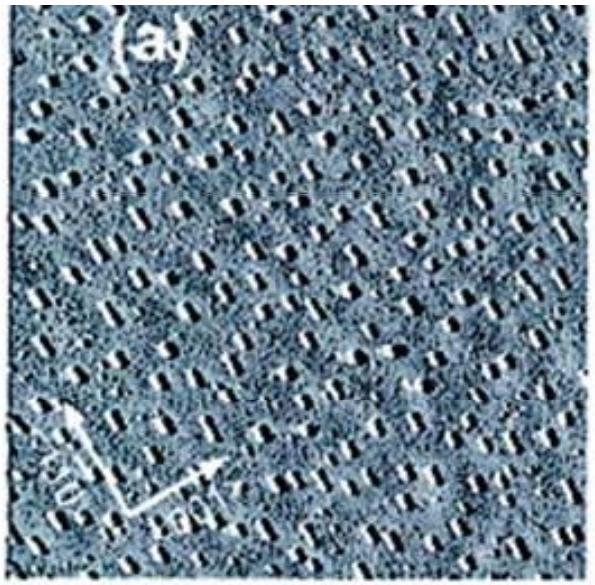
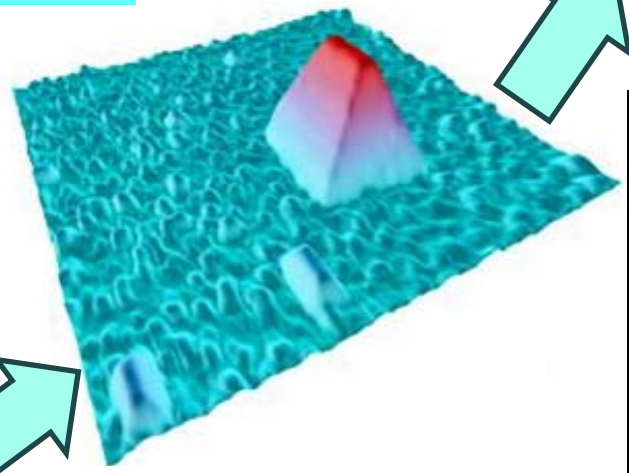
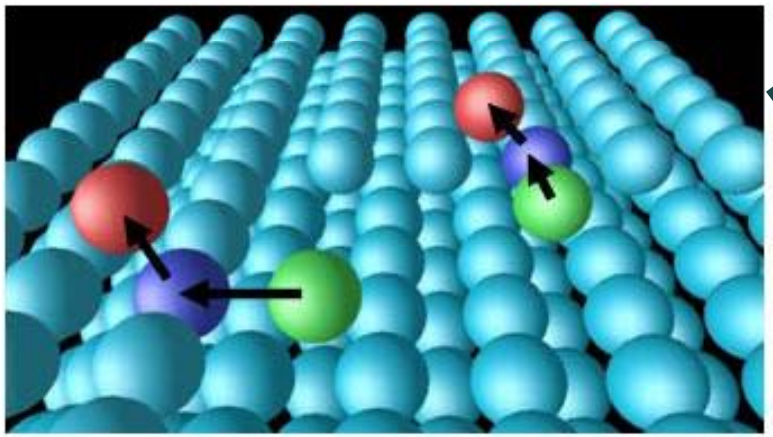
Multi-Scale Simulation of Assembly at Gas-Solid Interfaces: Al/Al(110)

Kristen A. Fichthorn
Penn State University

Sponsored by
NSF DMR-0514336







Yogesh Tiwary's PhD

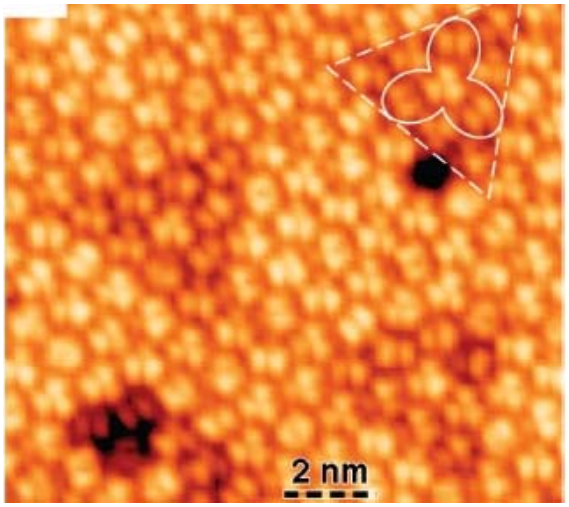
Patterned Substrates Are Useful!

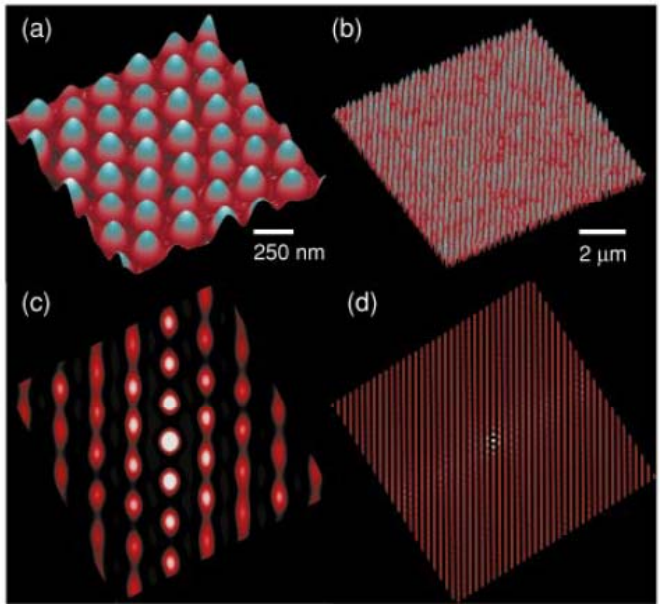
Templates for Molecular Assembly

C60 on Ag/Pt(111)

K. Ait-Mansour et al., J. Phys. Chem. C **113**, 5292 (2009).

J. Howe, …, K. Fichthorn, *PRB* **81**, 121410 (2010).

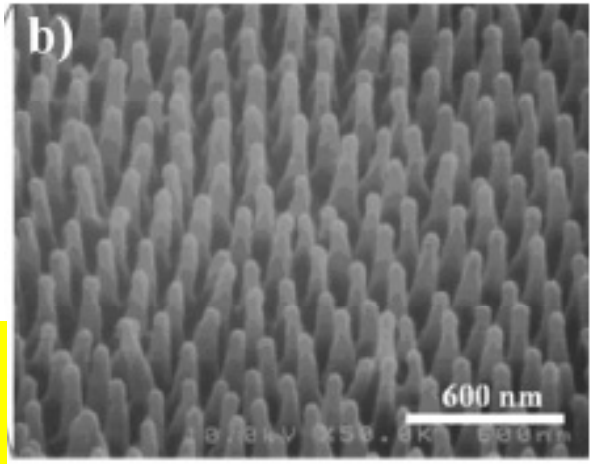




Superhydrophobic Properties

Cicada Wing

W. Lee et al., Langmuir **20**, 7665 (2004).



H. Wu, …, K. F. *J. Chem. Phys*. **133** 054704 (2010).

Optoelectronic Properties

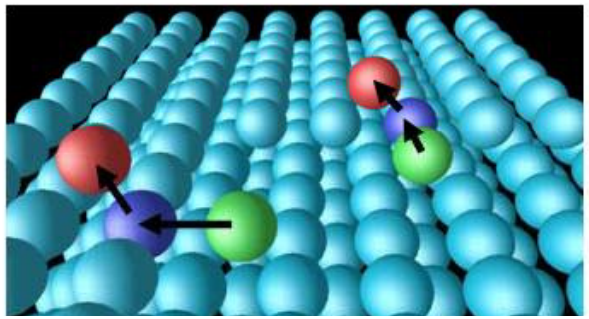
Ge/Si(001) Quantum Dots

O.G. Schmidt et al., Appl. Phys. Lett. **77**, 4139 (2000).

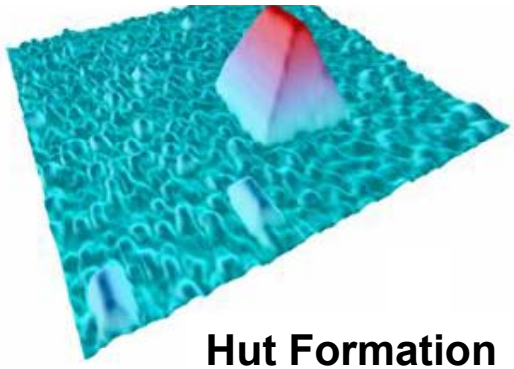
We want to Design Their Assembly From the Bottom Up!

Hut Formation in Al(110) Homoepitaxy

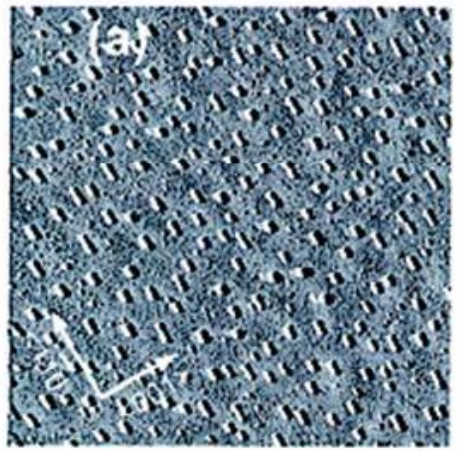
Bautier de Mongeot *et al.*, *Phys. Rev. Lett.* **91**, 016102 (2003).



Atoms Hopping (Å, ps)



Hut Formation (nm, min)



Hut Organization (μm, min)

Zhu et al., Phys. Rev. Lett. **92**, 106102 (2004).

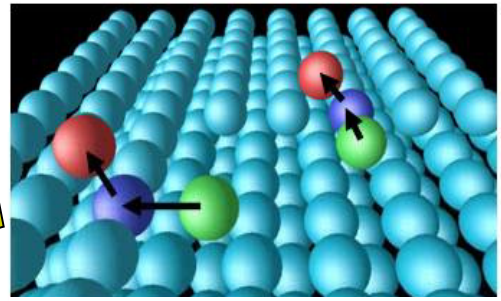
Multi-Scale Kinetic Self-Assembly

K. Fichthorn and M. Scheffler, *Nature* **429**, 617 (2004).

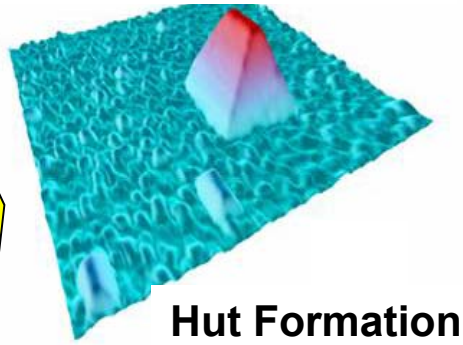
Describing Multi-Scale Self-Assembly in Al(110) Homoepitaxy

First-Principles DFT
VASP Code
Diffusion Barriers
Adatom Interactions

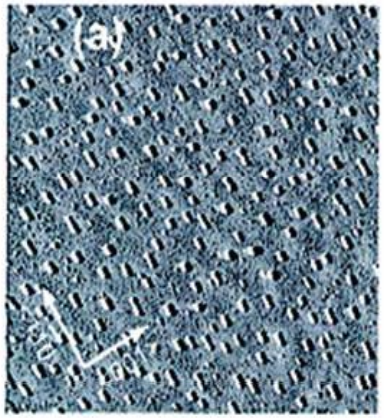
Y. Tiwary and K. Fichthorn,
Phys. Rev. B **75**, 235451 (2007);
Phys. Rev. B **78**, 205818 (2008);
Phys. Rev. B **81**, 195421 (2010);
Phys. Rev. B (submitted).



Atoms Hopping (Å, ps)



Hut Formation
(nm, min)



Hut Organization
(μm, min)

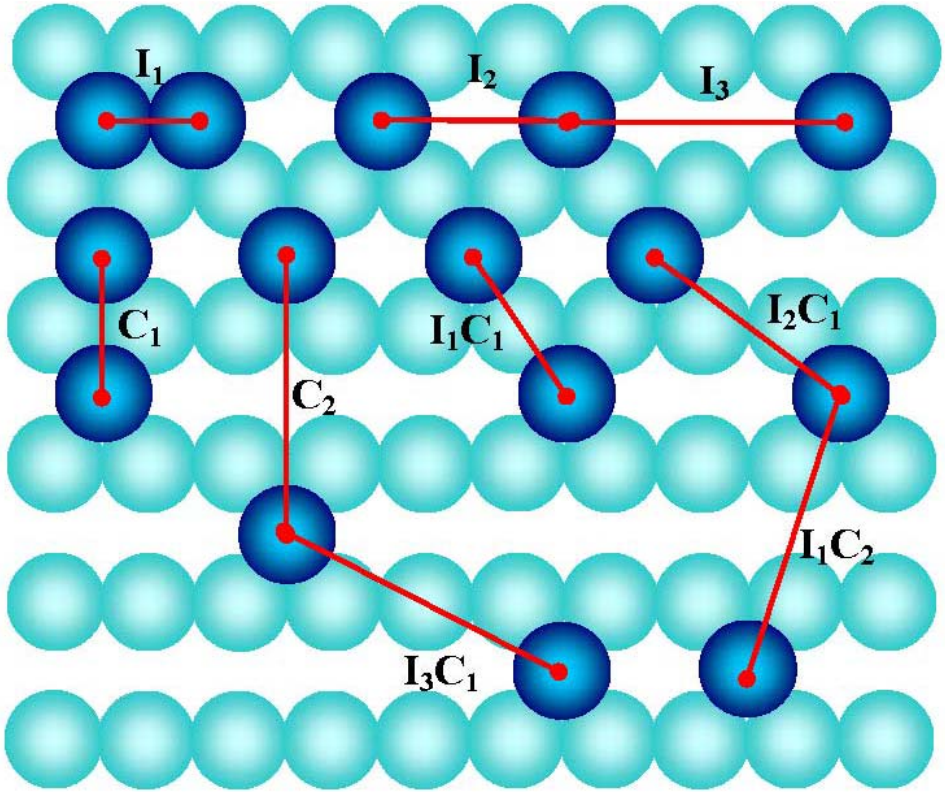
Ab initio Accelerated MD
Modified VASP Code
Diffusion Pathways

K. A. Fichthorn et al., *J. Phys. Cond. Matt.* **21**, 084212 (2009).

Kinetic Monte Carlo Continuum
Growth Simulations

Y. Tiwary and K. Fichthorn (In preparation).

Pair Interactions on Al(110) DFT GGA



E_{I1} = -0.091 eV

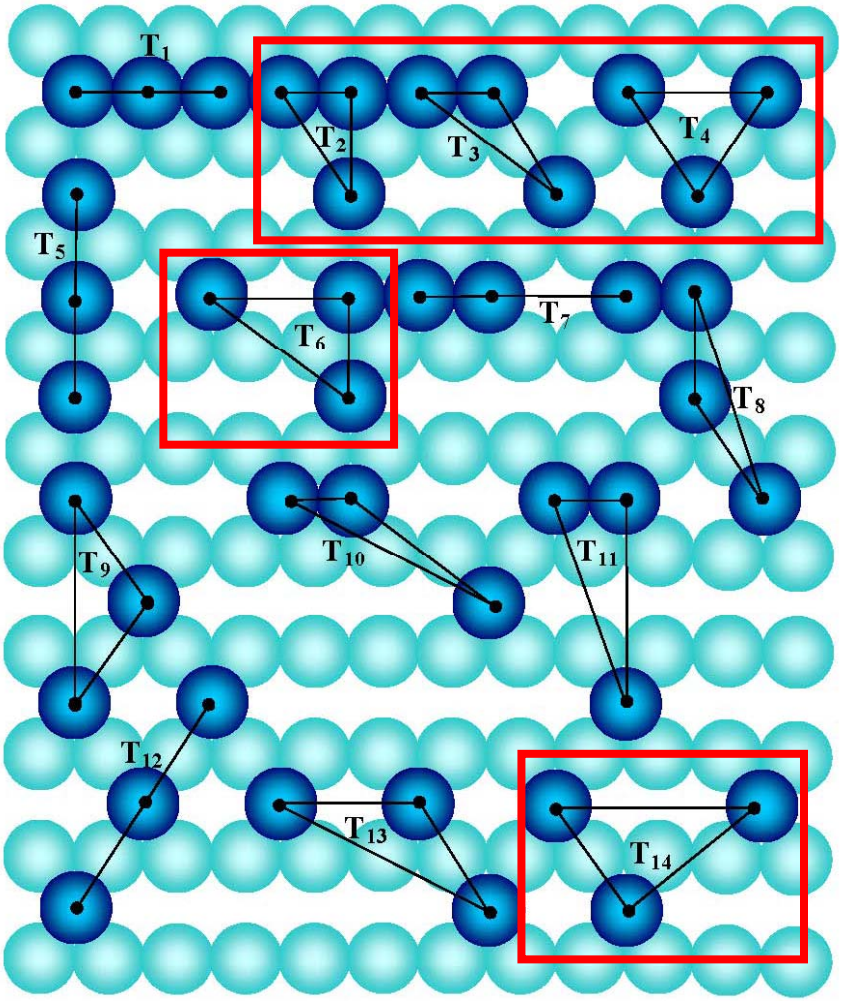
E_{C1}= 0.049 eV

All long-range pair interactions are repulsive!

Y. Tiwary and K. Fichthorn, *Phys. Rev. B* **75**, 235451 (2007)

How Can We Have Huts???

Attractive Trios…

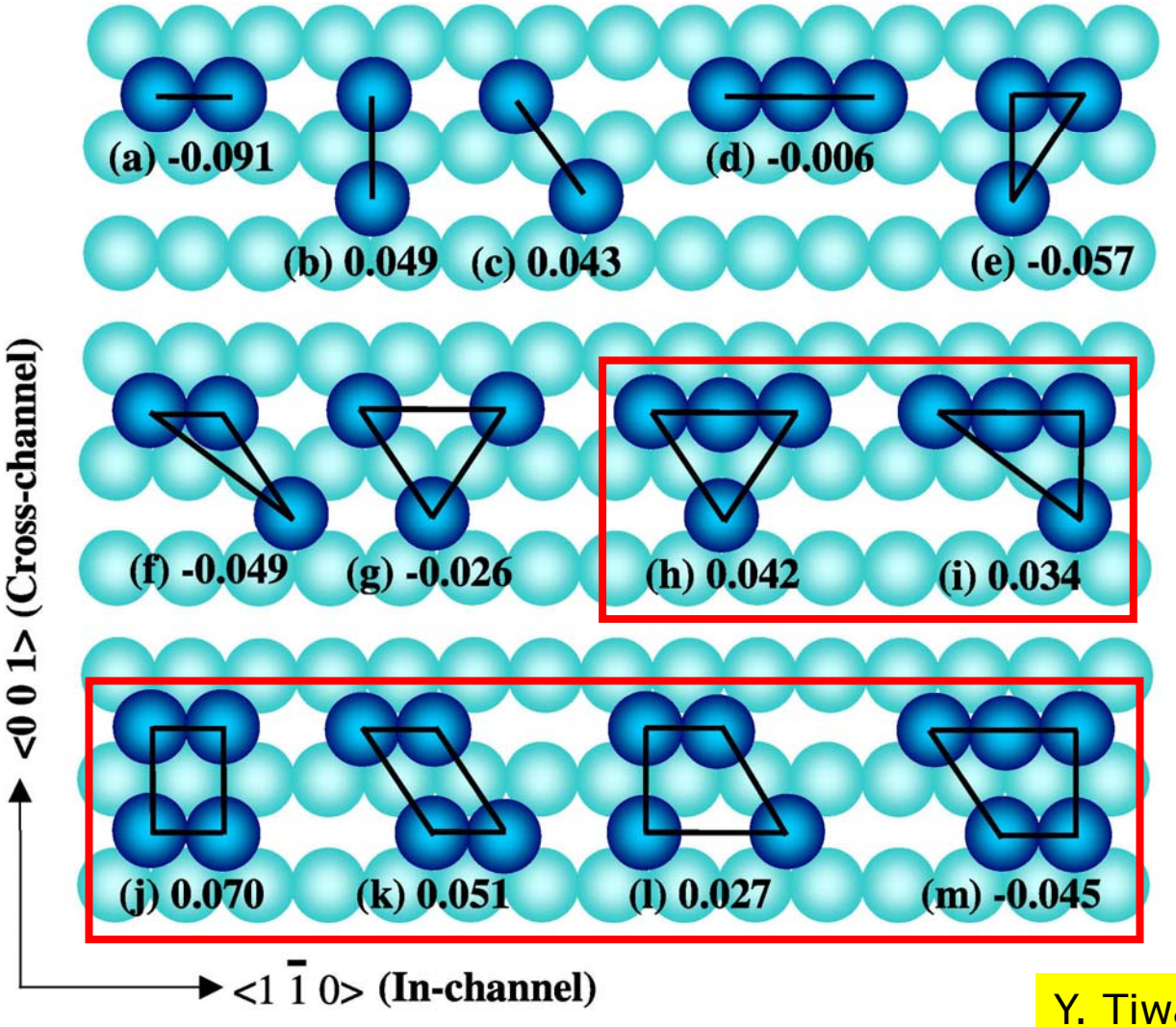


*T*1 = -0.006 eV	*T*8 = 0.011
*T*2 = -0.060	*T*9 = 0.019
*T*3 = -0.044	*T*10 = -0.005
*T*4 = -0.021	*T*11 = 0.015
*T*5 = 0.032	*T*12 = 0.004
*T*6 = -0.019	*T*13 = 0.017
*T*7 = -0.025	*T*14 = -0.017

Trios Can Stabilize Cross-Channel Bonding, But…

Y. Tiwary and K. Fichthorn, *Phys. Rev. B* **75**, 235451 (2007).

High-Order Many-Body Interactions Are Significant!!

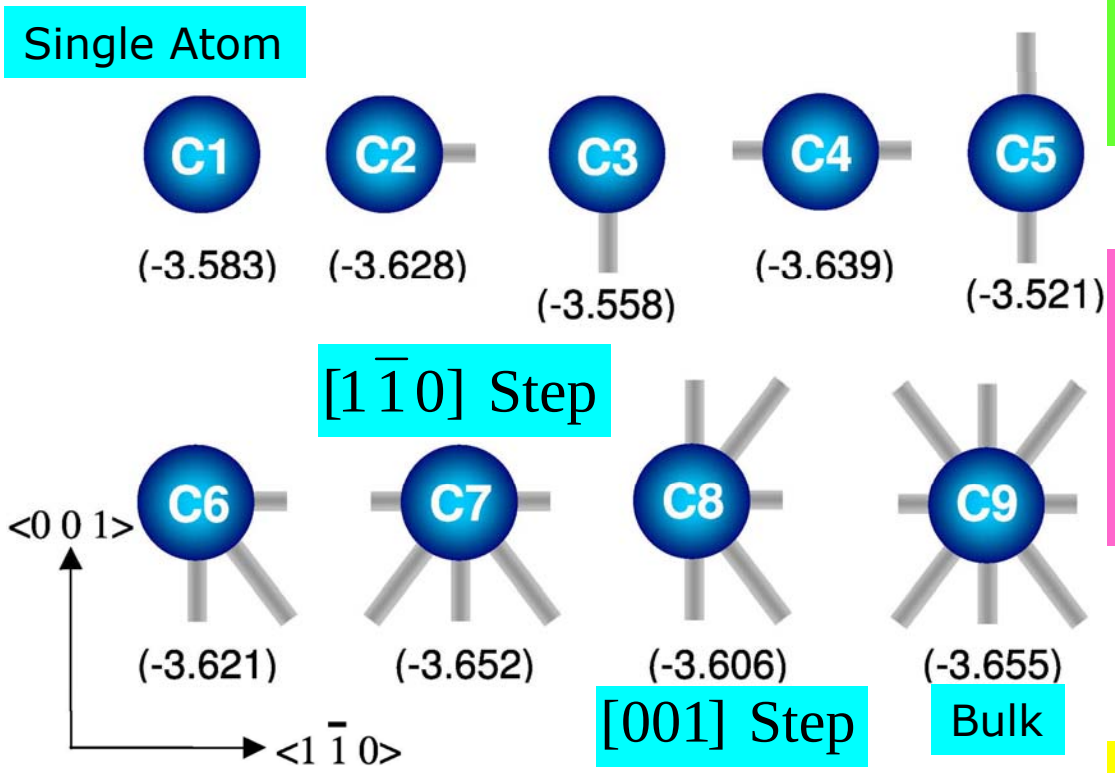


Many-Body (Elastic) Interactions Make the Lattice-Gas Approach Unwieldy…

Y. Tiwary and K. Fichthorn, *Phys. Rev. B* **78**, 205818 (2008).

The Connector Model

Combine groups of many-body interactions into structural units with a single interaction energy



Connectors Contain Key Energies in Thin-Film Growth e.g., Steps

$$\lambda_{[1\bar{1}0]} = C7 - C9 = 0.003 \text{ eV/atom}$$

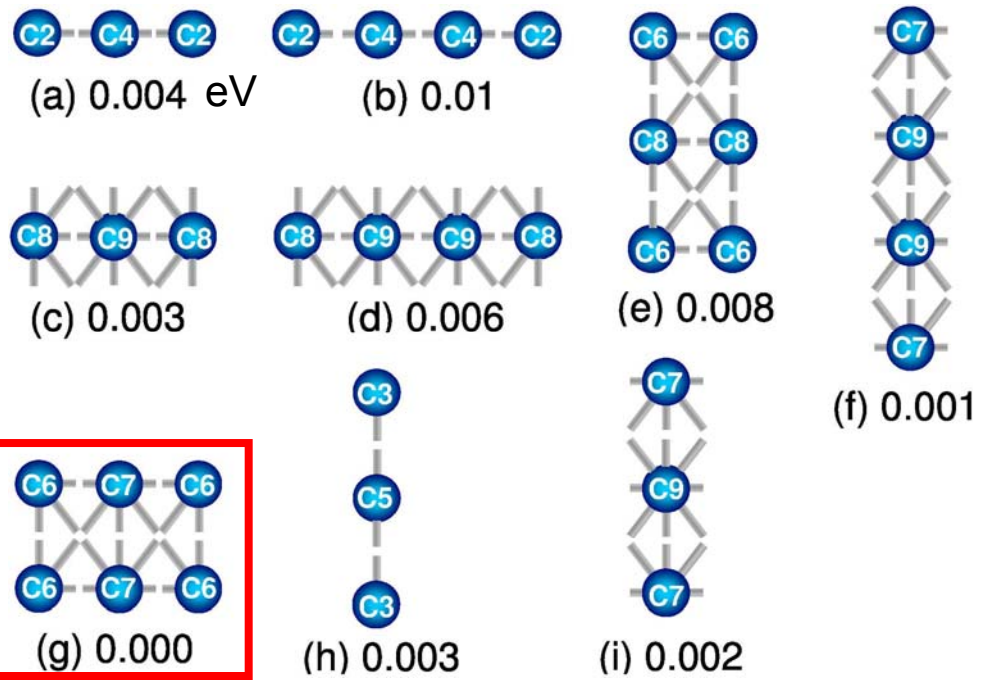
$$\lambda_{[001]} = C8 - C9 = 0.048 \text{ eV/atom}$$

$$\lambda_{[001]} / \lambda_{[1\bar{1}0]} = 16$$

Y. Tiwary and K. Fichthorn, *Phys. Rev. B* **78**, 205818 (2008).

The Connector Model is Accurate and Efficient

Connector vs. DFT



Connector

$$E = 4C_6 + 2C_7$$

vs. Lattice Gas

$$E = \sum E_0 + \sum pairs + \sum trios + \sum quartos + \sum pentas + \sum hexas$$

$$6 \quad + \quad 15 \quad + \quad 10 \quad + \quad 15 \quad + \quad 6 \quad + \quad 1$$

> 50 interactions

Y. Tiwary and K. Fichthorn,
Phys. Rev. B **78**, 205818 (2008).

Connector Model Compares Favorably To Fitted Cluster Expansion Model

$$CV = \sqrt{\frac{1}{M}\sum_{i=1}^{M}\left[\{E^{DFT}(i) - E^{CE}(i)\}^2\right]}$$

M Atom Configurations
n terms in CE

A. van de Walle and G. Ceder, J. Phase. Equilib. **23**, 348 (2002).

G. L. W. Hart, V. Blum, M. J. Walorski, and A. Zunger, Nature Mat. **4**, 391 (2005).

N. A. Zarkevich and D. D. Johnson, Phys. Rev. Lett. **92**, 255702 (2004).

R. Drautz and A. Díaz-Ortiz, Phys. Rev. B **73**, 224207 (2006).

Y. Tiwary and K. Fichthorn,
Phys. Rev. B **78**, 205818 (2008).

	Interaction Energy (eV)						
	FLG	n=18	n=14	n=10	n=6	n=4	Connector
$N1$	-0.091	-0.086	-0.092	-0.095	-0.093	-0.094	.
$N2$	0.050	0.050	0.052	0.053	0.053	0.062	.
$N3$	0.043	0.047	0.046	0.044	0.025	.	.
$N4$	0.045	0.045	0.040	0.045	0.039	0.041	.
$N5$	0.036	0.009	.	.	.	.	.
$N6$	0.010	0.010	0.010	0.009	0.011	.	.
$T1$	-0.006	-0.015	.	.	.	.	.
$T2$	-0.057	-0.067	-0.062	-0.052	-0.033	-0.021	.
$T3$	-0.049	-0.030	-0.015	-0.008	.	.	.
$T4$	-0.026	-0.038	-0.030	-0.032	.	.	.
$T5$	0.005	0.003	0.000	.	.	.	.
$T6$	-0.025	0.002	0.014	.	.	.	.
$Q1$	0.071	0.093	0.081	0.052	.	.	.
$Q2$	0.042	0.067	0.060	0.039	.	.	.
$Q3$	0.051	0.044	0.023	.	.	.	.
$Q4$	0.034	0.023	.	.	.	.	.
$Q5$	0.027	0.022	.	.	.	.	.
$F1$	-0.045	-0.058	-0.023	.	.	.	.
CV	0.014	0.021	0.009	0.009	0.013	0.020	0.007
$\epsilon(eV/atom)$	0.030	0.014	0.018	0.018	0.018	0.022	0.006

Are Huts Thermodynamically Stable?

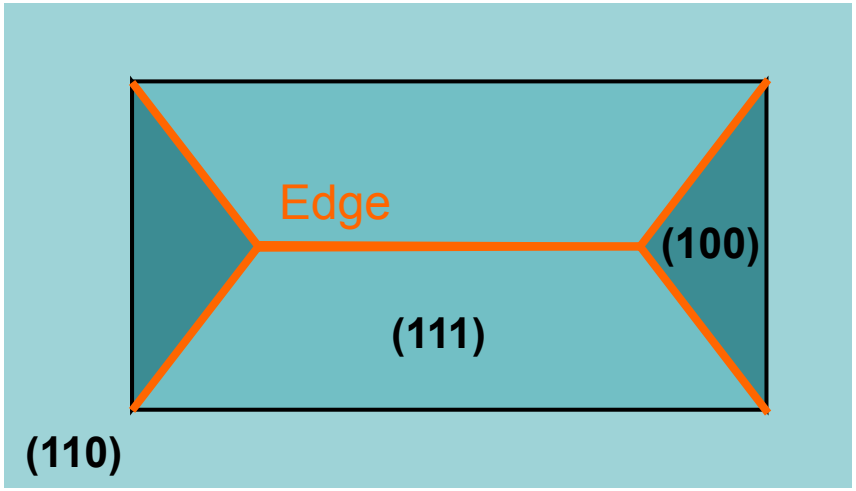
Hut Formation Energy

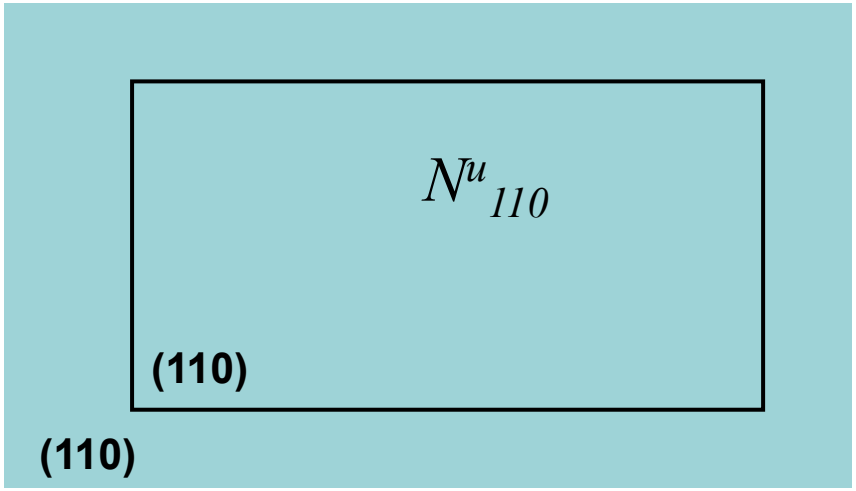
γ = Surface Energy (eV/atom)

N = # atoms

$$\Delta E_{hut} = E_{substrate+hut} - E_{substrate+ML}$$
$$= \left(N^{f}_{111}\gamma_{111} + N^{f}_{100}\gamma_{100} + N^{f}_{edge}\gamma_{110}\right) - N^{u}_{110}\gamma_{110}$$

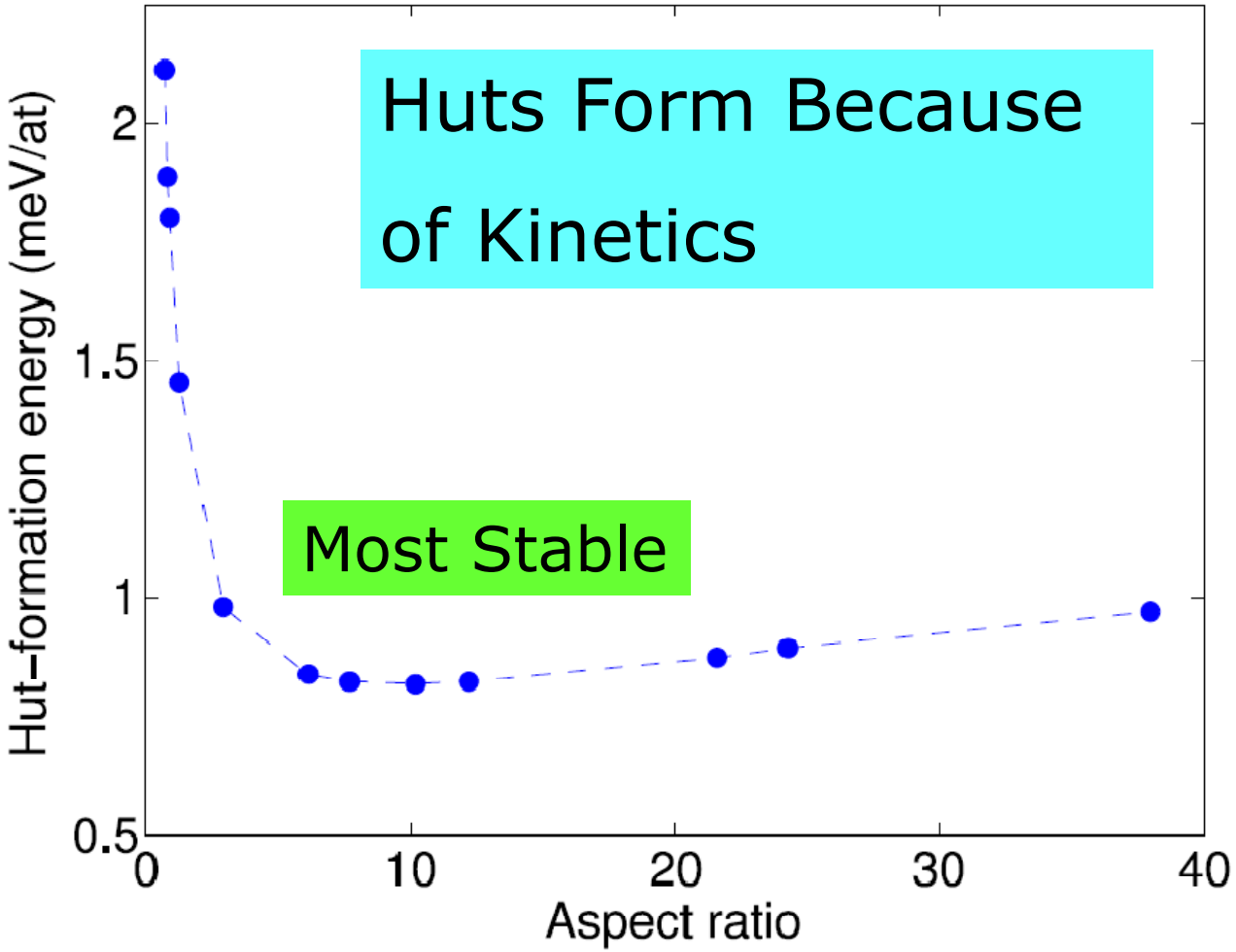
γ_{110} = 0.665 eV/atom, γ_{100} = 0.454 eV/atom, γ_{111} = 0.342 eV/atom





If $\Delta E_{hut} < 0$, Hut Favored Over Layer

Huts Are Not Energetically Favored



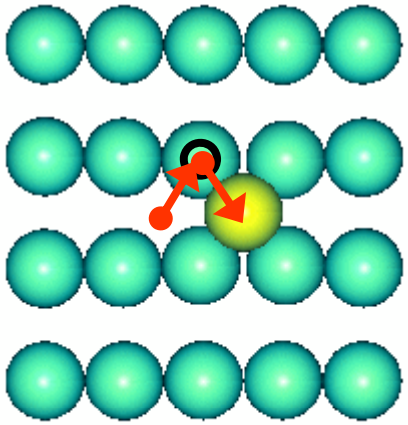
Consistent with Experiment….

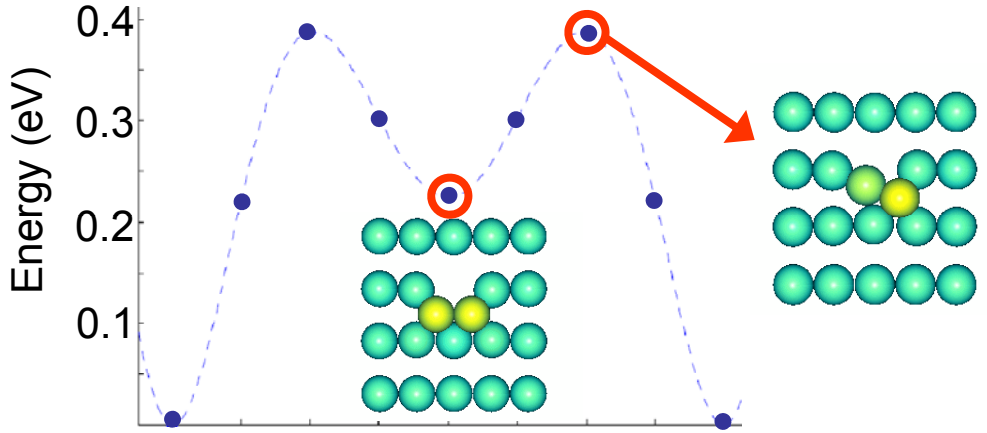
Bautier de Mongeot *et al.*, *Phys. Rev. Lett.* **91**, 016102 (2003).

Al Diffusion on Al(110)

Climbing-Image Nudged-Elastic Band Method
G. Henkelman, B.Uberuaga, and H. Jonsson, J. Chem. Phys. 113, 9901 (2000)

In-Channel





Local Minima in the Diffusion Pathway

ΔE = 0.40 eV
Stumpf: 0.33 eV
Zhu: 0.33 eV

R. Stumpf and M. Scheffler, Phys. Rev. B **53**, 4958 (1996).
W. Zhu et al., Phys. Rev. Lett. **92**, 106102 (2004).
Y. Tiwary and K. Fichthorn, *Phys. Rev.* B **81** 195421 (2010)

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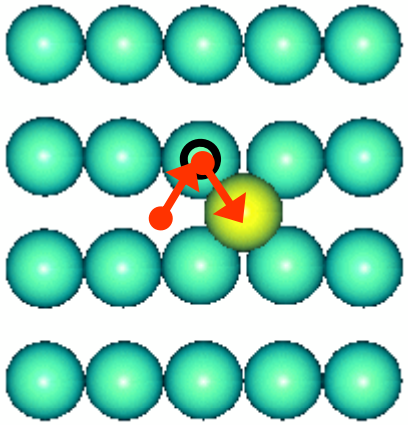

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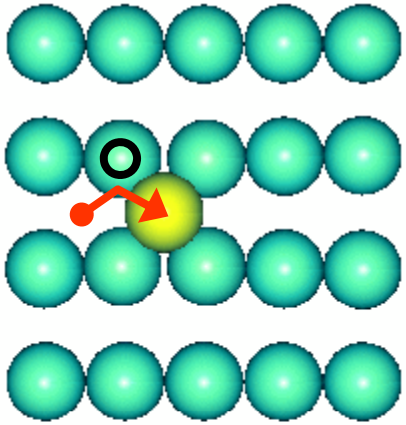
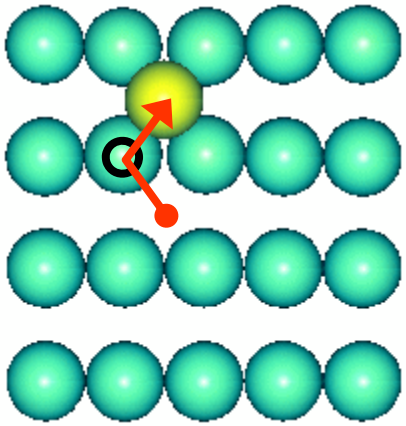
In-Channel



ΔE =0.38 eV

Cross-Channel

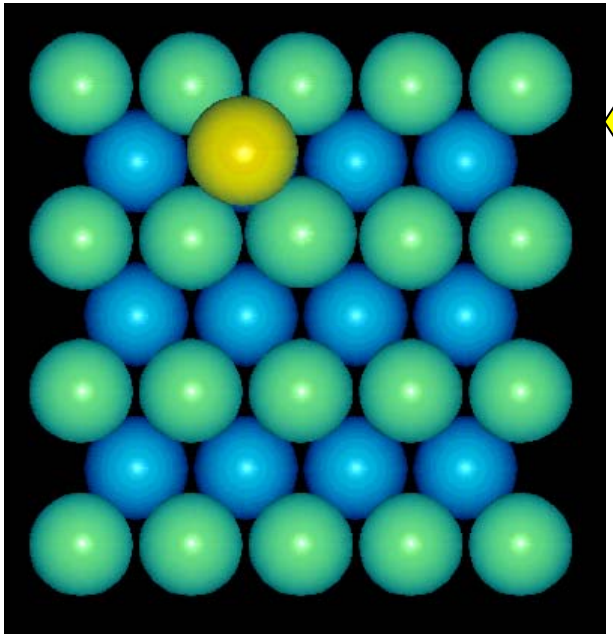


ΔE = 0.38 eV
Stumpf: 0.62 eV
Zhu: 0.49 eV

Isotropic Diffusion…

R. Stumpf and M. Scheffler, Phys. Rev. B **53**, 4958 (1996).
W. Zhu et al., Phys. Rev. Lett. **92**, 106102 (2004).
Y. Tiwary and K. Fichthorn, *Phys. Rev.* B **81** 195421 (2010)

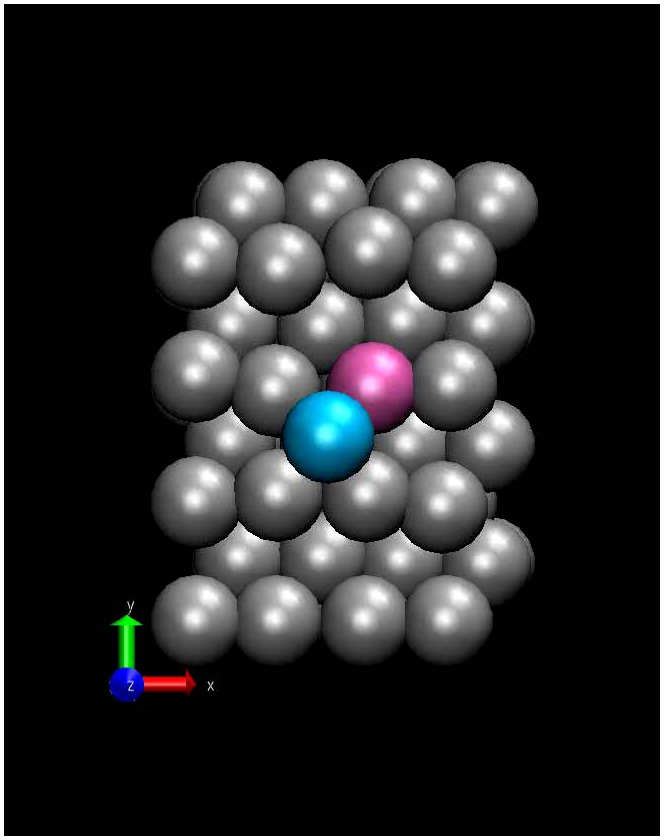
Accelerated Ab Initio MD

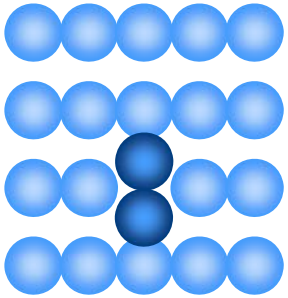


Climbing-Image Nudged Elastic Band Method

vs.

Accelerated AIMD

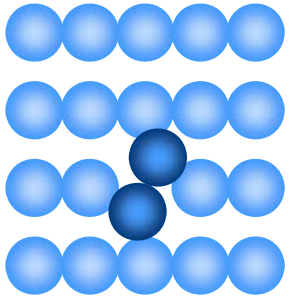




E_B = 0.38 eV

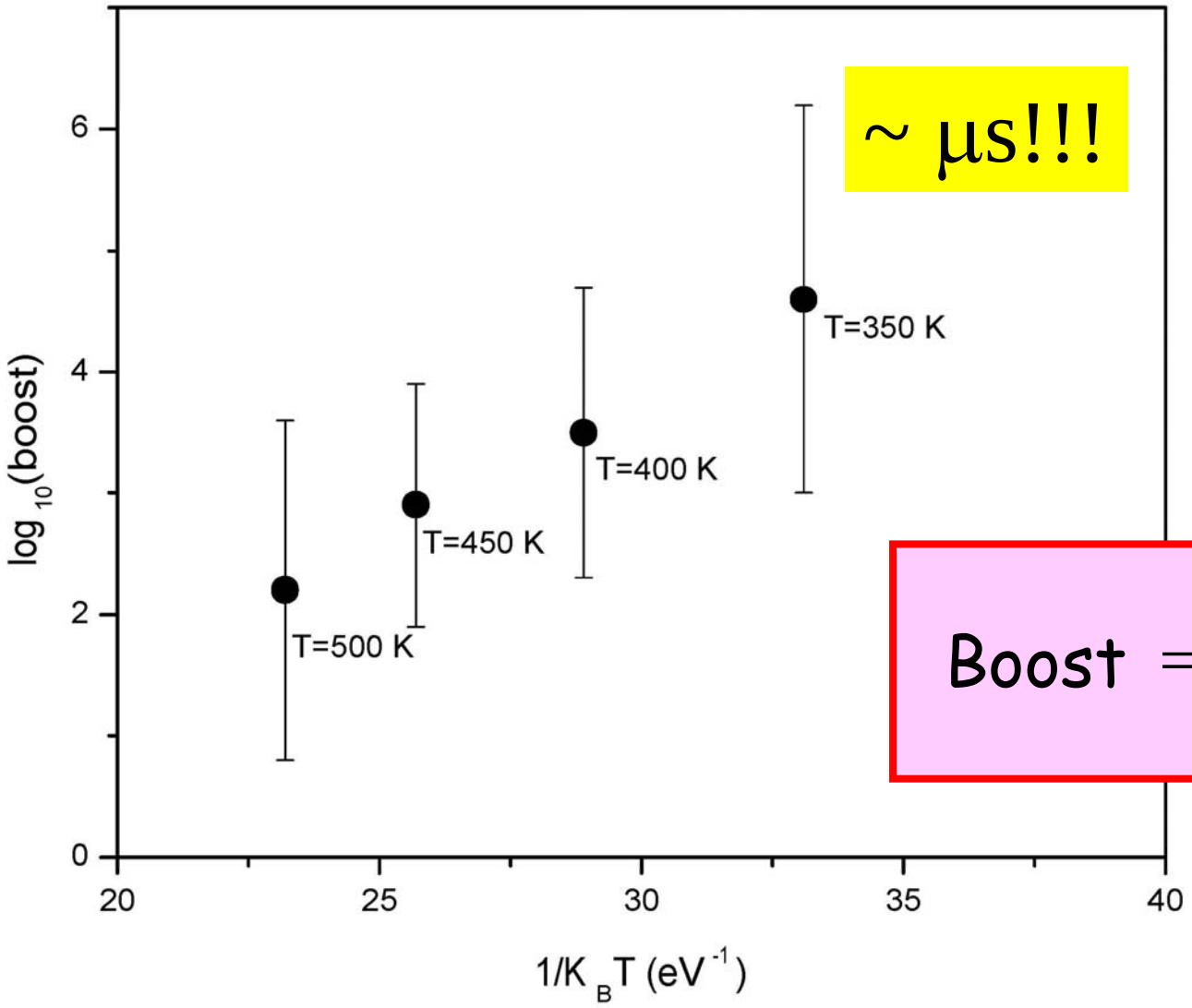
Cross-Channel Diffusion Is Faster!

K. Fichthorn et al., *J. Phys. Cond. Matt.* **21**, 084212 (2009).



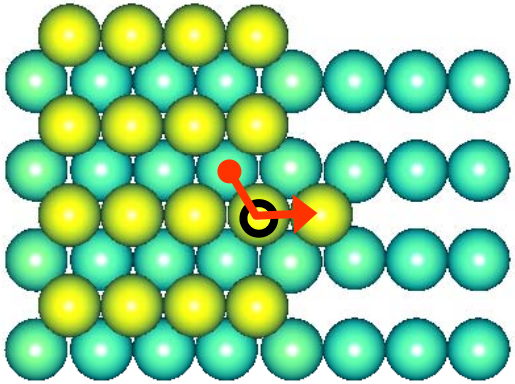
E_B = 0.33 eV

The Boost in *ab initio* MD

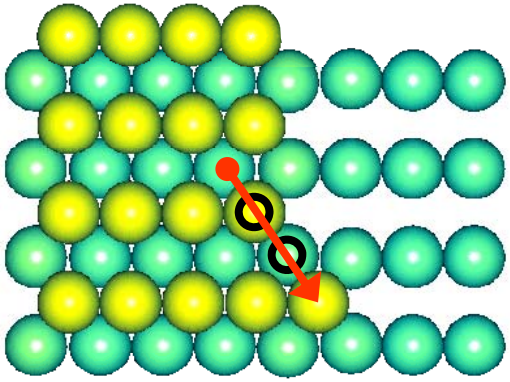


$$\text{Boost} = \left\langle \exp\left(\frac{\Delta V}{kT} \right) \right\rangle$$

Diffusion Up and Down Steps: Diagonal Dominance

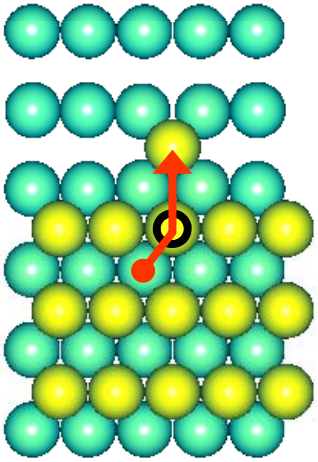


(100) Step

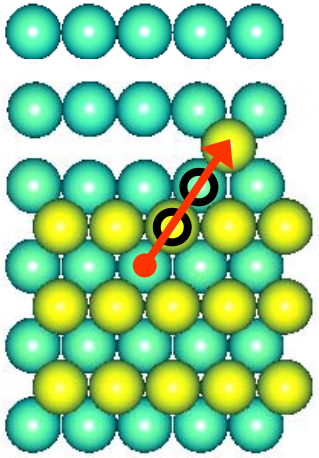


Up (Down): 0.58 (0.44)
Zhu : 0.60 (0.43)

Up (Down): 0.49 (0.36)



(111) Step



Up (Down): 0.65 (0.68)
Zhu : 0.67 (0.71)

Up (Down): 0.58 (0.62)

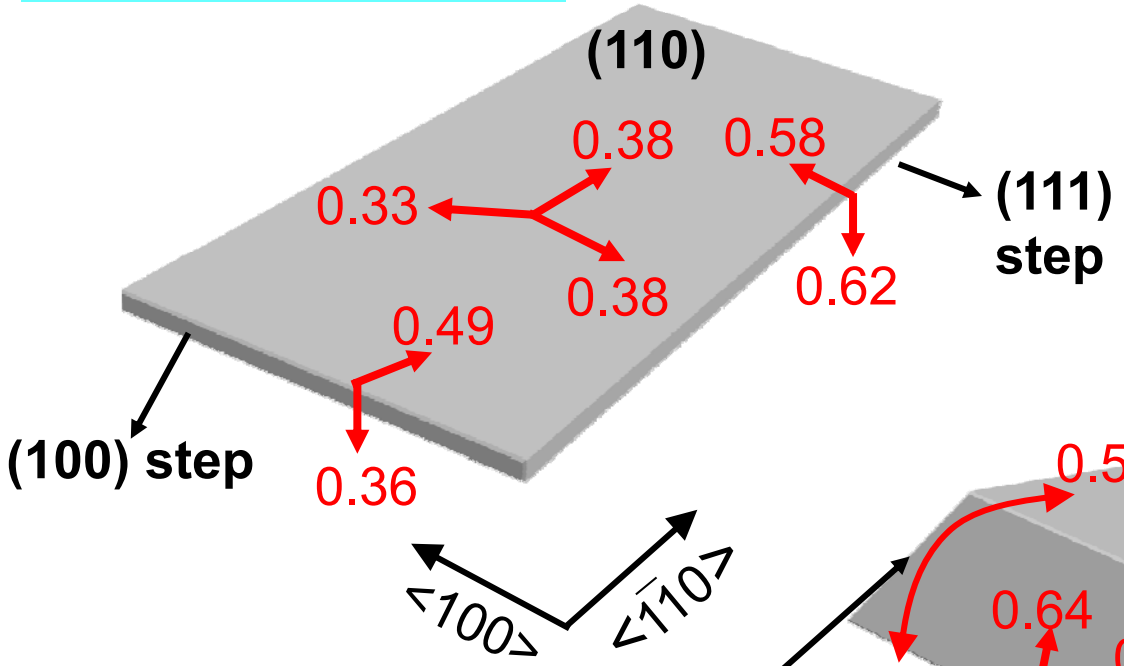
Zhu et al., PRL **92** 106102 (2004)
Y. Tiwary and K. Fichthorn PRB **81**, 195421 (2010).

Barriers for Single-Atom Hops (eV)

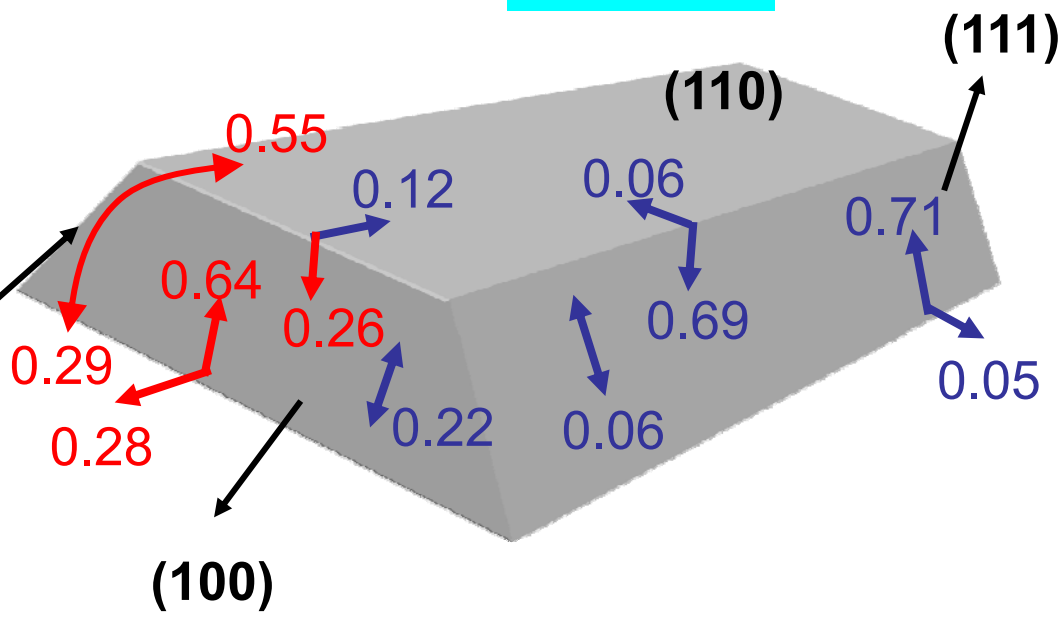
Mono-Atomic
High Island

New Mechanisms

Old Mechanisms



3D Hut

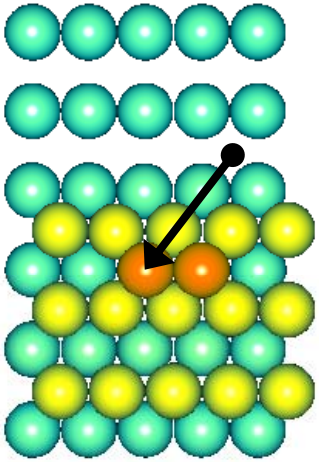


On a 2-Layer Facet

Y. Tiwary and K. Fichthorn , Phys. Rev. B **81**, 195421 (2010).

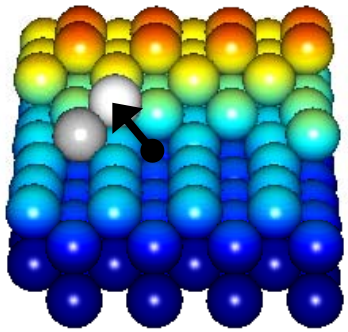
Co-operation Between Atoms

Atoms Pull Others Up



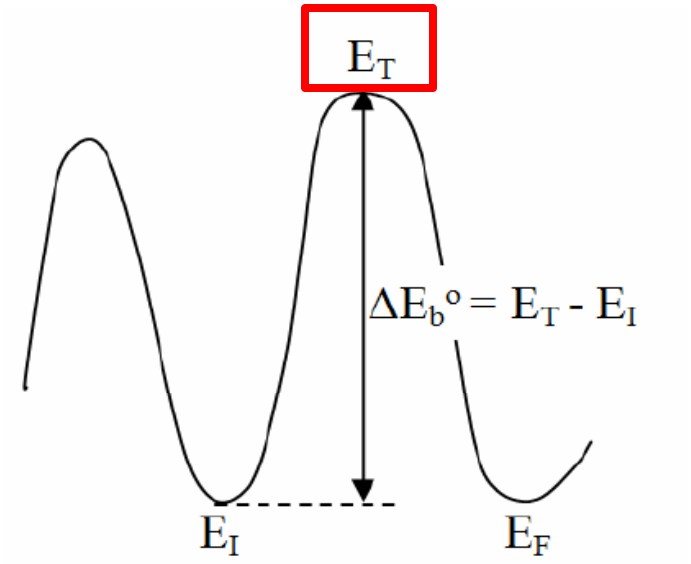
0.50 vs. 0.58 eV (isolated)

Atoms Push Others Up



0.47 vs. 0.67 eV (isolated)

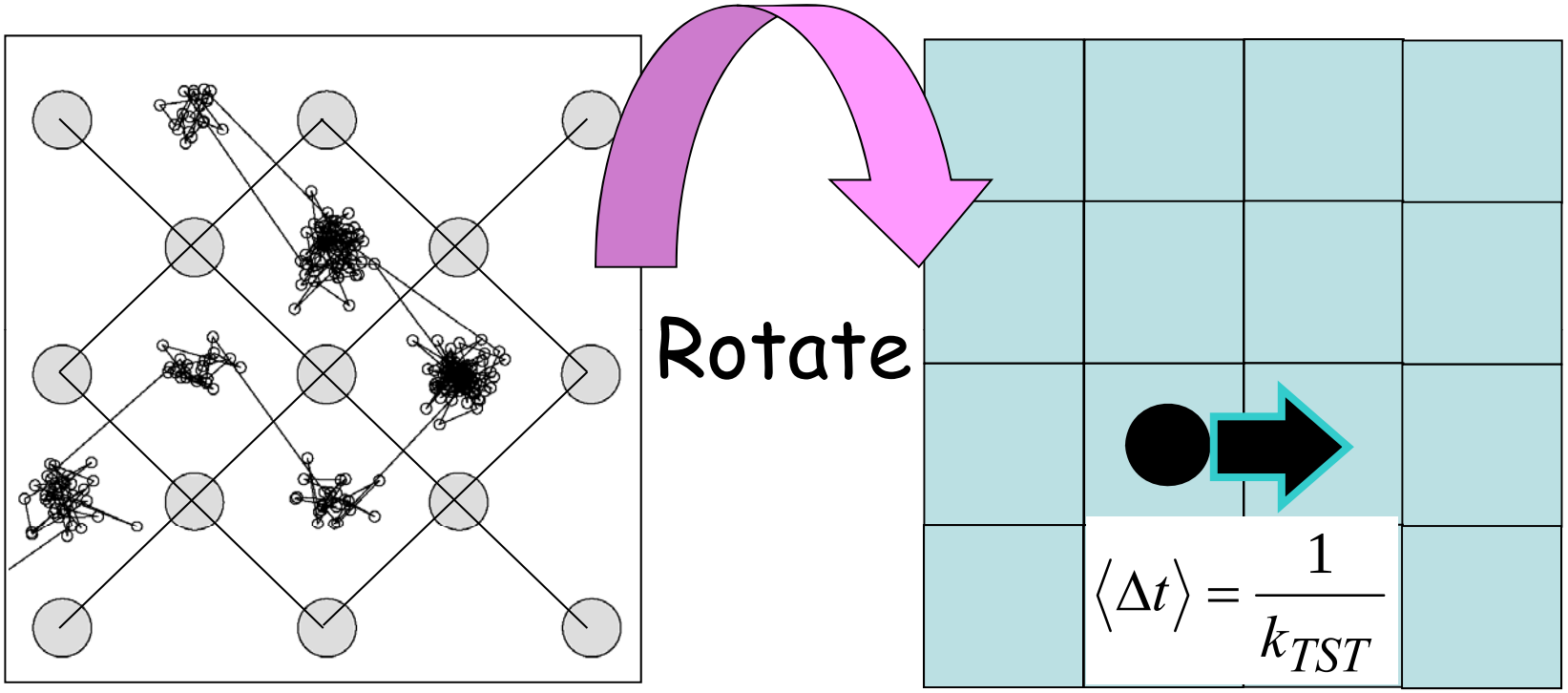
Transition-State Interactions are Important!



Y. Tiwary and K. Fichthorn , Phys. Rev. B **81**, 195421 (2010).

Kinetic Monte Carlo: Coarse-Graining MD

K. A. Fichthorn and W. H. Weinberg, J. Chem. Phys. 95, 1090 (1991).



MD of Co on Cu(001): The Whole Trajectory

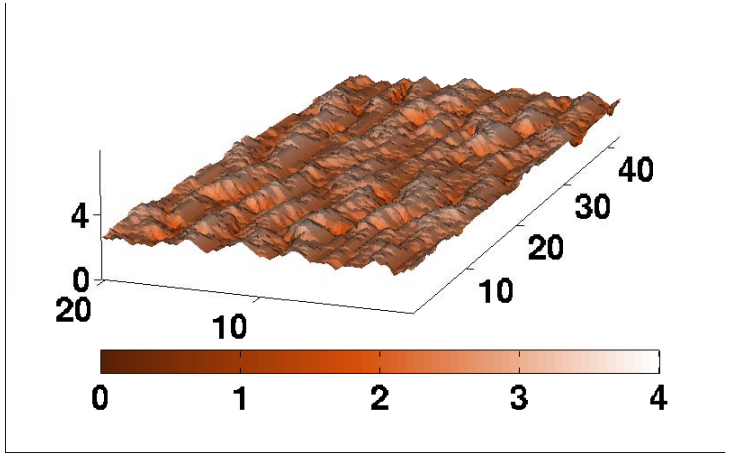
kMC: Coarse-Grained Hops

Rare Events: $k_{TST} = \left\langle \frac{\nu}{2} \right\rangle \frac{\int \delta(\mathbf{R}-\mathbf{R}^{\dagger}) \exp(-V(\mathbf{R})/k_B T)}{\int \exp(-V(\mathbf{R})/k_B T)}$

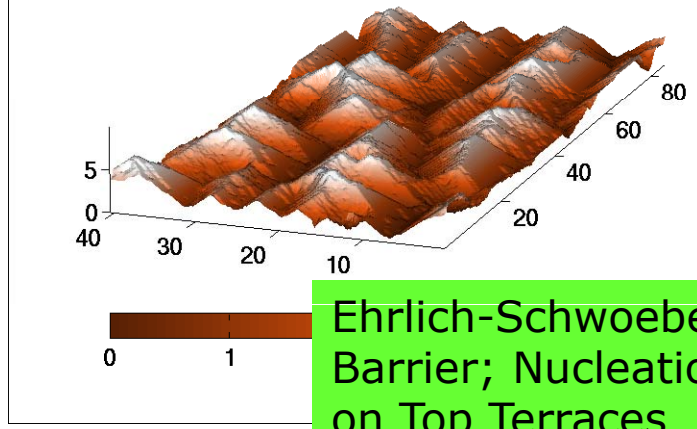
KMC Simulations of Al(110) Homoepitaxy

T=150 K; θ=20 ML

Dimensions in nm

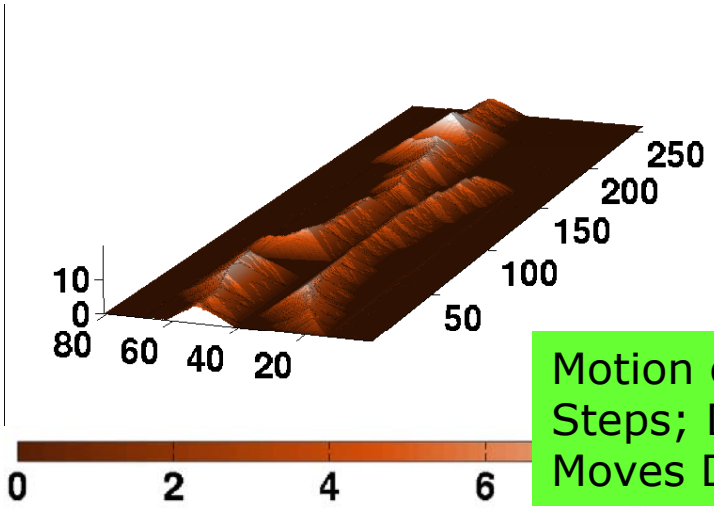


T=200 K; θ=20 ML

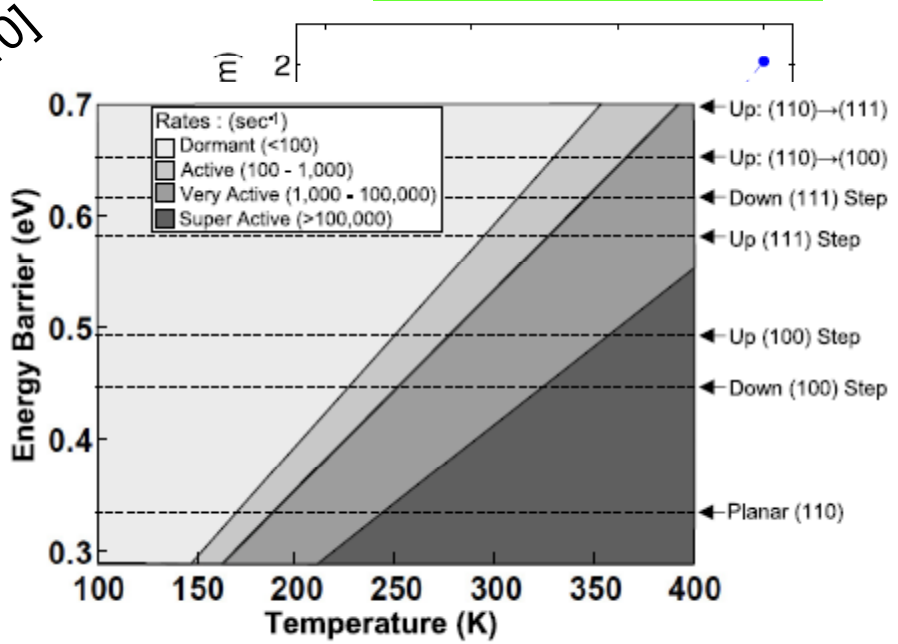


Ehrlich-Schwoebel Barrier; Nucleation on Top Terraces

T=250 K; θ=10 ML

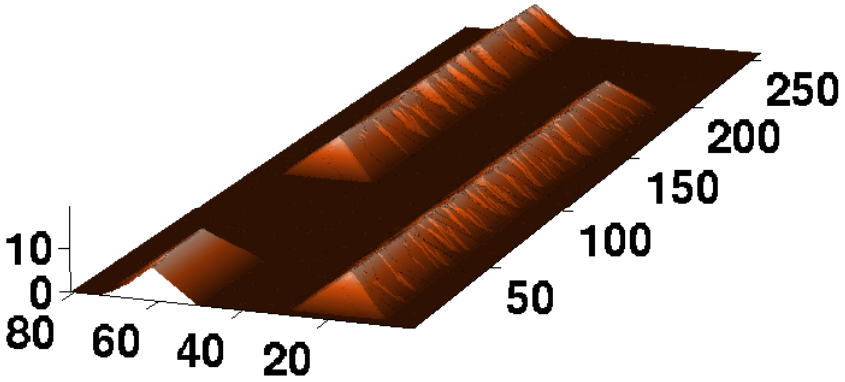


Motion on (100) Steps; Downward Moves Dominate



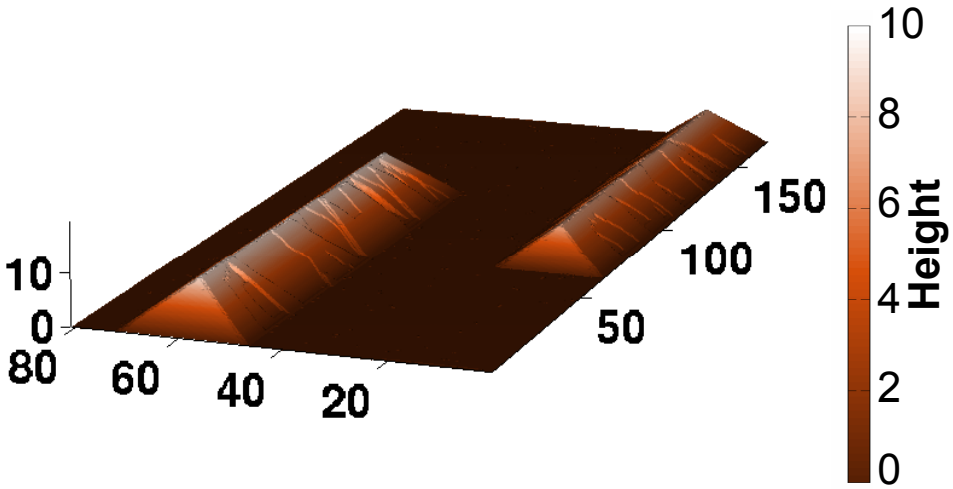
KMC Simulations: Rising Huts

T=350 K, θ=10 ML
(F=150 ML/min, θ=0.25 ML)



Aspect Ratio ≈ 8:1

T=400 K, θ=10 ML
(F=350 ML/min, θ=0.25 ML)

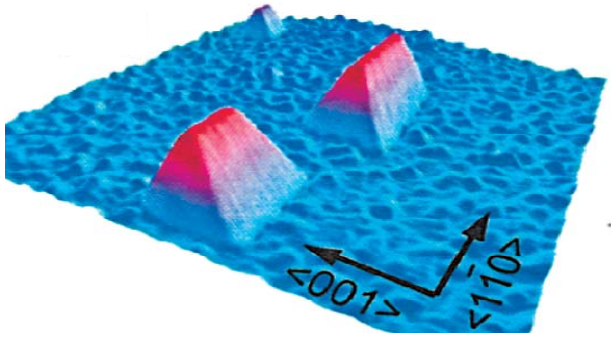


Aspect Ratio ≈ 5:1

Experiment (AFM)

Bautier de Mongeot *et al.*, *Phys. Rev. Lett.* **91**, 016102 (2003).

Zhu et al., Phys. Rev. Lett. **92**, 106102 (2004).



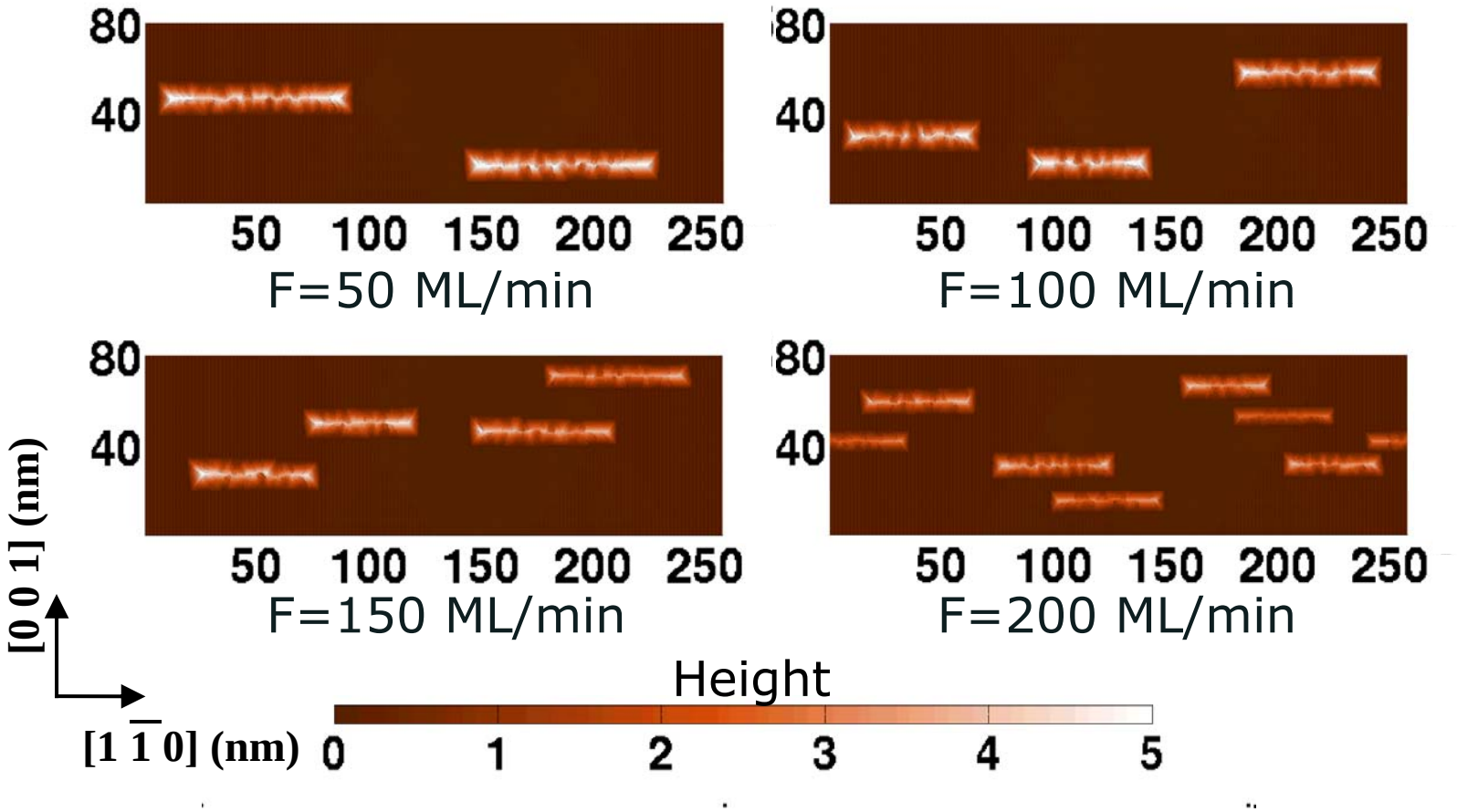
All dimensions in nm

T=450 K, F=1 ML/min,
θ=10 ML

Aspect Ratio ≈ 3:1

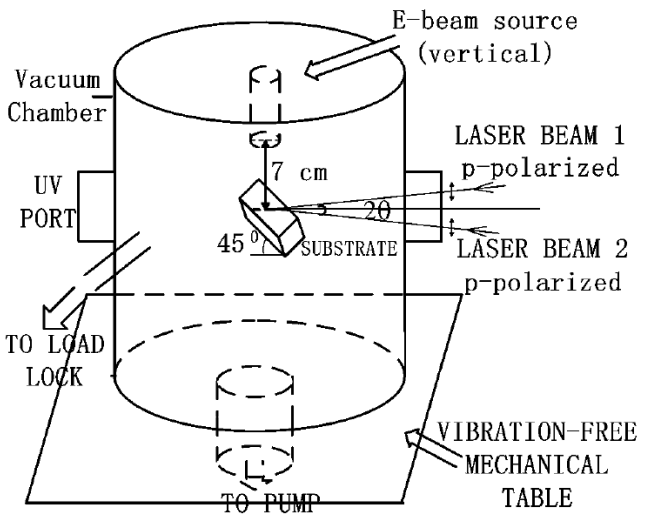
KMC: Controlling Hut Density via Flux

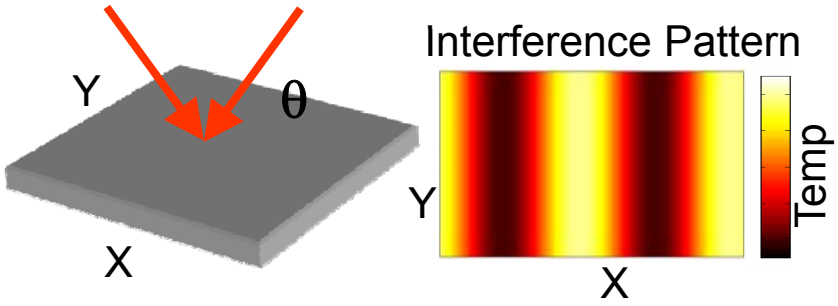
(T=325 K, θ=2 ML)



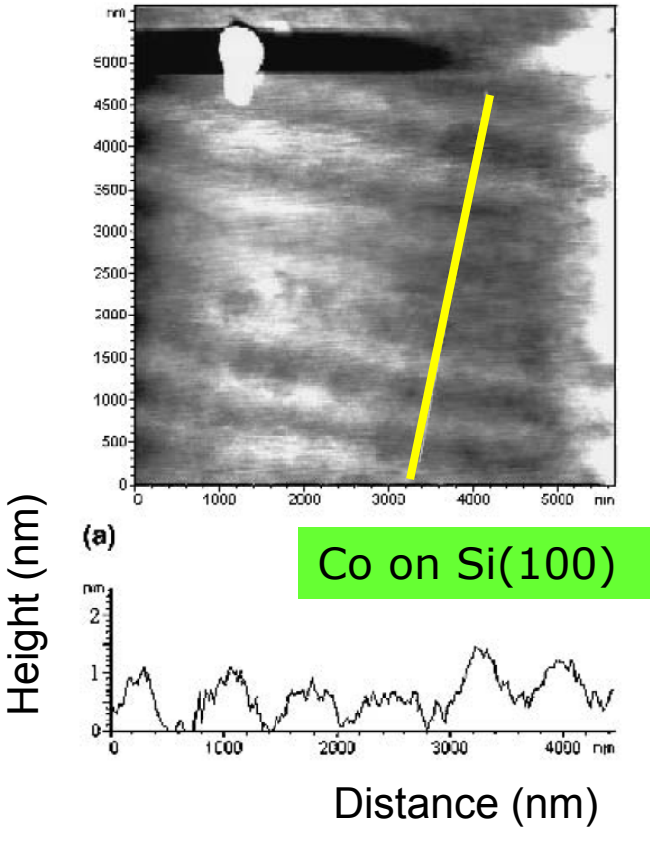
Now All We Need is Good Hut Placement

Hut Positioning: Pulsed Dual-Beam Laser Interference





Zhang & Kalyanaraman,
J. Mater. Res. **19**, 595 (2004)



Co on Si(100)

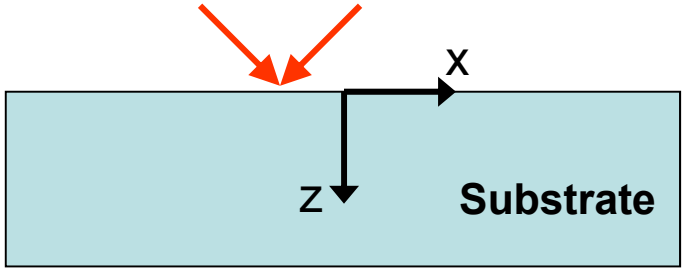
Laser Interference Parameters:

Temperature:
Energy Density of Laser
(5 mJ/cm^2 = 50 K)

Fringe Width or Wavelength (532 nm):
Wavelength of Laser (266 nm)
Interference Angle (29^o)

Temperature Profile: Pulsed Two-Beam Interference

$$\rho c_p \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial z^2}\right) + q$$



T(x,z,t): Temperature, ρ: Density, c_p: Specific heat,
k: Thermal conductivity

Power Generation

$$q = \alpha \frac{E(x)}{\sigma\sqrt{2\pi}} exp\left(-\frac{(t-t_p)^2}{2\sigma^2}\right)(1-R)exp(-z\alpha)$$

t_p: Pulse width of laser beam, α: Absorption coefficient, R: reflectivity

Interference Intensity

$$E(x) = 2E_o\left[cos\left(\frac{2\pi x}{\Lambda}\right) + 1\right]$$

E_o: Energy density of incident laser beam

Fringe Width

$$\Lambda = \lambda/[2Sin(\theta)]$$

λ: wavelength of laser

θ: Interference angle

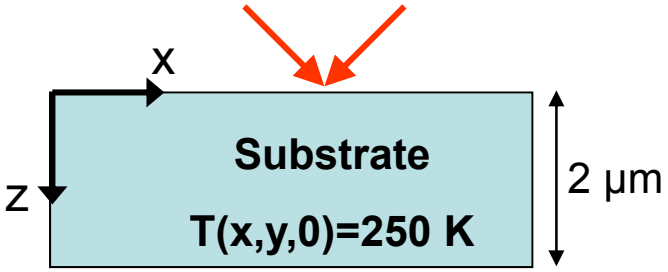
Lasagni *et al.*, Appl. Surf. Sci. 247, 32 (2005)

Temperature Profile

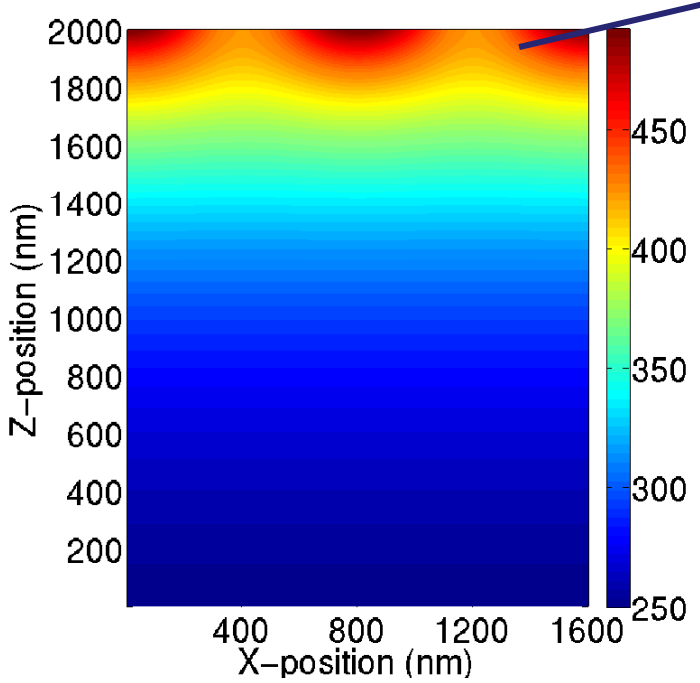
λ=266 nm, *t=Pulse Width* (t_p=9 ns)

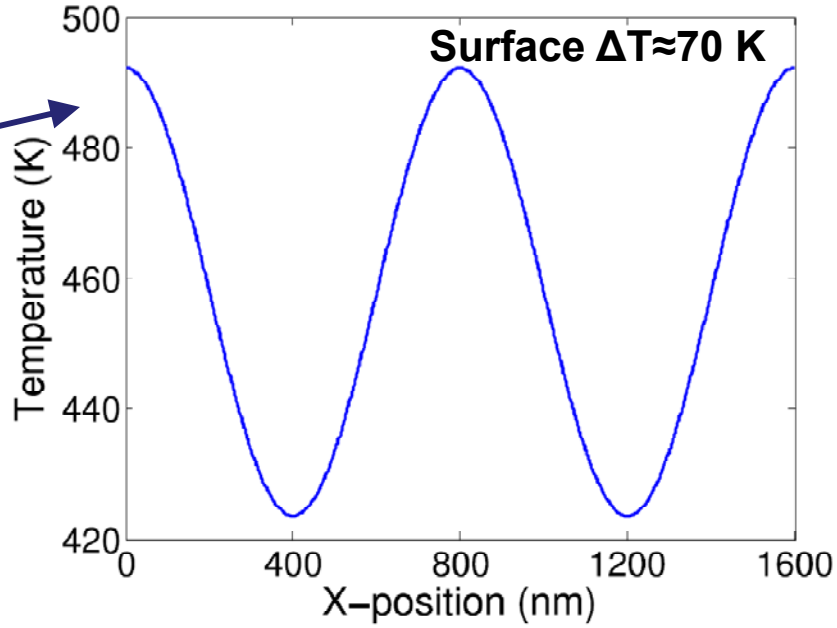
Optical Properties of Aluminum:

Weaver *et al.*, Physics Data, Optical Properties of Metals, Vol. 18 (1981)



E=0.4 J/cm², Λ=800 nm
(Nanohut spacing at 450 K)

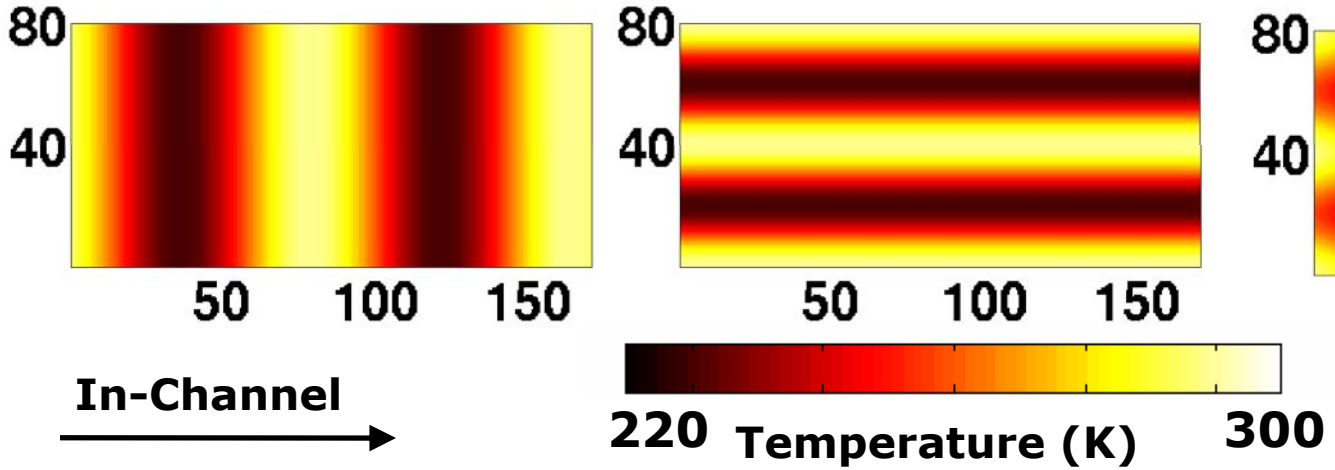


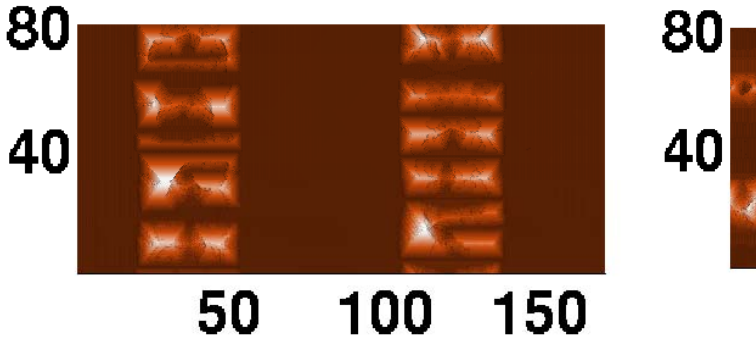


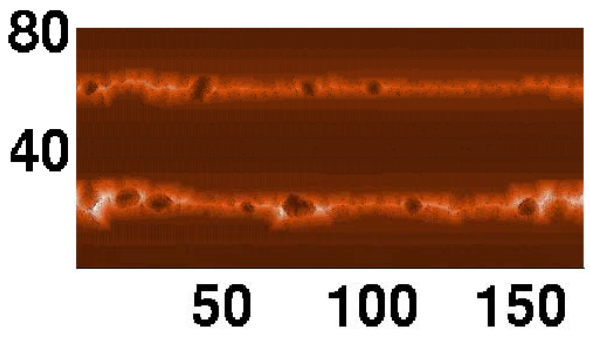
Significant temperature gradients for relevant spacings!

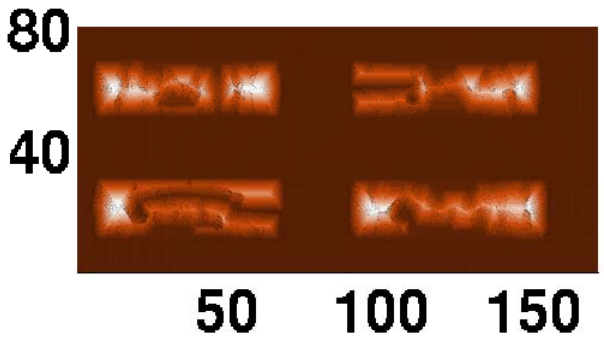
KMC Simulation of Hut Placement

Dual/Four-Beam Laser Interference , F=1 ML/min, θ=5 ML









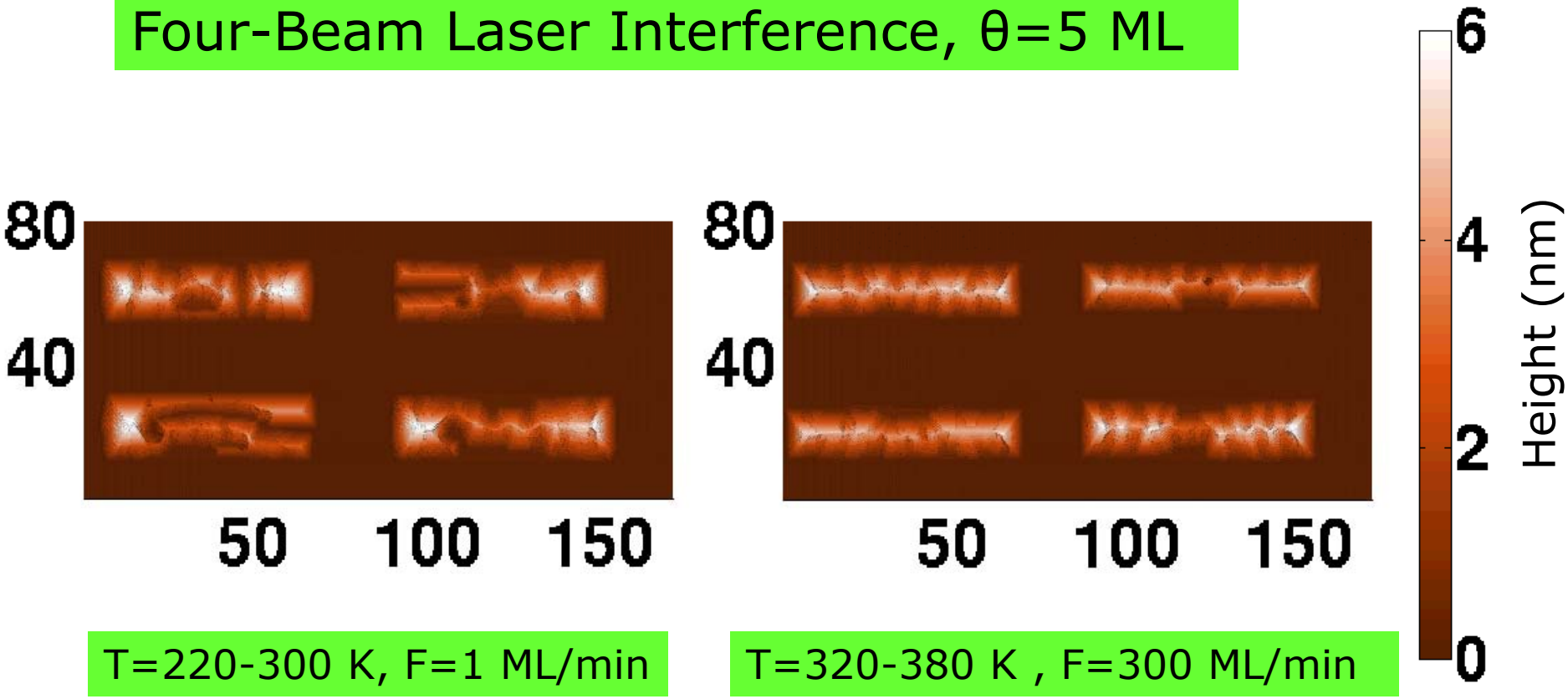
Nano-Ripples

Array of Mounds

Dimensions in nm

KMC Simulation of Hut Placement

Four-Beam Laser Interference, θ=5 ML

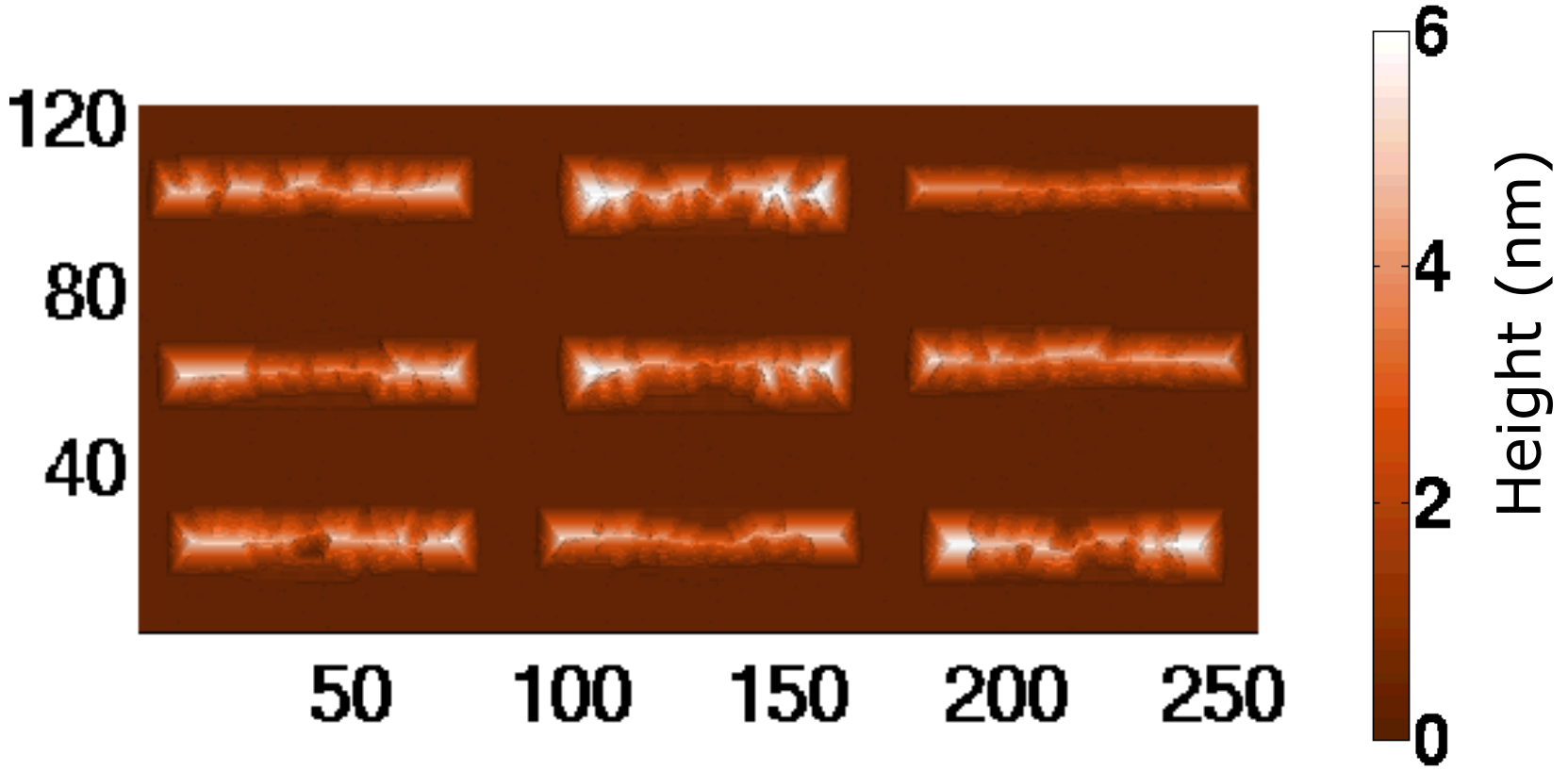


T=220-300 K, F=1 ML/min

T=320-380 K , F=300 ML/min

Tune Hut Morphology by Adjusting Temperature

KMC: Four-Beam Laser Interference



T=300-360 K, F=200 ML/min, θ=5 ML

Conclusions

- Al(110) [and possibly other fcc(110)]
  Homoepitaxy is Interesting:
  Increased Roughening with Increasing Temperature: HUTS

- Many-Body Interactions and Diffusion are Key
  - Connector Model
  - Ab initio Accelerated Molecular Dynamics

- Hut Placement by Pulsed Dual- or Four-Beam Laser Interference