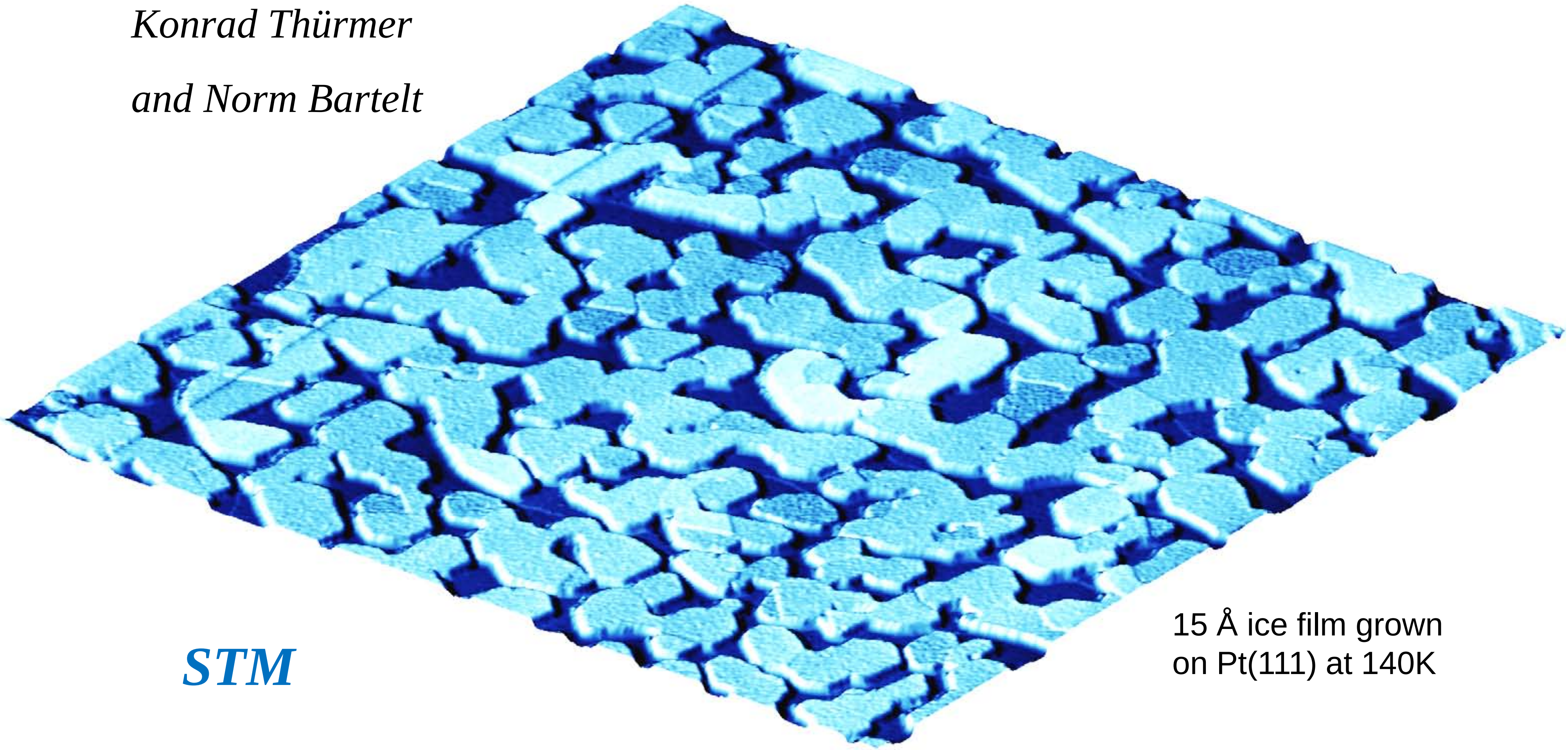
SAND2010-1685C

Growth and stability of ice multilayers on Pt(111)

Konrad Thürmer

and Norm Bartelt



STM

15 Å ice film grown
on Pt(111) at 140K

What does ice film morphology reveal about water-solid interactions?

This research was completely supported by the
Office of Basic Energy Sciences, Department of Energy

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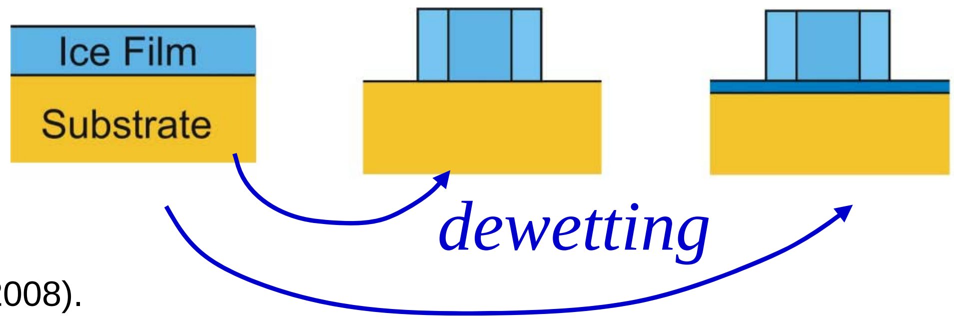
What determines ice-film morphology, energetics or kinetics?

Two case studies for ice/metals:

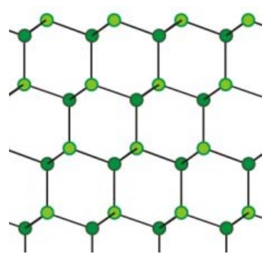
- How does dewetting occur?



Basic modes of growth (wetting)

K. Thürmer and N. C. Bartelt, Phys.Rev. Lett. **100**, 186101 (2008).

- Why does cubic ice form at low T?



K. Thürmer and N. C. Bartelt, Phys. Rev. B **77**, 195425 (2008).

H. König, Z. Kristallogr. **105**, 279 (1944).

ice/Pt(111) STM

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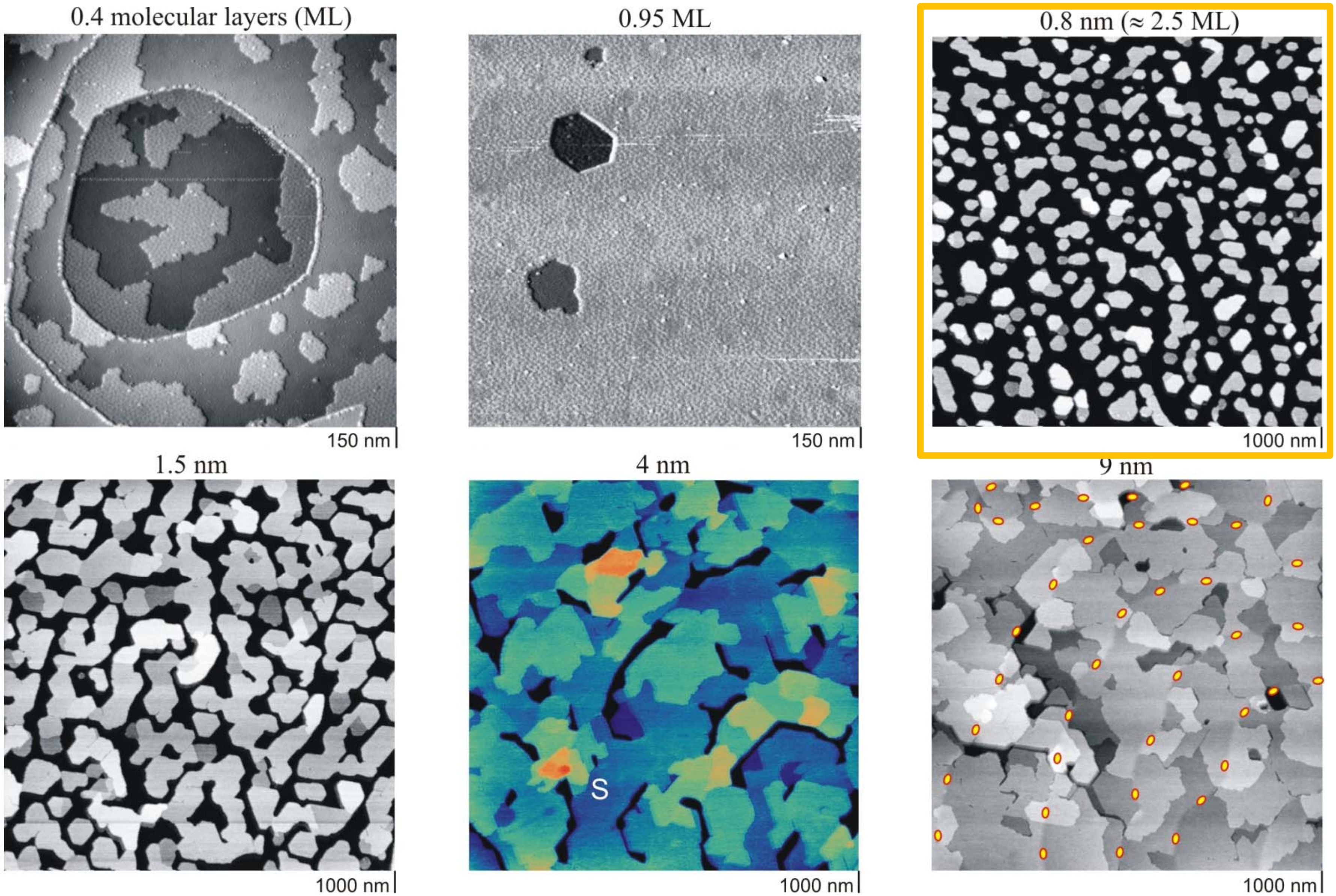
Growth of crystalline ice on Pt(111) at 140 K



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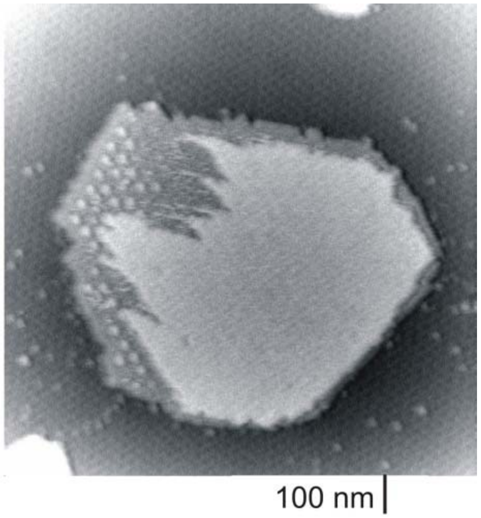
STM on ice films using usual scanning conditions:

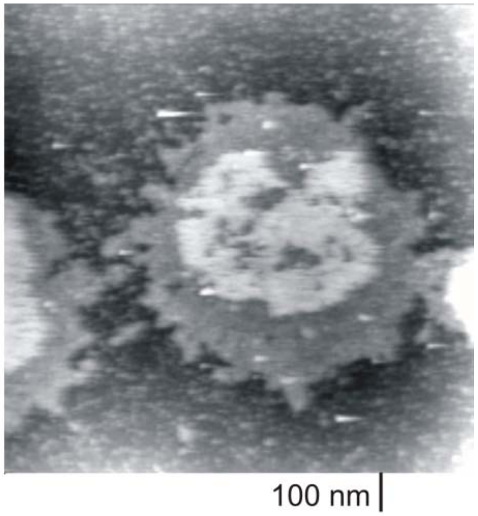
Examples of samples damaged by STM:

~3 layers thick island



V_{sample}= -0.9 V
I_t= 0.8 pA

4 or 5 layers thick island



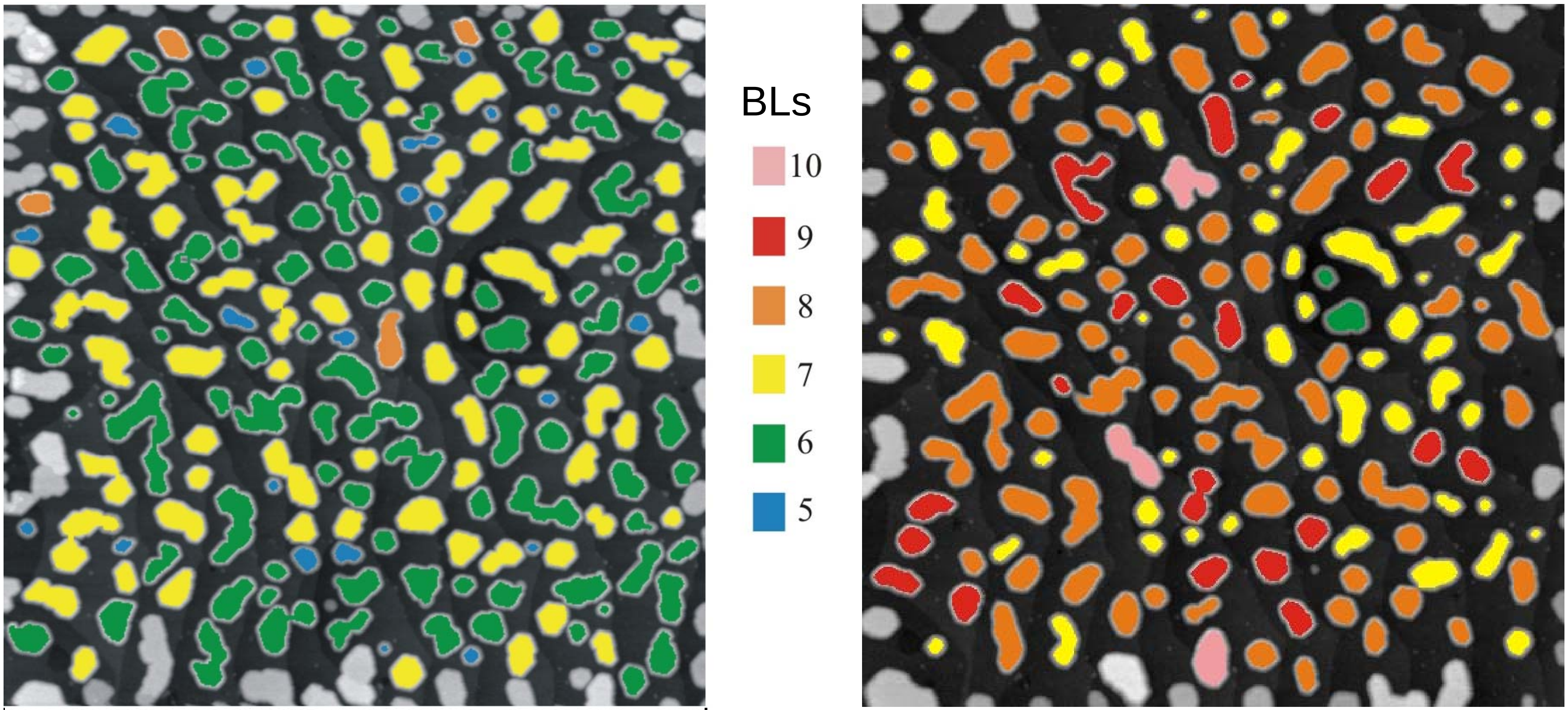
V_{sample}= -0.4 V
I_t= 0.4 pA

Damage minimized for V < -6V and I < 0.3pA

Probing the Stability of Ice/Pt(111)

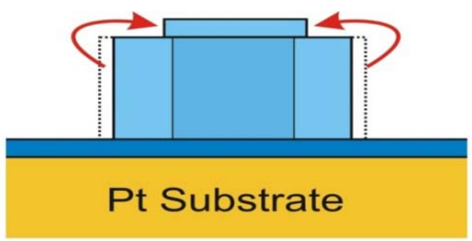
8 Å thick ice film grown at 140K

After 1 hour annealing at 140K



1 μm

Same surface region



Captured hundreds of nucleation events.

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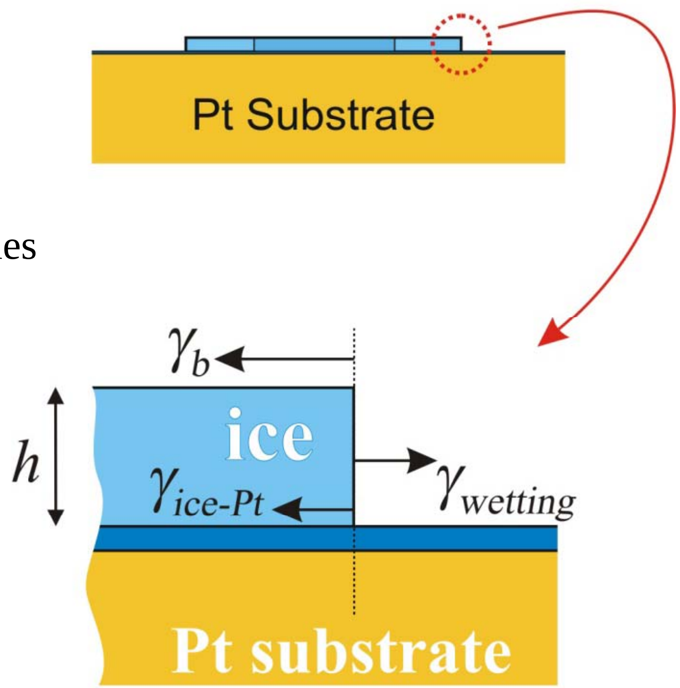
The dewetting process

The driving force:

Realistic aspect ratio:

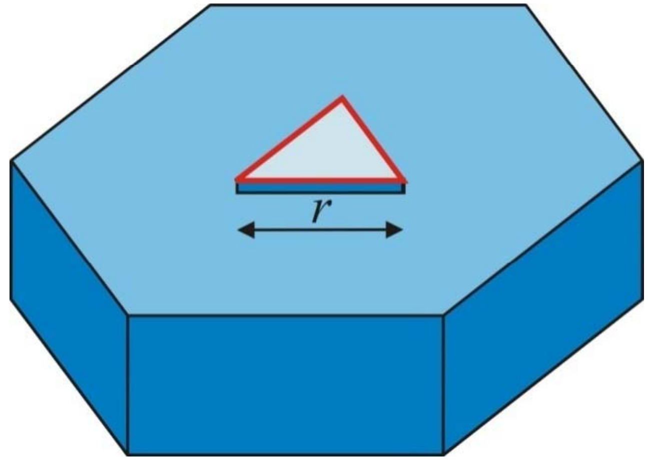


γ_i = free energies per area

$$\gamma_{wetting} < \gamma_b + \gamma_{ice-Pt}$$

supersaturation of water ad-molecules (higher for smaller h)

The opposing force:



Creating new steps costs energy:
$E=3r\beta$ (β – free energy/step length)

Balance determines nucleation rate *J*

[no nucleation observed for metal/metal Ag, Au, Cu/Ru(0001) and Cr, Fe/W(011)]

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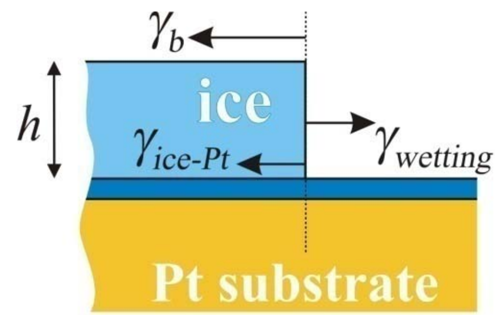
Quantifying the dewetting process

Applying nucleation theory to the dewetting yields nucleation rate J:

$$J(h/h_0) = J_0 \exp\left[-\frac{1}{\gamma_b+\gamma_{ice-Pt}-\gamma_{wetting}}\,\frac{3\sqrt{3}\beta^2}{kT}\,\frac{h}{h_0}\right]$$

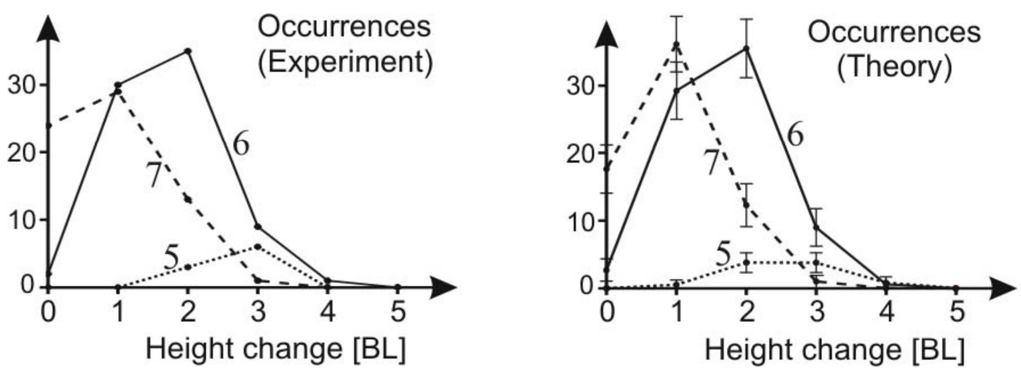
$$= J_0 \exp(-\alpha h/h_0)$$

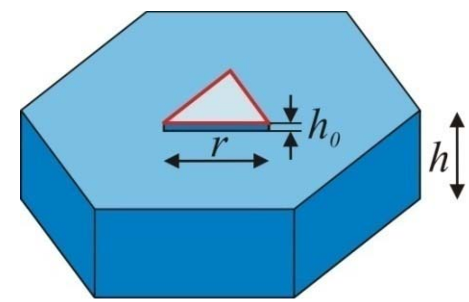
Legend: γ_i = free energies per area



Analysis of layer-nucleation rates:

fit: α≈1





$E_{step} = 3r\beta$
(β – free energy/step length)

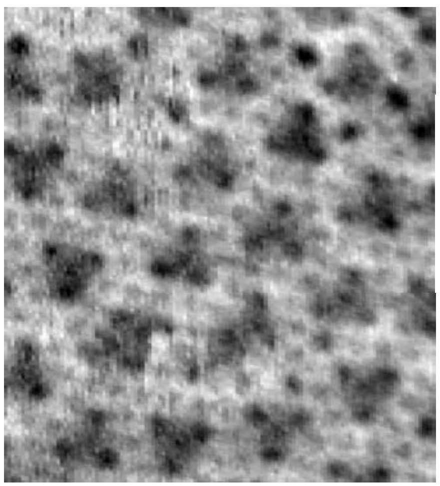
Driving force of dewetting is large enough to cause nucleation.

→ ***Water in the wetting layer binds more strongly to the substrate than the water of the ice crystals.***

Open question:
What is the molecular structure of the wetting layer?

Evidence for nanometer-scale patterns

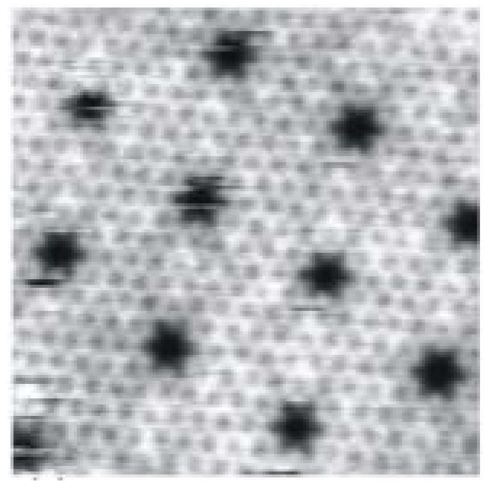
Depends on deposition temperature



140K

STM
FOV = 10 nm

Disordered arrangement of triangular depressions.

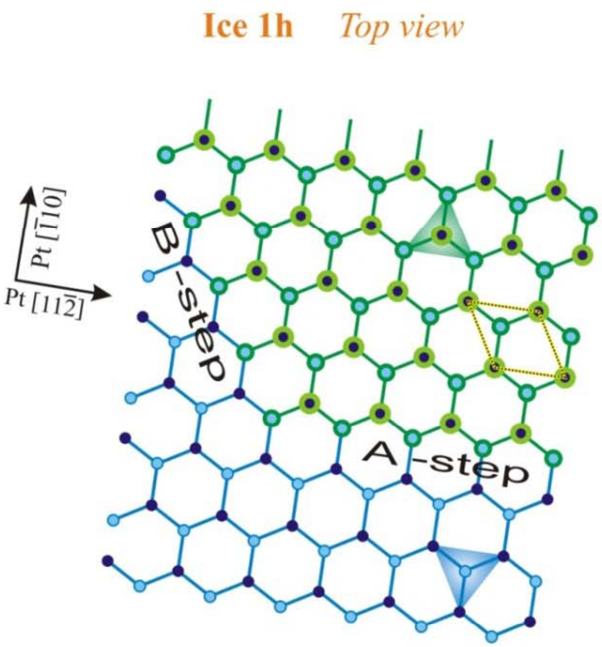


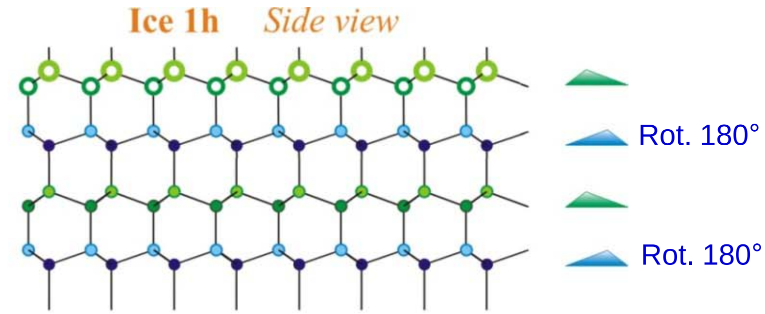
160K

STM
FOV = 10 nm

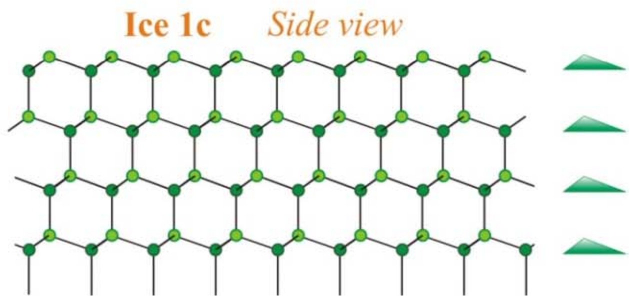
Long-range order due to water dissociation?

Formation of (metastable) cubic ice 1c





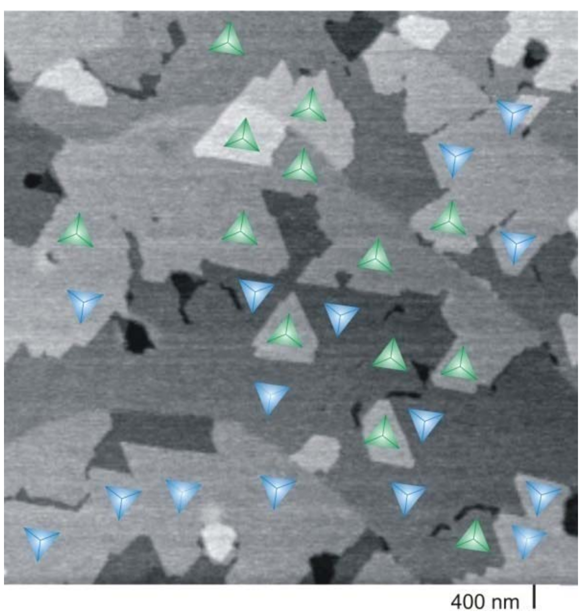
Equilibrium structure: Hexagonal Ice 1h



Metastable low-T structure: Cubic Ice 1h

3-fold symmetry within each bilayer (BL):

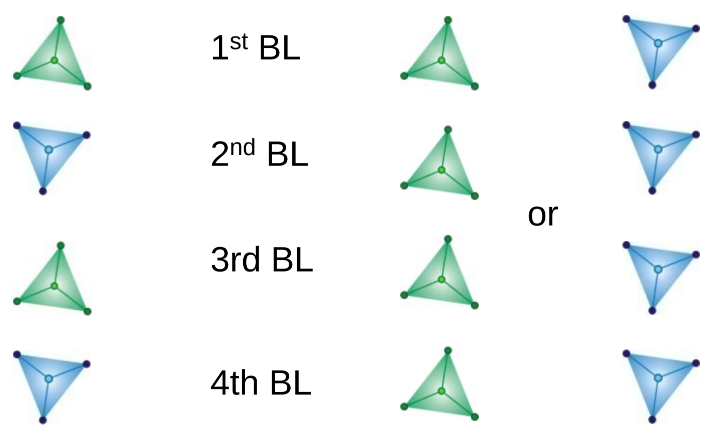
4 nm Ice/Pt(111) deposited at 140K



stacking sequence top view:

hex ice

Cubic ice

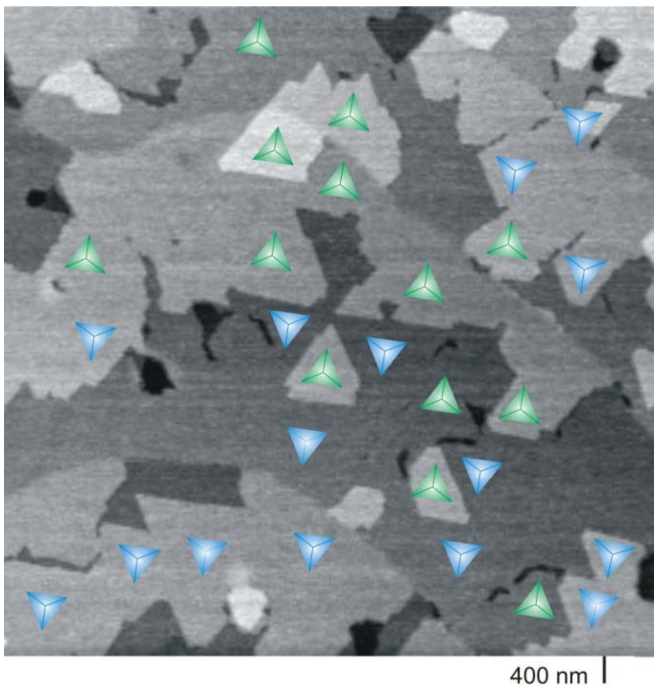


Cubic ice as a small-size effect?

G. P. Johari, J. Chem. Phys. **122**, 194504 (2005):

Cubic ice has lower surface energy and is stable in films thinner than 10 nm.

4 nm Ice/Pt(111) grown at 140K



3 nm grown at 145K, then
2D islands deposited at 115 K
annealed at 125 K For 135 min

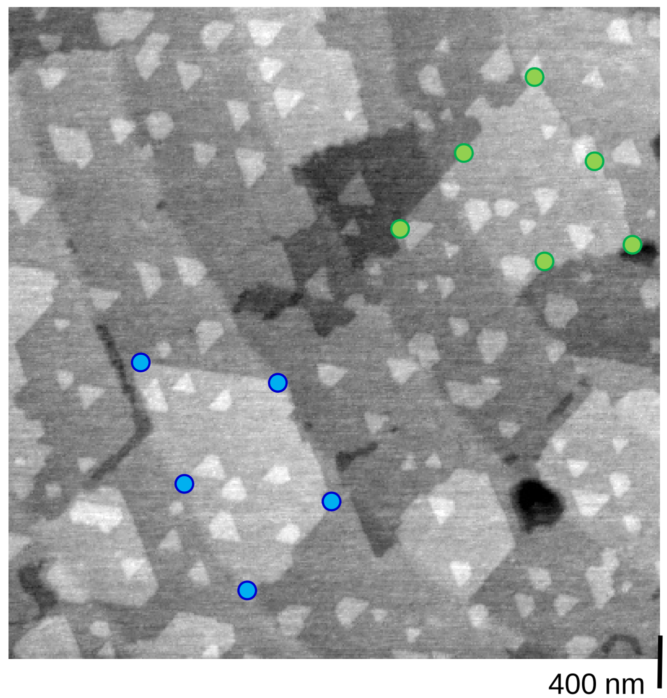
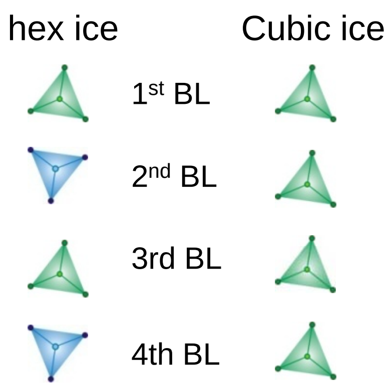


Image:
Shu
Nie



Layers nucleate as hexagonal ice (no small-size effect)

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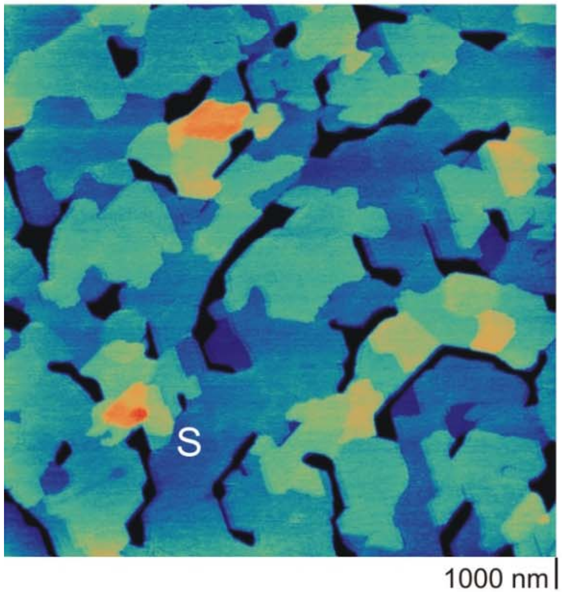
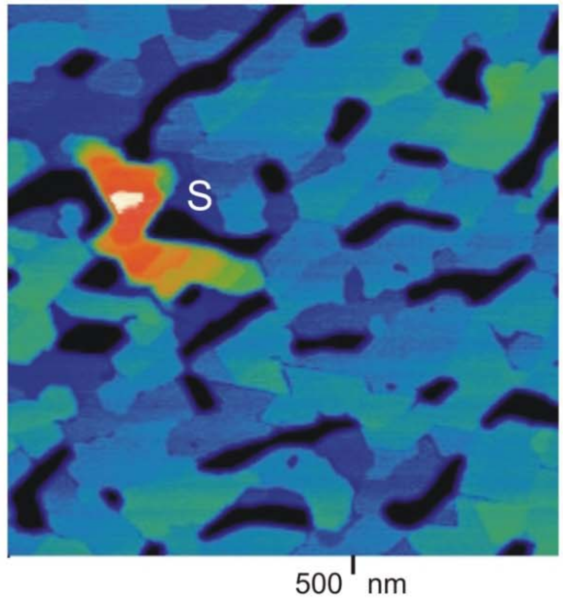
Fastest growth occurs via growth spirals

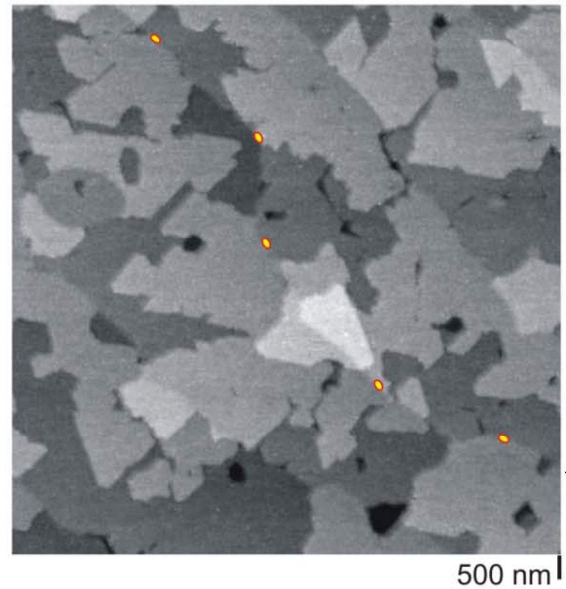
4 nm grown at 140K



6 nm grown at 150K

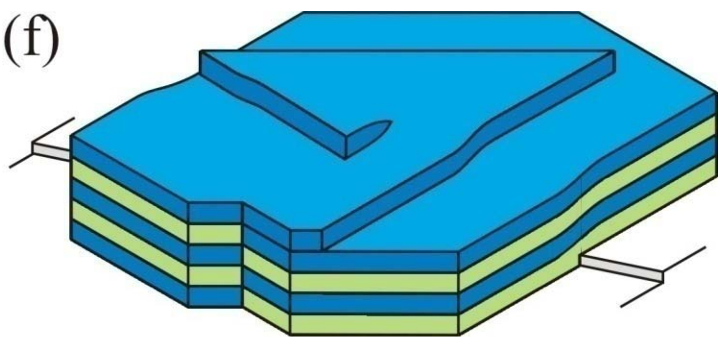


4 nm grown at 140K



Buried substrate step

(f)

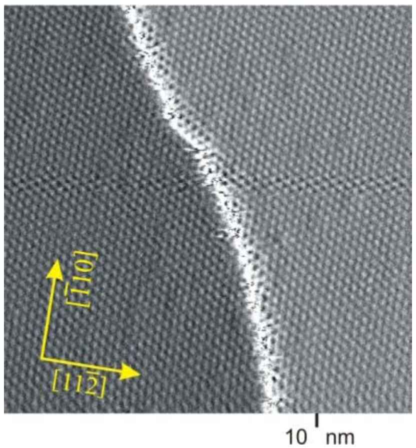


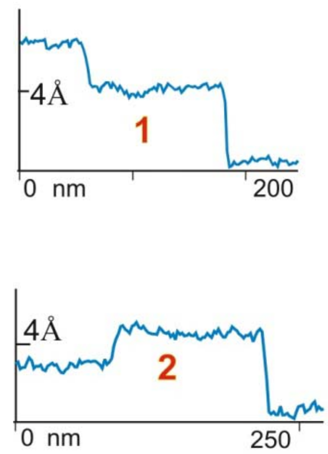
Triangular spirals form cubic ice?

Why do they form above substrate steps?

Role of substrate steps

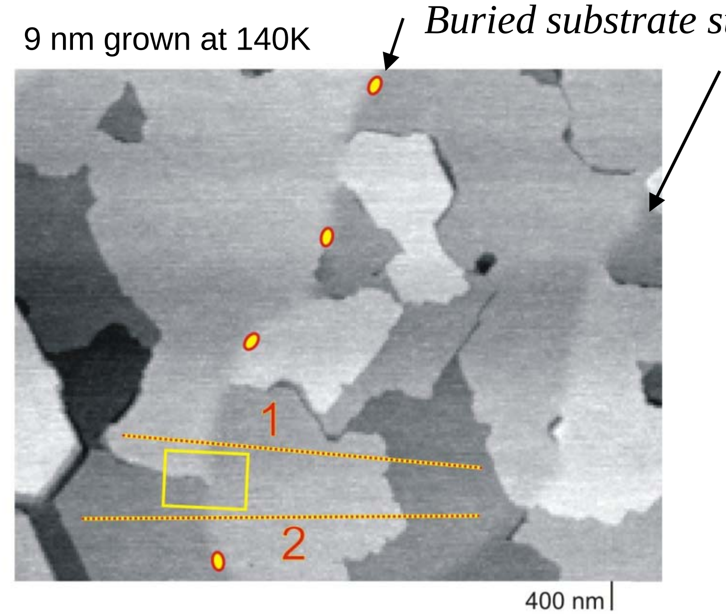
Pt(111) step:



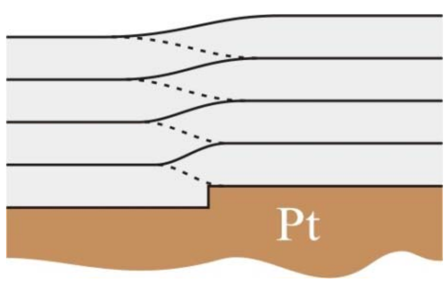


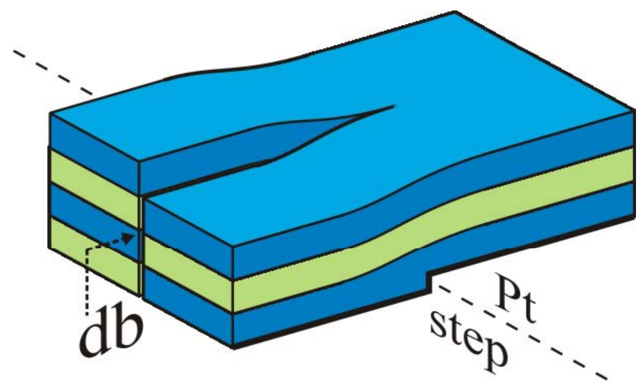
9 nm grown at 140K

Buried substrate steps



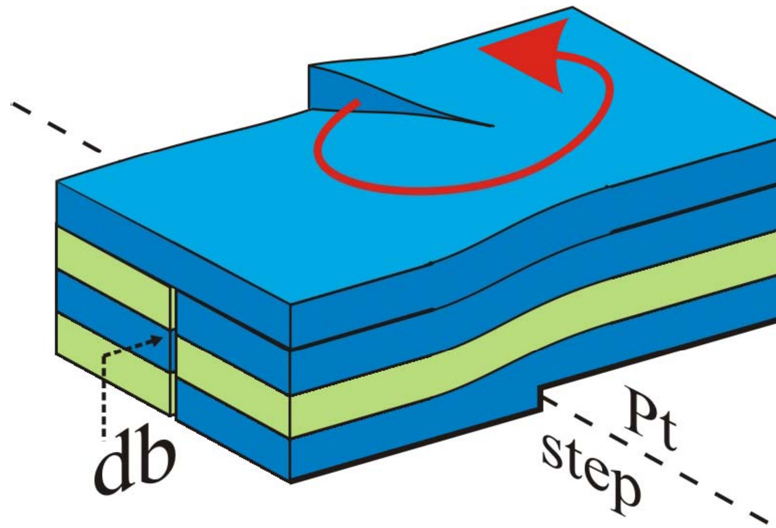
Ice layers connect across a substrate step
by bending upwards or downwards:





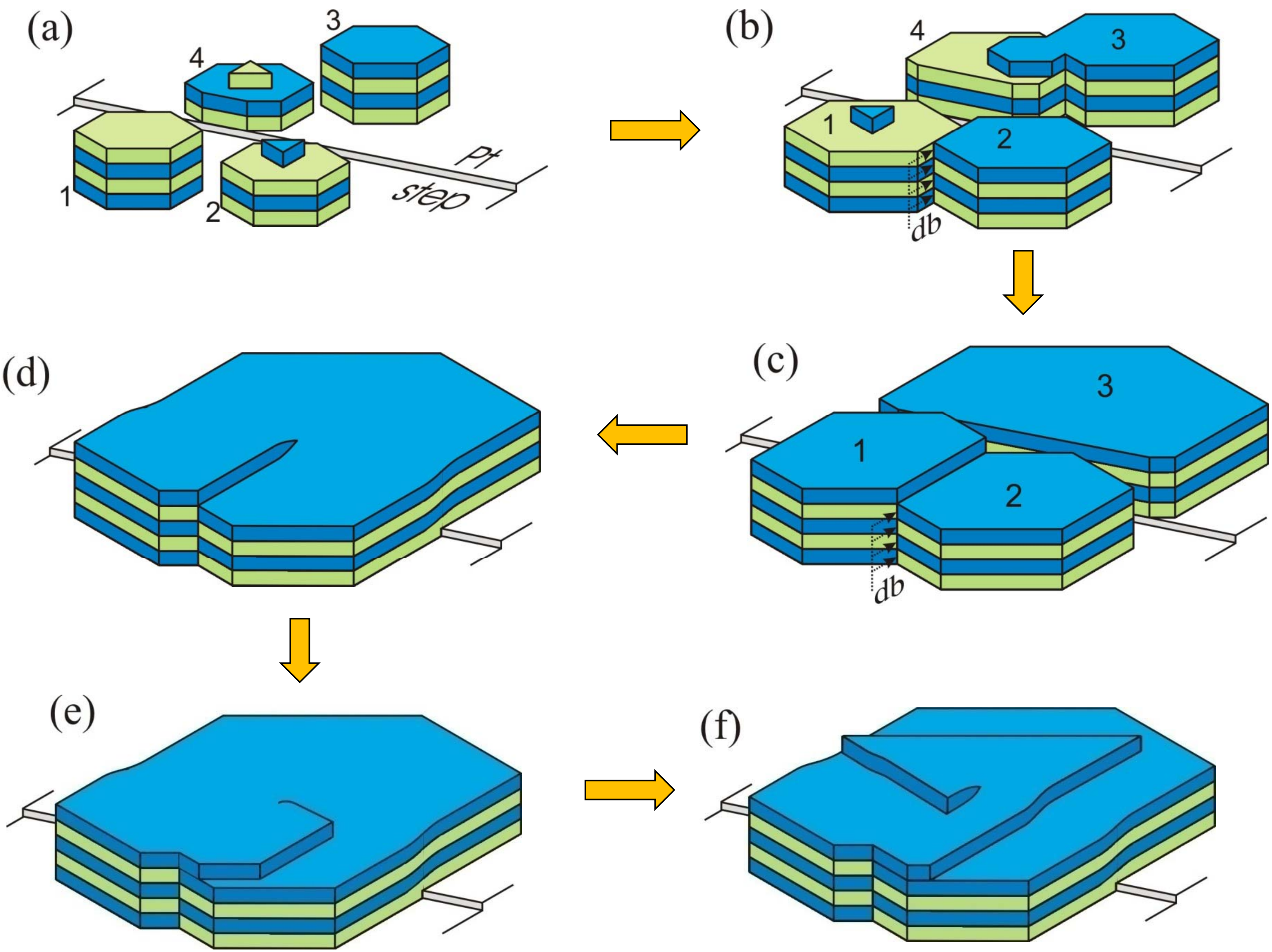
Substrate steps promote screw dislocations.

Growth around screw dislocations



…and propagating the top layer leads to cubic ice!

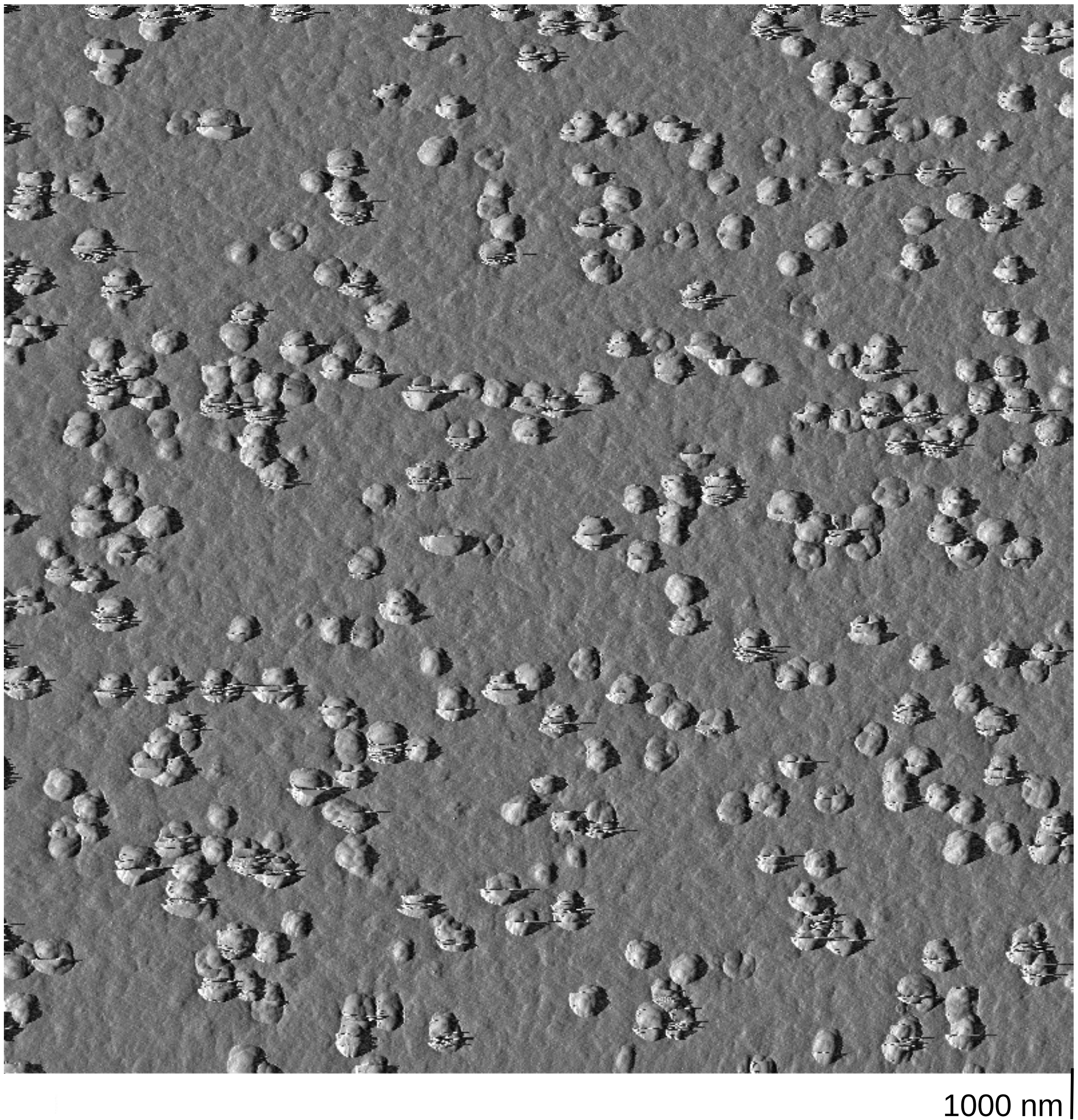
A scenario of cubic ice formation



Open question:

Transition from amorphous to crystalline ice

6 nm grown at 120K



- What are the relevant atomic-scale processes?

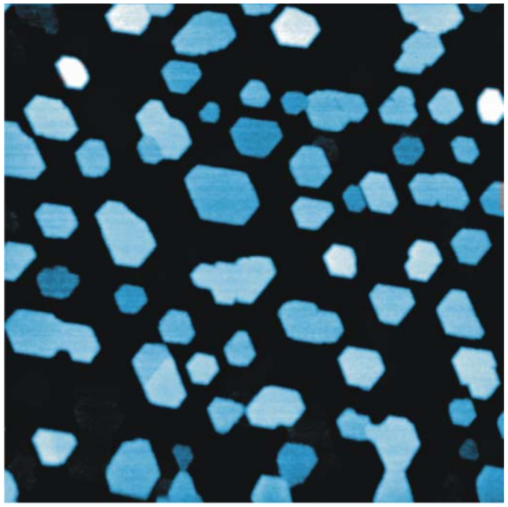
- What determines the rate?

Challenges:

- imaging tall crystallites
  (easier with AFM ???)

-simultaneous dewetting and amorphous-to-crystalline transition

Summary



- Quantify dewetting of ice/Pt(111) yields insights into ice energetics:

    - Driving force of dewetting is large enough to cause layer nucleation (in contrast to metal/metal systems).

- We now understand why cubic ice grows at low T: kinetics!

Posters:

1) S. Nie: Observations of surface-self diffusion on ice

S. Nie et al. PRL **102**, 136101 (2009).

2) K. Thürmer: Proton order in near-substrate ice layers

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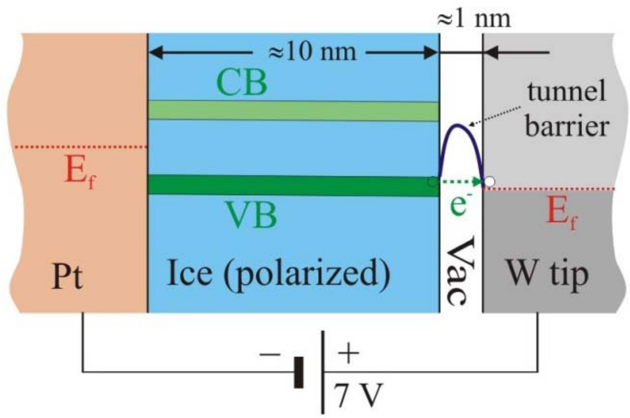
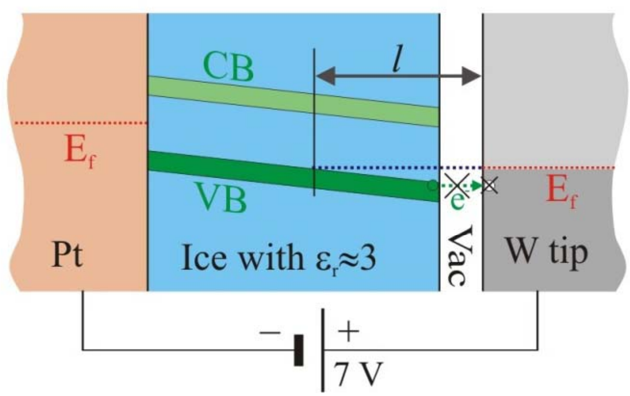
Proposed work:

Imaging ice multilayers / electronic properties

? ? ?





Corroborate/refine imaging model:

- Is conductance through the valence band possible?
  - ab-initio electronic transport calculations
- Can ice be polarized by the applied bias?
  - non-activated process?
  - DFT structure relaxation with electric field
- Probe electronic states locally with Scanning Tunneling Spectroscopy

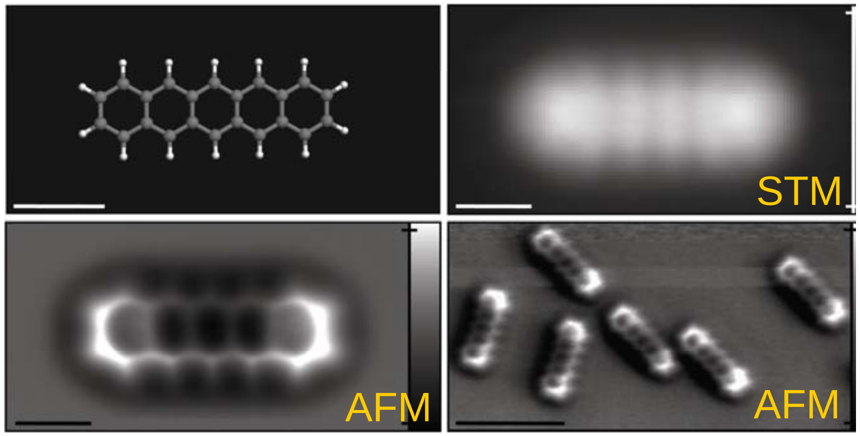
Proposed work:

Extend Scanning Probe studies to non-conducting substrates

Exploit high-resolution capability of "Q-plus" sensor for AFM …

Pentacene on Cu(111):

Leo Gross, *et al.* *Science 325, 1110 (2009);*



… to study structure and evolution of ice films on important non-conducting substrates such as oxides