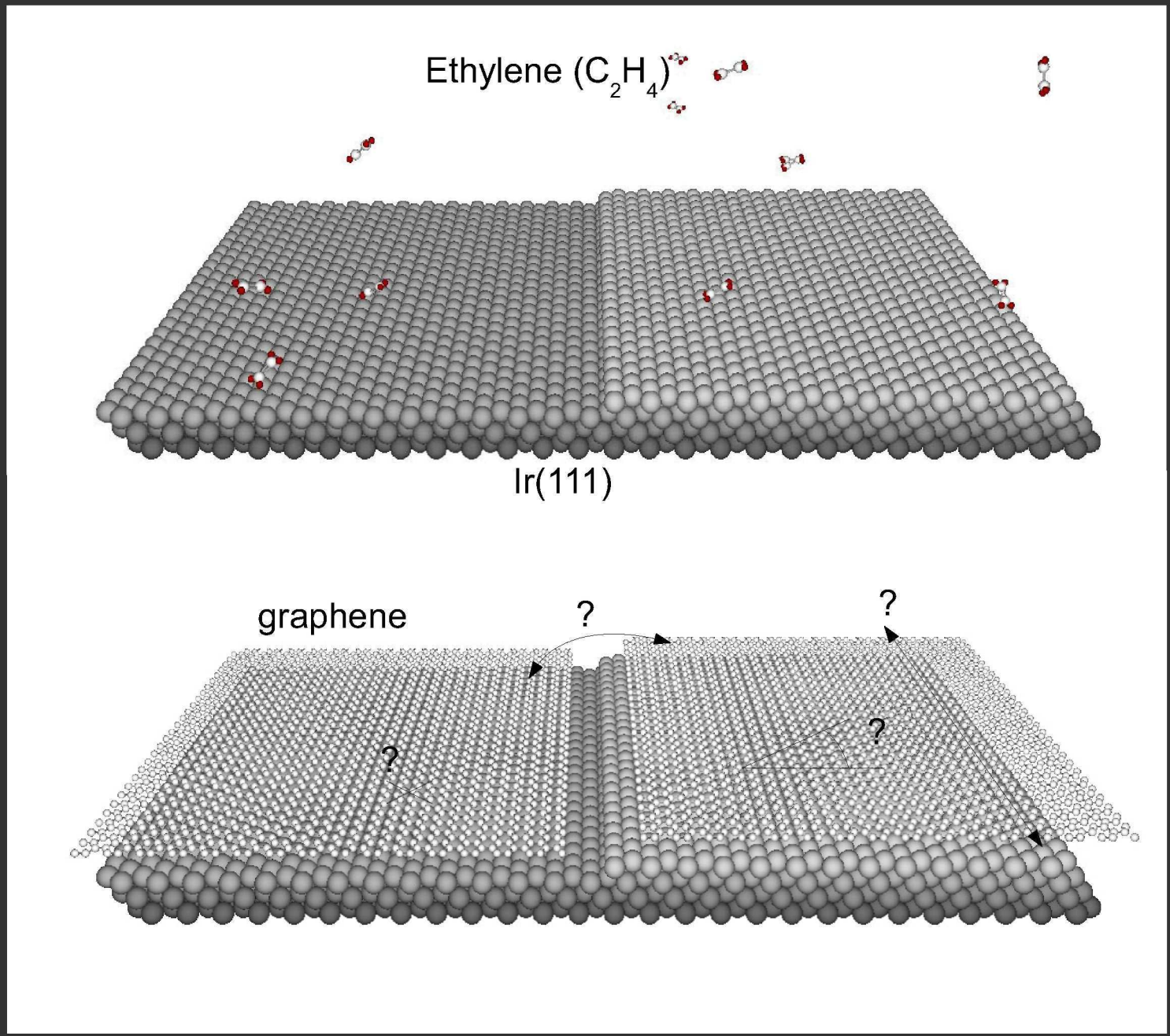
C/Ni(111):
hybridization of
graphene's bands with
the metal ones
Gruneis *et al.*, PRB 2008



→ see Poster "Nearly neutral graphene on Ir(111)"
Kralj & Pletikosić, Tuesday

- Self-assembly of graphene based nanostructures

UHV

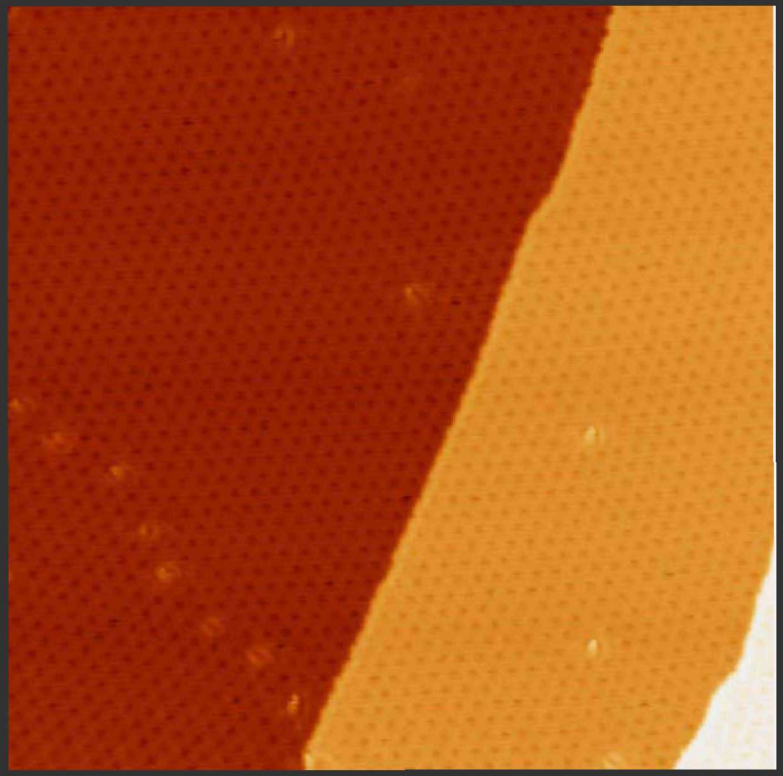


→ *in situ* scanning tunneling microscopy (STM)

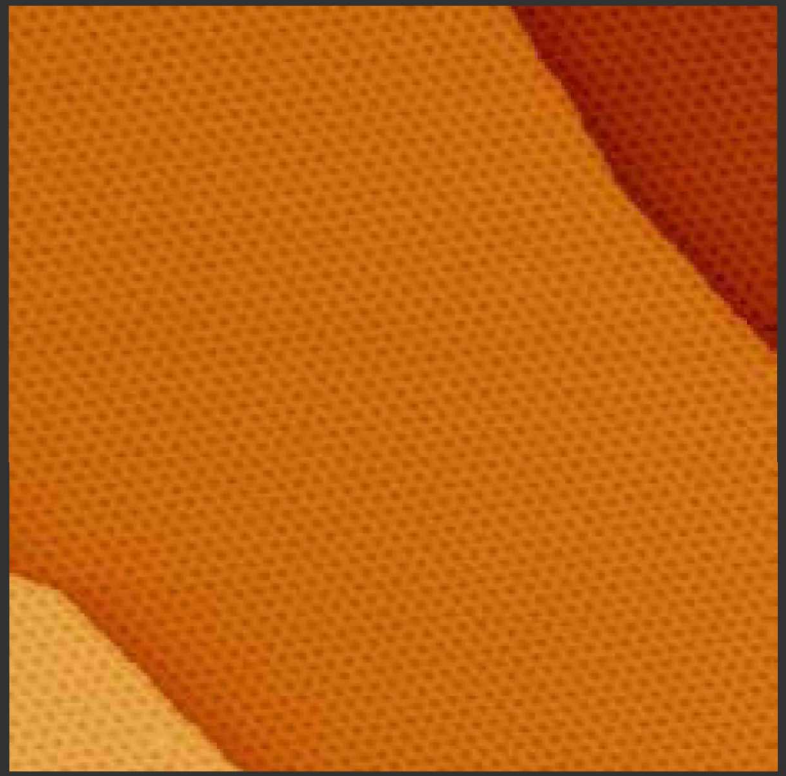
Structural coherency of graphene/Iridium

Coraux, N'Diaye, Busse, Michely, Nano Lett. 2008
N'Diaye, Coraux, Plasa, Busse, Michely N. J. Phys. 2008

Moiré of graphene on Ir(111) - orientation

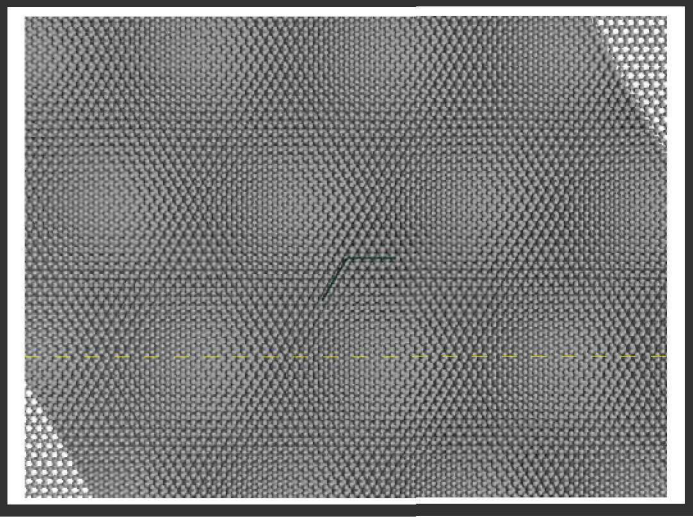


1120 K

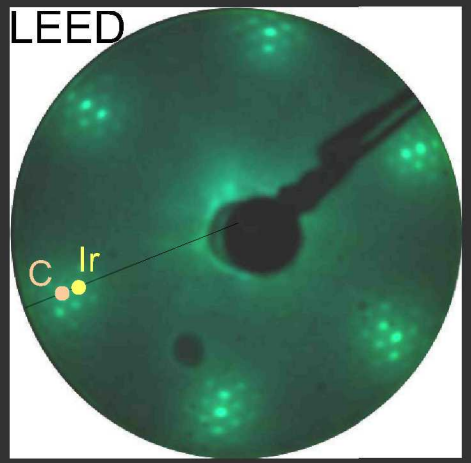


110×110 nm^2

1320 K



- Superstructure = moiré
  $a_{Ir} \sim 1.1 \times a_C$



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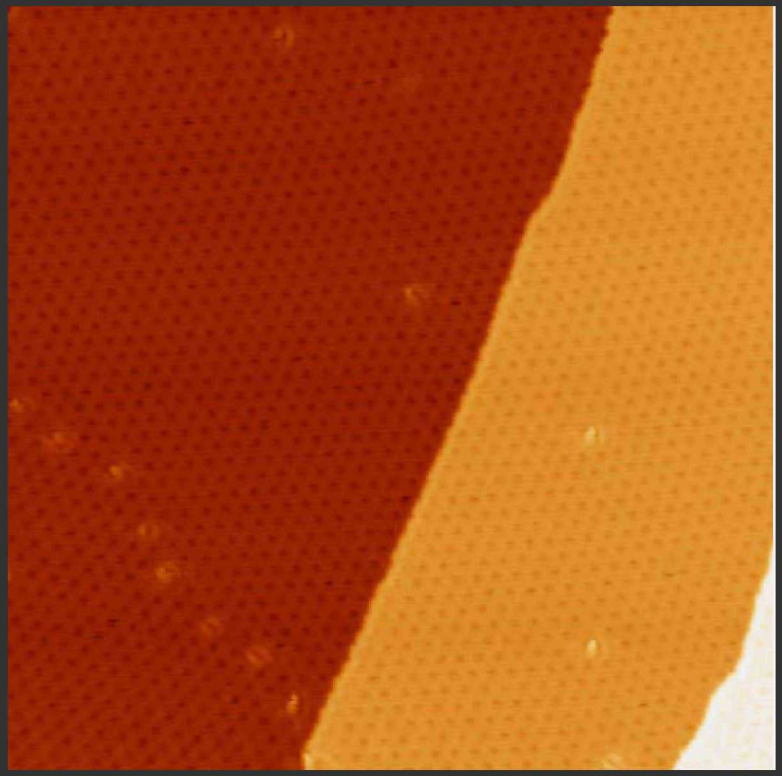

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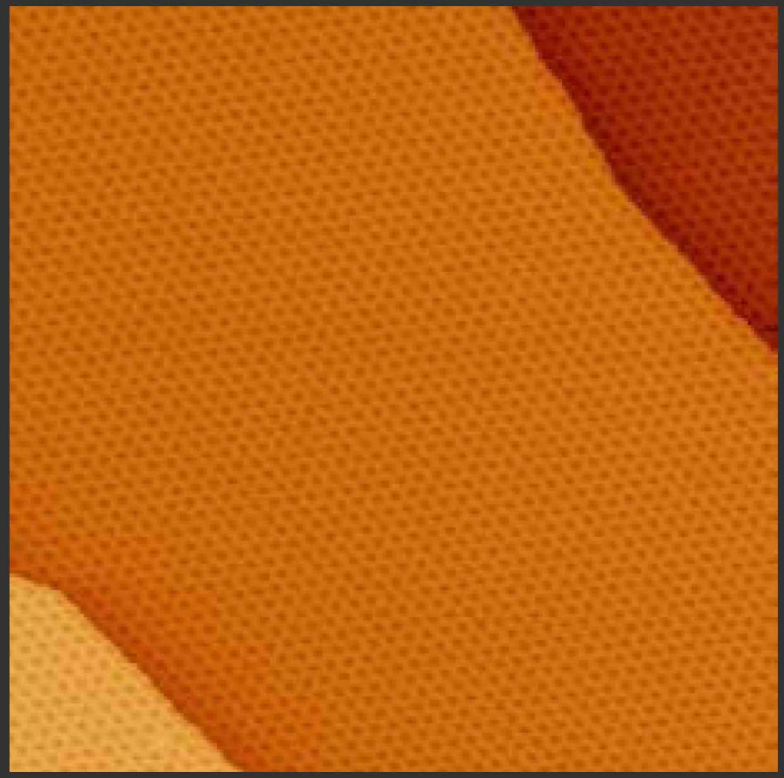

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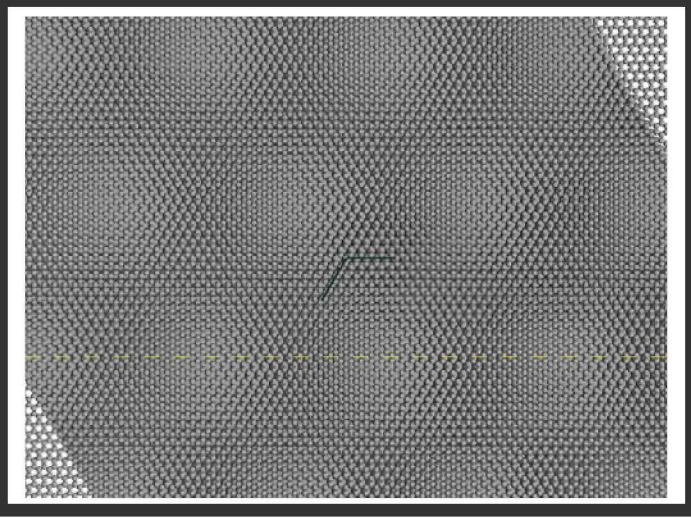

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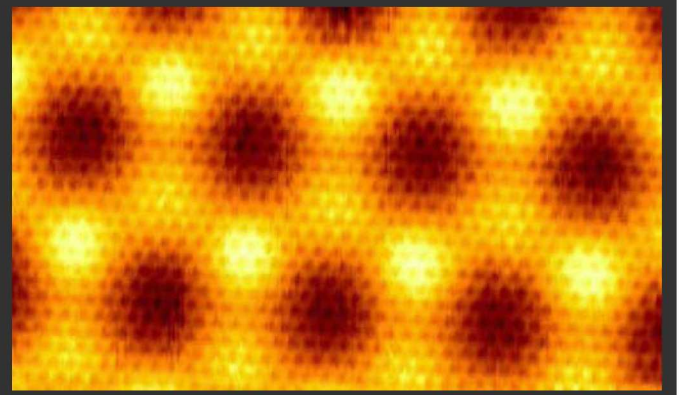
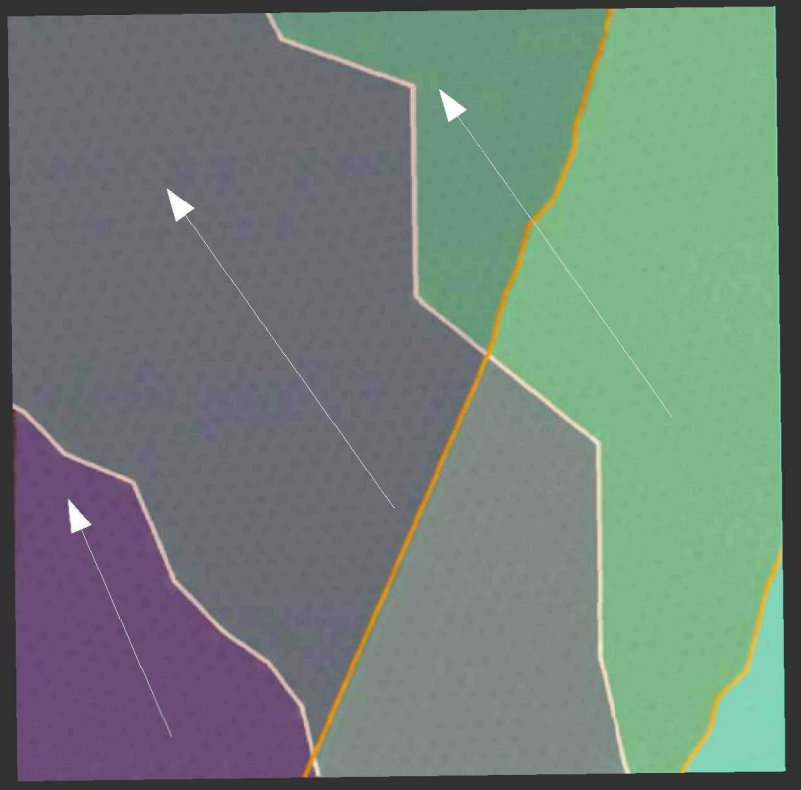
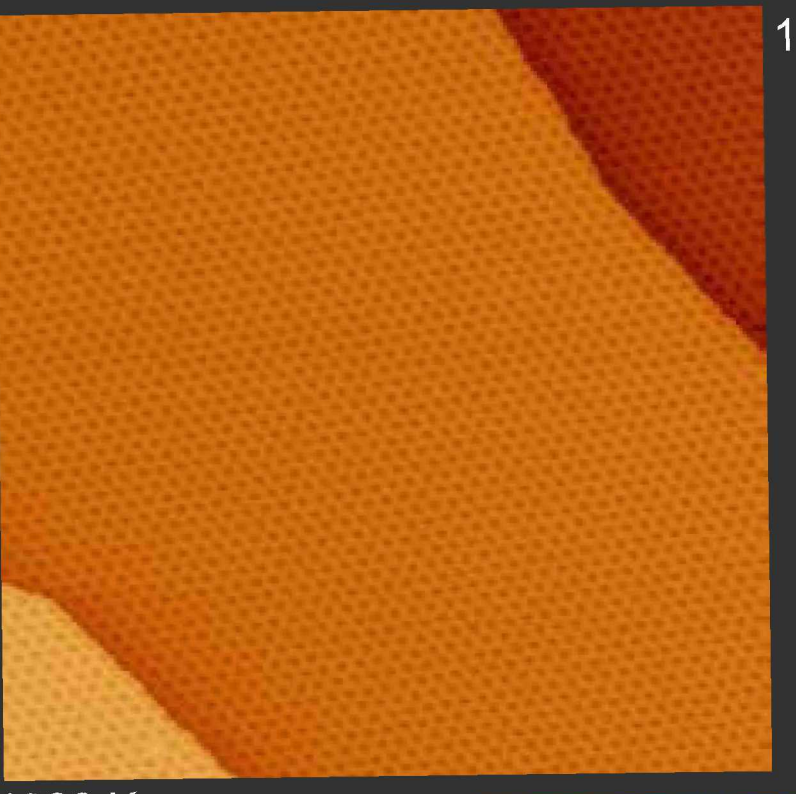


10×5 nm^2

Moiré of graphene on Ir(111) - orientation

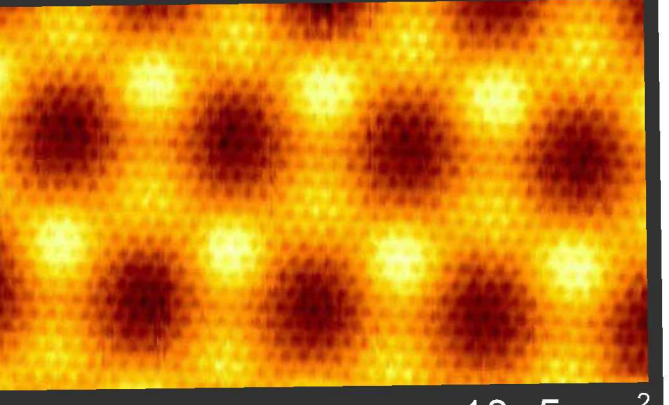


1120 K



110×110 nm^2

1320 K



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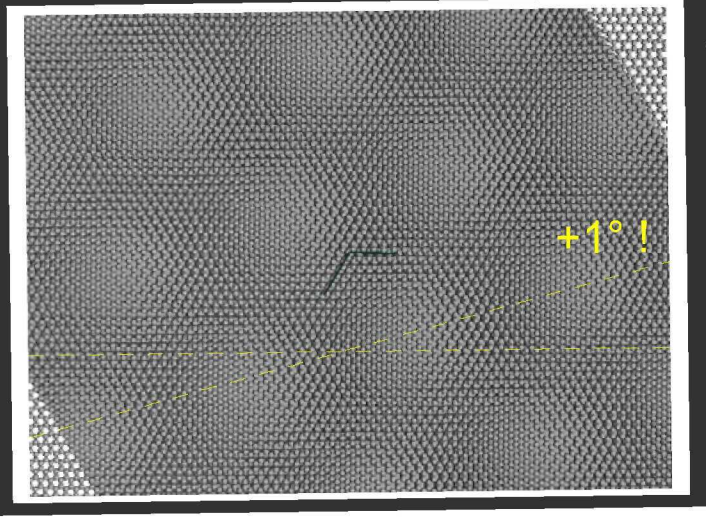

- Superstructure = moiré
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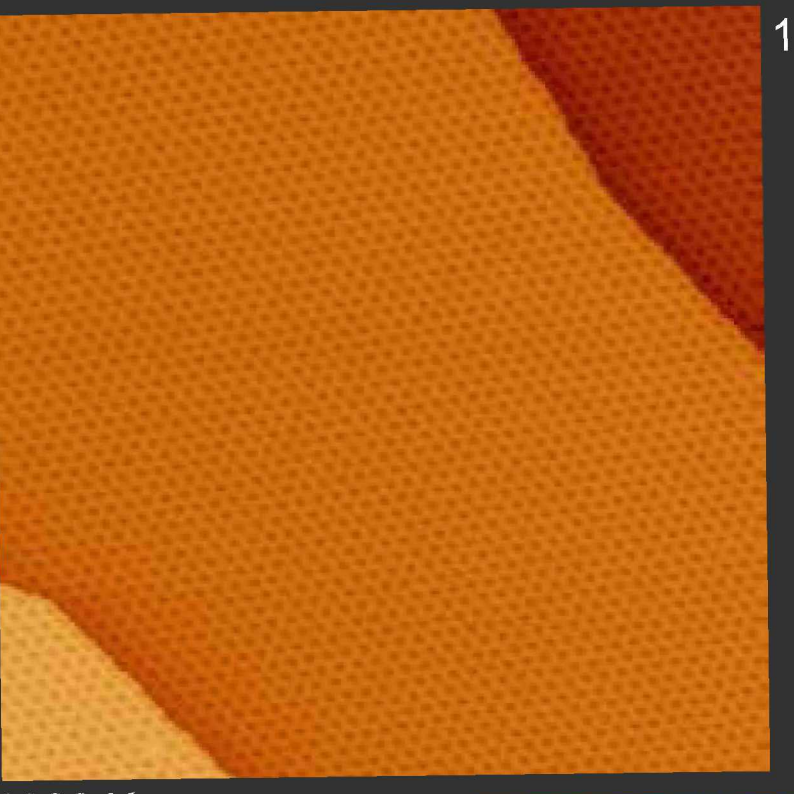
- Moiré tilts ~
  10× tilts of C rows !
  → limited disorder

- Unique orientation over
  µms above 1300 K !!!

Moiré of graphene on Ir(111) - orientation

1120 K



110×110 nm^2

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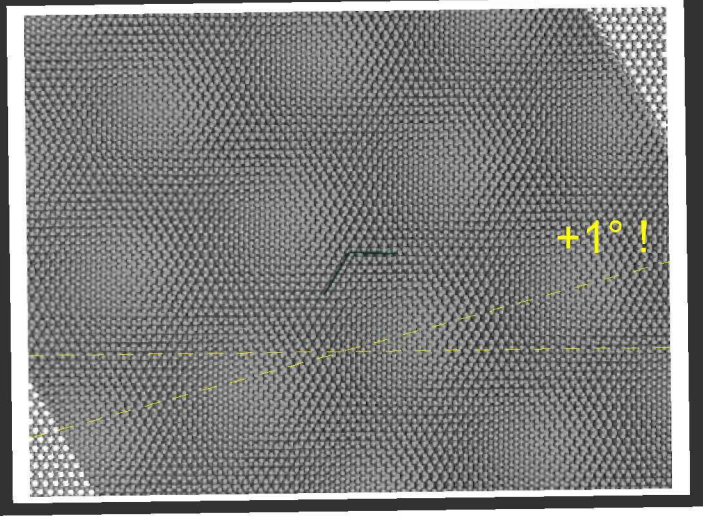

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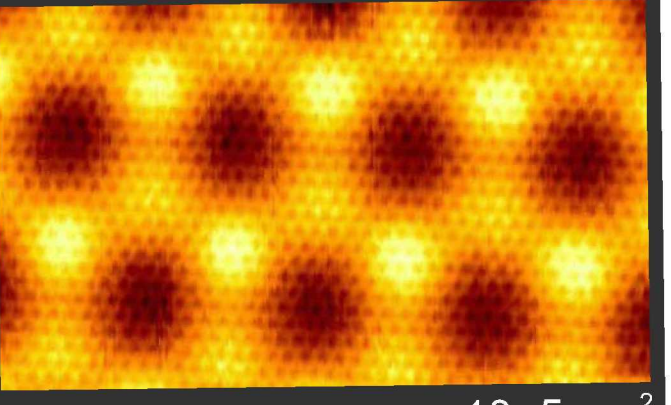
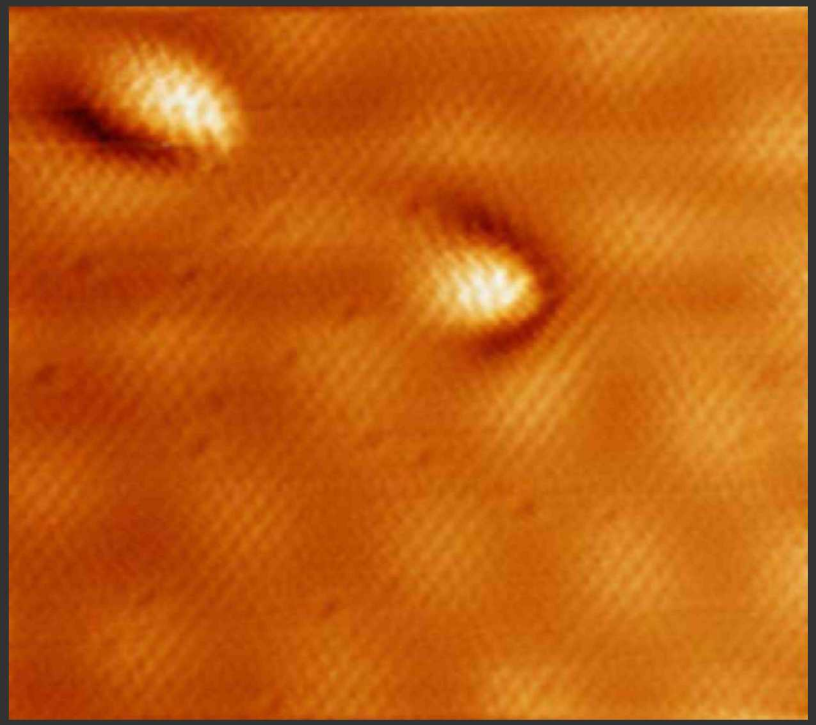


10×5 nm^2

Edge dislocations in graphene

14×12 nm^2



Edge dislocations in graphene

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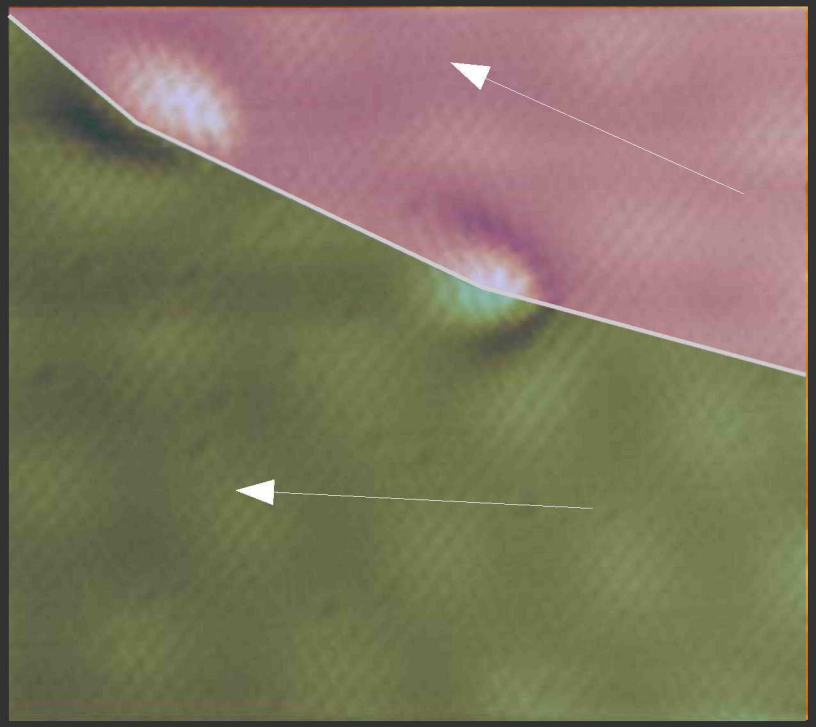

Edge dislocations in graphene

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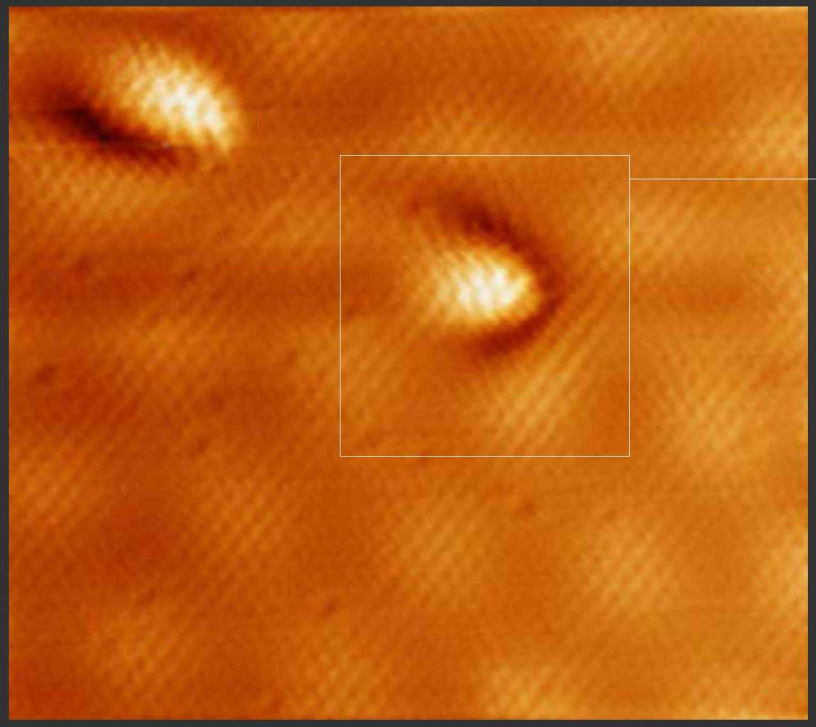
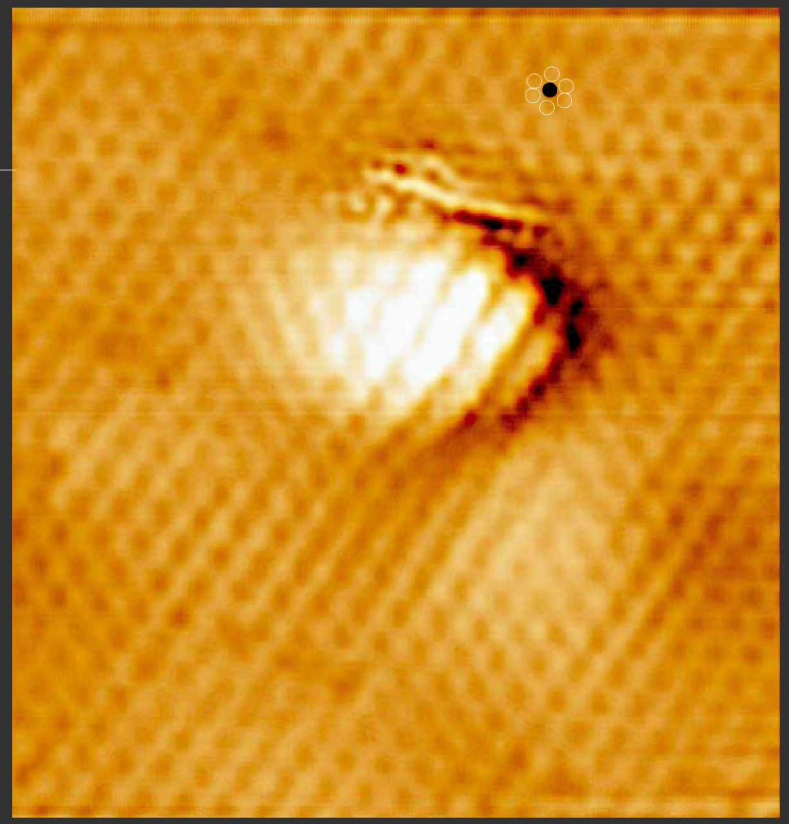


5.5×5.5 nm^2



Edge dislocations in graphene

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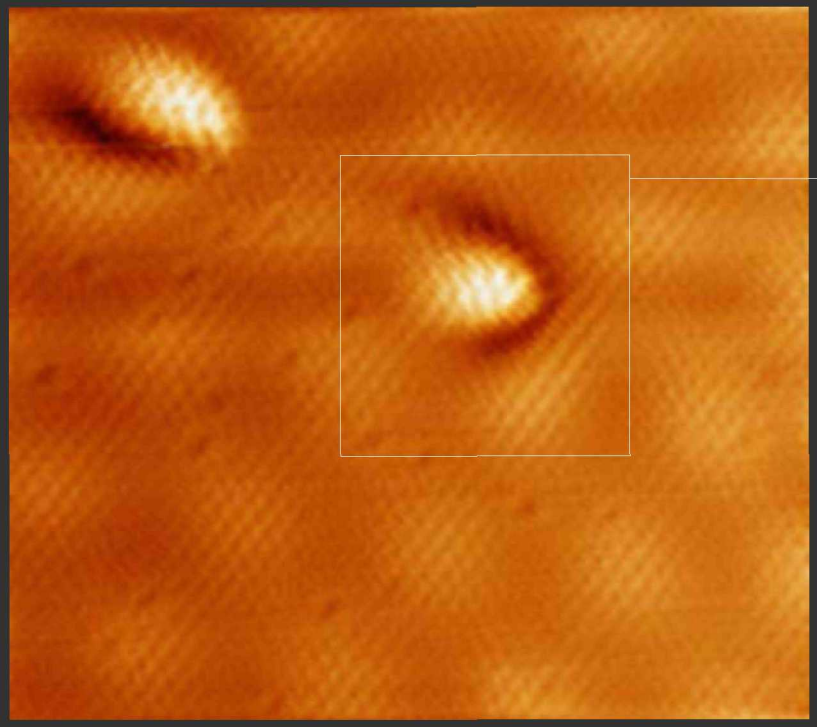
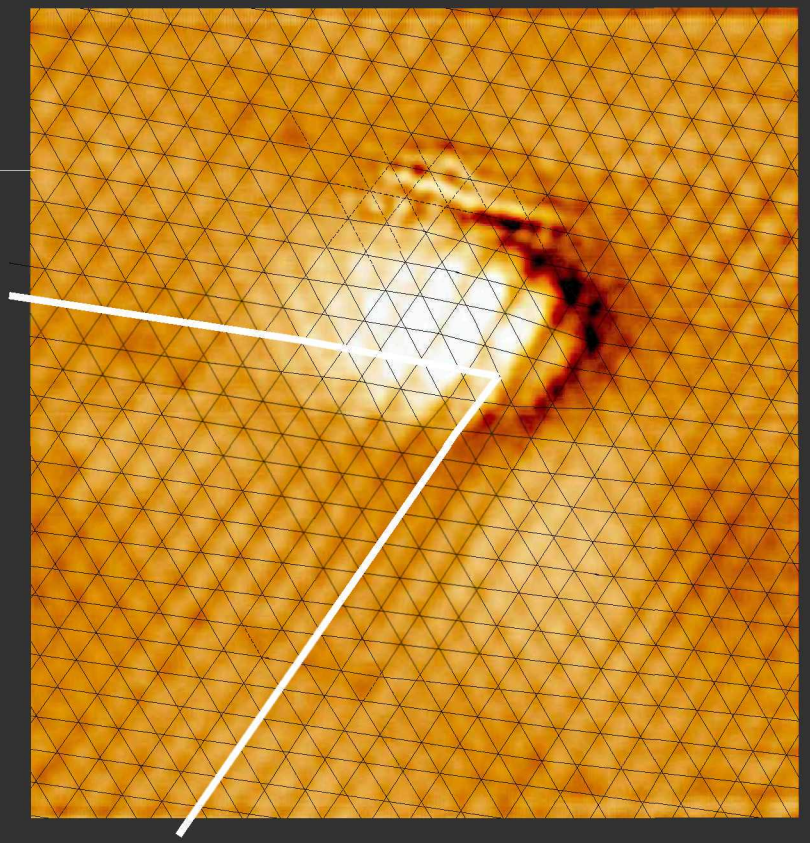
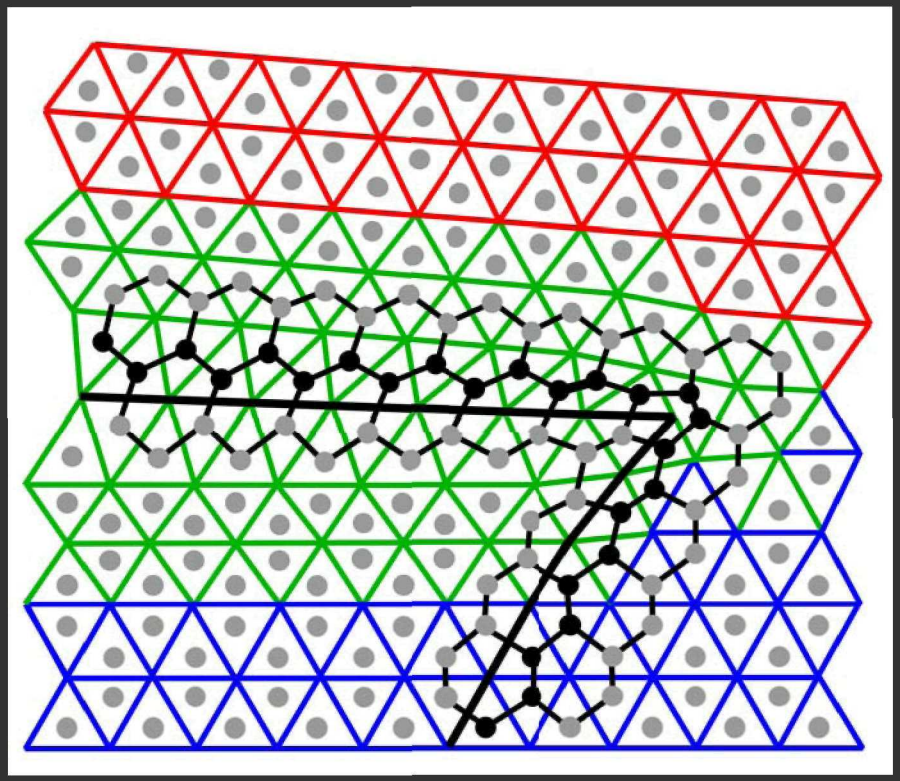


5.5×5.5 nm^2

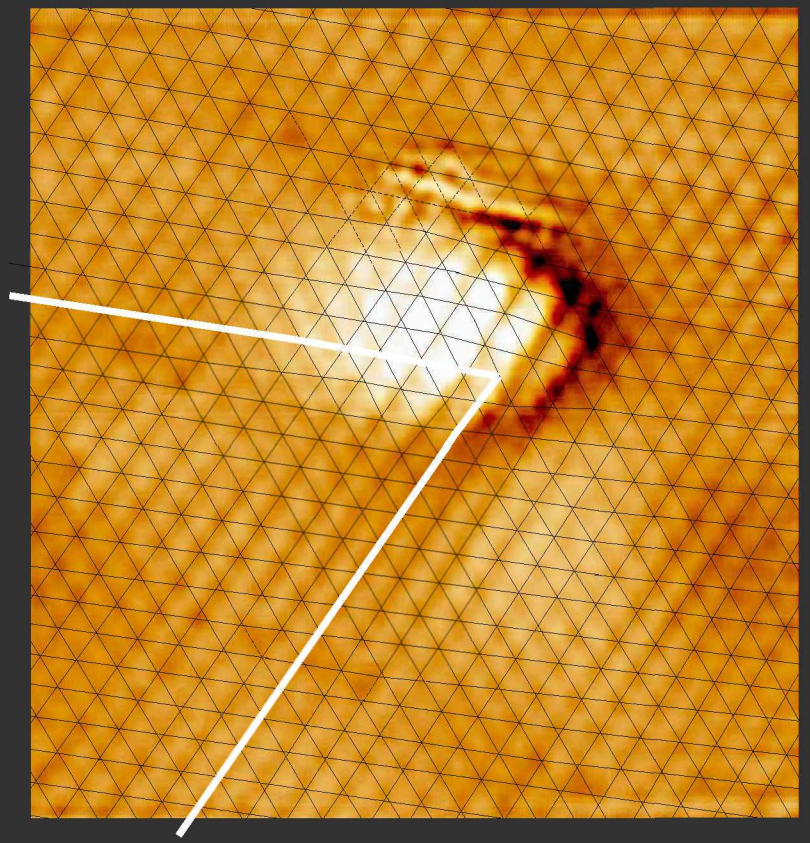


Two extra lines !

Edge dislocations in graphene



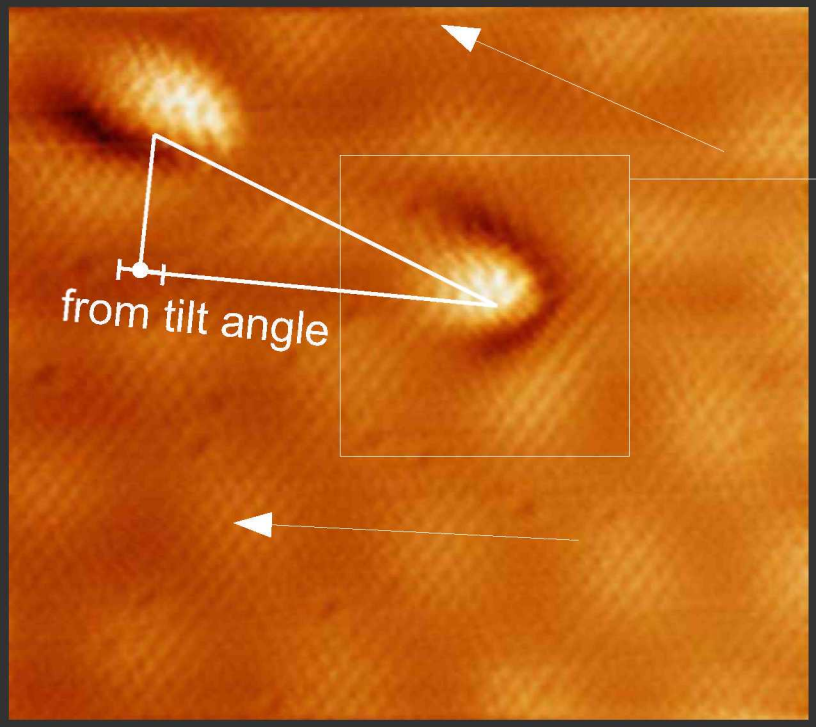
5.5×5.5 nm^2



Two extra lines !
= two extra zigzag C rows + one heptagon/pentagon pair
= edge dislocation in a 2D hexagonal crystal

Edge dislocations in graphene

14×12 nm^2



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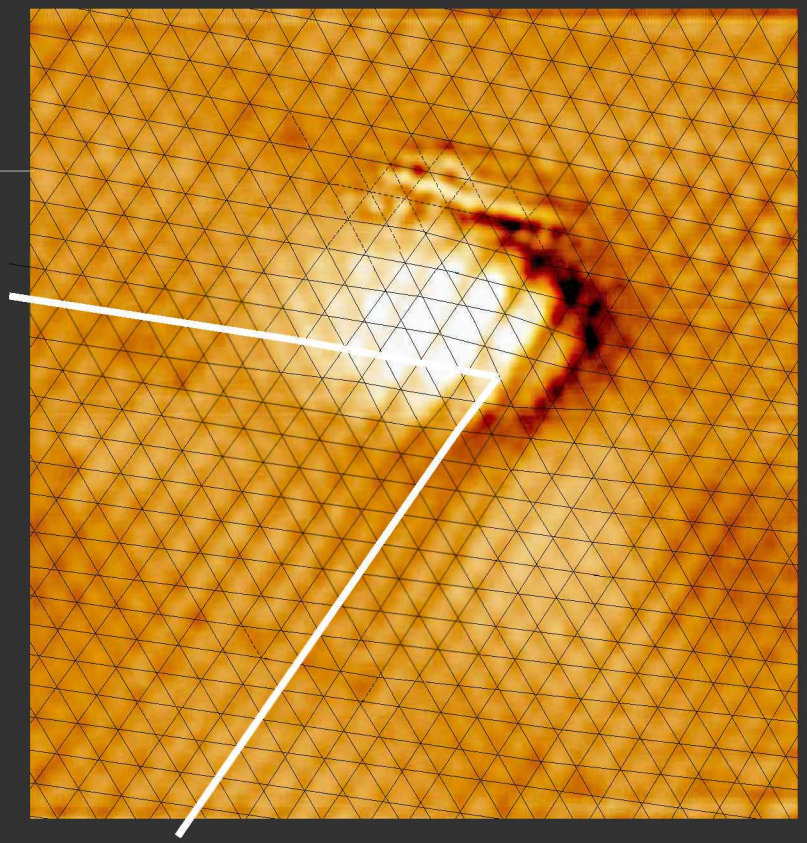
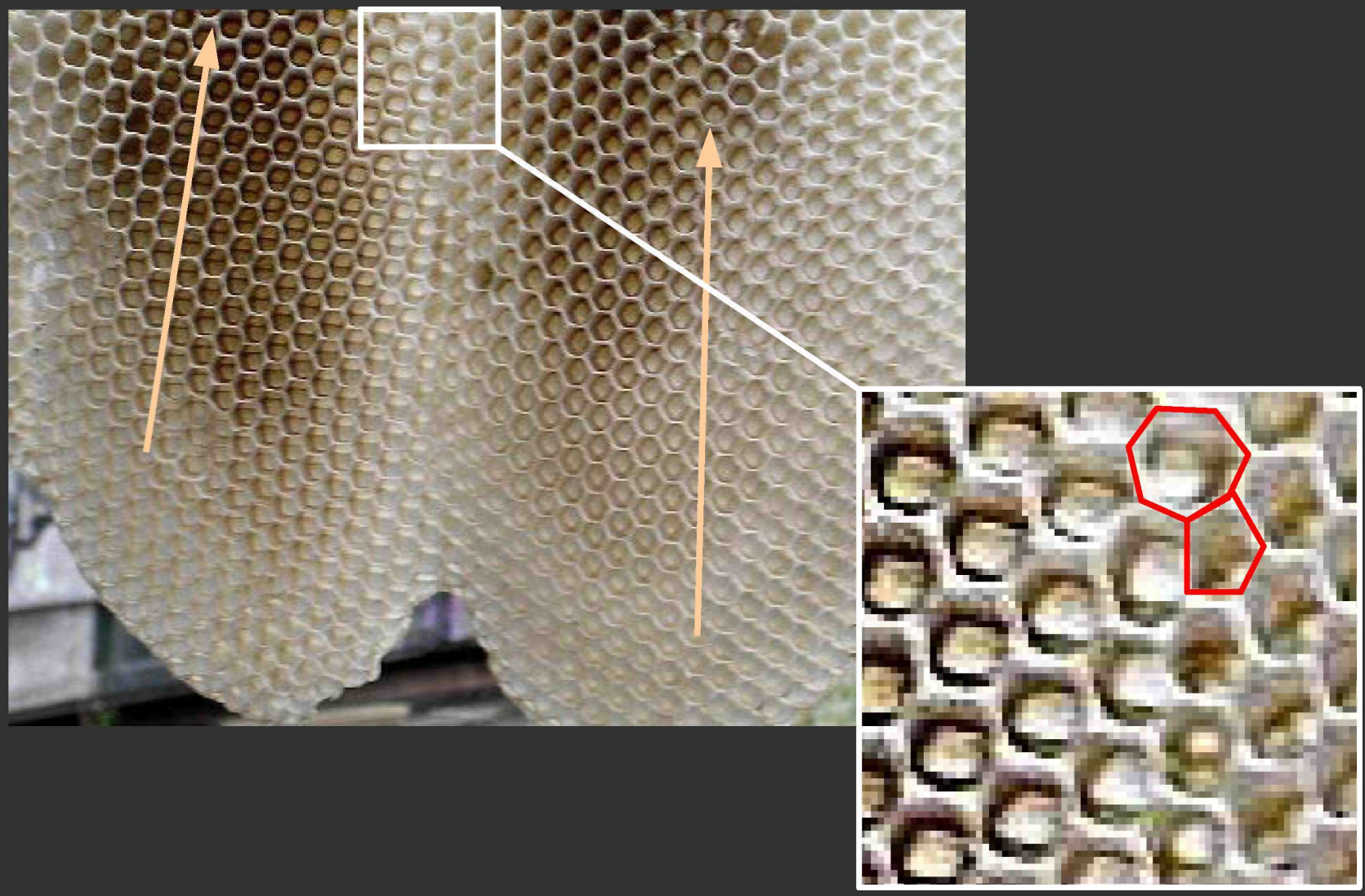


Two extra lines !
= two extra zigzag C rows + one heptagon/pentagon pair
= edge dislocation in a 2D hexagonal crystal

Driving force for formation = tilt accommodation

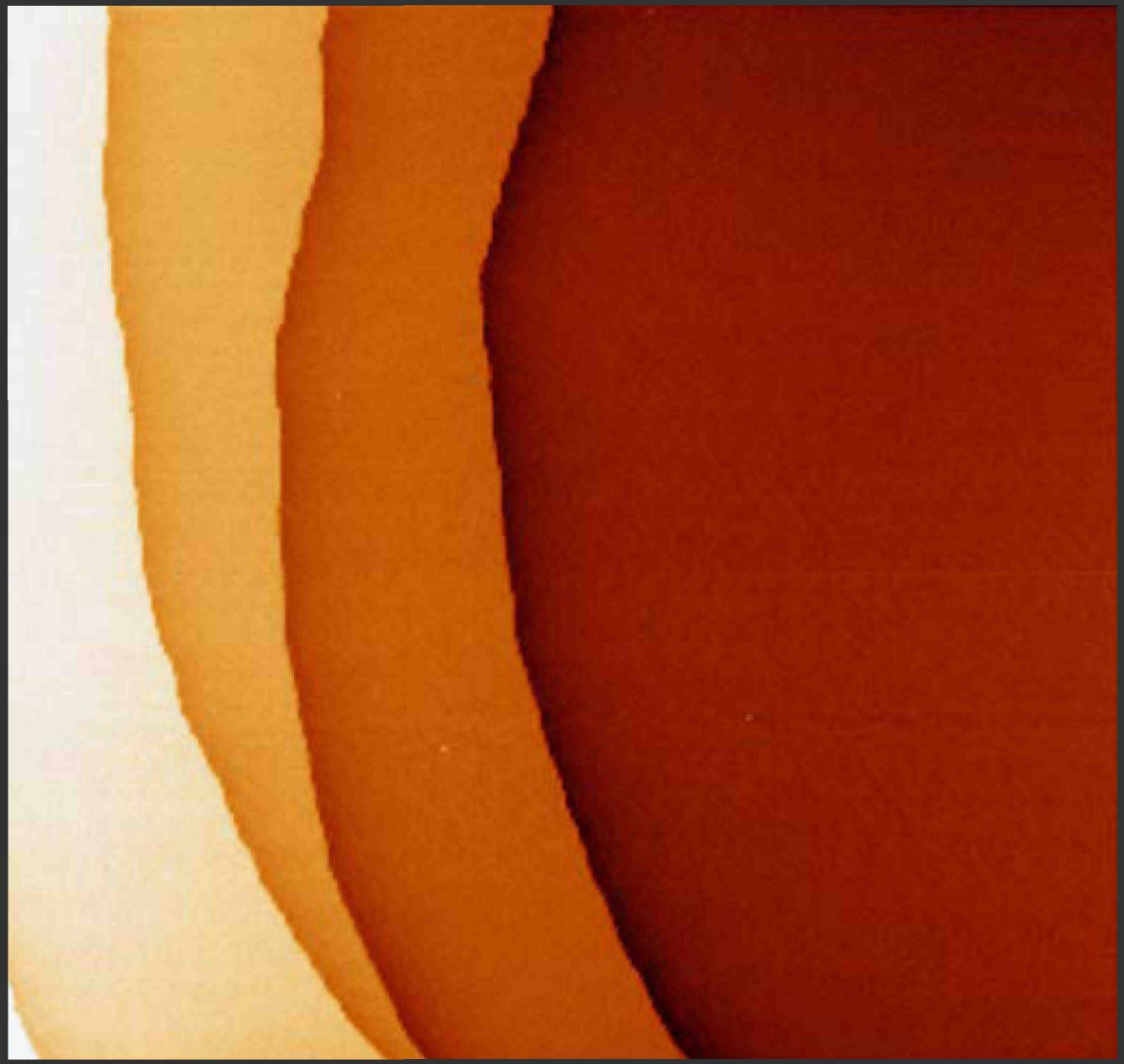
What about the bees ?



heptagon/pentagon pair at the boundary between two meeting honeycombs...

... is minimization of wax quantity the driving force ?

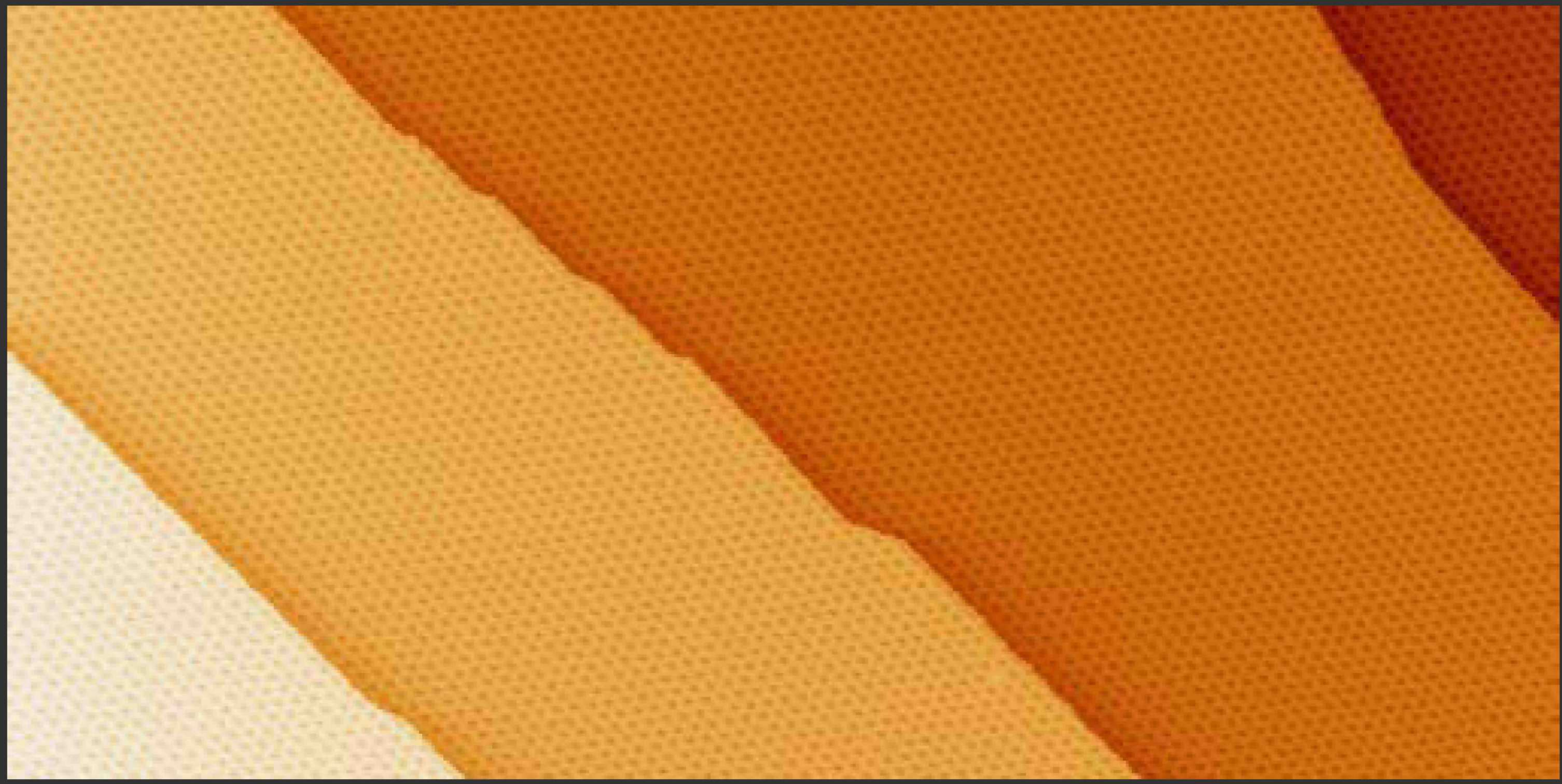
Coherency across step edges



Full coverage,
Growth at 1320 K

STM, 0.5×0.5 μm^2

Coherency across step edges



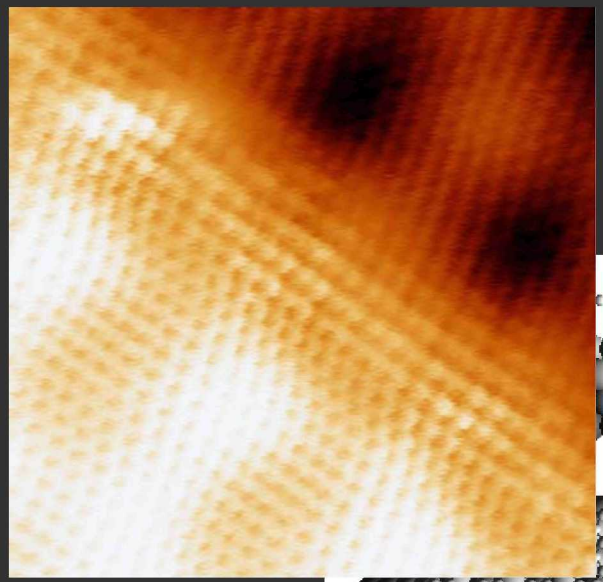
Growth at 1320 K

250×125 nm^2

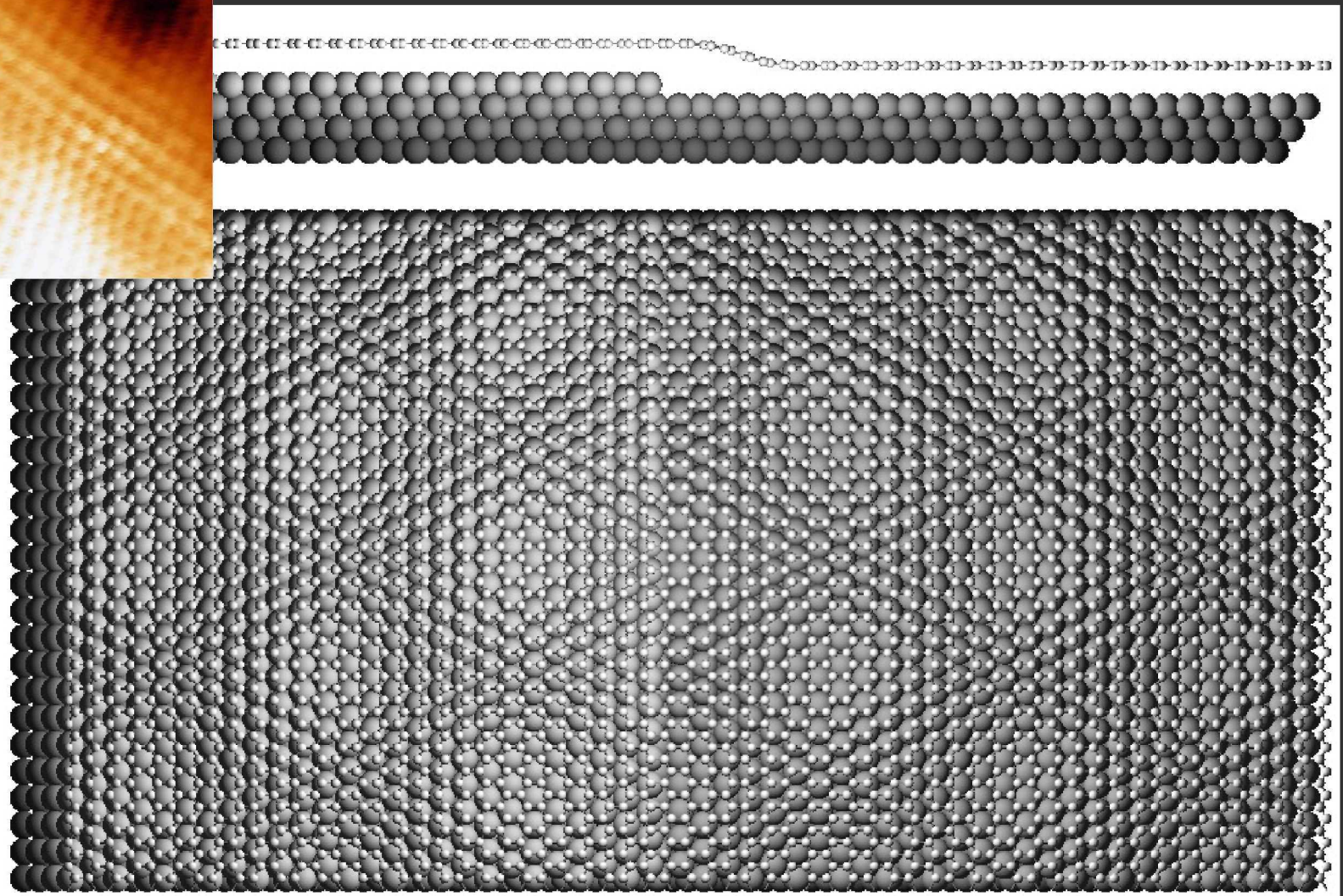
Extremely high order:
- Single orientation over step edges and µms
- No edge dislocation over µms

Coherency across step edges

5×5 nm^2



C rows are continuous across the step edge
→ graphene preserves its orientation

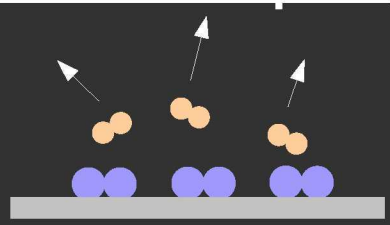


Growth of graphene/Iridium

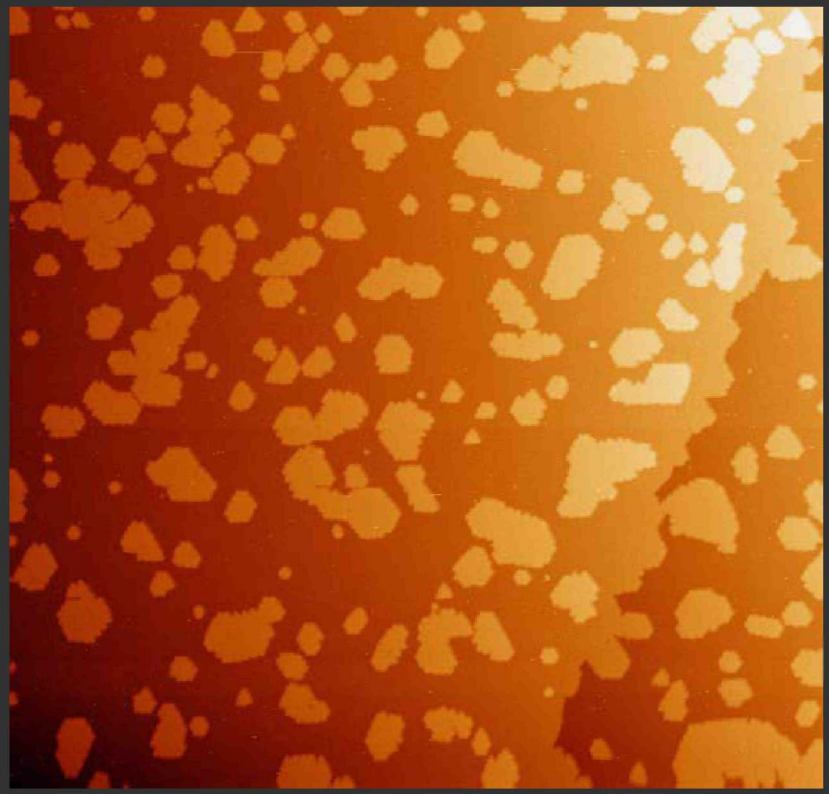
Coraux, N'Diaye, Engler, Busse, Michely, submitted

First approach: temperature programmed growth

1. 300 K adsorption

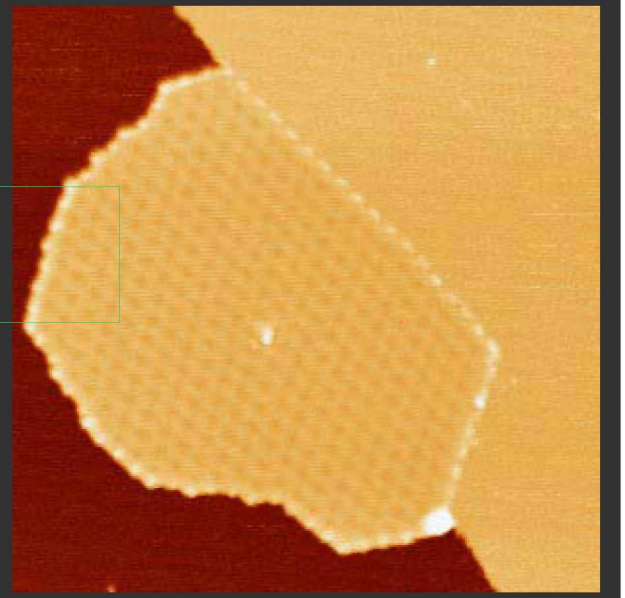


2. T>700 K decomposition & growth

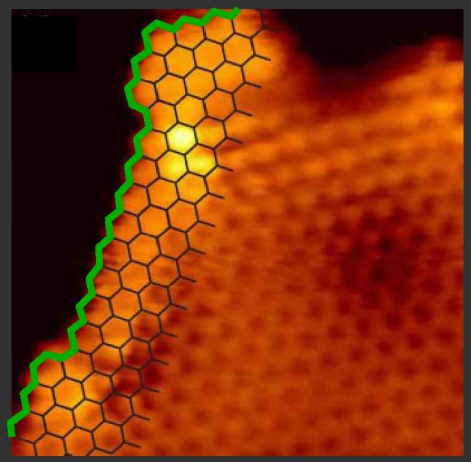


250×250 nm^2

Nano-islands
with zigzag edges



70×70 nm^2

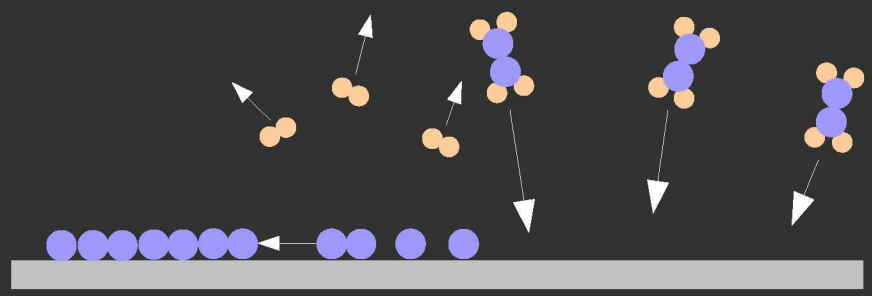


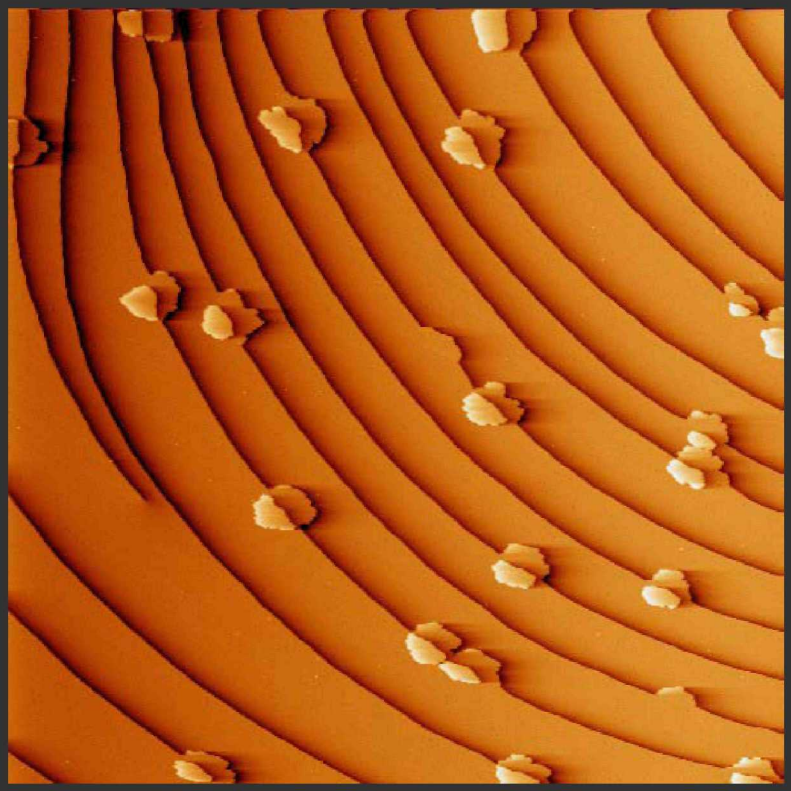
4×4 nm^2

Zigzag edge state ?

Also cf. Vázquez de Parga *et al.*, PRL 2008

Second approach: chemical vapor depostion (CVD)

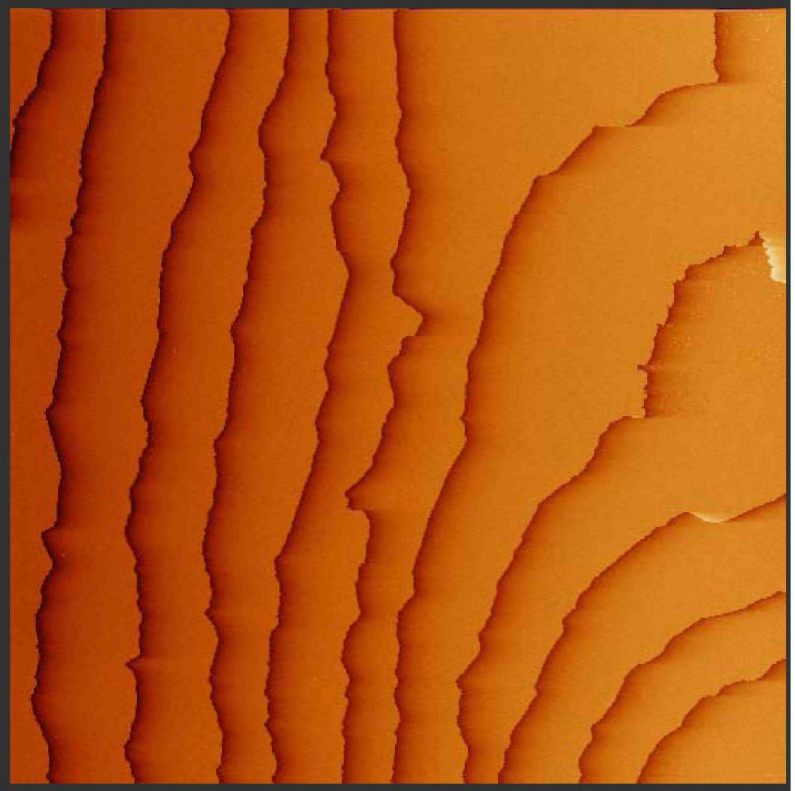




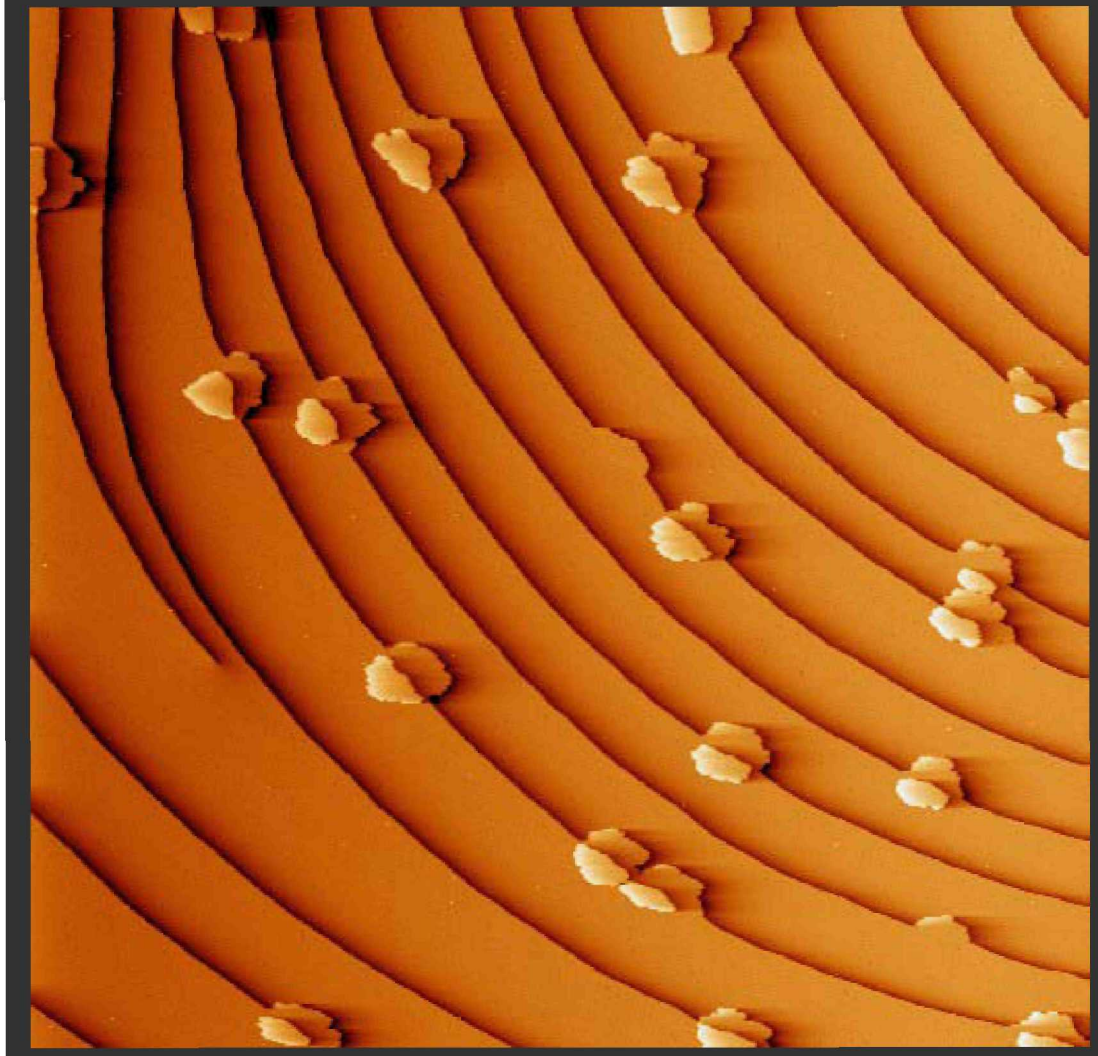
1×1 μm^2

From islands...

...to full coverage

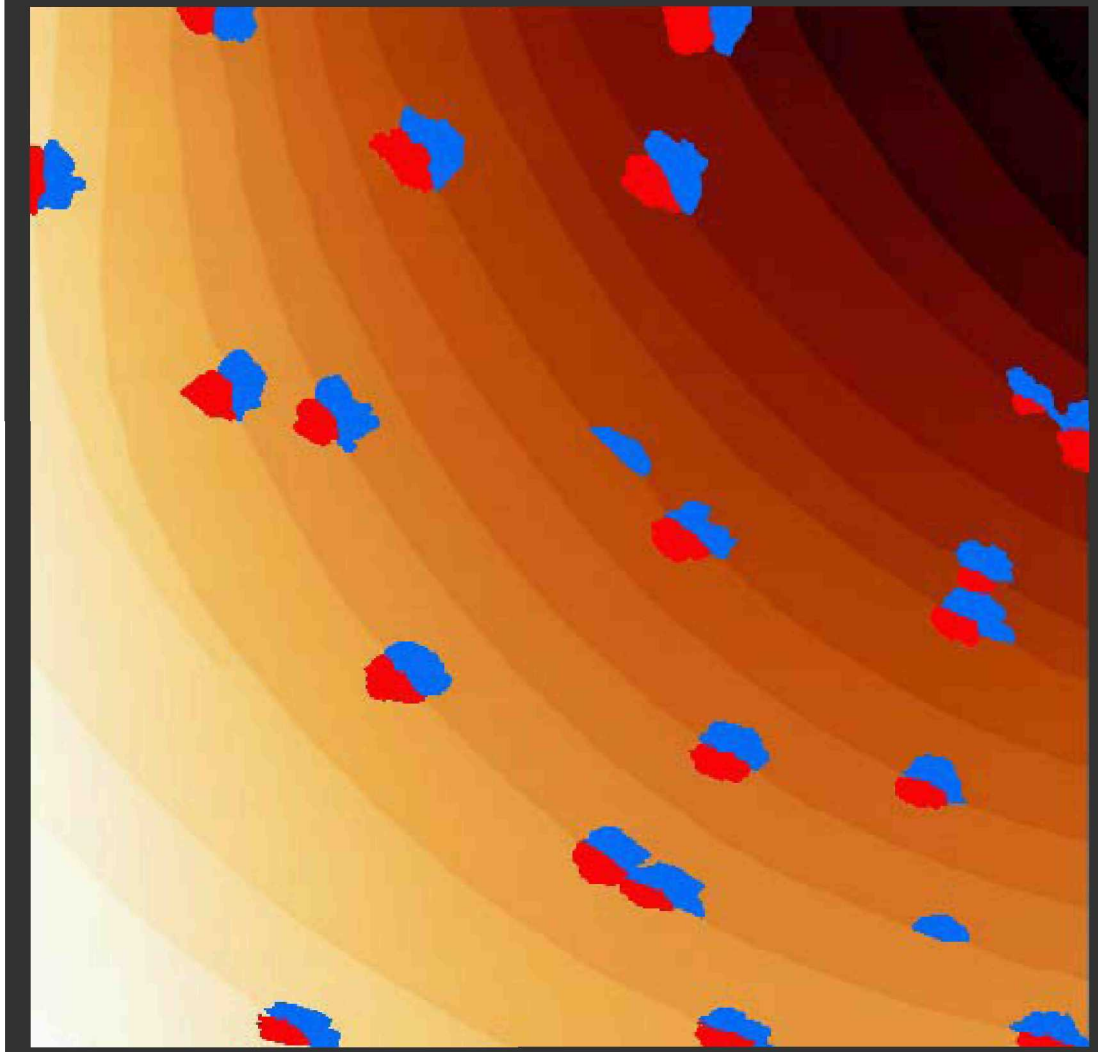


CVD: graphene nucleation (1)

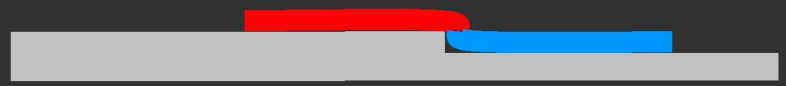


Growth at 1120 K, differentiated image, 1×1 μm^2

CVD: graphene nucleation (1)



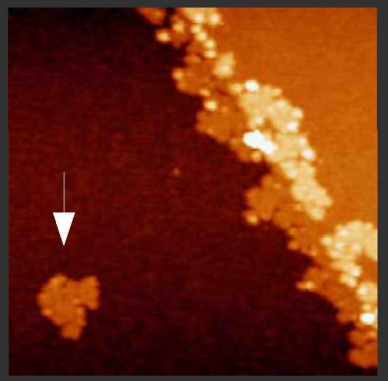
Growth at 1120 K, 1×1 μm^2



side-view

- Exclusive nucleation at substrate steps at T>1000K

- Ethylene decomposes everywhere:



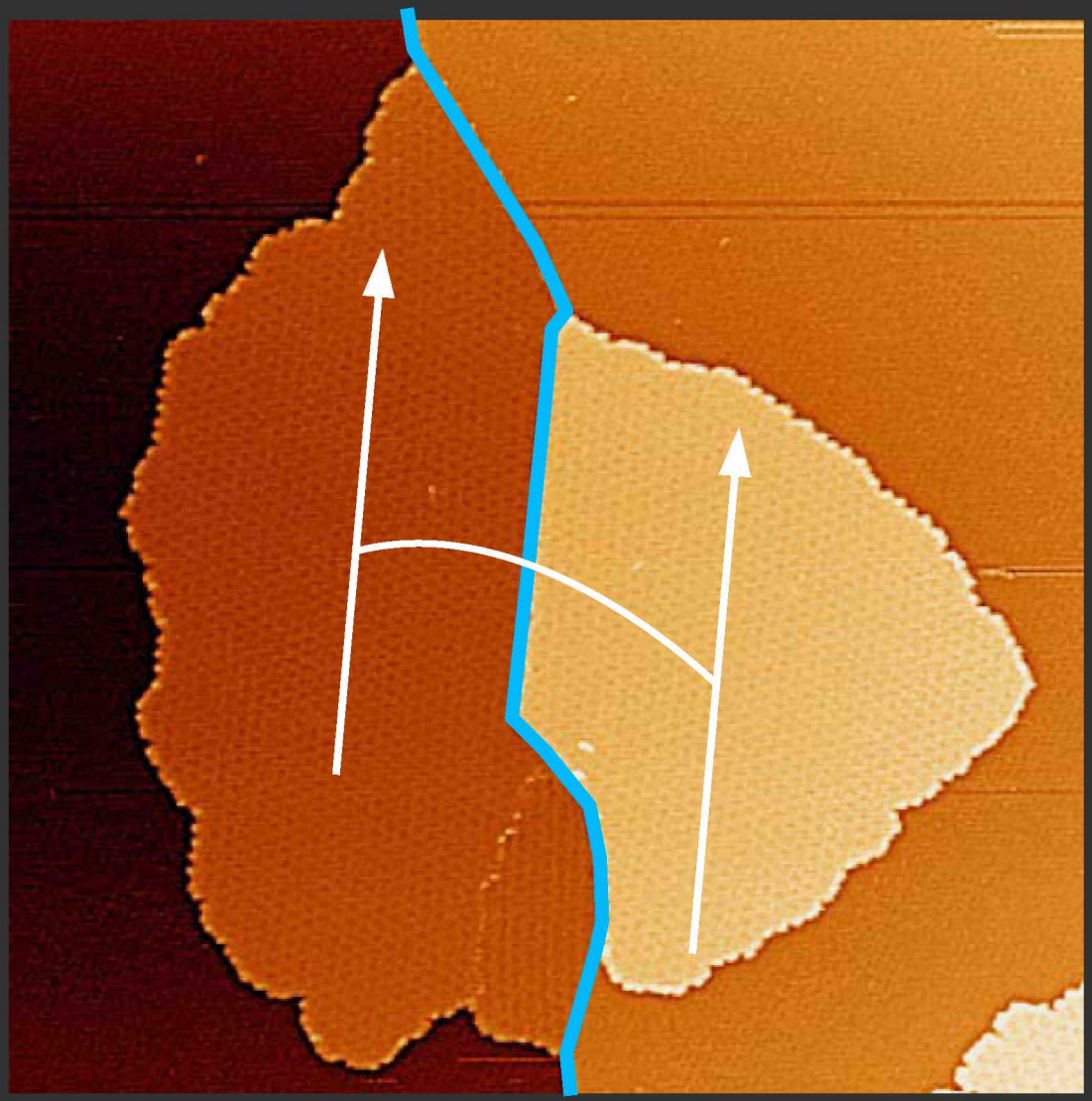
870 K
70×70 nm^2

→ efficient C transport

- blue/red ~ 7/3 & no isolated red islands
→ nucleation at ascending step edge

→ C-Ir σ bond

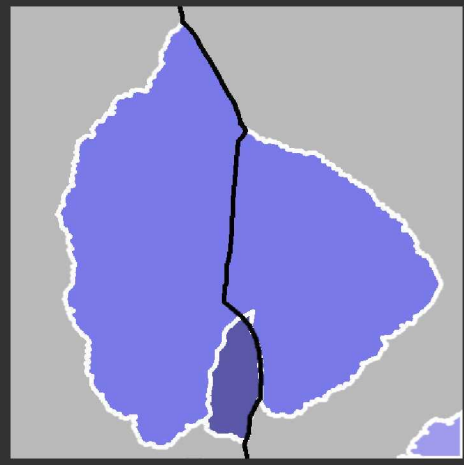
CVD: graphene nucleation (2)



Growth at 1120 K, 170×170 nm^2

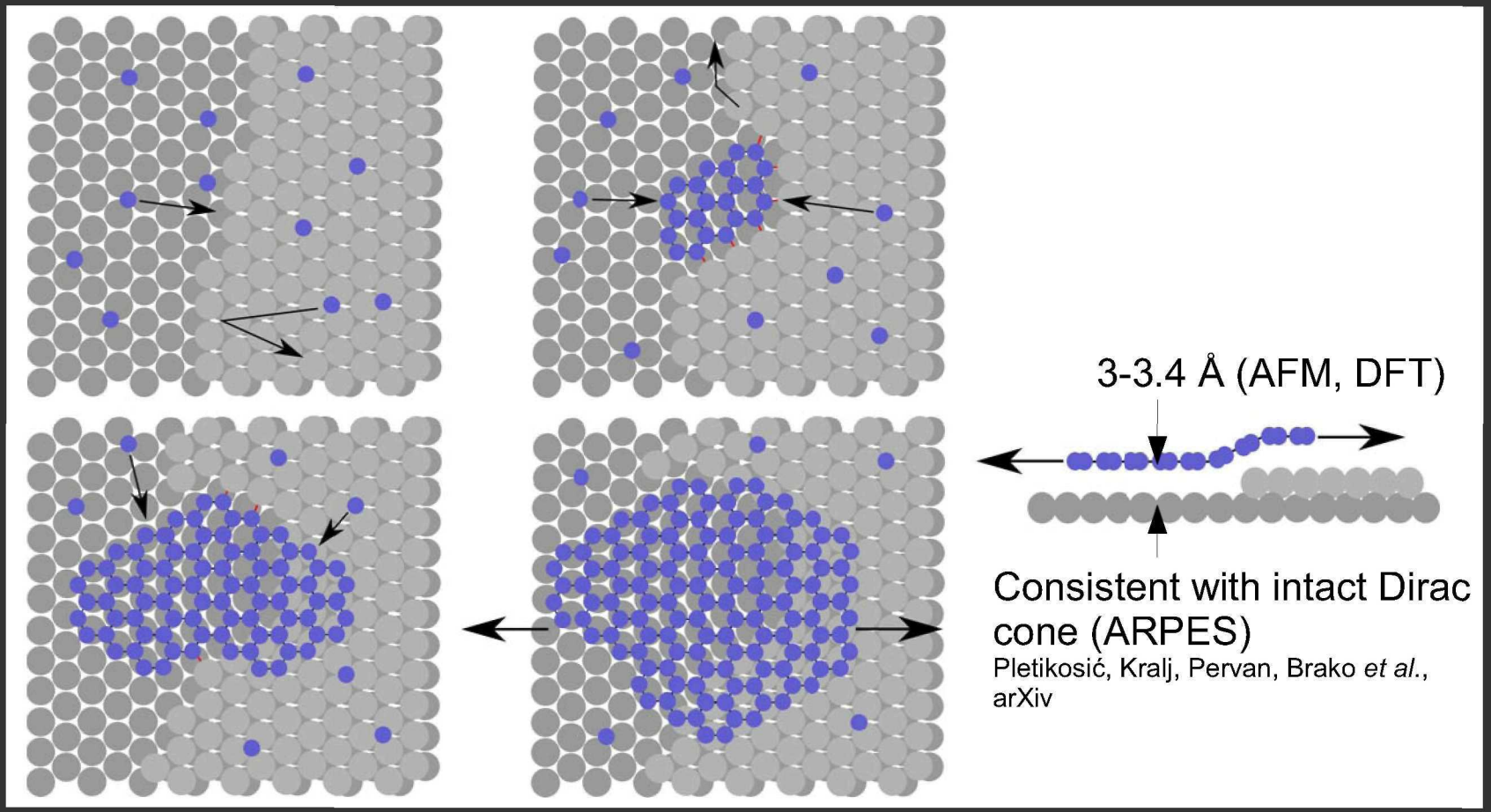
- Profound reshaping of Ir steps
  → Ir steps locally align C zigzag rows
  → maximizing number of C-Ir σ bonds

- Moiré orientation preserved across step edge



→ graphene spans across step edges without defects

CVD: graphene nucleation - mechanism

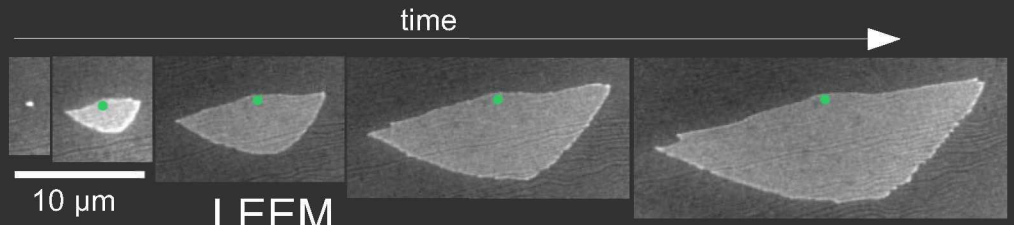


3-3.4 Å (AFM, DFT)

Consistent with intact Dirac cone (ARPES)

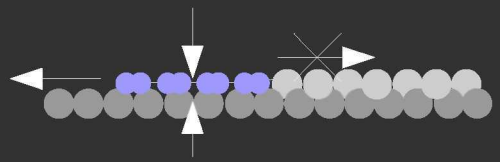
Pletikosić, Kralj, Pervan, Brako *et al.*, arXiv

Graphene/Ru(0001):
growth exclusively at ascending step edge



LEEM

Sutter *et al.*, Nature Mat. 2008

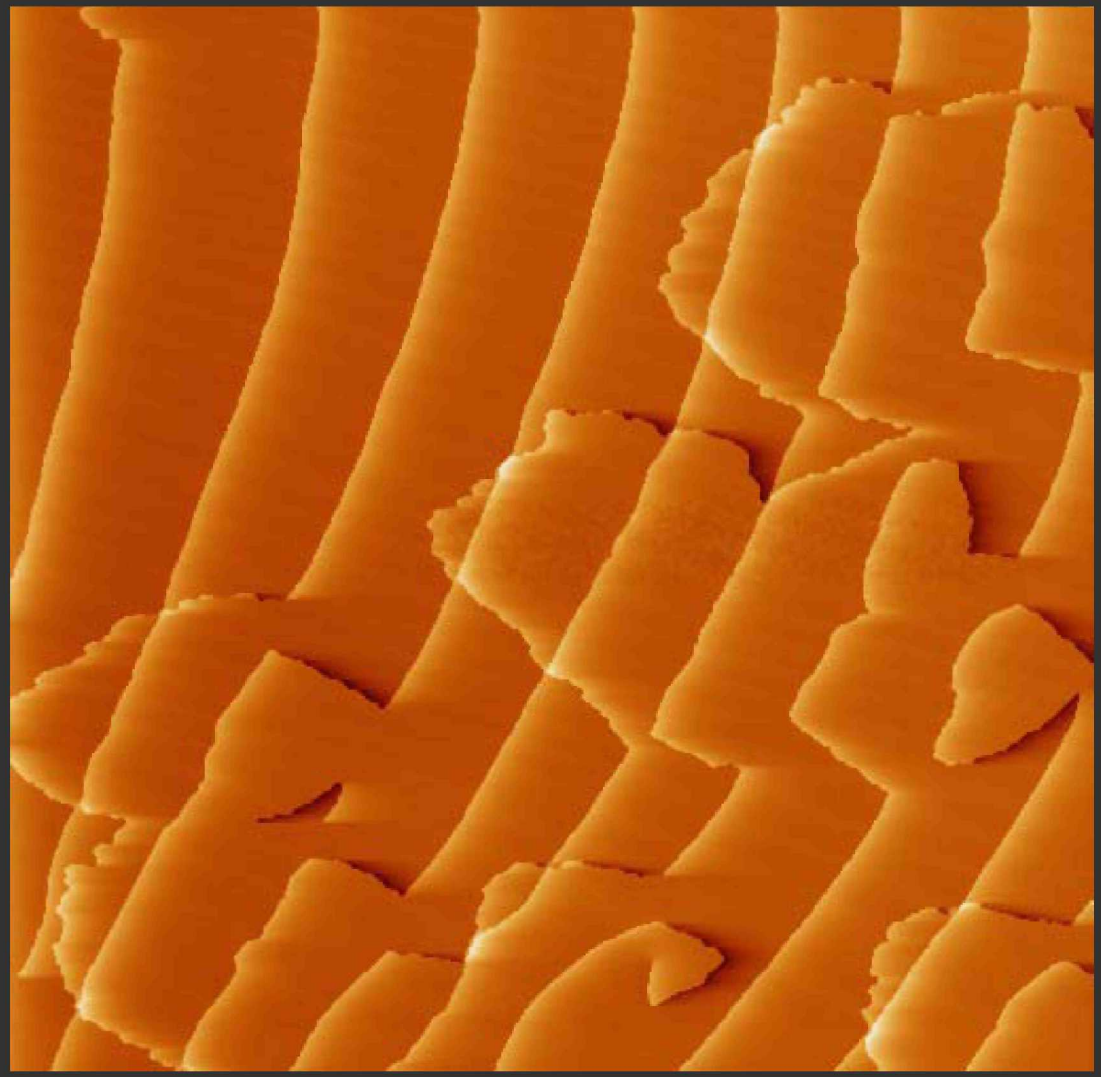


1.5-2 Å (LEED, DFT)

Consistent with deep modification of π-bands (ARPES)

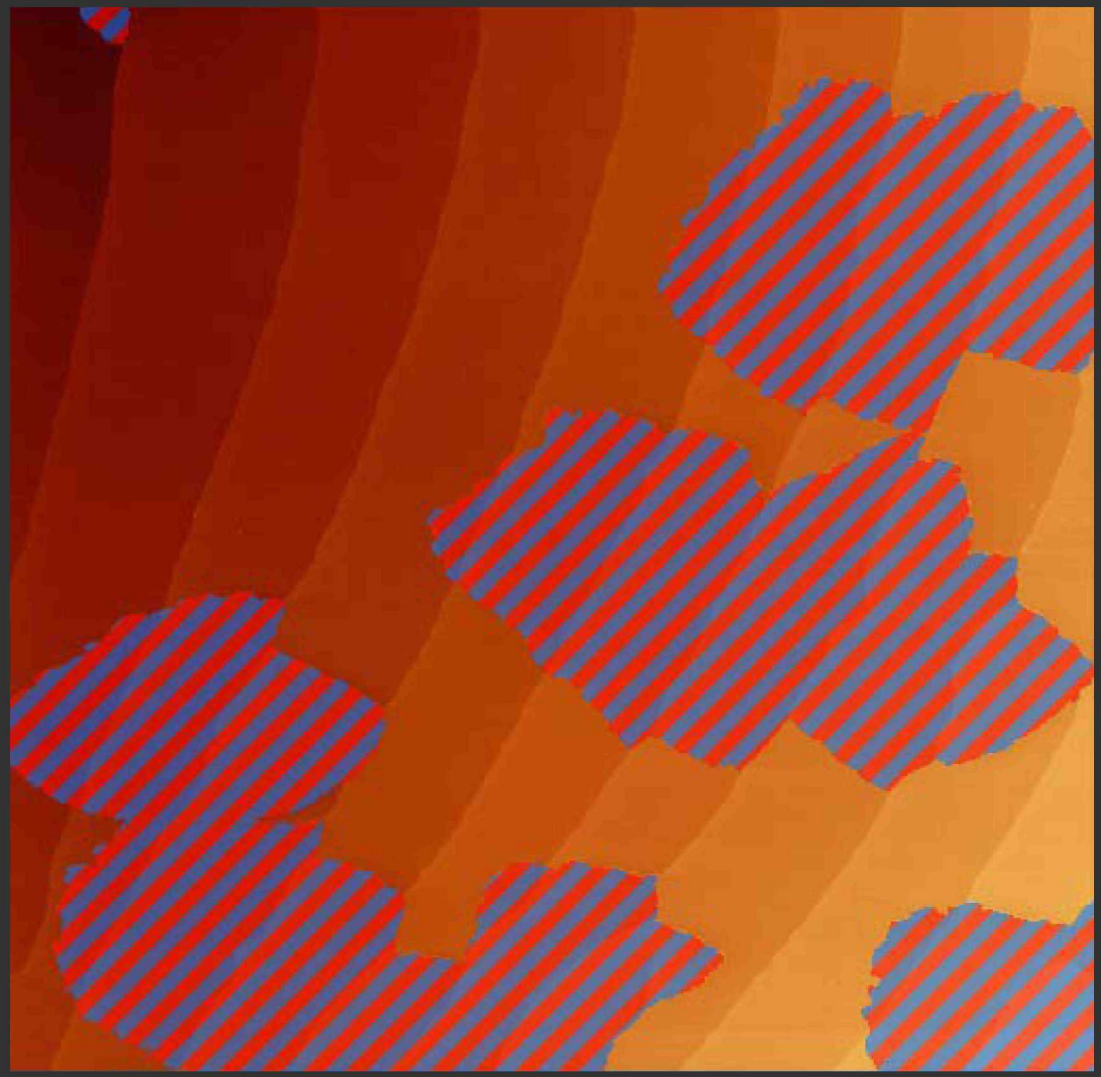
Brugger *et al.*, arXiv

CVD: from islands to full coverage (1)



Growth at 1120 K, differentiated image, 1×1 μm^2

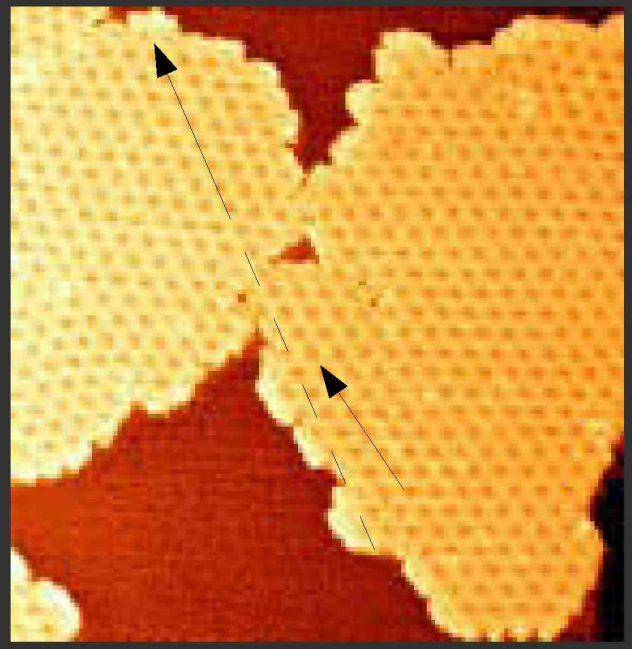
CVD: from islands to full coverage (1)



Growth at 1120 K, 1×1 μm^2

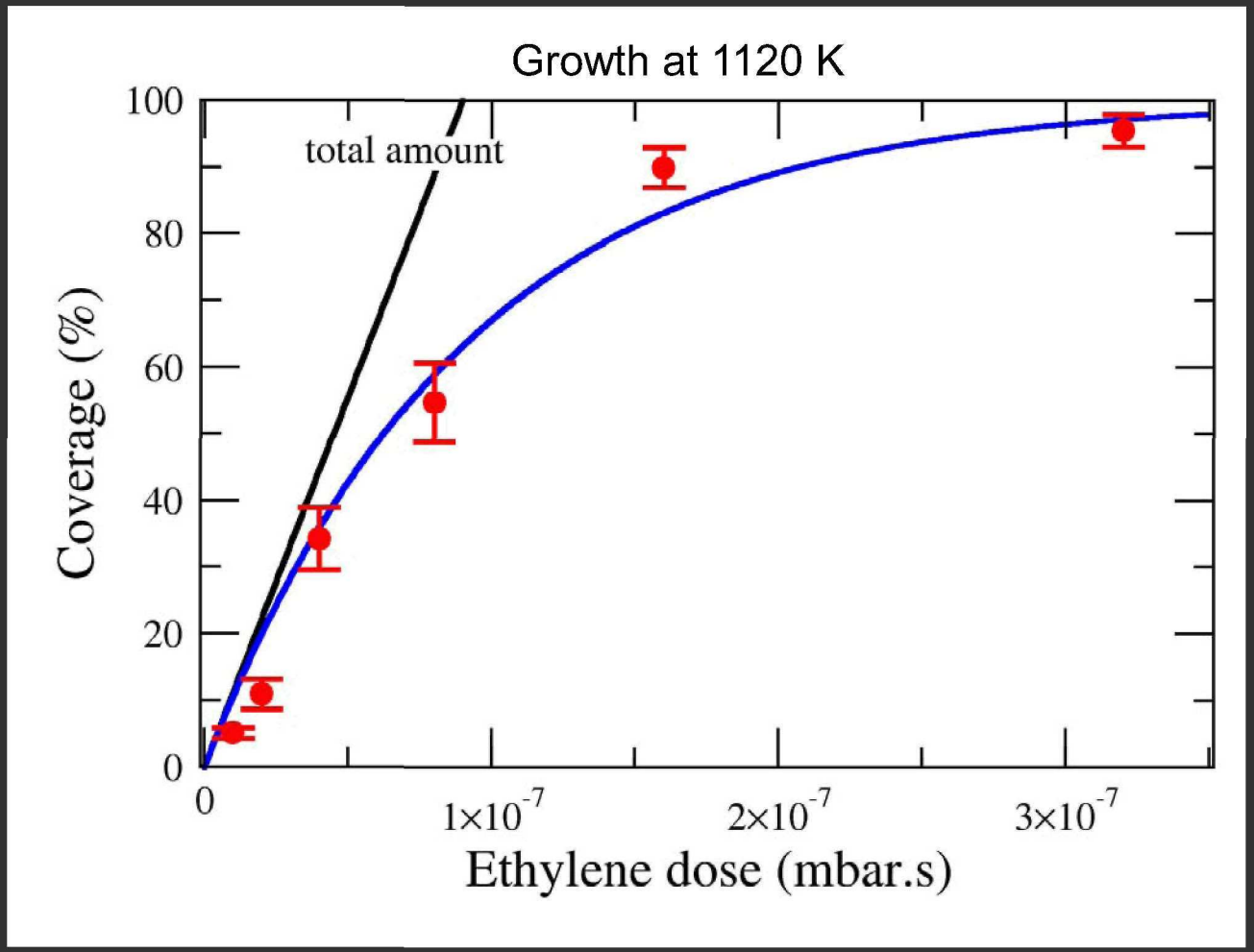
- islands cross Ir steps coherently

- Moiré uninterrupted upon coalescence of islands
  → islands meet coherently

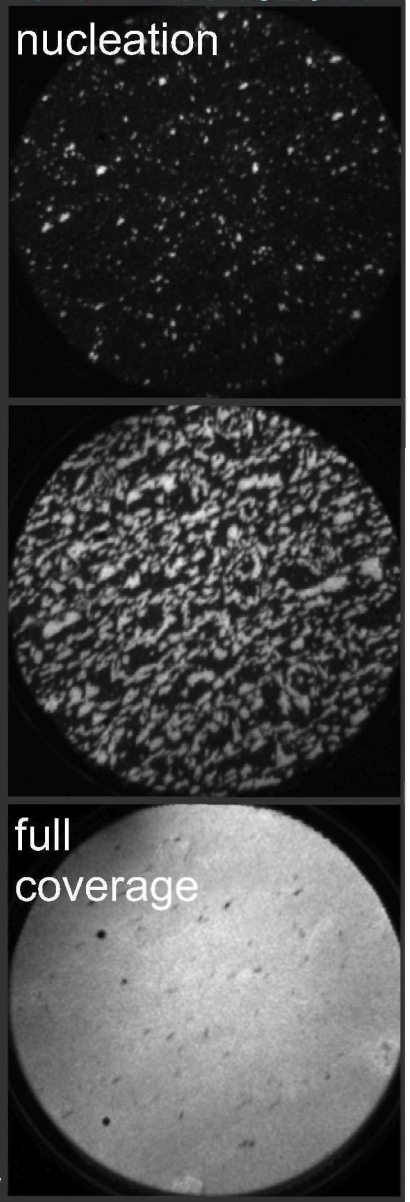


70×73 nm^2

CVD: from islands to full coverage (2)



Growth at 1320 K



Best fit with simple model **excluding ethylene desorption** on Ir:
- probability=1 to decompose on Ir and form graphene
- probability=1 to desorb on graphene

$$\rightarrow \quad \Theta = 1 - e^{-\Phi \times \Omega / \sqrt{2\pi M k_B T}}$$

PEEM, 50 µm
D. Wall, N. Buckaniea, F. Meyer zu Heringdorf

Summary

Graphene growth

→ nanoislands with well defined zigzag edges – full coverage (CVD)

- CVD: nucleation at ascending step edges, islands cross step edges and meet coherently

Structural coherency

- heptagon/pentagon pairs accommodate tilt boundaries
- limited disorder from 1100 K growth temperature
- µm-scale (at least) full coherency above 1300 K

Graphene on Iridium as a model system

high structural quality and low interaction with the substrate

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