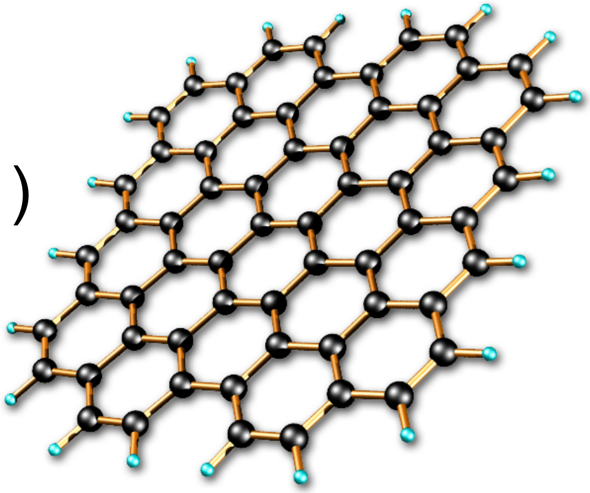
T.J. Watson Research Center

Optimizing Graphene Morphology on SiC(0001)

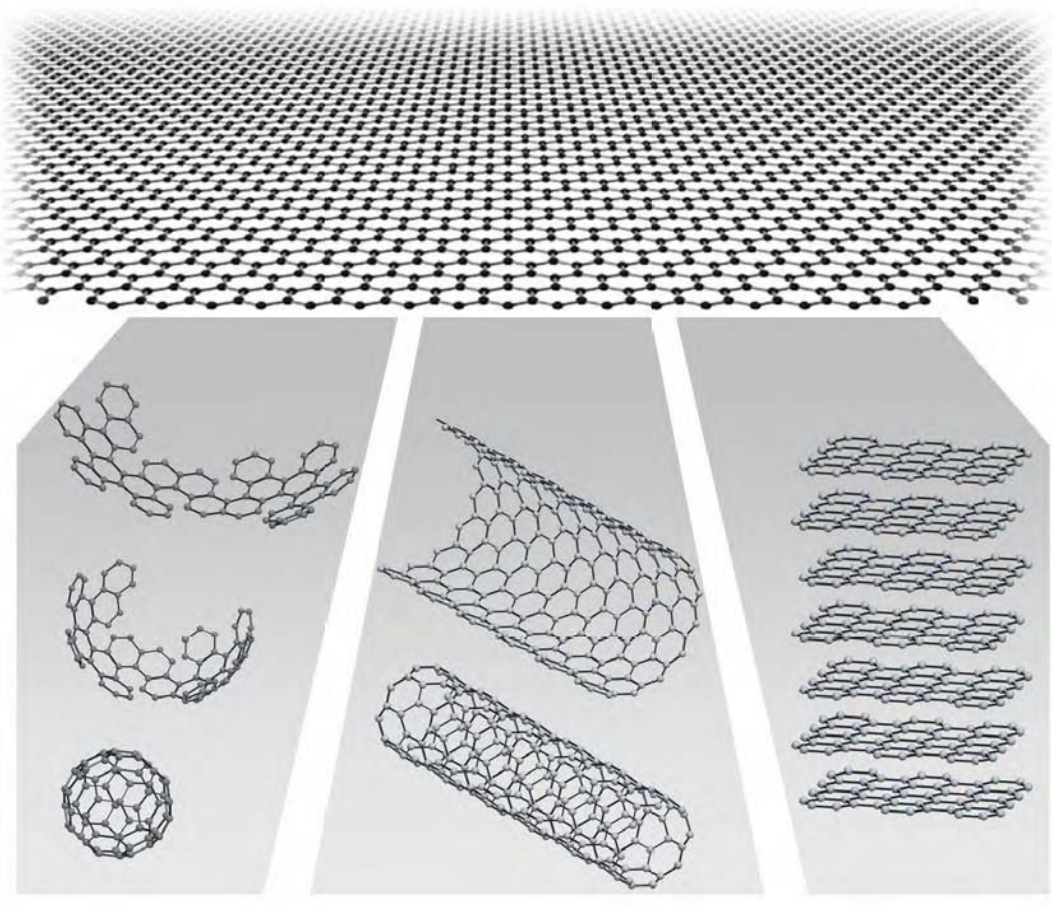


James B. Hannon
Rudolf M. Tromp

The 1st GCOE International Symposium, Tohoku University, March 5, 2009

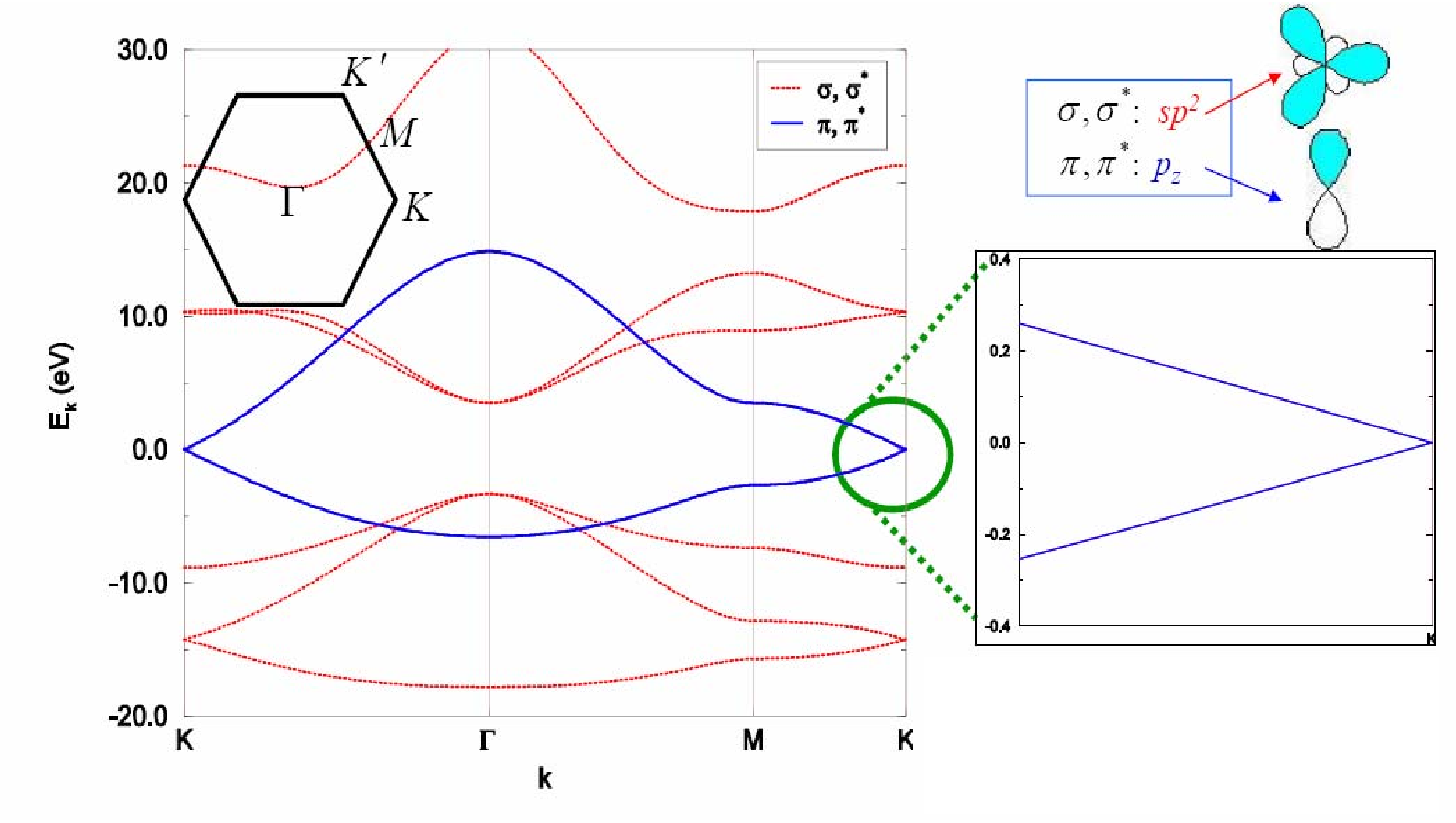
Graphene sheets

- Graphene sheets can be formed into 0D,1D, 2D, and 3D structures
- Chemically inert
- Intrinsically high carrier mobility
- Interesting physics – see next talk!



Geim, Novoselov, Nature Mater, 6, 183 (2007)

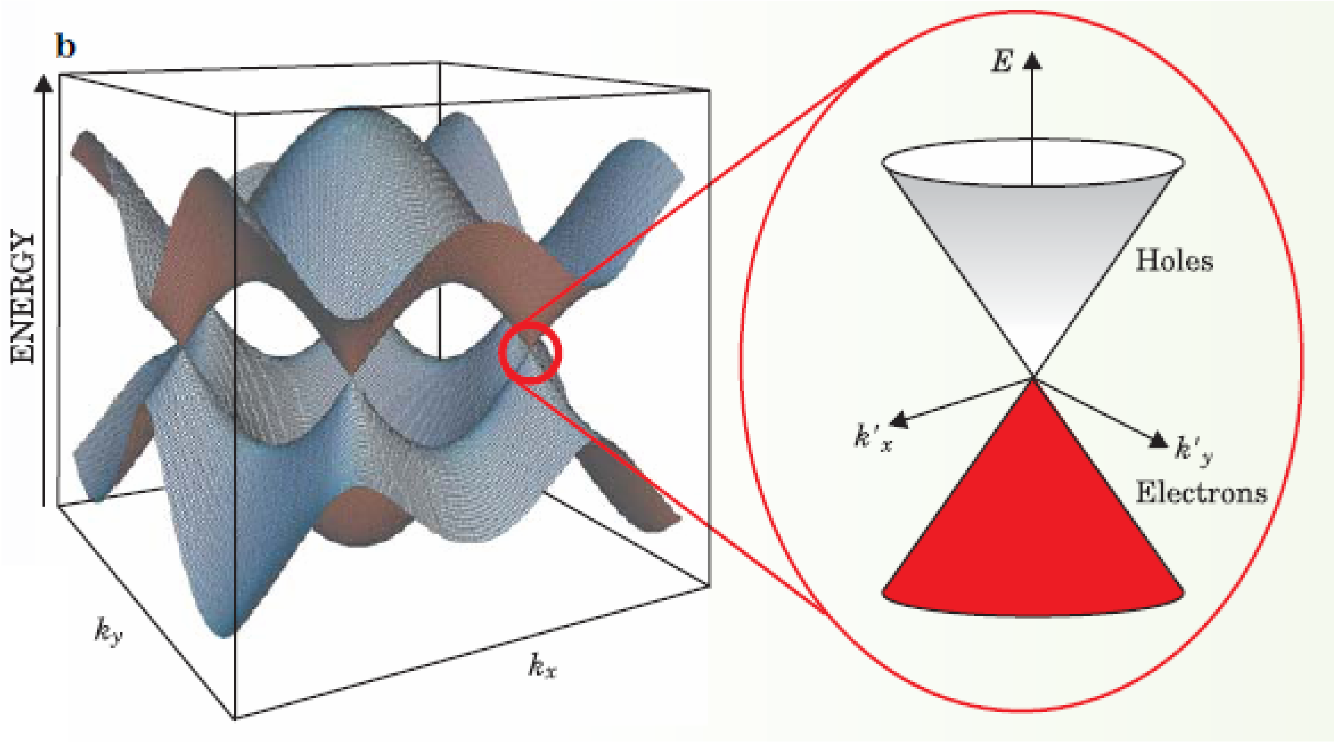
Electronic structure of graphene



Min, “Electron Structure of Graphene” (2006)

Dirac Point

Linear dispersion relation, vanishing density of states at E_F

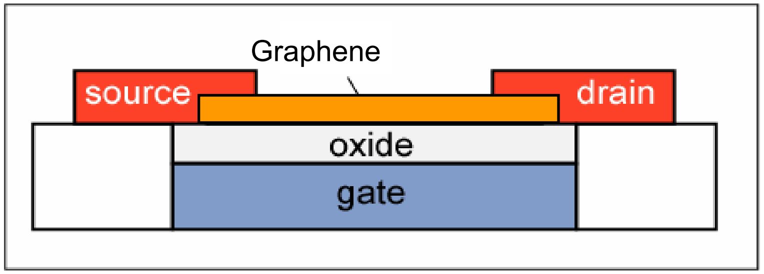


$$E = \hbar v_F k$$

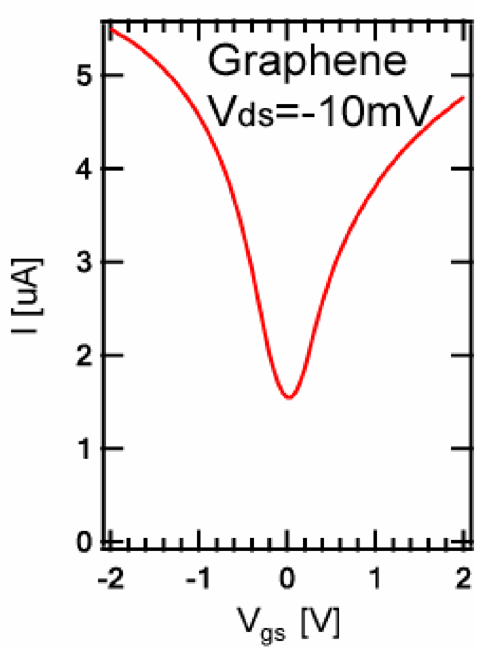
$$\mathrm{DOS} = \frac{2E}{\pi \hbar^2 v_F^2}$$

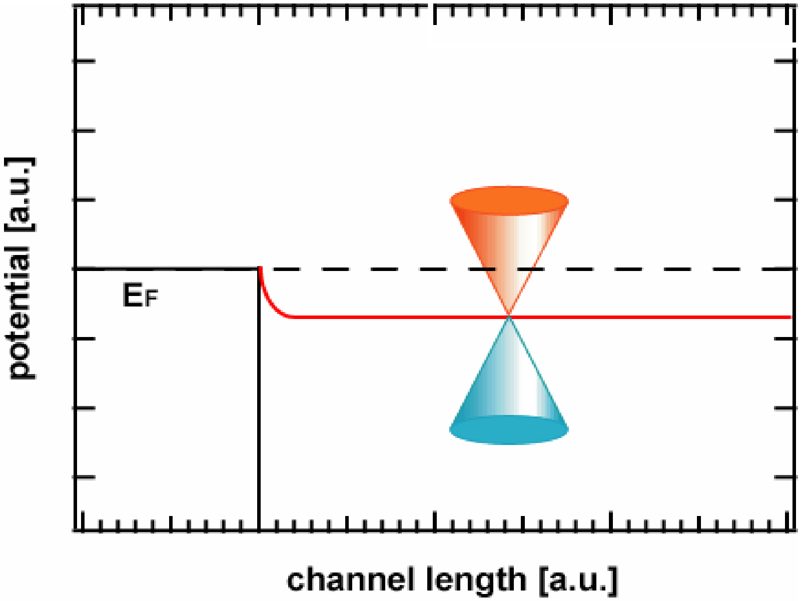
M. Wilson, Physics Today, Jan 2006

Graphene FET (2D, without gap, ballistic)

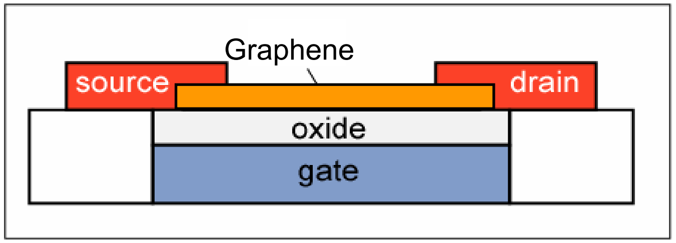


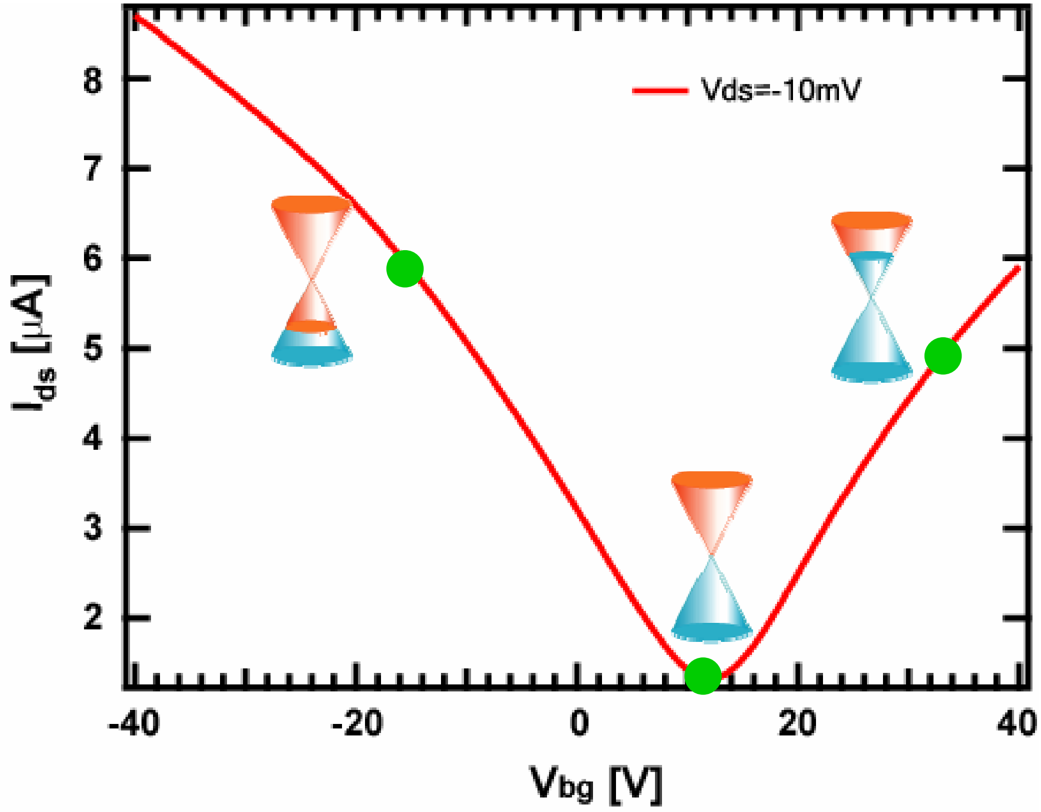
$$I_d \propto \int_{V_{gs}} dE\, \underline{D_{2D}}\,(E)$$





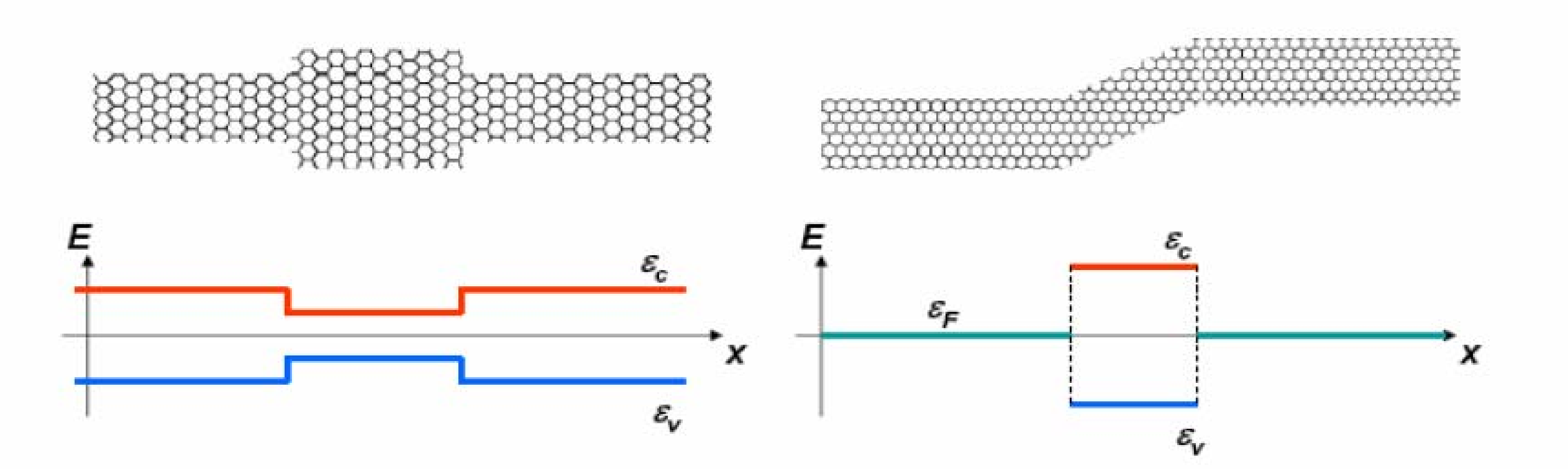
Current modulation linked to density of states





Graphene for high-performance electronics

- High carrier mobility – 200,000 cm^2/Vs demonstrated (Si < 2000 cm^2/Vs)
- Same effective mass for electrons and holes
  - identical *p*- and *n*- type FET characteristics
- Compatibility with conventional Si technology
- Band gap engineering



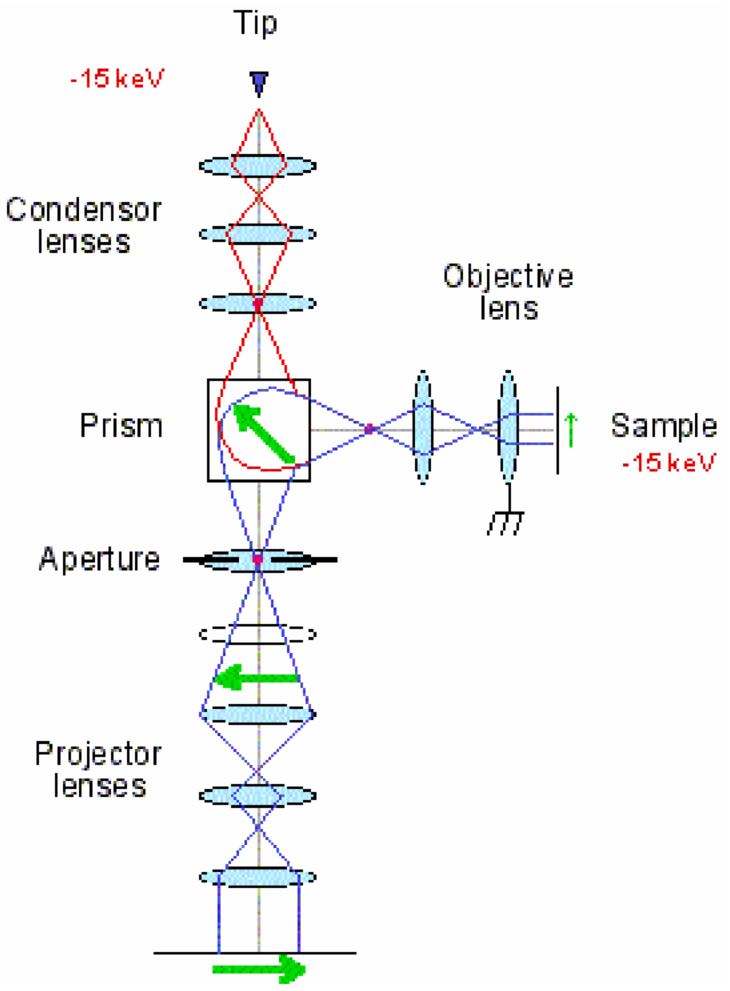
P. Kim, “Electron transport in graphene” (2008)

Challenges for synthesizing high-quality material:

- Need to synthesize large graphene domains
  - Need to maintain a flat SiC substrate during synthesis
  - Control nucleation of graphene domains to prevent domain boundaries
- Need to synthesize films of uniform thickness in a controlled manner
  - Control the step density on SiC substrate (decomposition is easier at steps)
- Need to maintain electrical properties of the SiC substrate
  - High performance devices require low-loss substrate (especially for RF applications)
  - Prevent generation of bulk defects
  - Understand and control how substrate dopes graphene

Low-energy electron microscopy

- Real-time *in situ* imaging
  - Growth, etching, oxidation, sublimation
- Chemical, structural, magnetic contrast
  - Low energy electrons (0-100 eV) = surface sensitivity
  - Contrast mechanisms are similar to those used in TEM
- Ideal for direct modeling of surface structure evolution
  - “Local” rather than “average”
- Real-space & reciprocal space
  - 5 nm spatial resolution



LEEM review: E. Bauer, Rep. Prog. Phys. 57 (1994) 895
IBM LEEM: R.M. Tromp et al., Surface Reviews and Letters 5 (1998) 1189

Advantages of LEEM for investigations of graphene

- Phase identification (e.g. graphene, buffer layer, bilayer stacking)
  Spatially-resolved diffraction, dark-field imaging

- Graphene layer thickness is easy to measure
  Quantum well states: Hibino *et al*, PRB 77 (2008) 075413

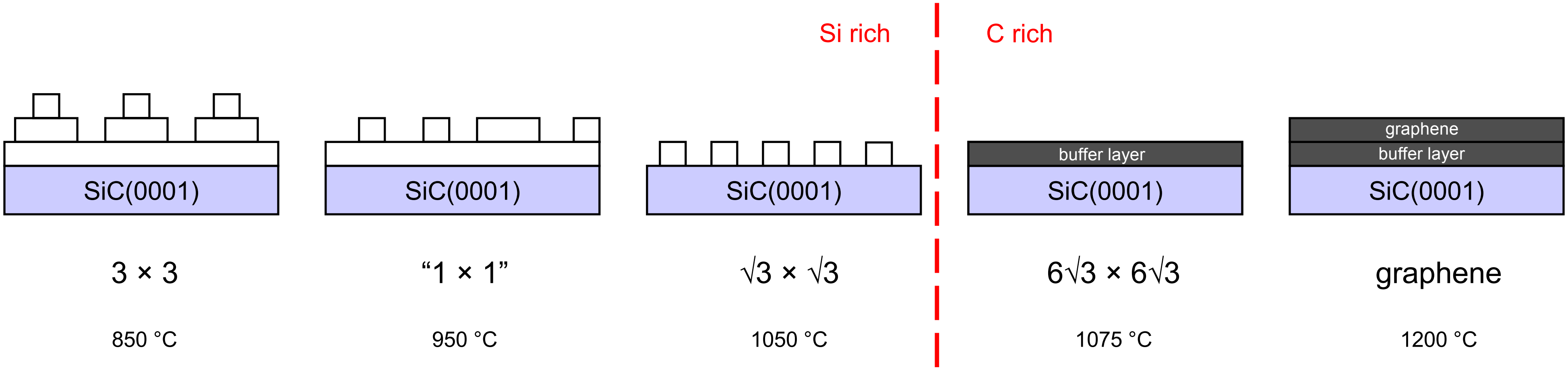
- Atomic structure (e.g. stacking of SiC bilayers in the bulk) and stoichiometry
  Quantitative analysis of reflectivity (e.g. image intensity) versus electron beam energy

- Step motion / surface smoothing
  Domain and island coarsening, island growth, step smoothing

- *Local* electronic structure can be measured
  Spatially-resolved photoemission, electron-energy loss spectroscopy (plasmons)

SiC(0001) Surface Structure Taxonomy

- Clean SiC surface by exposing to Si in ultra-high vacuum (Si + O → SiO)
- A well-defined sequence of surface phases forms as temperature is raised
- Si-rich phases give way to C-rich phases at high temperature

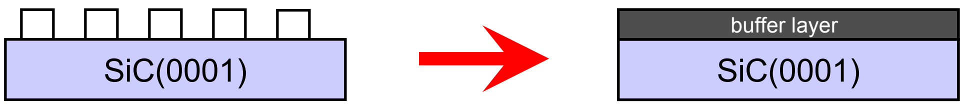


3 × 3	“1 × 1”	$\sqrt{3} \times \sqrt{3}$	$6\sqrt{3} \times 6\sqrt{3}$	graphene
850 °C	950 °C	1050 °C	1075 °C	1200 °C

Forbeaux *et al*, PRB 58 (1998) 16396.

The kinetics of graphene formation in UHV

- Above ~1100 °C, SiC decomposes in UHV.
- Liberated Si evaporates, C condenses into the graphene structure
- First graphene-like layer ("buffer layer") is covalently bound to substrate
  - Electronic structure is not like graphene



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

1050 °C

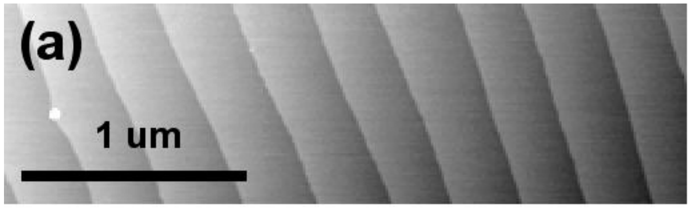
$6\sqrt{3} \times 6\sqrt{3}$

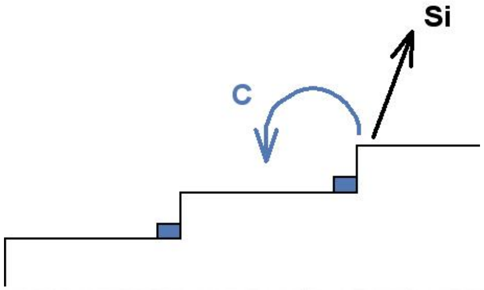
1075 °C

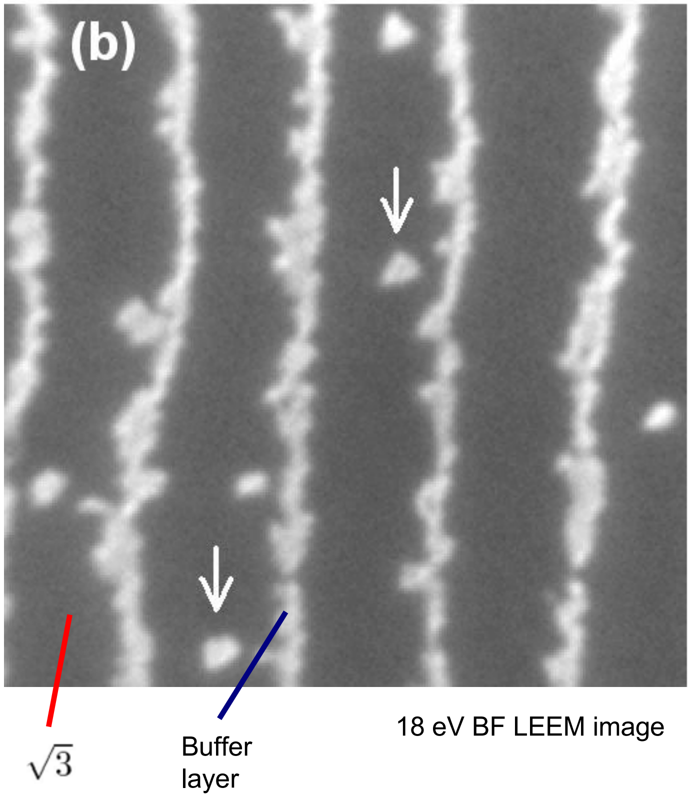
Initial formation of buffer layer from the √3 phase (1060 °C)

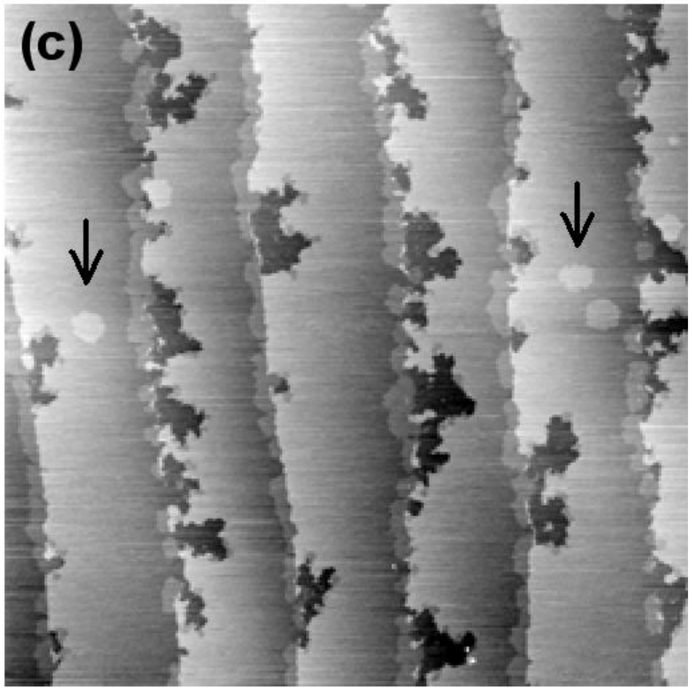
- √3 steps are eaten away – terraces are intact.
- √3 steps decompose in units of three SiC bilayers
- ‘ribbon’ of buffer layer nucleates at the lower sides of steps.
- Buffer layer islands seen on the terrace, indicating that C atoms can freely diffuse

AFM image of starting surface – 3 bilayer steps







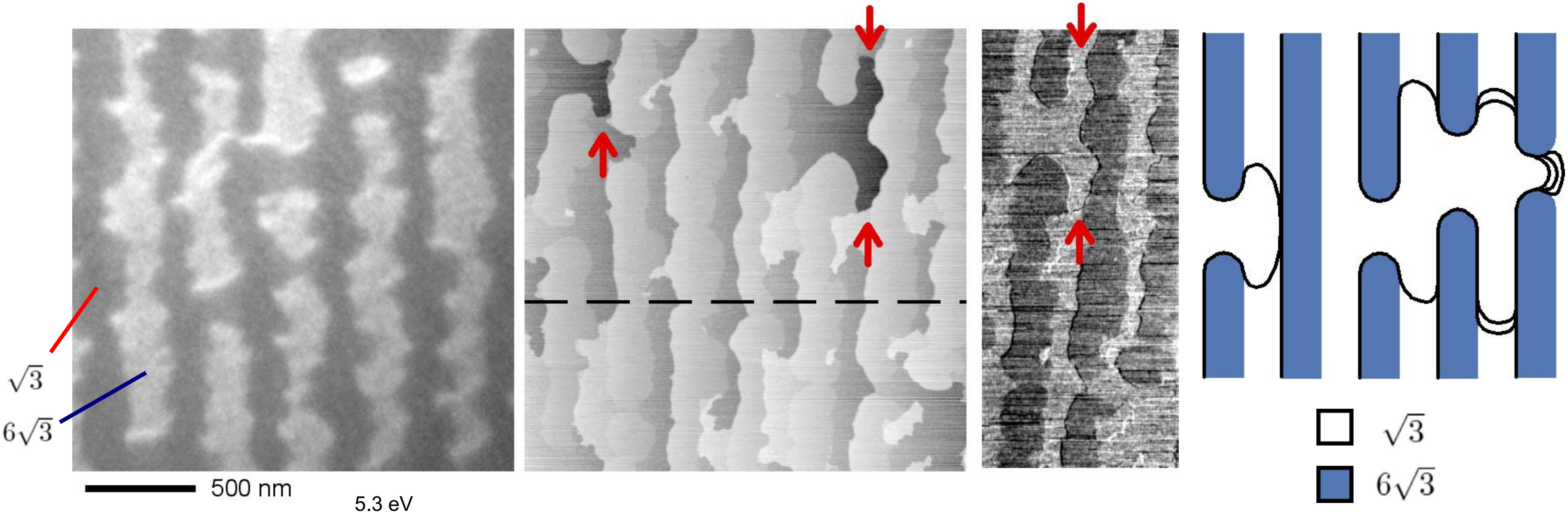


18 eV BF LEEM image

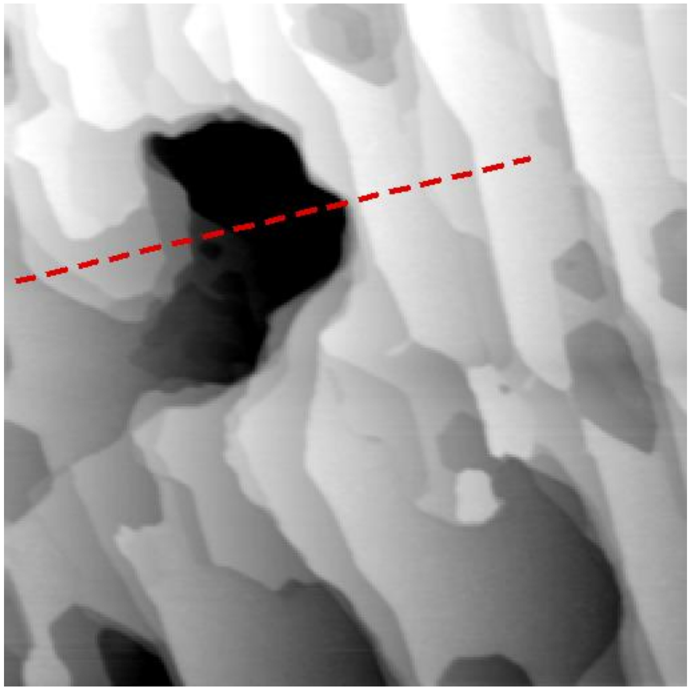
Hannon & Tromp, PRB 77, 241404R 2008

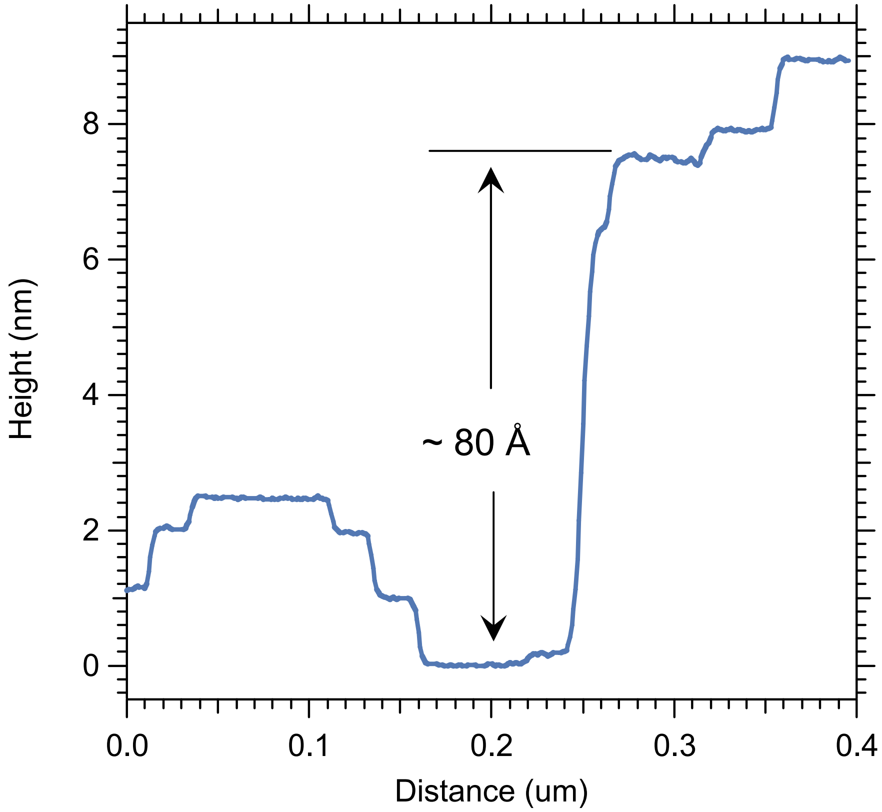
Further annealing – buffer layer grows, √3 steps decay

- √3 steps flow <u>through</u> gaps in the buffer layer domain structure
- This ‘up-hill’ step migration leads to pit formation



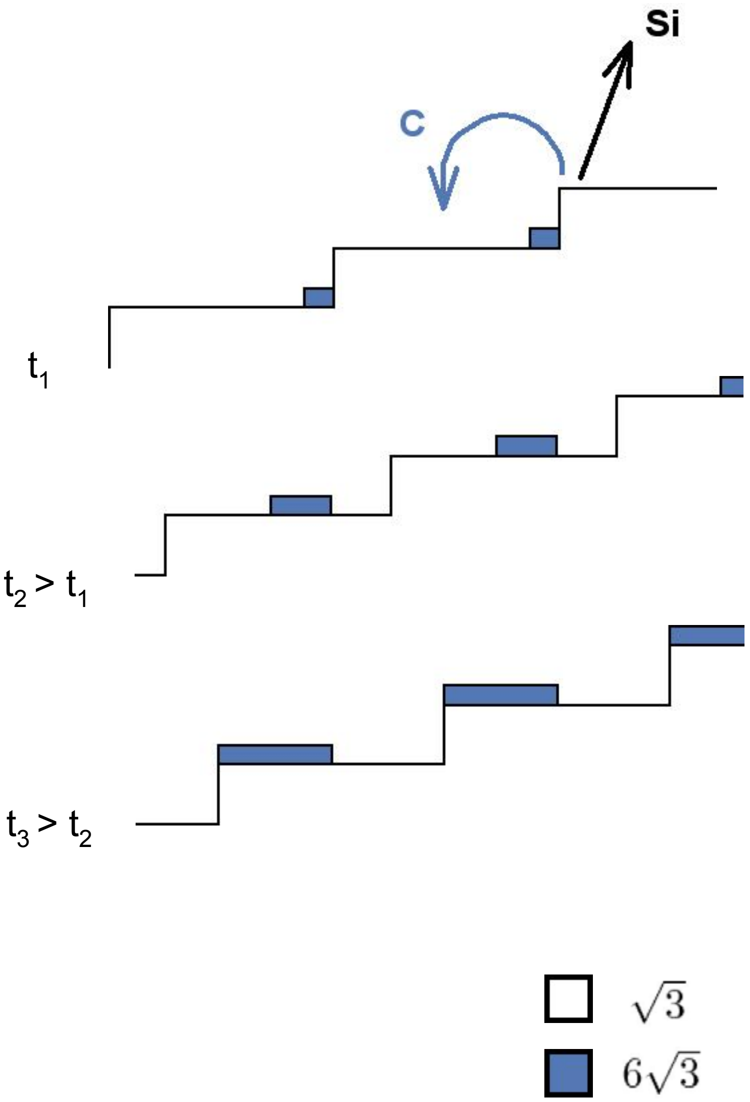
The pits can be ~ 100 Å deep

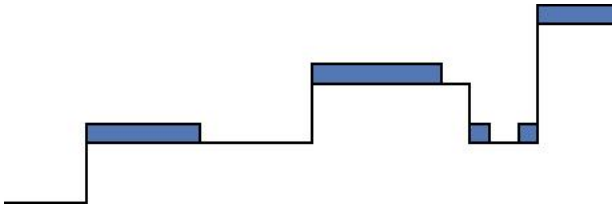




Step morphology suggests a model

- Buffer layer grows at the expense of √3 steps, which easily decay
- Buffer layer is immobile at 1060 C – no coarsening
  - Makes sense – it's basically graphene
- Frustrated state, with no √3 steps, is reached at about 50/50 coverage
- What happens next ?!





...you nucleate a (3 bilayer deep) pit

A fundamental problem

- Buffer layer grows at expense of √3 steps. Terraces remain intact at 1060 °C.
- Buffer layer is very stable – it does not coarsen at 1100 °C
  - √3 steps flow around pre-existing 6√3 domains
- Incomplete step coverage of buffer layer enhances pit formation
- Difficult to grow flat, thin (1 ML) graphene films by slowly heating in UHV.