ATOMISTIC MODELS FOR LOW-TEMPERATURE EPITAXIAL GROWTH OF METAL FILMS

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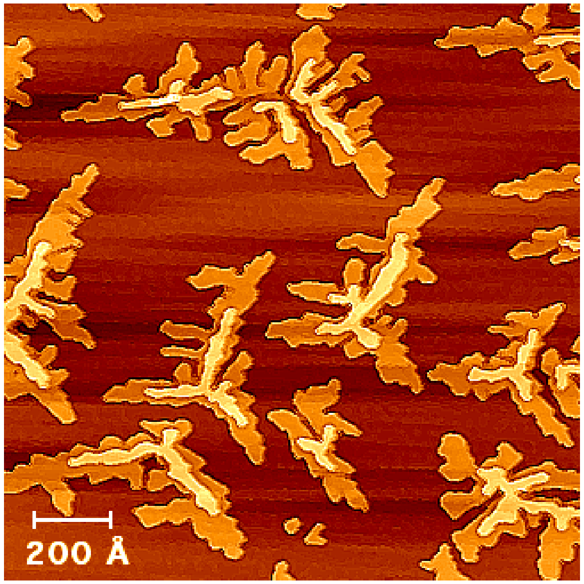
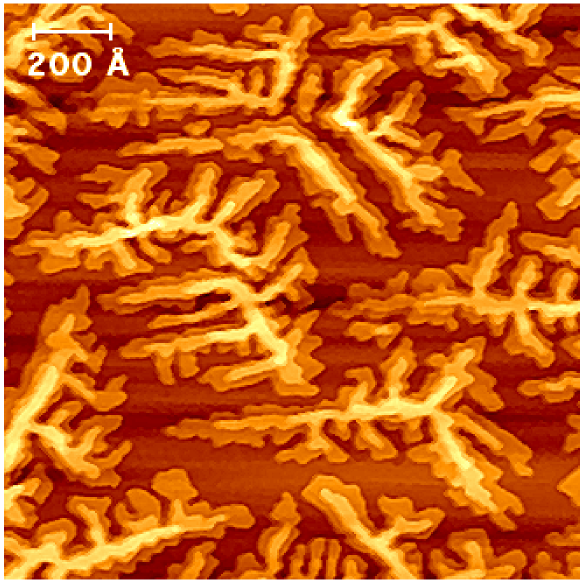
STM Expt: C. Stoldt, A. Layson, E. Cox, C. Chung, Patricia Thiel

Iowa State University **$$$ NSF Grant CHE-0414387**

KINETICALLY CONTROLLED GROWTH STRUCTURES IN LOW-T EPI GROWTH



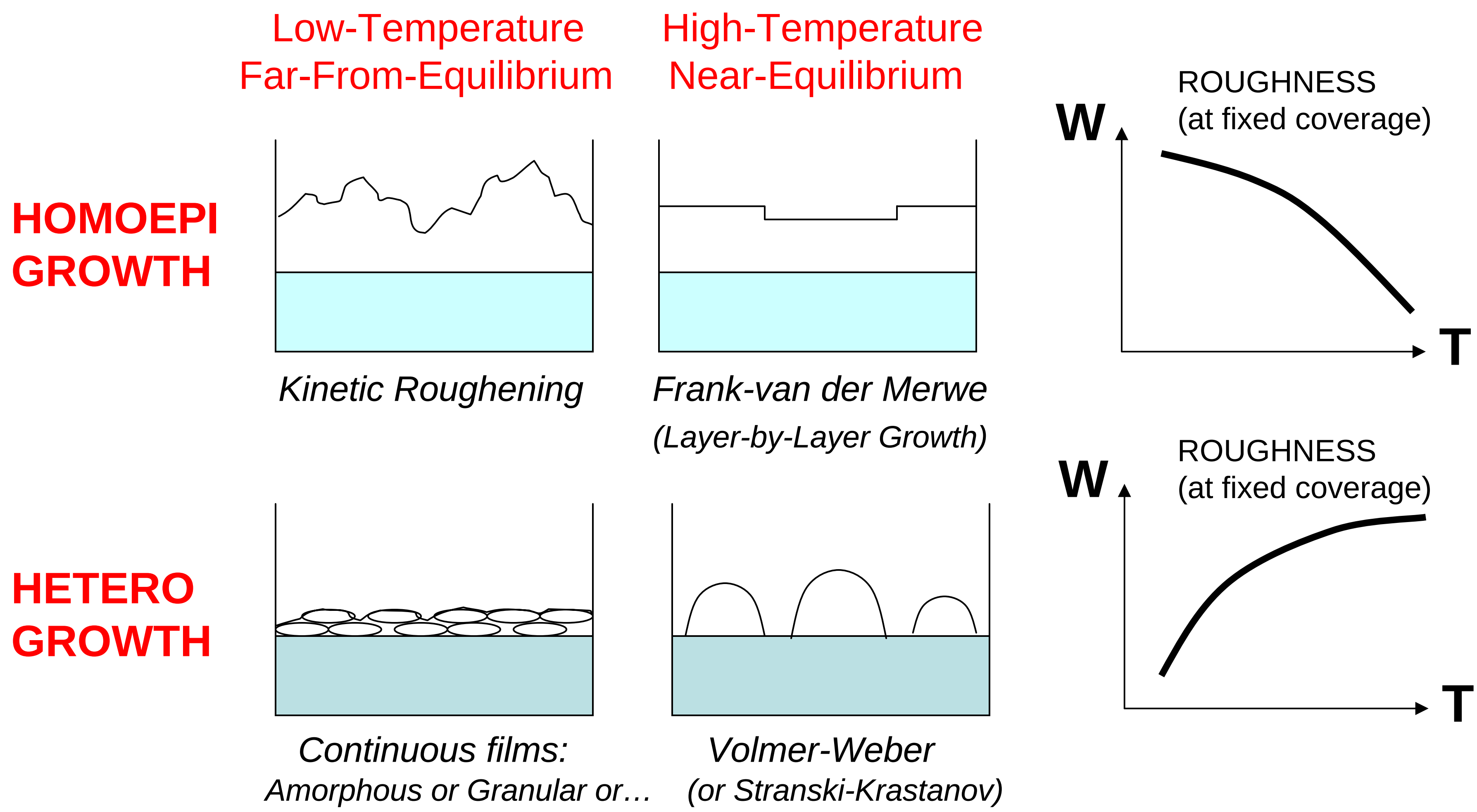


Ag/Ag(111) @ 135K
F=0.004 ML/sec

STM Images:
150×150 nm^2
Left Frame: 0.35 ML
Right Frame: 1.10 ML

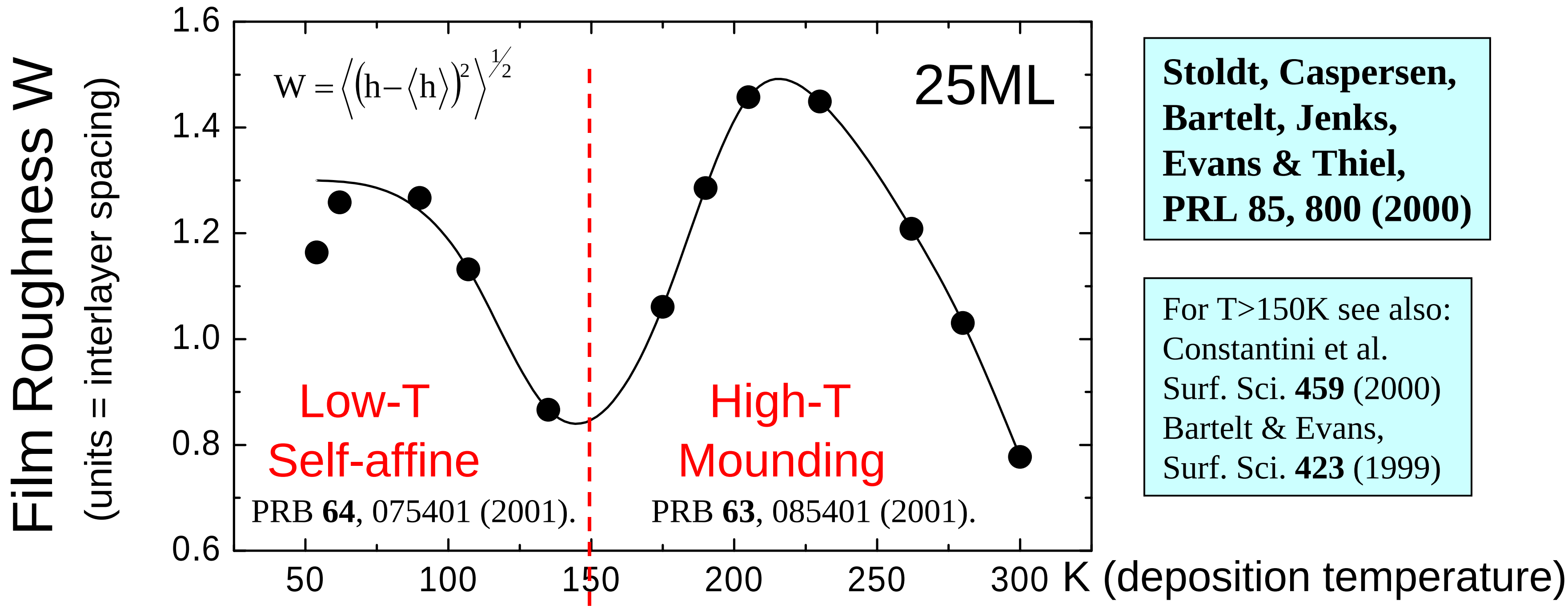
Cox, Li, Chung, Ghosh, …Jenks, Evans & Thiel, Phys. Rev. B **71** (2005)

OVERVIEW: T-DEPCE of HOMOEPITAXIAL vs HETERO GROWTH



High-T Equilibrium: determine by minimization of free energy (surface energy; strain)
Low-T Non-Equilibrium: goal is to develop atomistic models which can predict the rich variety of far-from-equilibrium film morphologies

OVERVIEW: TEMPERATURE-DEPENDENCE OF AG/AG(100) FILM GROWTH



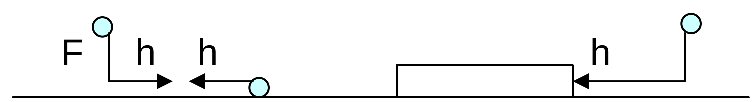
Stoldt, Caspersen, Bartelt, Jenks, Evans & Thiel, PRL 85, 800 (2000)

For T>150K see also:
Constantini et al. Surf. Sci. **459** (2000)
Bartelt & Evans, Surf. Sci. **423** (1999)

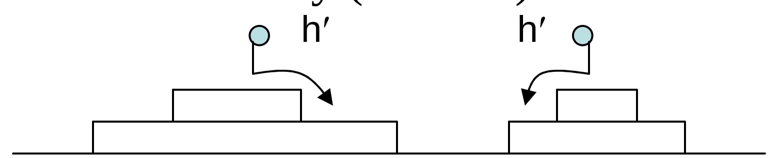
- ♦ Terrace diffusion inoperative
- ♦ Self-affine surface structure
- ♦ Overhangs form and then internal vacancies or voids:

Restricted Downward Funneling and low-barrier interlayer diff.n

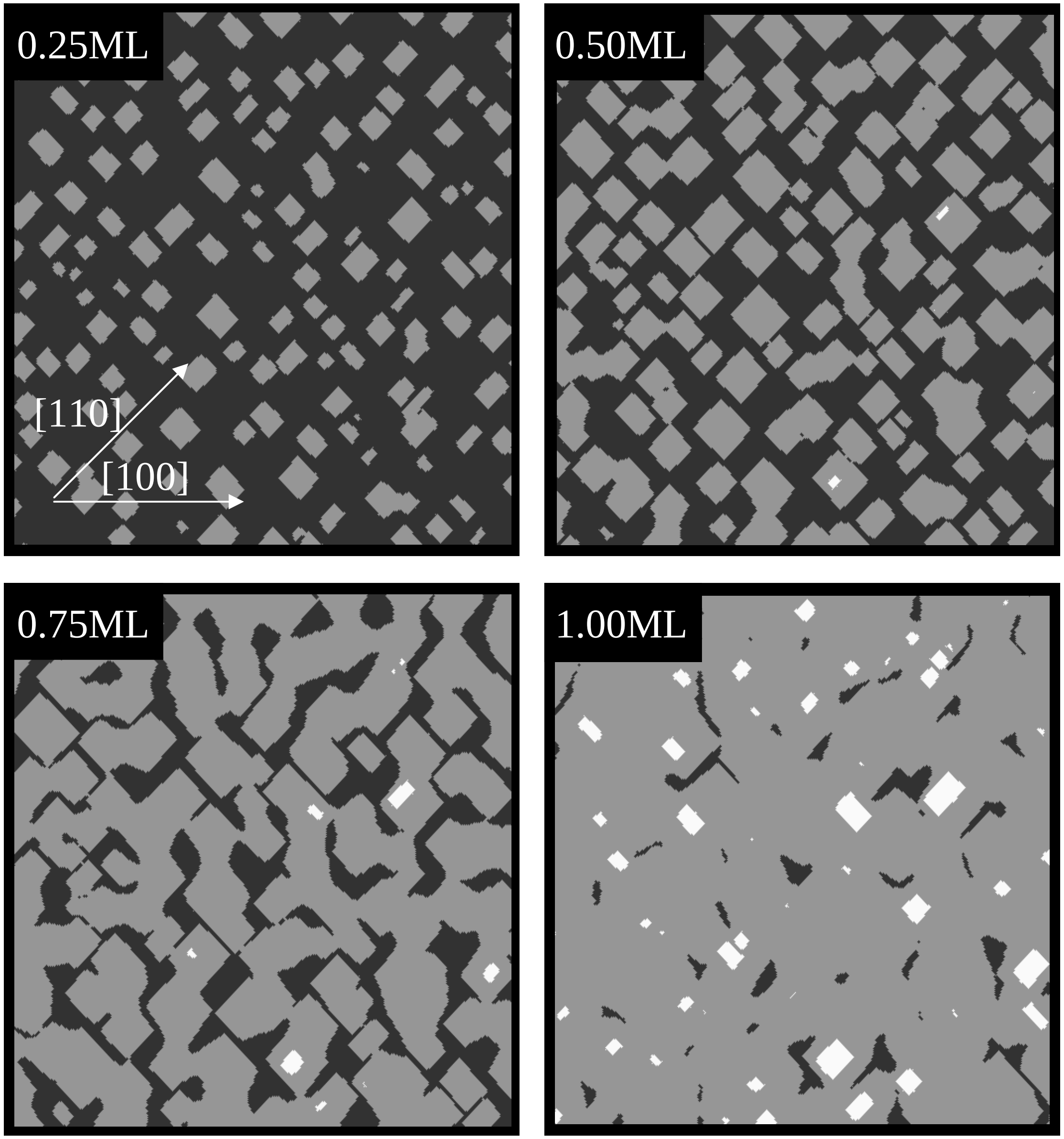
- ♦ Terrace diffusion is active (hop rate = h; E_{act} = 0.4eV)
- ♦ Formation of near-square 2D islands in each layer



- ♦ Growth instability (mounds) due to *small* step-edge barrier (h′<h)



Ag/Ag(100) @ 300K: PROTOTYPE FOR "LAYER-BY-LAYER" GROWTH



KMC SIMULATION

(100×100 nm^2 images)

T=300K F=0.055ML/s

Terrace Diffusion: E_{act}= 0.40eV

Rapid Edge Diffn: E_{act}= 0.25eV

⇒ **compact island growth shapes**

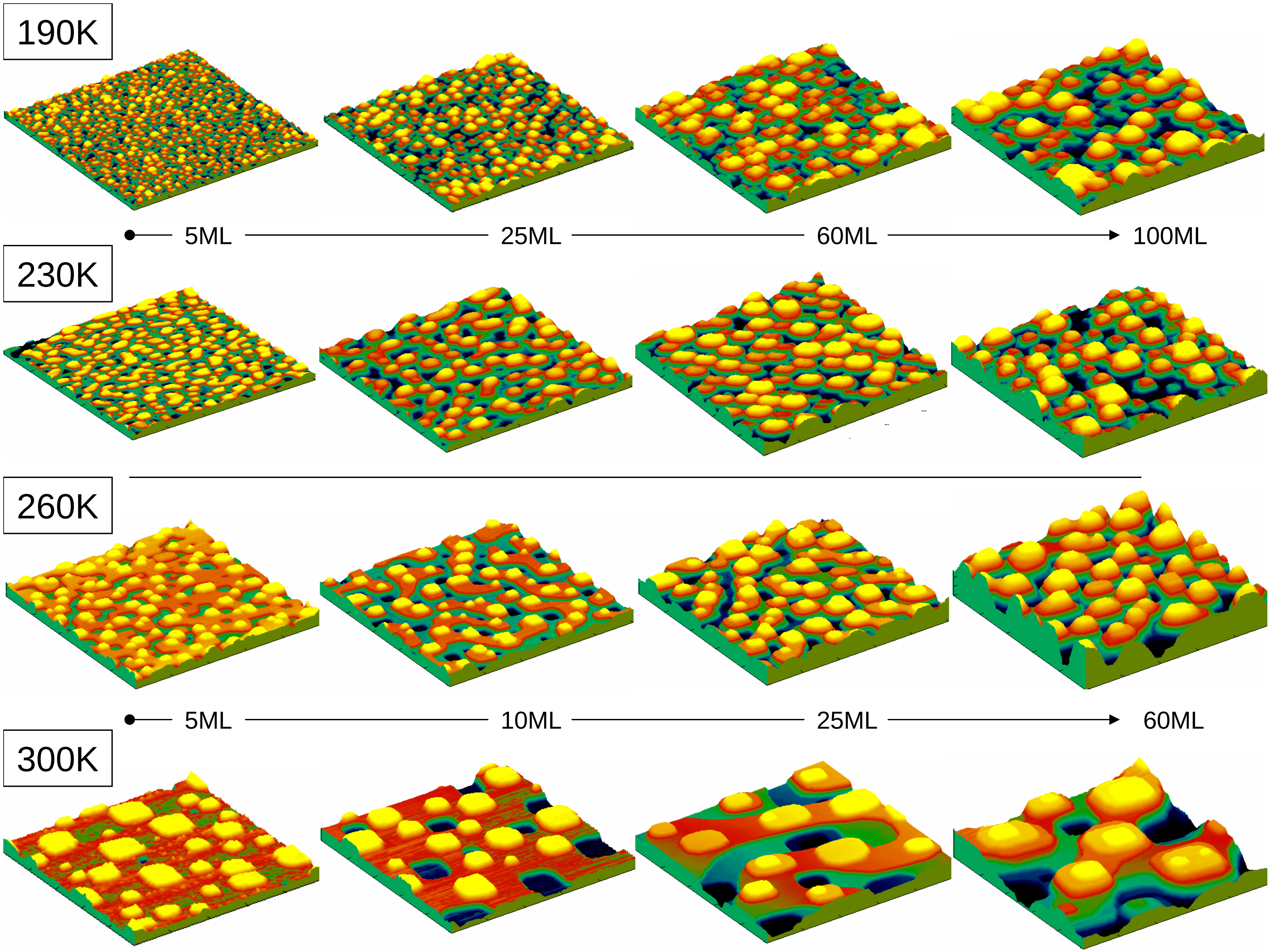
Caspersen et al., PRB **63** (2001) 085401

ONSET OF 2ND LAYER POPULATION after Island Coalescence @ ~0.3ML

SIGNIFICANT 2ND LAYER POPULATION after Island Percolation @ ~0.75ML*

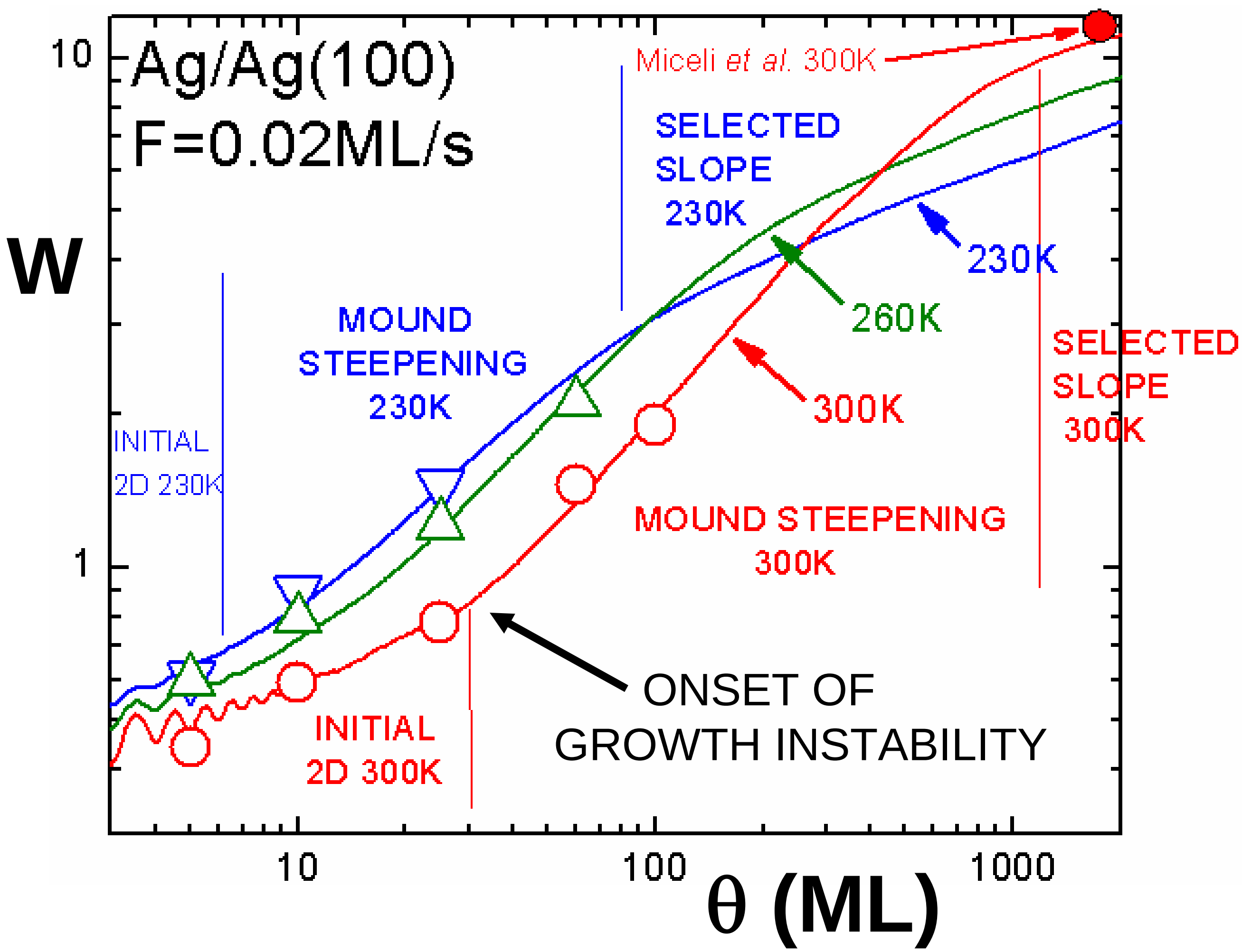
***exceeds standard continuum percolation value of ~0.7ML**

QUASI-LAYER-BY-LAYER GROWTH for up to ~30ML


190K
5ML
25ML
60ML
100ML
230K
260K
5ML
10ML
25ML
60ML
300K

Ag/Ag(100) @ 300K: UNEXPECTED VERY ROUGH GROWTH FOR >30ML

Film Roughness W (in units of interlayer spacing)

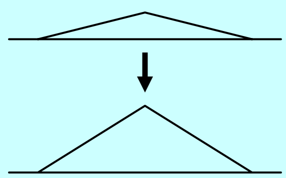


Modeling with <u>small</u> non-uniform step-edge barrier (E_{act}=0.07eV)
Caspersen et al., PRB **65** (2002) 193407

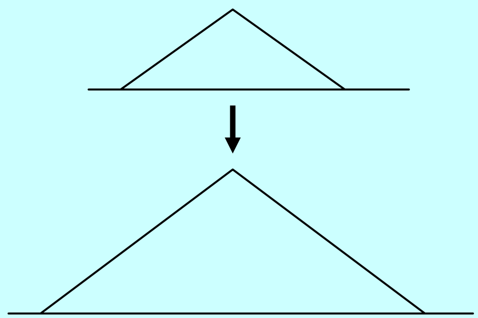
GROWTH REGIMES:

(i) INITIAL QUASI-LBL
…expected behavior

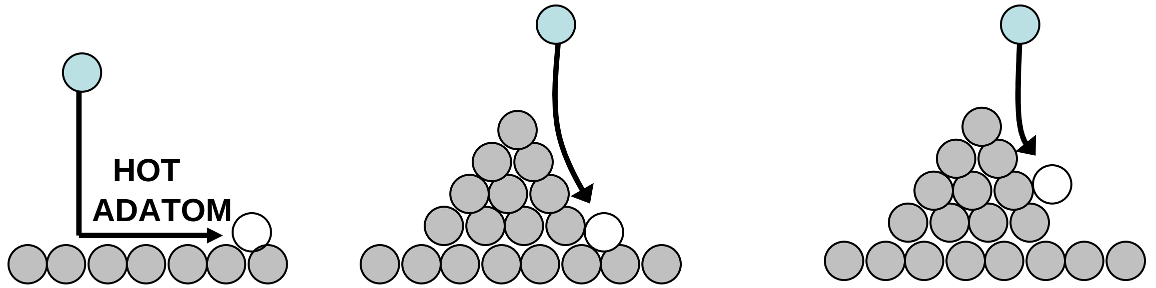
(ii) MOUNDS FORM & SIDES STEEPEN



(iii) SLOPE SELECTION & COARSENING



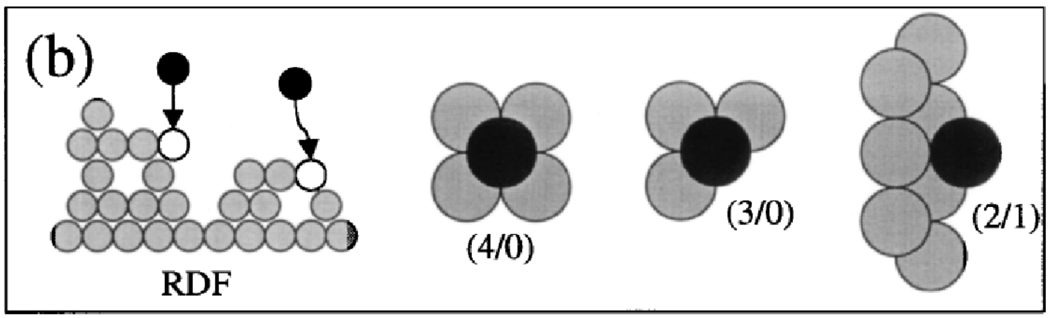
MODELING OF Ag/Ag(100) GROWTH BELOW 150K

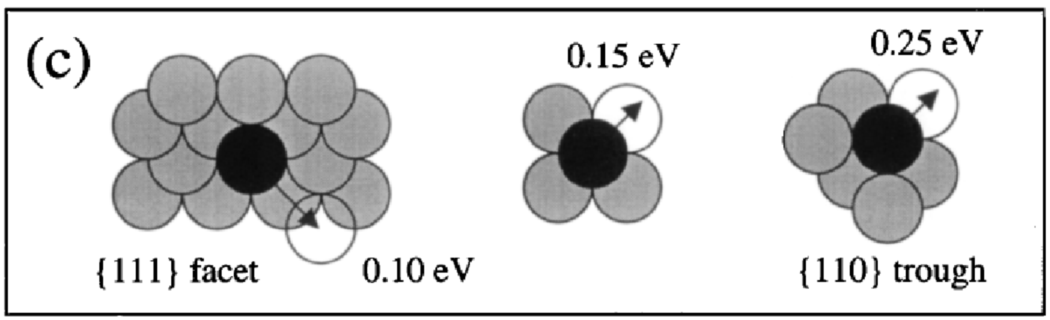


Transient Mobility | Downward Funneling (DF) | Restricted DF (RDF)

Early Models for Smooth Low-T Growth
Transient mobility: Egelhoff *et al.* PRL (89)
Downward Funneling: Evans *et al.* PRB (90)
Refinements:
Restricted Downward Funneling (RDF)
Analysis:
MD-DePristo *et al.* (90's); KMC-ISU group

ADSORPTION SITES FOR RDF:

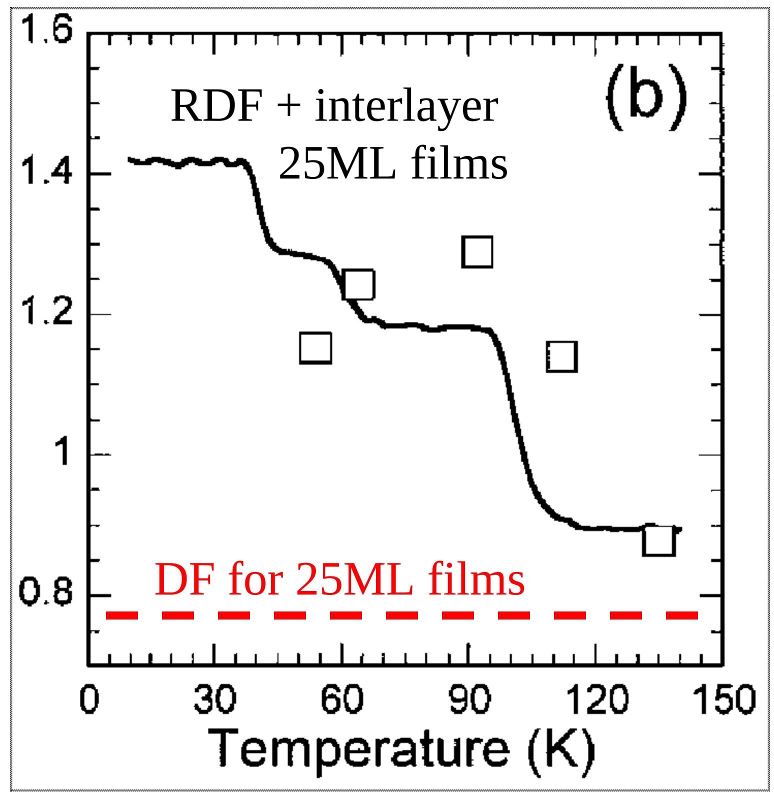




LOW-BARRIER INTERLAYER DIFF. PROCESSES

Stoldt et al. PRL **80** (2000); Caspersen & Evans, PRB **64** (2001)

FILM ROUGHNESS (W) vs. T



PHYSICAL REVIEW B **66**, 075418 (2002)

Vacancy formation in homoepitaxially grown Ag films and its effect on surface morphology

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Department of Physics, State University of New York, Stony Brook, N
(Received 20 December 2001; revised manuscript received 27 March 2002; pu

Synchrotron x-ray diffraction was used to investigate the low-temperature homoepitaxial growth on Ag(001) and Ag(111) surfaces. For both orientations, the Ag films deposited at $T = 100$ K were observed to exhibit a 1% surface-normal compressive strain, indicating that an appreciable vacancy concentration (~2%) is incorporated in the growing film. Concomitantly with the incorporation of vacancies, the growth on Ag(111) leads to the formation of pyramidlike structures with a non-Gaussian distribution of heights, whereas a similar effect was not observed for Ag(001).

T=0K

OTHER STUDIES:

- Kelchner & DePristo, Surf. Sci **393** (97): direct MD @ low T ⇒ overhangs; voids
- Caspersen & Evans PRB **64** (2001): Detailed KMC modeling of Ag/Ag(100) growth
  Explores kinetic roughening, inverse ES barrier to climbing up, compacting via PD
- Montalenti, Sorensen, Voter PRL **87** (2001): Temp - accelerated MD for Ag/Ag(100)
  Explores “steering effects”& RDF, multi-atom moves, compacting via PD
- Henkelman & Jonsson PRL **90** (2003): Off-lattice KMC with unrestricted TS search:
  Explores multi-atom moves in smooth growth of Al/Al(100).

Ag/Ag(111): TEMPERATURE-DEPENDENCE of ISLAND GROWTH SHAPES

Terrace diffusion: E_{act} =0.1eV ⇒ very active well below 100K Cox *et al.* PRB **71** (05)
Slow Edge Diffusion: E_{act} ≥0.3eV ⇒ inefficient shape relaxation/shape instability

(a) 120K
(b) 135K

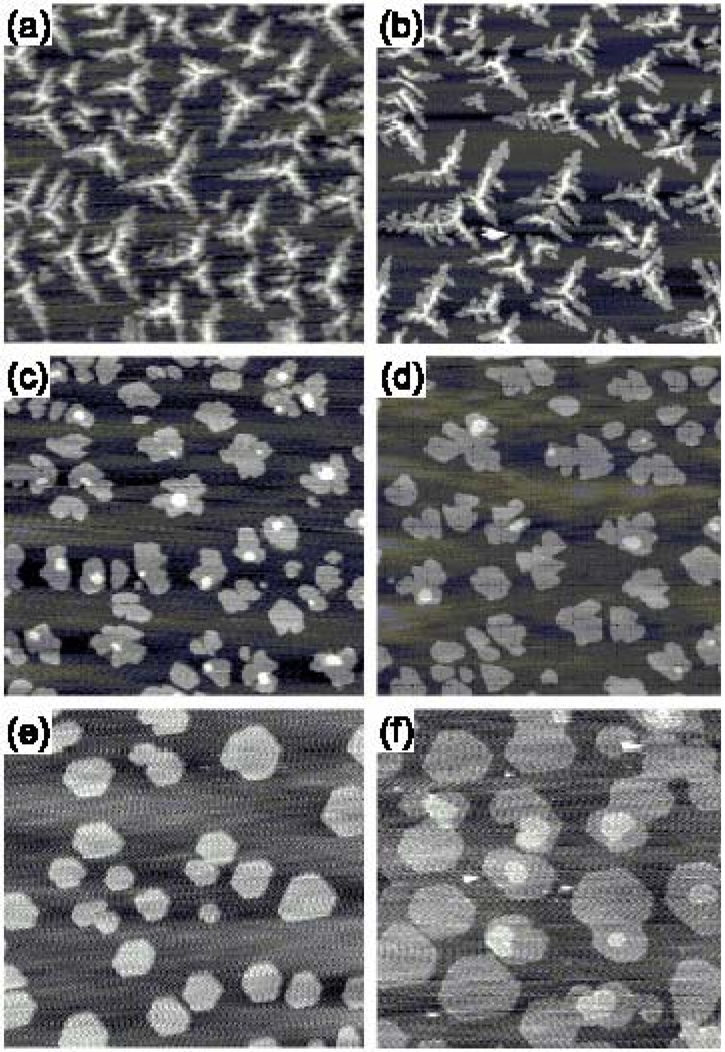
Triangular
Dendrites

(c) 150K
(d) 165K

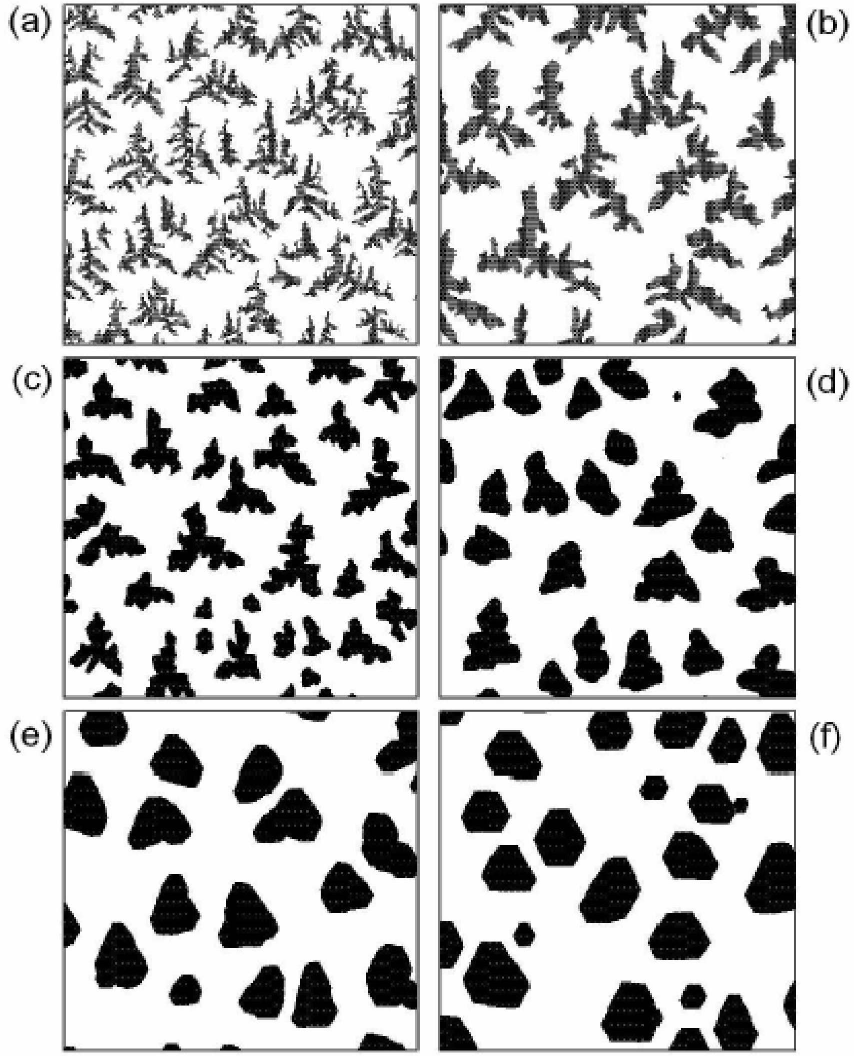
Isotropic
Fat
Fractals

(e) 180K
(f) 200K

Distorted
Hexagons



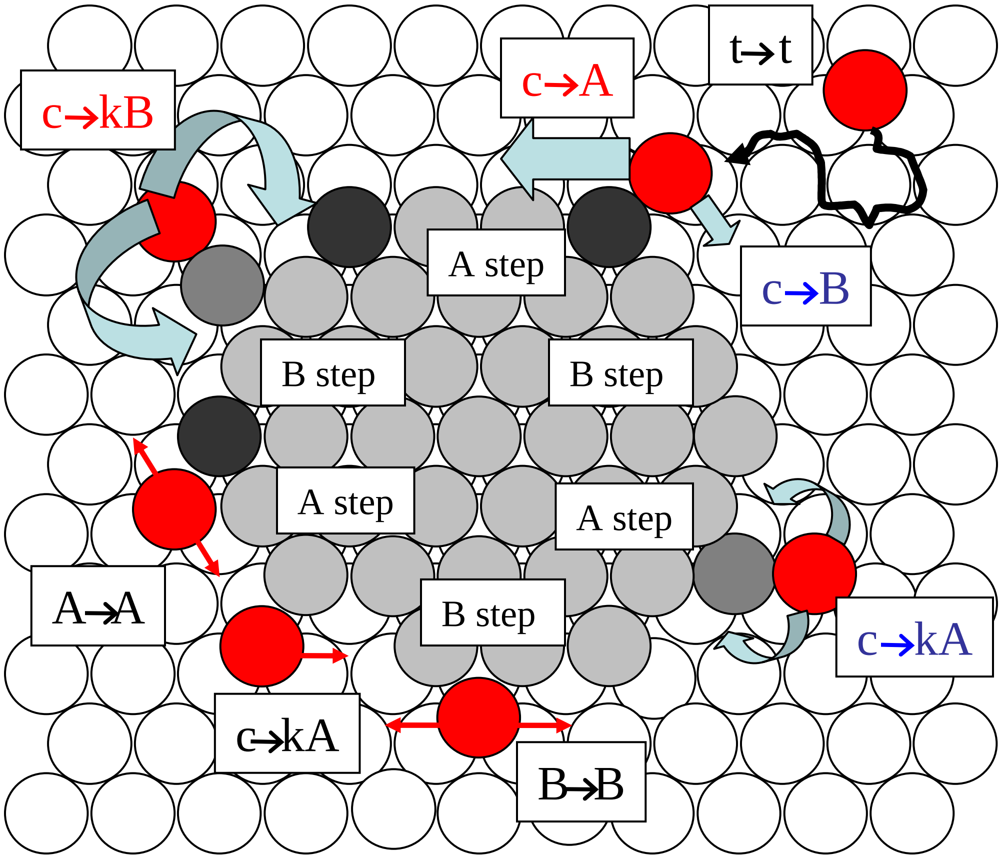
VT-STM IMAGES (300×300 nm^2)



KMC SIMULATIONS (~ 300×300 nm^2)

Ag/Ag(111): ATOMISTICS OF KINETICALLY CONTROLLED GROWTH SHAPES

E. Cox, M. Li, P.-W. Chung, C. Ghosh, T. Rahman, J.W. Evans, P.A. Thiel, Phys. Rev. B **71** (2005), in press.



Distinct A- and B-type step edges border any compact island:

A & B step energies almost identical
⇒Equilibrium island shape = hexagon

Deviations from 6-fold symmetry
(triangular dendrites & distorted hexagons)
observed in island growth shapes reflect a "kinetic anisotropy"…
the ***Corner Diffusion Anisotropy***

Discussed for Pt/Pt(111) by Hohage *et al.* PRL 76 (96); Al/Al(111) by Ovesson *et al.* PRL 83 (99) …unequal A & B step energies (both thermodynamic & kinetic symmetry breaking)
Ag/Pt(111) by Brune *et al.* Surf. Sci. 349 (96)

Distorted hexagons at 180-200K: adatoms aggregating at corners more likely to hop to A-steps ⇒ A-steps advance more quickly and thus tend to "grow out"

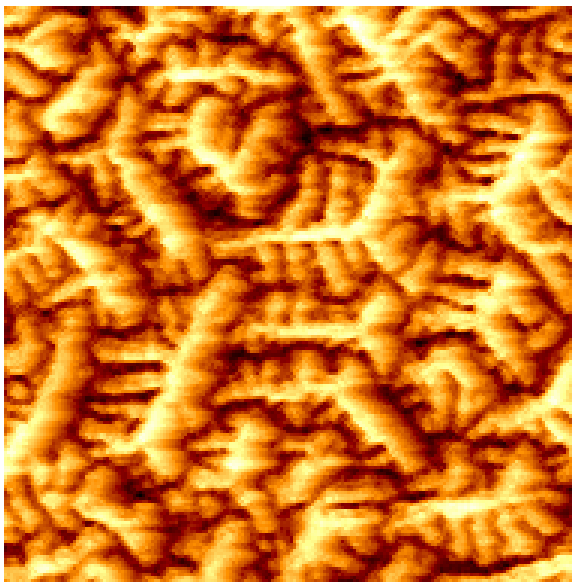
Triangular dendrites at 120-135K: adatoms aggregating at single atoms more easily relax to B-steps than A-steps ⇒ fingers grow out from A-steps faster

Ag/Ag(111): MOUNDED MULTILAYER GROWTH MORPHOLOGIES

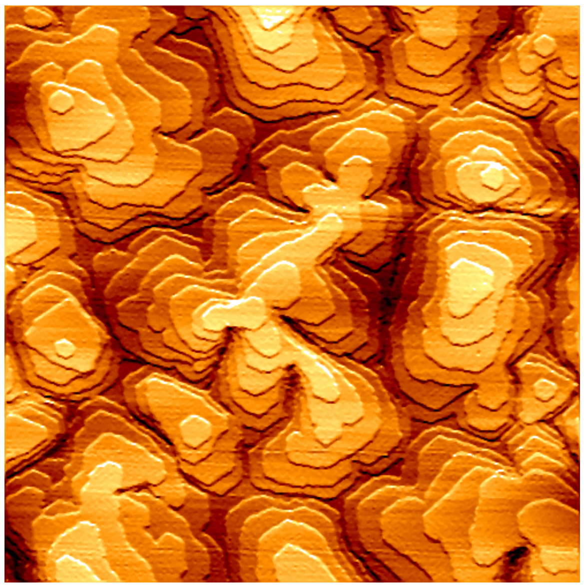
Ag/Ag(111) barriers: E_{act} =0.10eV (terrace diff); ≥0.3eV(edge diff); =0.15eV(step edge)

Large step-edge barrier to downward transport ⇒ rapid roughening & wedding-cake-like mounds
Ag/Ag(111) is the prototype for rough "Poisson growth" (limited interlayer transport) even at 300K

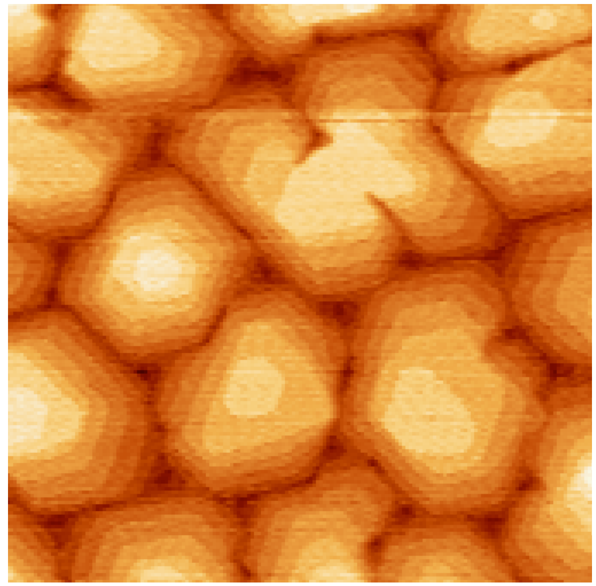
cf. Ag/Ag(100) barriers: E_{act} =0.40eV (terrace diff); ≥0.25eV (edge diff); =0.07eV (step edge)



135K: 200×200 nm^2 3ML
Dendritic mounds (Δ-envelopes)



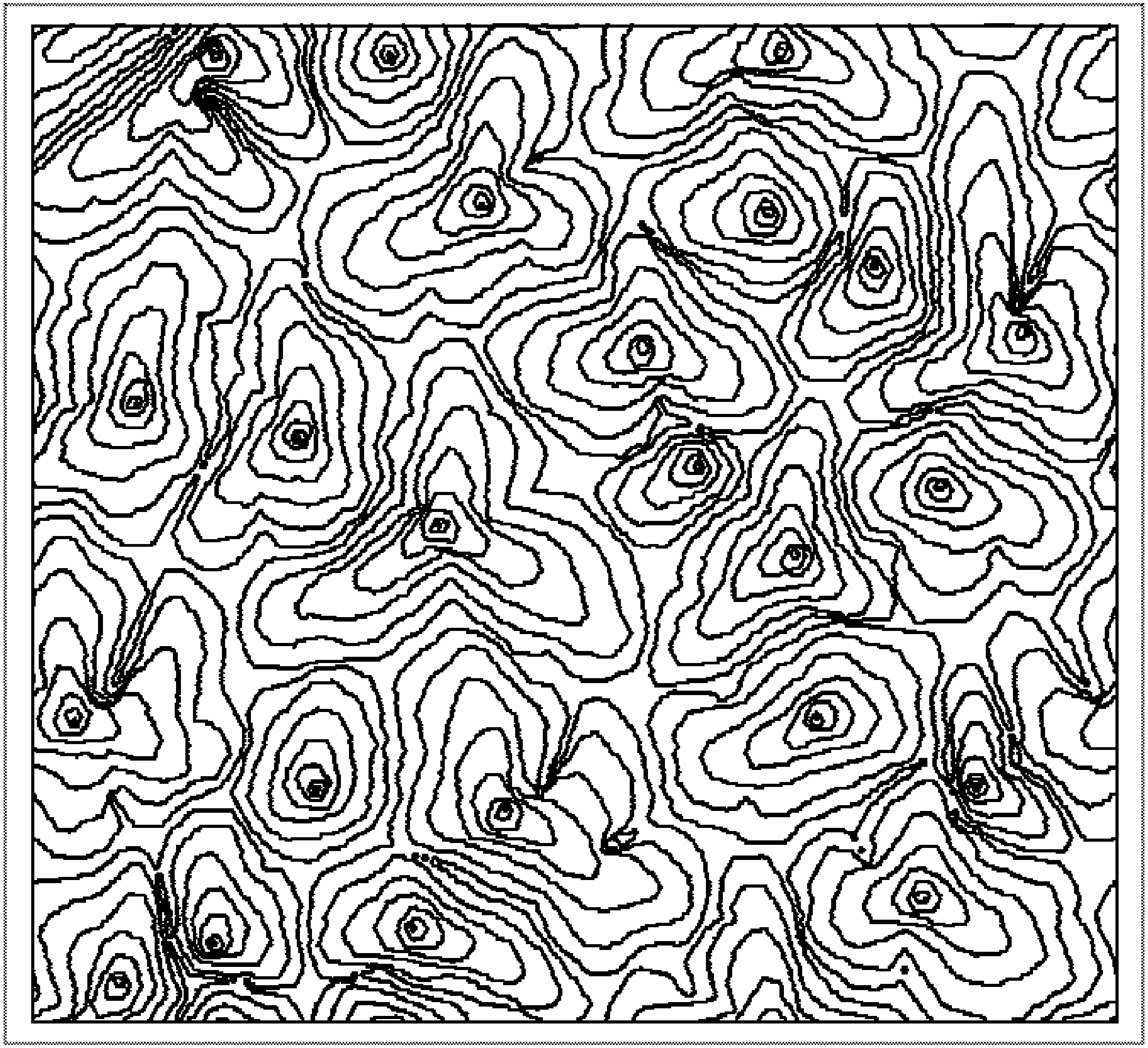
150K: 123×123 nm^2 3ML
Isotropic fat fractal mounds



180K: 350×350 nm^2 4ML
Distorted hexagonal mounds

Key observation: submonolayer island structure propagated into multilayer morphology

SIMULATION OF AG/AG(111) GROWTH AT 150K



KMC SIMULATION
…extending model for submonolayer deposition to the multilayer regime

T=150K
F=0.0035ML/s
θ=2ML

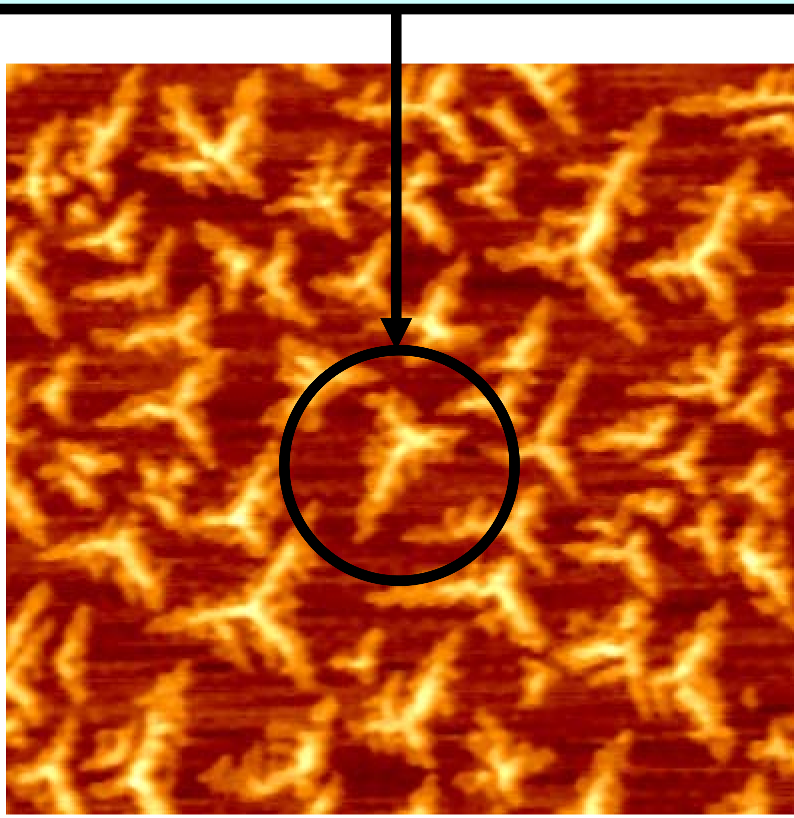
Image size:
500$\times$500 sites

Large ES barrier

Ag/Ag(111): STACKING-FAULT ISLANDS (LOW-T KINETIC EFFECT)

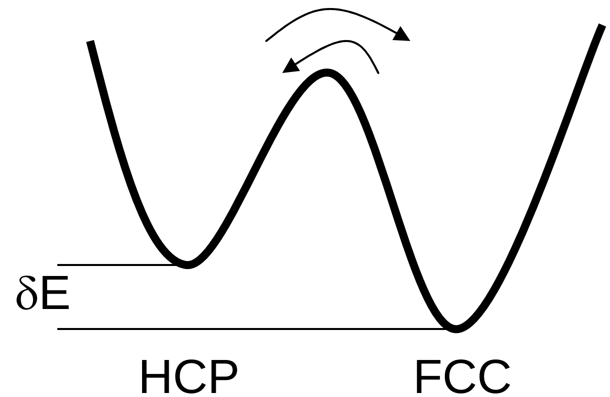
STACKING-FAULT ISLAND
POINTS IN "WRONG DIRECTION"

ATOMS RESIDE ON HCP (NOT FFC)
THREE-FOLD HOLLOW SITES



0.3 ML Ag/Ag(111) at 120 K

SMALL CLUSTERS TRANSITION BETWEEN FCC AND HCP SITES:



$$\mathrm{Prob(HCP)/Prob(FCC)} = \exp(-\delta E/kT)$$

with $\delta E \propto$ cluster size

OBSERVED FRACTION OF HCP DETERMINED BY δE FOR LARGEST MOBILE CLUSTER AT THAT TEMP.

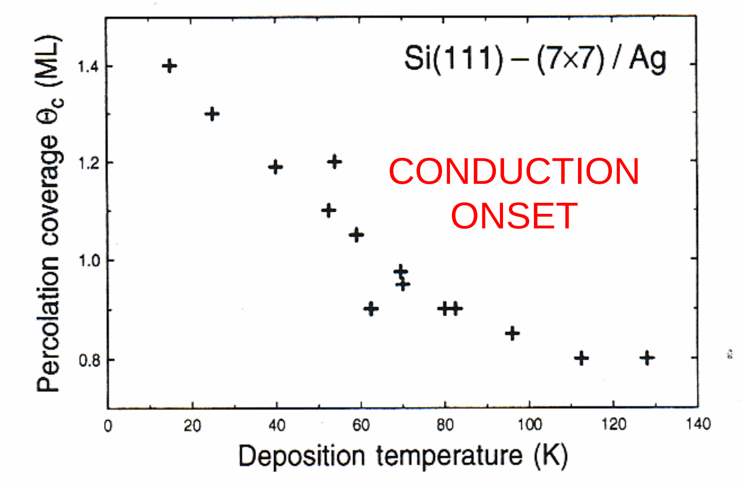
LOWER T ⇒ LESS MOBILE CLUSTERS
⇒ LOWER δE ⇒ MORE HCP

Michely et al. PRL **91** (2003) for Ir/Ir(111)

Ag/Si(111)7×7 AT LOW-TEMPERATURE

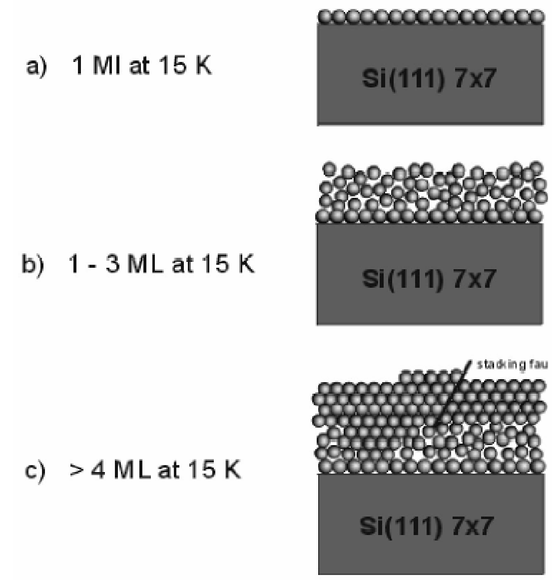
Horn-von Hoegen, Henzler, Meyer in "Morphological Organization in Epitaxial Growth…" (World Sci., 1998)

…small Ag clusters inside both halves of 7×7, corner holes



Pb/Si(111)7×7 at 15 K

Henzler et al. Surf. Sci. (01); PRB 65 (02)

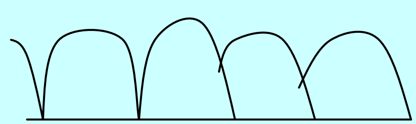


QUENCH-CONDENSED (QC) FILMS OF Ag, Pb, Au,… on HOPG or glass etc.

Amorphous-to-Crystalline Transition: atoms stick where land ⇒ amorphous structure; Converts when thick enough to overcome substrate interaction; utilizes heat of condensation;…

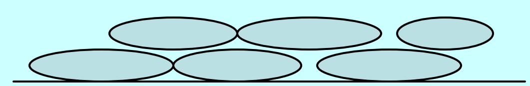
Danilov *et al.,* PRB (95) JLTP (96)

3D Islands Merging: conduction via tunneling



Strongin, Dynes,….

Stacks of plate-like islands: approx. 2 layers for conduction



Valles *et al.* PRB (98); PRL (99)

CONCEPTS AND TECHNIQUES FOR LOW-T DEPOSITION:

DYNAMICS OF DEPOSITION…and assoc. pathways to induce nano-crystallinity
Transient mobility, knock-out, downward funneling,… (Evans, PRB 91)

EFFICIENCY OF ENERGY DISSIPATION: can be restricted due to stiff substrate; limited vibrational energy transport through topologically disordered amorphous film?

VERY-LOW BARRIER MULTI-ATOM REARRANGEMENT PROCESSES

ACCELERATED-MD TECHNIQUES: bridge gap between time-scales accessible In between conventional MD (~10^{-6} sec) and deposition processes (~10^{3} sec): temperature-accelerated dynamics; hyperdynamics, parallel replica dynamics
[Voter and coworkers, PRL 87 (2001) 126101]

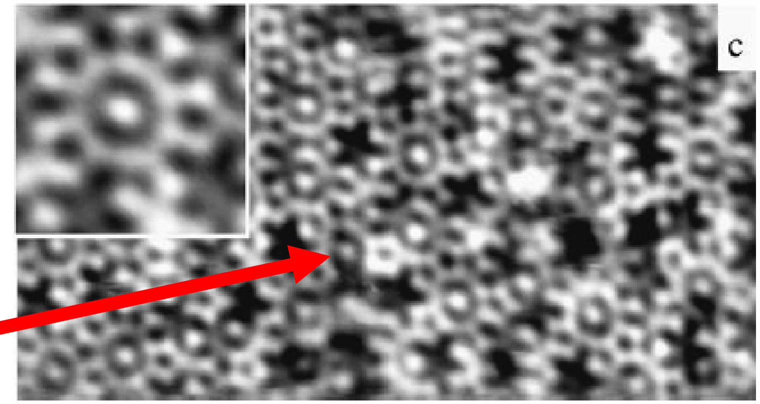
OFF-LATTICE KMC WITH AUTOMATED TRANSITION-STATE SEARCH
…on-the-fly or self-teaching KMC exploiting the dimer-method for TST searches
[Jonsson and coworkers, PRL 90 (2003) 116101]

OFF-LATTICE KMC FOR STRAINED-LAYER HETEROEPITAXY:
onset of dislocations after critical thickness; SK-growth …so far just for 1+1D models
[Biehl and co-workers, EPL 63 (2003) 14; 56 (2001) 791]

Ag DEPOSITION ON 5-FOLD AlPdMn QUASICRYSTAL (QC !)

Fournee et al. (ISU group) PRB **67** (03); Surf. Sci. **537** (03)

Motivation: five-fold QC order of the substrate might be propagated into metal overlayer. A 1-element quasicrystal valuable for studies of..



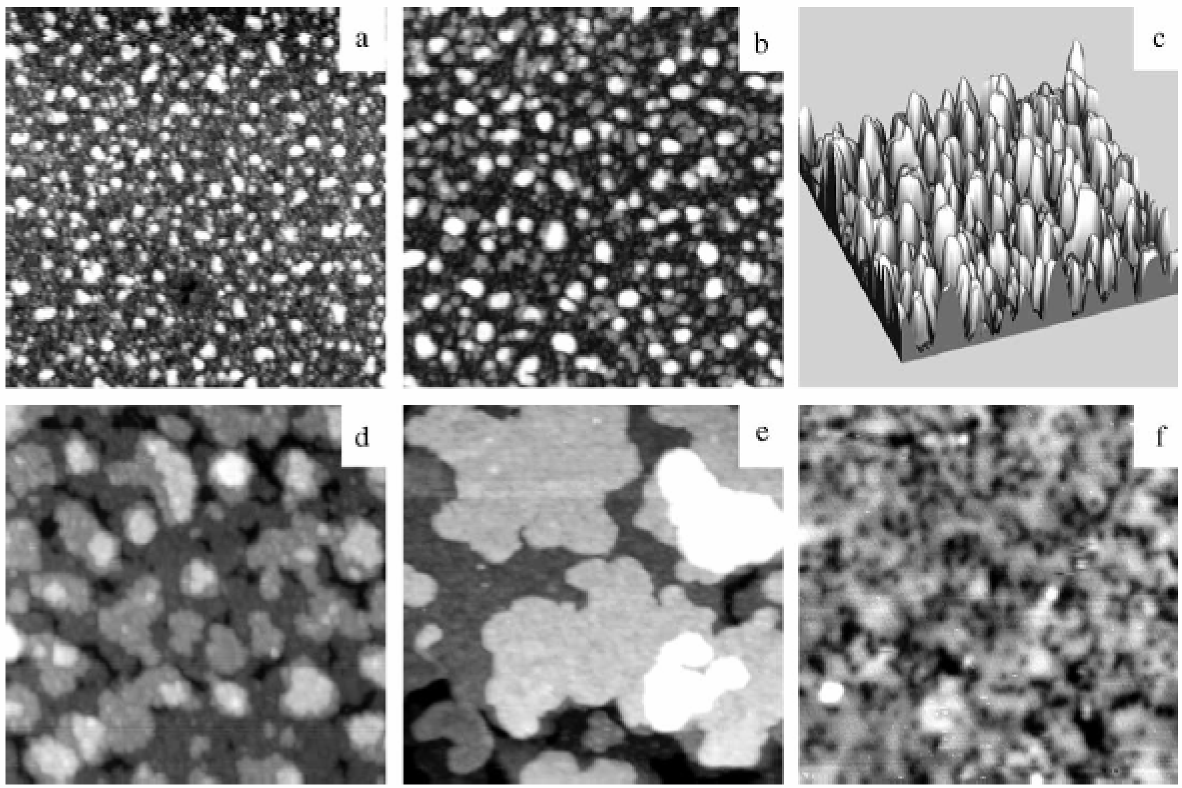


Fig. 5. (a)–(e) 100 × 100 nm^2 STM images of Ag deposited on the 5-fold $Al_{72}Pd_{19.5}Mn_{8.5}$ IQC surface at 0.2 (a), 0.5 (b), 1.0 (c), 1.7 (d) and 5 ML (e). (f) 27.6 × 27.6 nm^2 STM image on top of a Ag island at 5 ML. (c) is a 3D view.

← GROWTH AT 300K

(i) <0.5ML: nucleation of islands at "trap" sites
(ii) 1-2 ML: development of 3D needle-like islands
(iii) >2ML: lateral spreading
(iv) >10ML: hexagonal wedding-cake mounds as for Ag/Ag(111) @ 300K, but with overall 5-fold symmetry

GROWTH AT LOW T~130K

…smoother, avoids growth of 3D needle-like islands