Temperature-accelerated dynamics and KMC simulations of metal epitaxial growth

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- Introduction: *Parallel kinetic Monte Carlo (KMC) and temperature-accelerated dynamics (parTAD)* *Y. Shim and J.A., PRB (2005), Y. Shim et al, PRB (2007)*

APPLICATIONS:

- Vacancy formation and strain in low T Cu/Cu(100) growth

  Y. Shim, V. Borovikov, B.P. Uberuaga, A.F. Voter, and J.G. Amar, PRL (2008)

- Complex behavior in a simple system: low-T Ag/Ag(100) growth revisited *Y. Shim and J.A., Phys. Rev. B (2010); Y Shim and J.A., Phys. Rev. B (2011).*

- Effects of strain on island-shape in Cu/Ni(100) growth

  Y. Shim and J.A., Phys. Rev. Lett. (2012)

- Conclusions

THE UNIVERSITY OF TOLEDO 1872

Supported by NSF DMR

OSC

Modeling Thin-Film Growth

The ability to probe and manipulate matter on an atomic scale has made it possible to grow thin-films with novel structures and materials properties

- High purity crystal layers
- Heterostructures, quantum dots and wires

  "Nanotechnology"

- Thin-films for industrial applications

  "Coatings, Photovoltaic devices, Sensors"

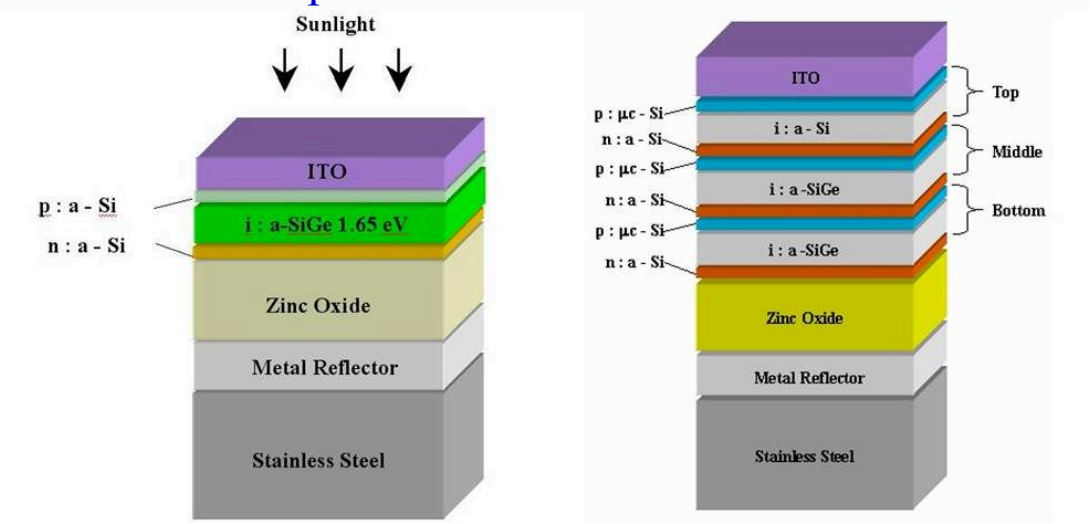
Understanding thin-film growth is a challenging scientific and technical problem

"Surface and Interface Physics"

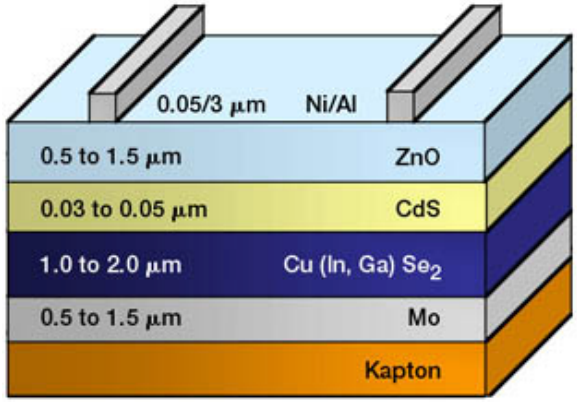
"Far-from-equilibrium growth"

Thin-Film Solar Cells

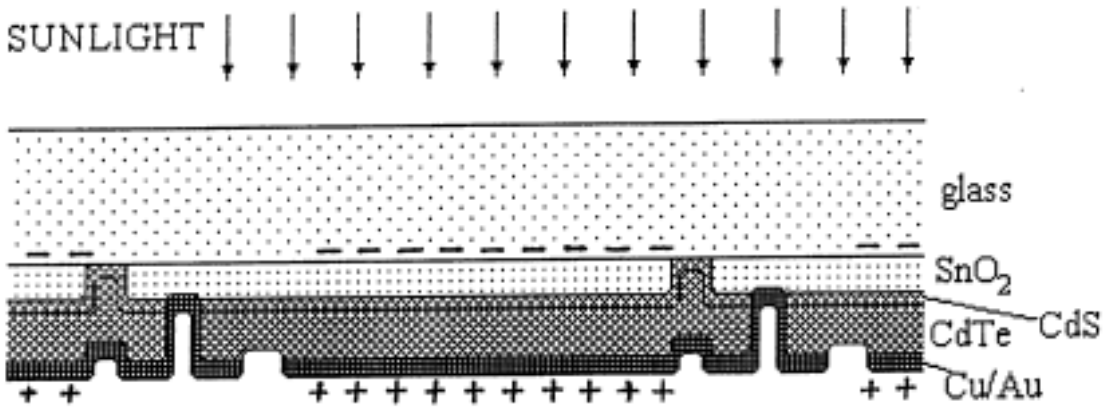
Amorphous silicon



CIGS

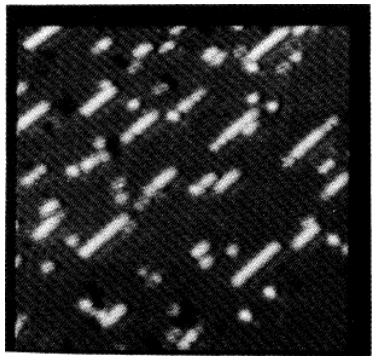


CdTe



Two Regimes in Thin-film Growth

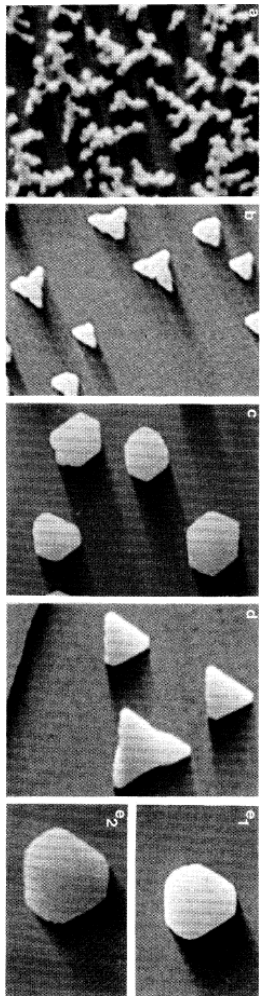
Submonolayer (nucleation) Regime

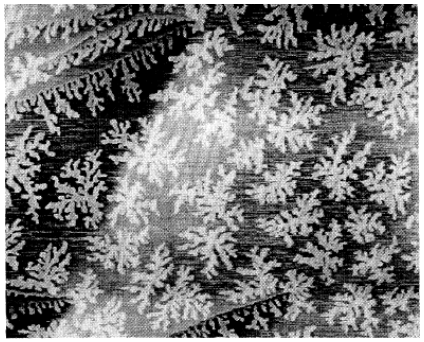


Si/Si(001)

Pt/Pt(111)

Low T

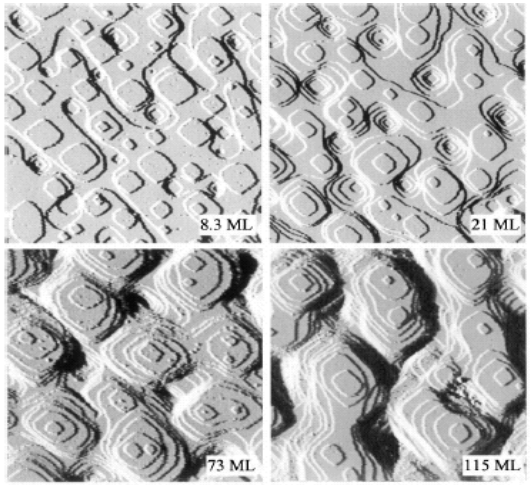




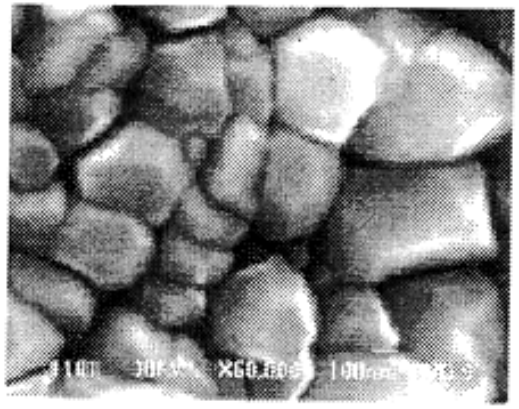
Au/Ru

High T

Multilayer Regime



Cu/Cu(100)



CdTe/glass

Theoretical Approaches

* • Kinetic Monte Carlo Simulations — *Atomic Scale*

  'TETRIS'

1D thin-film growth

* • Analytical Calculations — *Mesoscopic Scale*

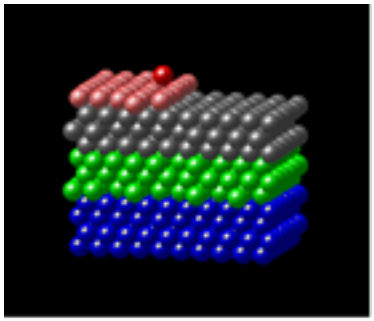
  Surface current, island density

* • Rate Equations — *Mesoscopic Scale*

  Ignore fluctuations, mean field

* • Molecular Dynamics

  simulate dynamical processes on atomic scale



Cu/Cu(100) deposition

• Accelerated Dynamics

extend molecular dynamics to experimental timescales

Other Theoretical Approaches

- Density Functional Theory (DFT) *Atomic Scale*

  Quantum-mechanical calculations of activation energies, atomic-scale structures

- Solution of Continuum Equations *Macroscopic Scale*

$$\frac{\partial h}{\partial t} = -\nu_2 \nabla^2 h \; - \nu_4 \nabla^4 h \; + \lambda_2 |\nabla h|^2 \; + \lambda_4 \nabla^2 (|\nabla h|^2) \; + \xi$$

Evap. Step barrier/ attraction — *Surf. Diffusion* — *Void formation (sideways growth)* — *Density Fluctuations* — *Dep. noise*

Y. Kryukov, N. Podraza, R. Collins, and J.A., Phys. Rev. B (2009)

Kinetic Monte Carlo (KMC)

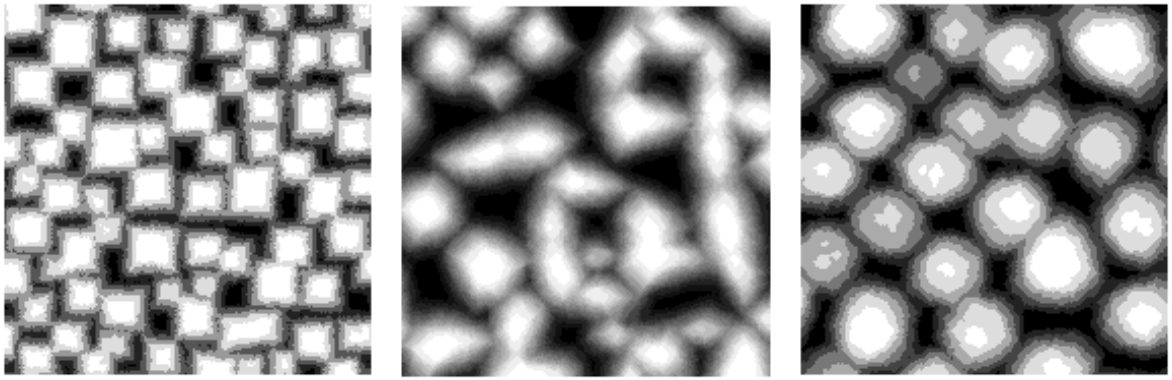
- Extremely efficient method to carry out dynamical simulations of a wide variety of stochastic and/or thermally activated processes when relevant atomic-scale processes are known

Applicable to Markov processes (no correlations between events)

Discard short-time motions of atoms (vibrations) and focus on activated events

- Serial KMC simulations have been used to model a variety of non-equilibrium processes ranging from catalysis to thin-film growth

n = 1/4 **n = 1/3** **n = 1/4**



Edge-diffusion **Edge + Corner** **Reversible growth**

J.A. (PRB 99)

KMC Algorithm

(1) Update list of all possible events (transitions) that can occur and rates for each event: assume each event i has rate R_i

Calculate total event rate $R_T = \Sigma R_i$

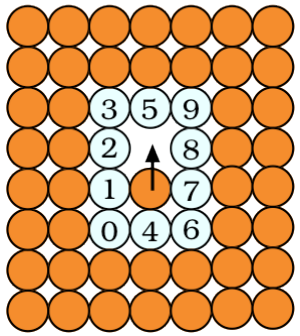
Select event j to occur with probability $P_j = R_j/R_T$

Perform event j

Update time $t = t - ln(\xi)/ R_T$ where ξ is a uniform random number between *0* and *1*

Go to (1) and repeat

Note: typically event rate $R_i = \nu_i \, exp(-E_a/k_BT)$ where E_a is activation barrier, T = temperature, and ν_i = prefactor (10^{12} s^{-1}) depend on ***local environment***



Limitations of kinetic Monte Carlo

In presence of low-barrier repetitive events (e.g. edge-diffusion, vacancy diffusion) simulation slows down significantly- computational time is wasted doing repetitive events

Possible Solutions

- First-passage-time KMC (FPKMC)

  G. Nandipati, Y. Shim and J.G. Amar, PRB 2010

  Calculate "escape-times" from basins (such as diffusion along an island edge)

- Parallel KMC

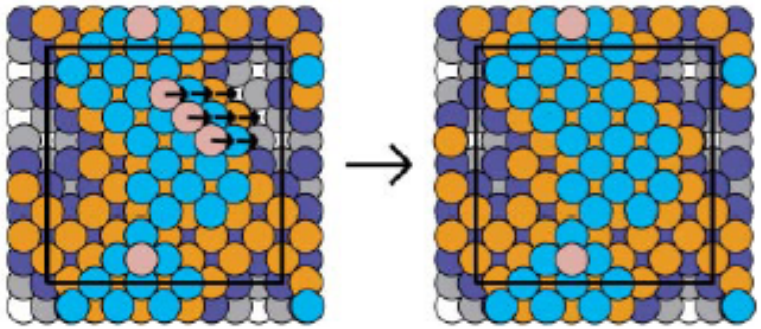
  Y. Shim and J.G. Amar, PRB 2005, G. Nandipati, J.Amar et al, J. Phys. Cond. Mat 2009

  Limited number of processors, each processor still slowed down by repetitive low barrier events

Problems with kinetic Monte Carlo

- Kinetic Monte Carlo simulations are limited by requirement that catalog of *all relevant processes* and rate constants must be specified

Since relevant transition mechanisms often involve ***concerted motion****, they may be difficult to predict and so it may be effectively impossible to pre-calculate all transitions*



8-atom concerted mechanism *observed in TAD simulations of Cu/Cu(100) epitaxial growth:* $E_a = 0.046$ *eV (45.2 ns at 77 K)* *Voter et al, Annu. Rev. Mater. Res. (2002)*

Even if relevant transition mechanisms are ***known****, it may still be effectively impossible to pre-calculate rates for all transitions due to* ***range of interactions*** *and/or* ***multiplicity of states***

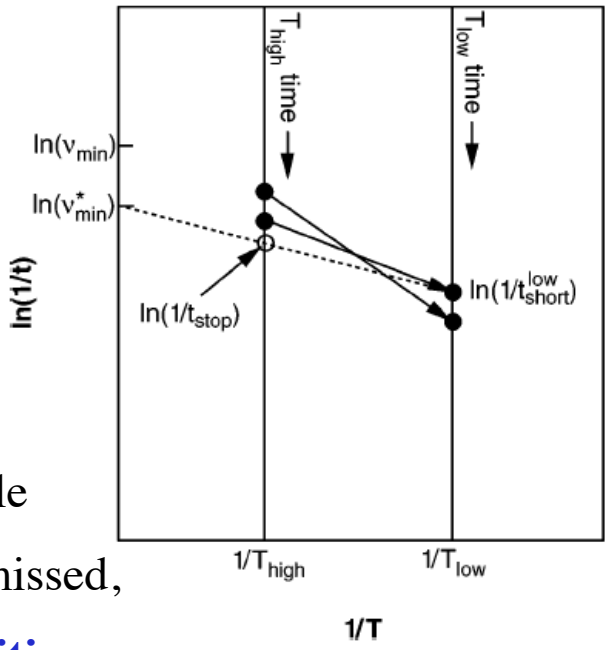
Temperature Accelerated Dynamics (TAD)

Sorensen & Voter, 2000

- Accelerate dynamics of infrequent events (transitions) by carrying out **basin-constrained MD** simulation at **high temperature T_{high}**

- Determine activation energy E_a for each high-T event, and use to obtain time t_{low} that event would have happened at **T_{low}**

- Assuming a minimum prefactor ν_{min} as well as acceptable **"confidence level"** that an 'earlier' event has not been missed, can use TAD to efficiently find **low-T sequence of transitions**



- **TAD can accelerate MD by factors as large as 10^6 !**

Realistic simulations of non-equilibrium processes over experimental time scales!

Perez, Uberuaga, Shim, Amar, Voter, Annu. Rep. Comp.Chem. (2009)

Problem: Serial TAD does not scale!

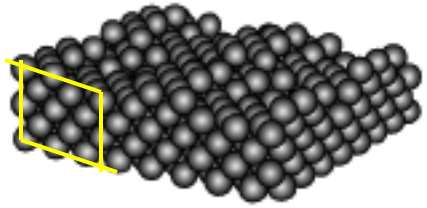
Computational work *w* scales approximately as $w \sim N^3$!

(where N = # of atoms in system)

$w \sim N^{3+1/3-\gamma}$ **where** $\gamma = T_{low}/T_{high}$ **for unlocalized saddle-point searches**

$N^{2-\gamma}$ **for localized saddle-point searches**

- As a result simulations of ***both*** extended time and length scales have ***not*** been possible.



Sim. cell repeated 4 times (2x2)

***Serial* TAD simulation of Ag/Ag (100) growth**
(Montalenti, Sorensen, Voter, PRL 2001)

SOLUTION: parallel TAD (Y. Shim et al, PRB 2007)

Synchronous sublattice (SL) algorithm

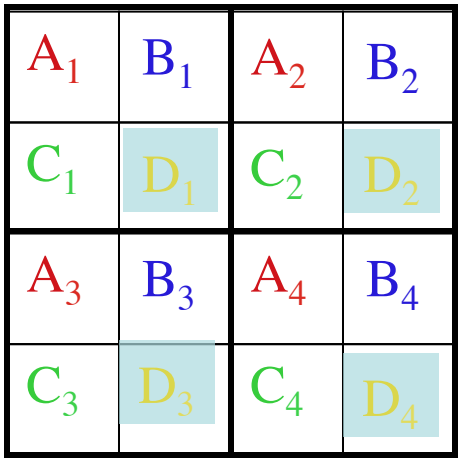
(Shim & Amar, PRB, 2005)

- System divided into different processor regions with each processor region divided into sublattices (A,B,C, or D)

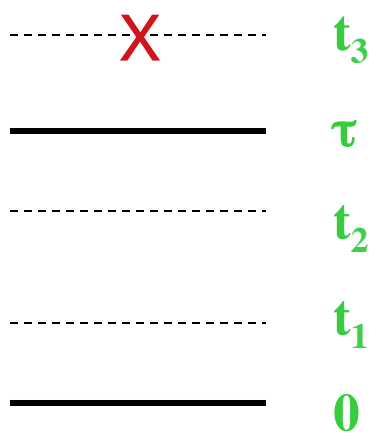
- At beginning of each synchronous cycle one sublattice in each processor's region is selected. All processors update atoms in selected sublattice only: **eliminates conflicts between PE's**.

At end of cycle processors communicate changes to neighboring processors.

- Maximum time interval τ determined by maximum ***possible* single**-event rate in simulation: $\tau = 1/D$



4-processors



2 events

Advantages:

- Only local communication required
- Multiple events per cycle: reduced communication overhead due to latency

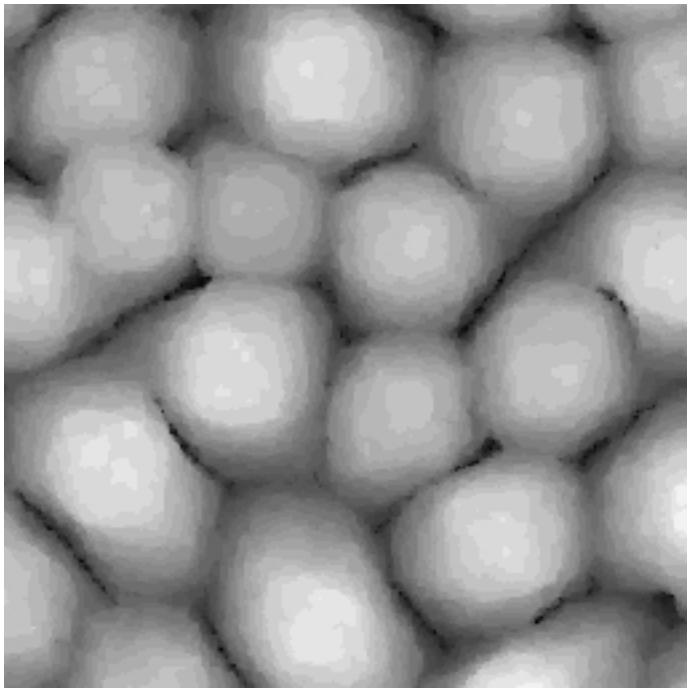
Disadvantages:

- Not rigorous & parallel efficiency is reduced by fluctuations
- Event-size limited by processor/sublattice-size

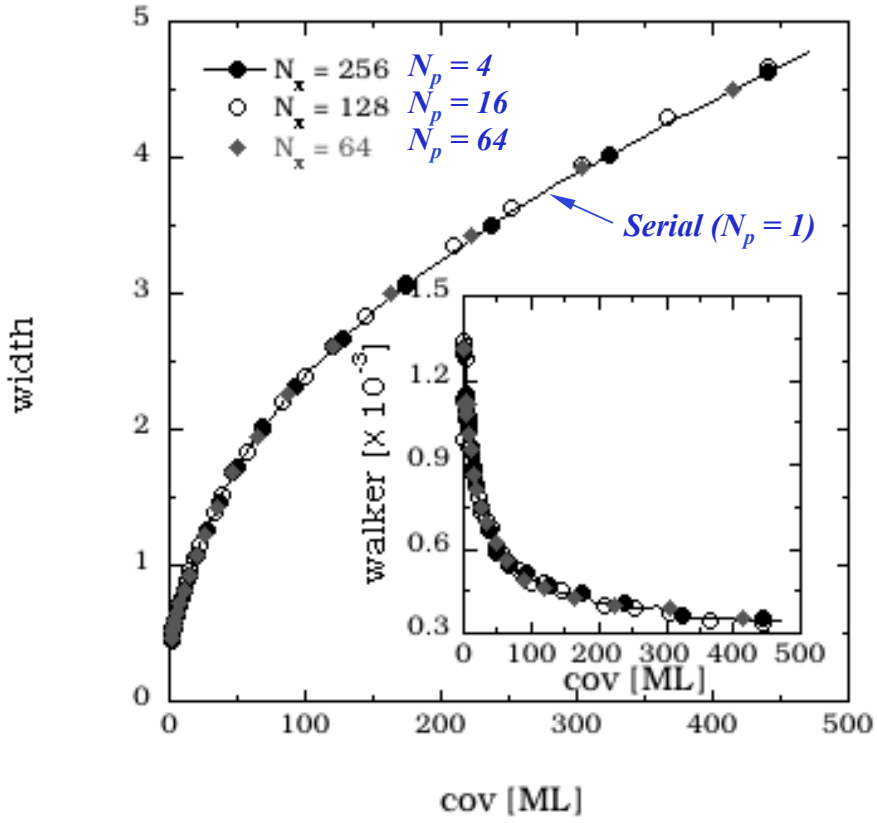
Parallel KMC: reversible growth model

T = 300 K, D/F = 10^5, E_1 = 0.1 eV, and E_b = 0.07 eV

N_x = 64 *N_y = 1024 N_p= 16* 128

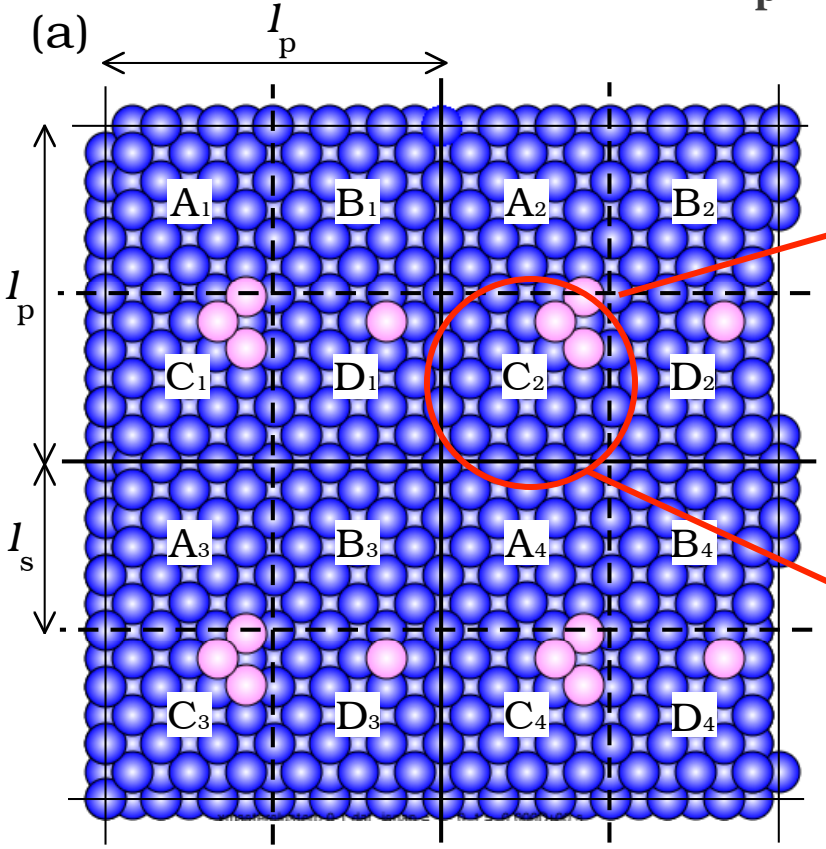


*512 by 512 portion of **1k by 1k system***



Parallel TAD: square decomposition *(Y. Shim et al, PRB 2007)*

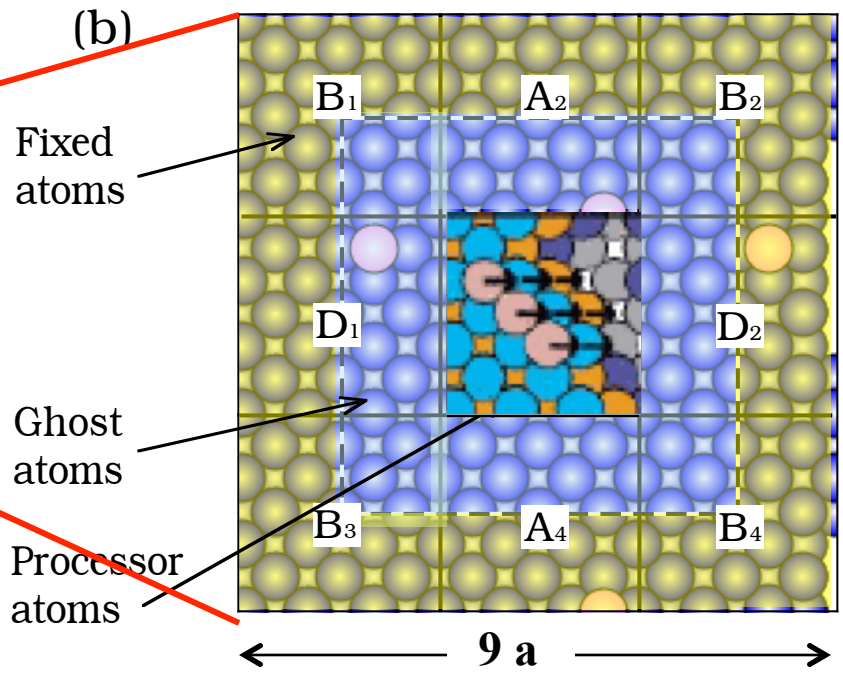
Sublattice decomposition ($N_p = 4$)



l_p = **6 a** (where a = 3.61 Å)

Cu EAM potential is used with r_{cut} = 4.961 Å
(Voter, PRB 57, 1998)

Processor, **Ghost**, and **Fixed** regions

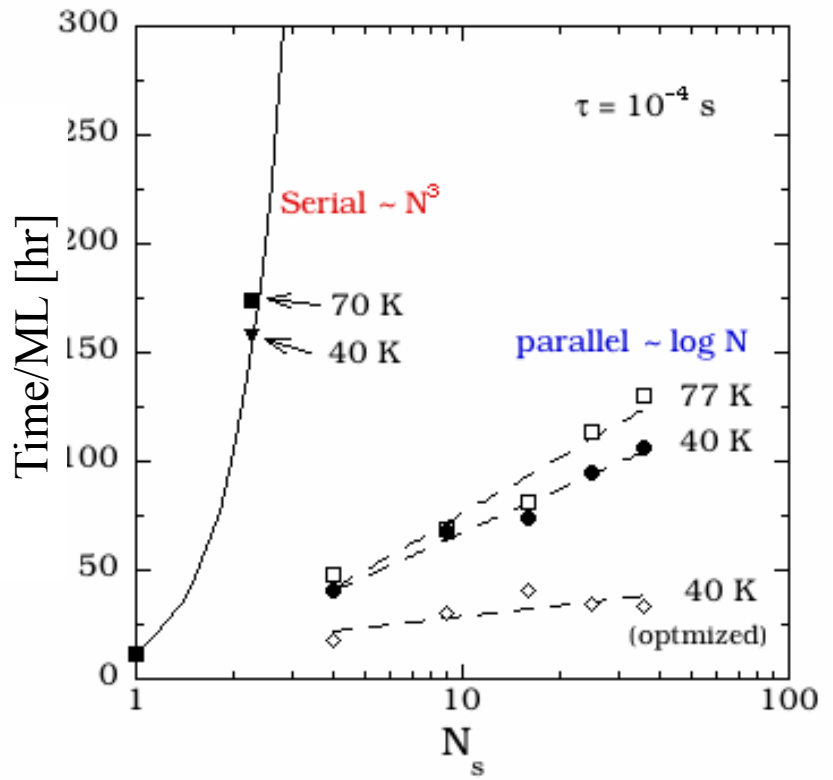


"Center-of-displacement" of event determines if event belongs to ghost region (rejected) or processor region (accepted)

Scaling in Parallel TAD (parTAD): Cu(100) growth

Cov = 0.5 ~ 1 ML, F = 500 ML/s

Scaling of serial and parallel TAD

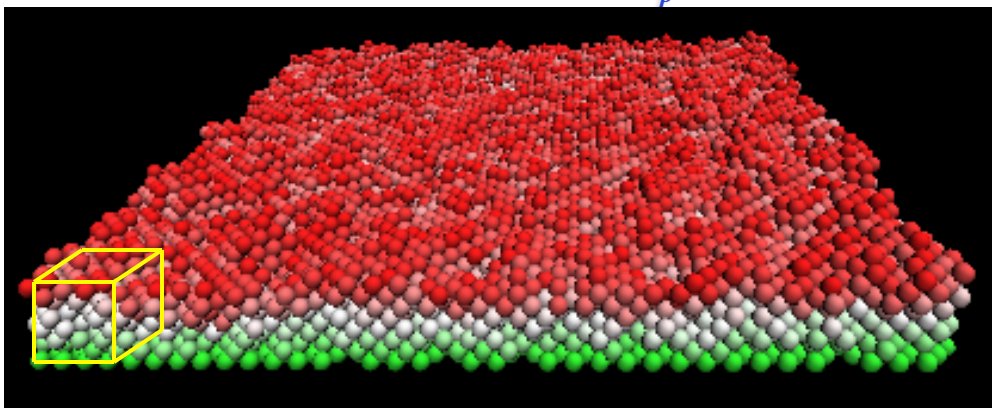


Y. Shim, J. Amar, B. Uberuaga, A. Voter, PRB 2007

Parallel TAD (parTAD) extends ***both*** time and length scales significantly !

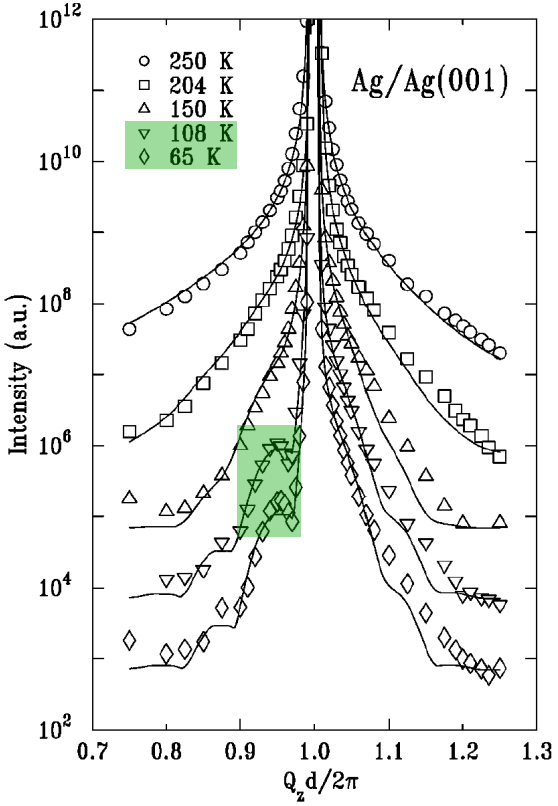
Log N scaling instead of N^3 !

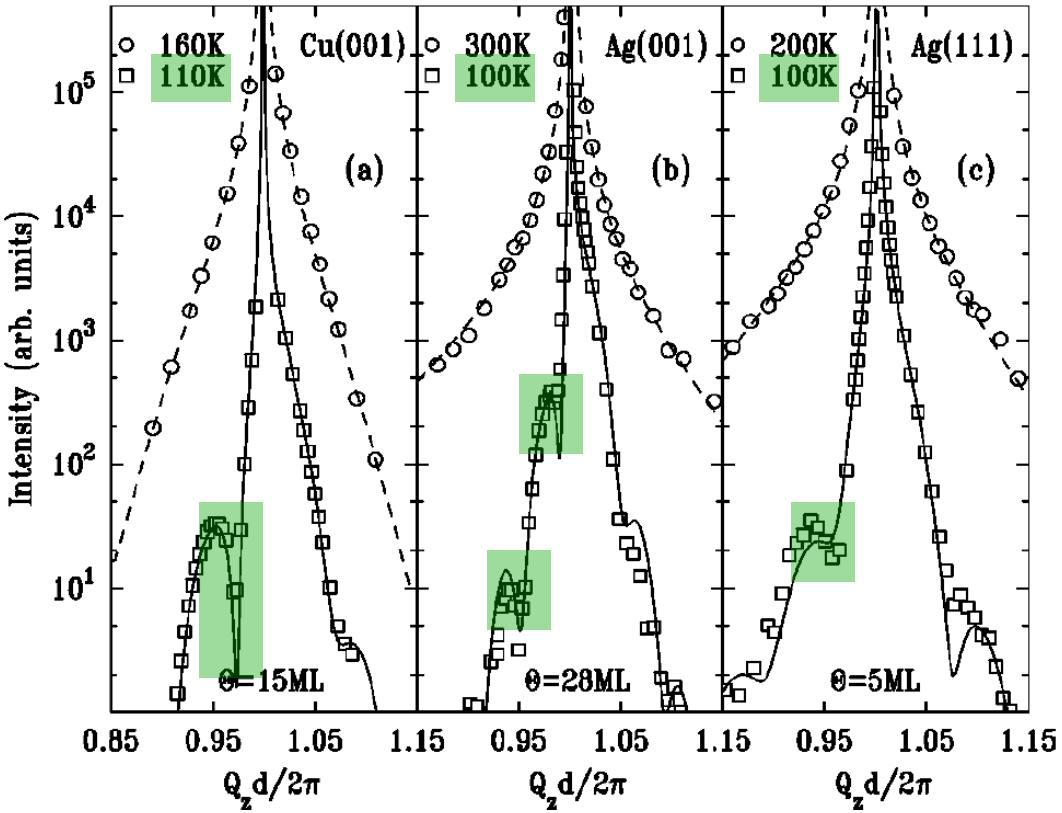
Parallel TAD Simulations: $N_p = 36$



Application: XRD experiments on low T epitaxial growth

C.E. Botez et al, APL 81,4718 (2002); C. Kim et al, APL (2007)

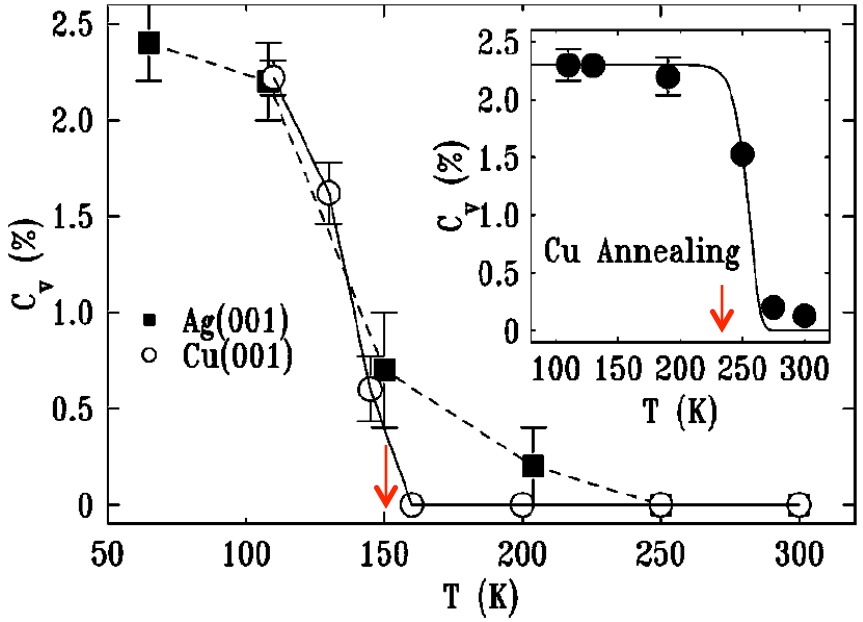




⇒ Oscillations in $I(Q_z)$ at low T indicate significant compressive strain

Interpretation: Vacancy trapping at low T!

C.E. Botez et al, APL 81,4718 (2002); C. Kim et al, APL (2007)



Vacancy density C_v estimated **indirectly** from uniaxial strain measured by X-ray diffraction:

$$C_v = -\frac{\Delta d}{d}[\alpha\,(1+2\frac{C_{12}}{C_{11}})]^{-1}$$

Can we use parTAD to "verify" the experimentally observed behavior?

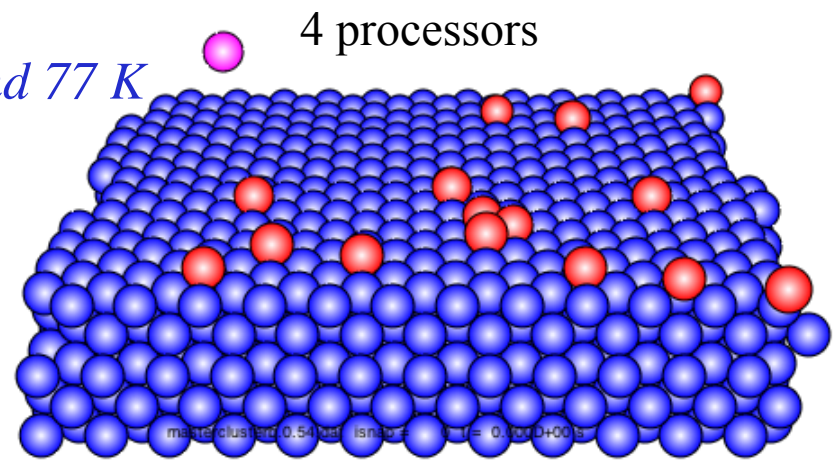
What determines transition temperature for vacancy formation (~ 150 K)?

What are key mechanisms, activation barriers?

ParTAD simulations of low T Cu/Cu(100) growth

Y. Shim, V. Borovikov, A.F. Voter, B. Uberuaga, J.A., PRL (2008)

- *Deposition rate F = 5000 ML/s*
- *Simulations carried out at T = 40 K and 77 K*
- *Deposition angles: 0^o, 30^o, 55^o, 60^o*
- *System size L = 72 (N_p = 36)*



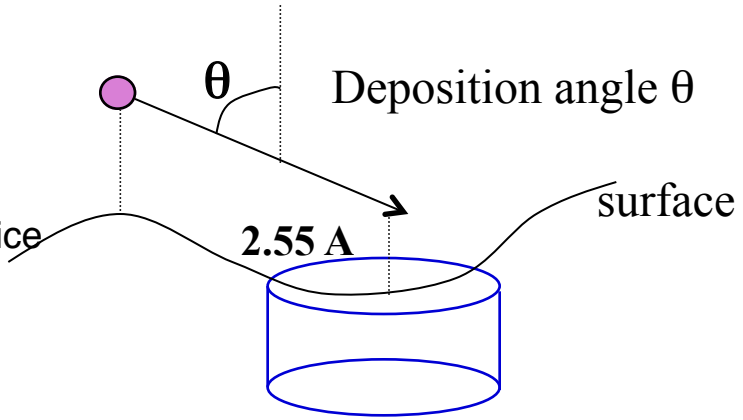
ParTAD Simulation:

1. **Deposit atom** in selected sublattice (A,B,C, or D) with probability ½ at beginning of each cycle (5 ps)

2. **Carry out TAD** in selected sublattice (Cycle-time $T = 1.1 \times 10^{-5}\ s^{-1}$)

3. **Communicate** any accepted events with neighboring sublattices before selecting next sublattice

4. **Globally relax** system every 1/8 ML



ParTAD simulations of low

Y. Shim, V. Borovikov, A.F. Voter, B. L

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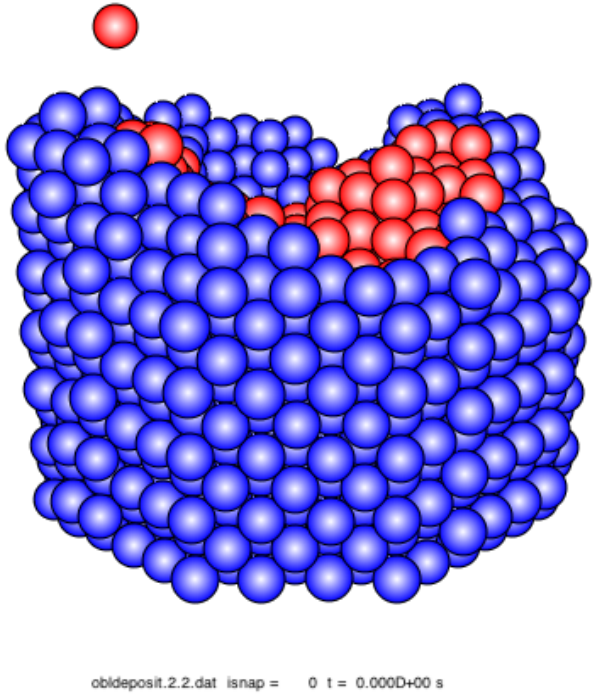

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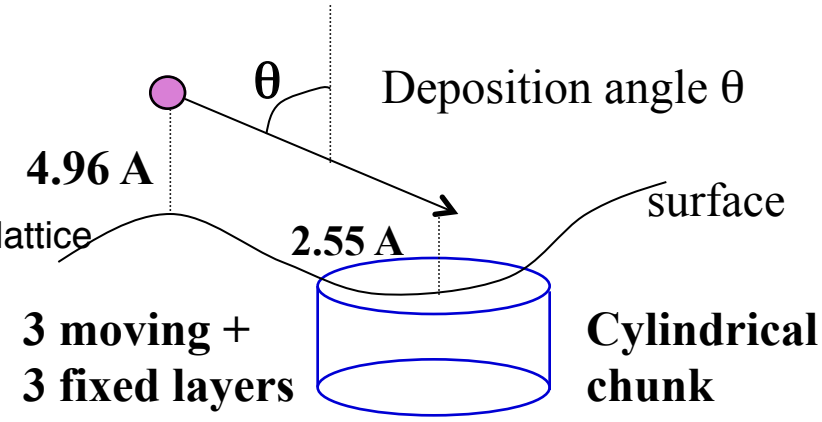

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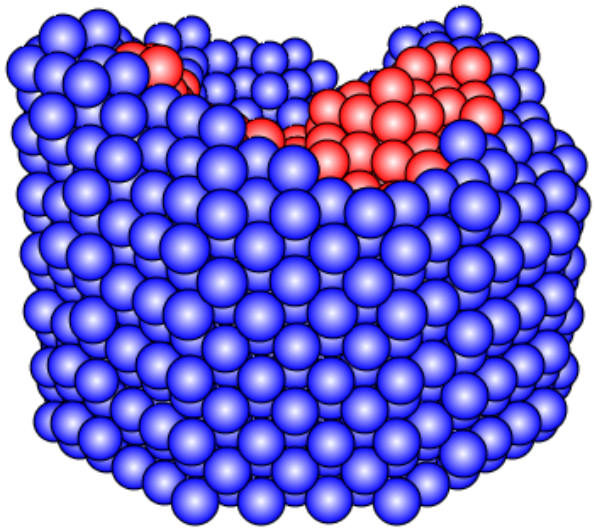
MD simulations also carried out for comparison



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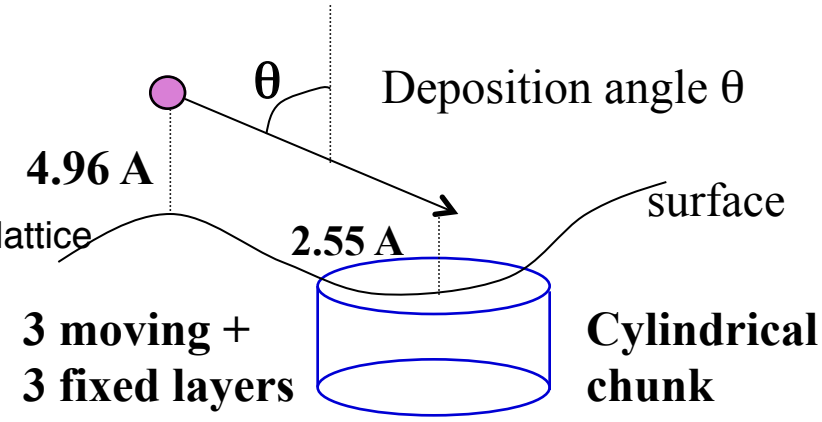
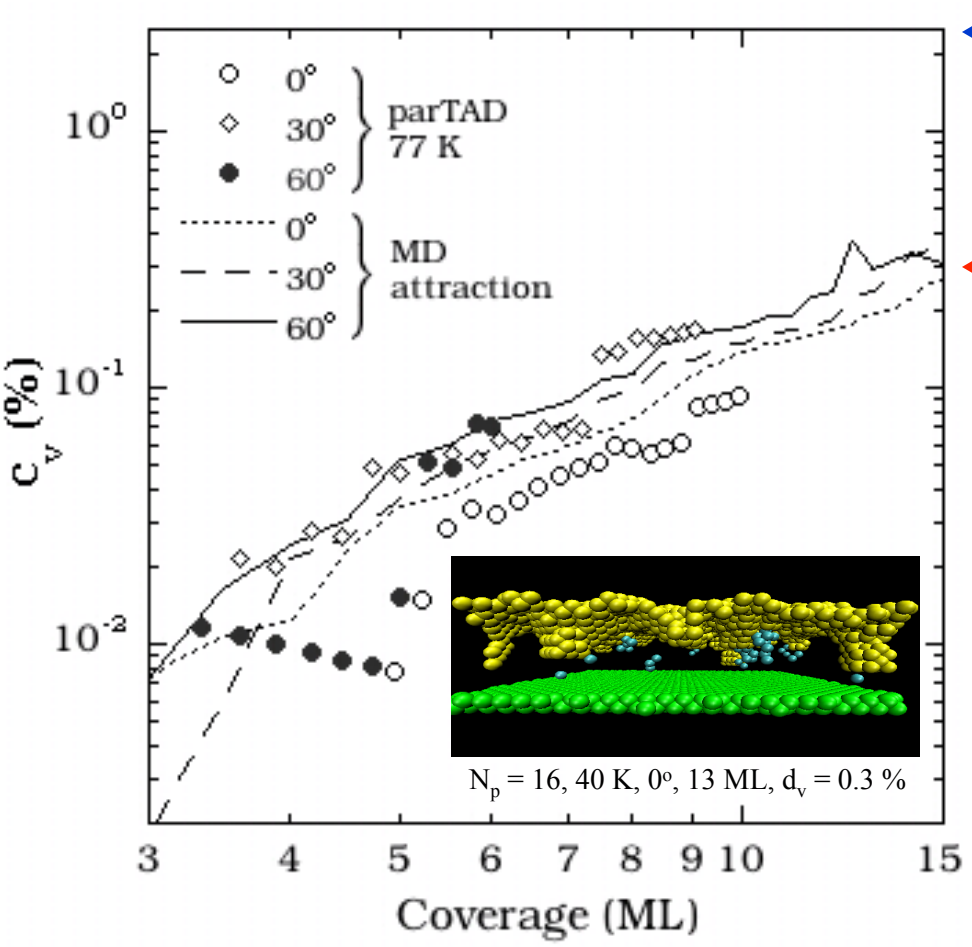


Vacancy density

=> ***Weak dependence on deposition angle!***

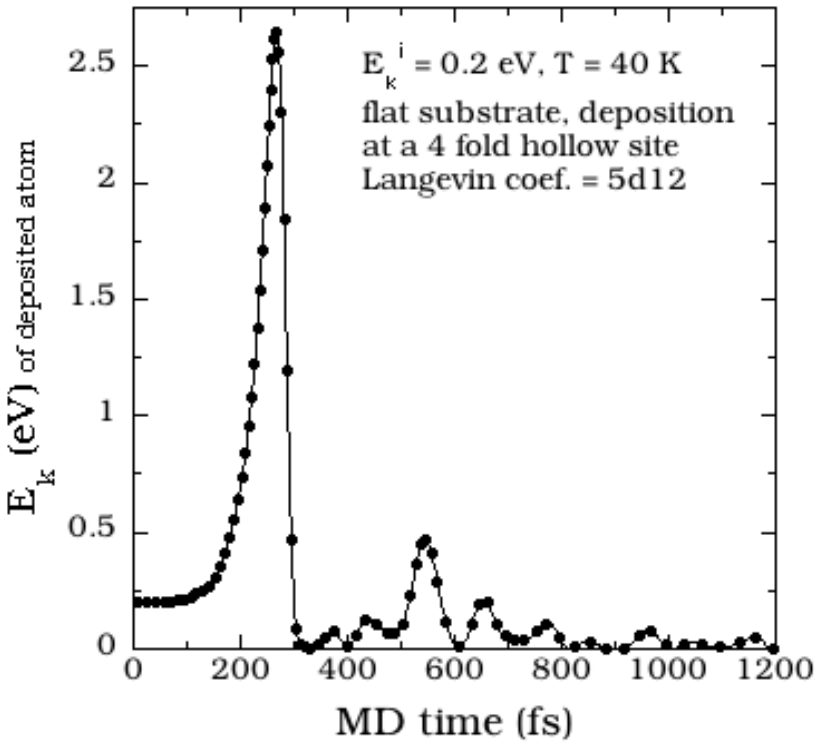


← Experiment

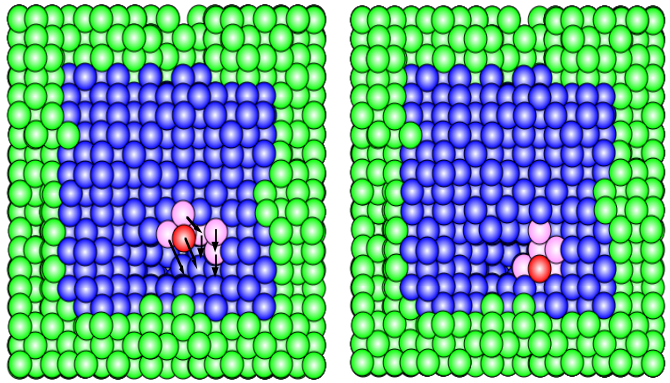
← *Much smaller than experimentally determined value !*

Deposition-triggered events

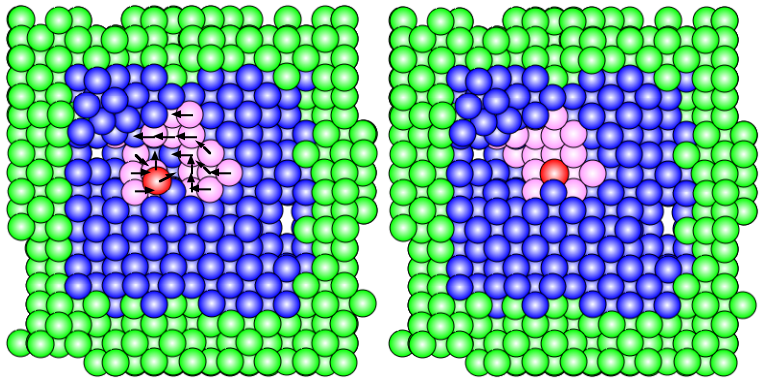
KE ≈ 2.5 eV



6 atom move



23 atom move



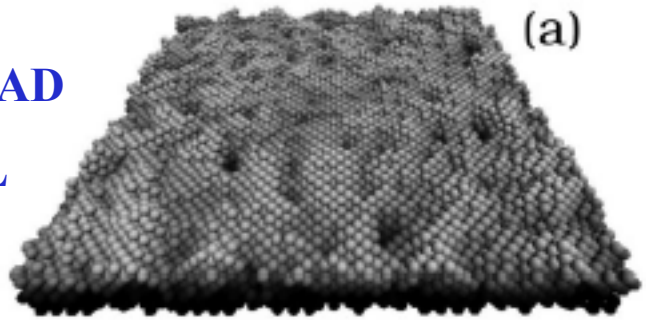
ParTAD simulations of low T Cu/Cu(100) growth

Y. Shim, V. Borovikov, A.F. Voter, B. Uberuaga, J.A., PRL (2008)

=> Strong dependence of morphology on deposition angle!

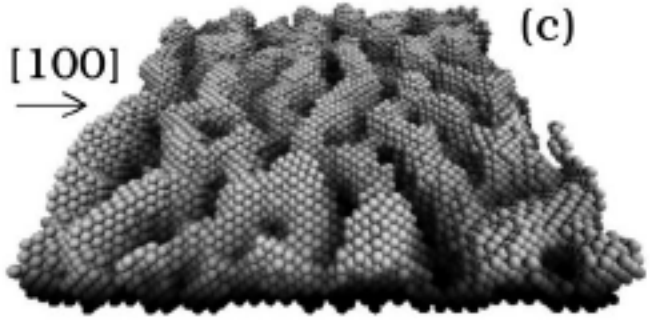
parTAD

7 ML



0°

Relatively smooth



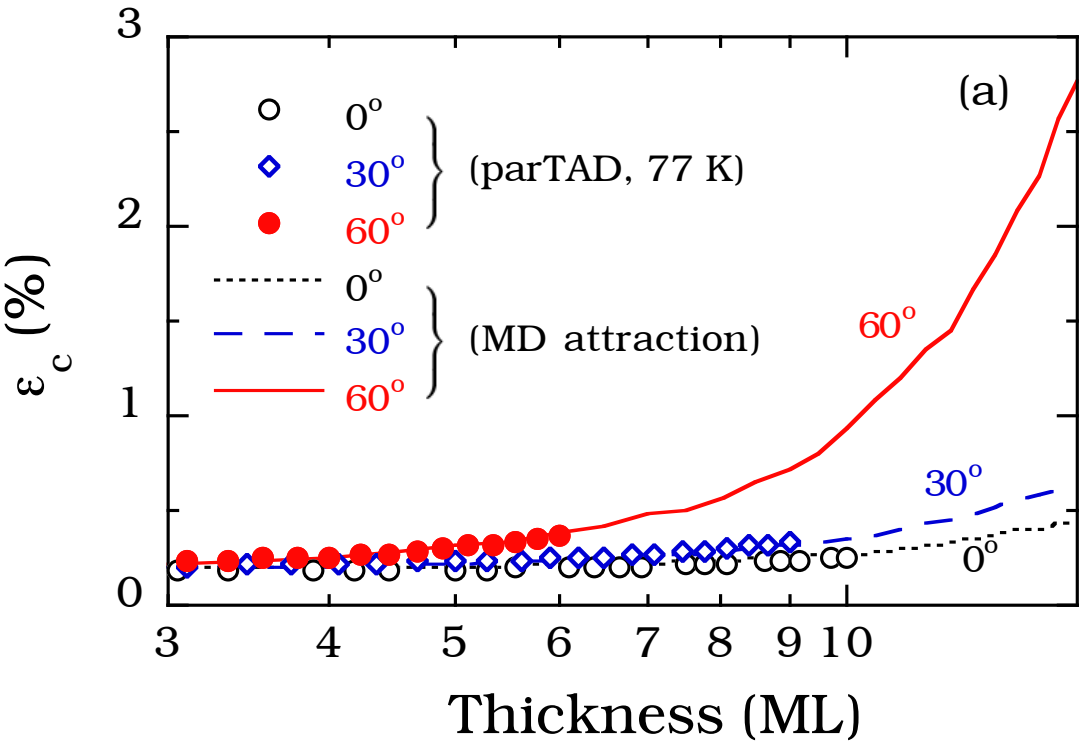
60°

Ripples!

ParTAD simulations of low T Cu/Cu(100) growth

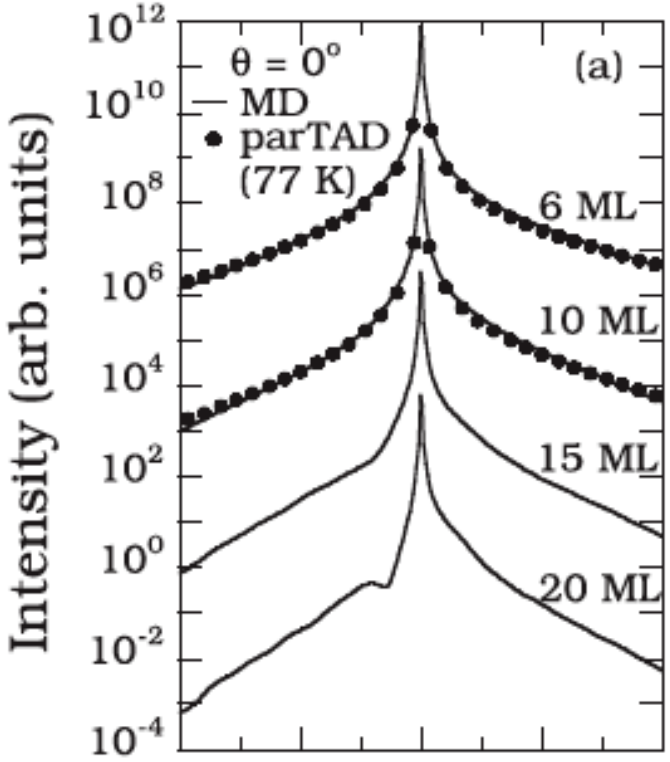
Y. Shim, V. Borovikov, A.F. Voter, B. Uberuaga, J.A., PRL (2008)

Strong dependence of compressive strain $\varepsilon_c = \Delta z/z$ on deposition angle!

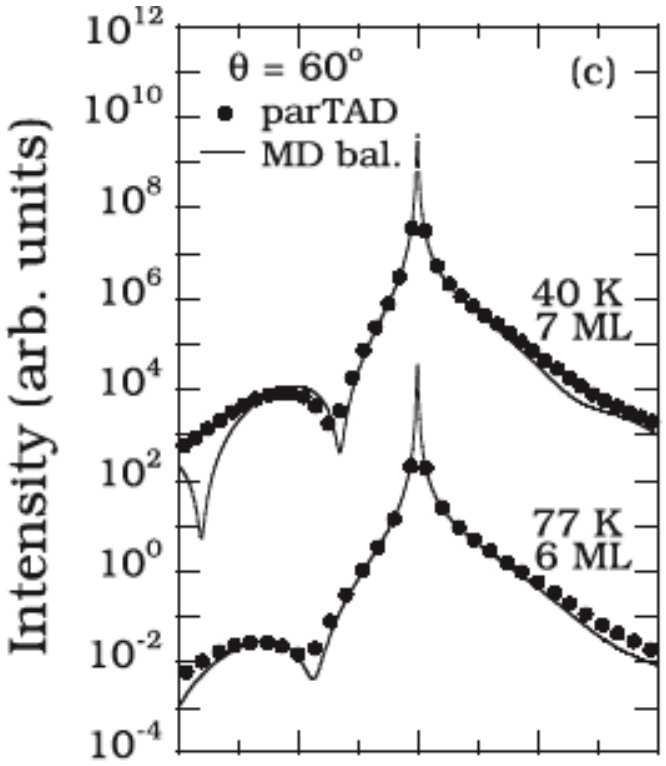


Strong dependence of XRD on deposition angle!

Normal incidence

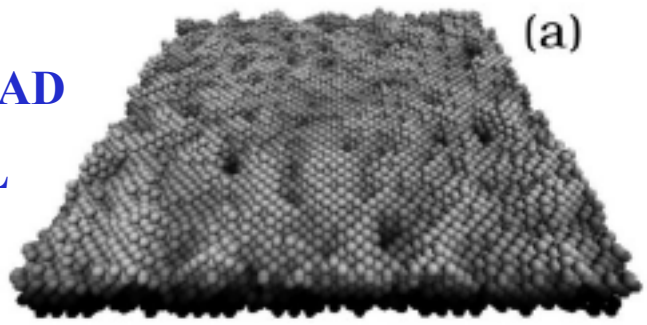


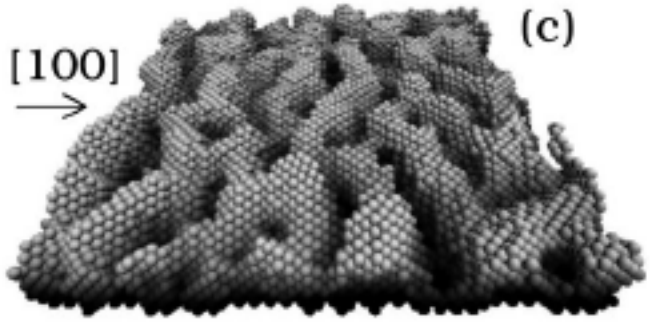
Oblique incidence



parTAD

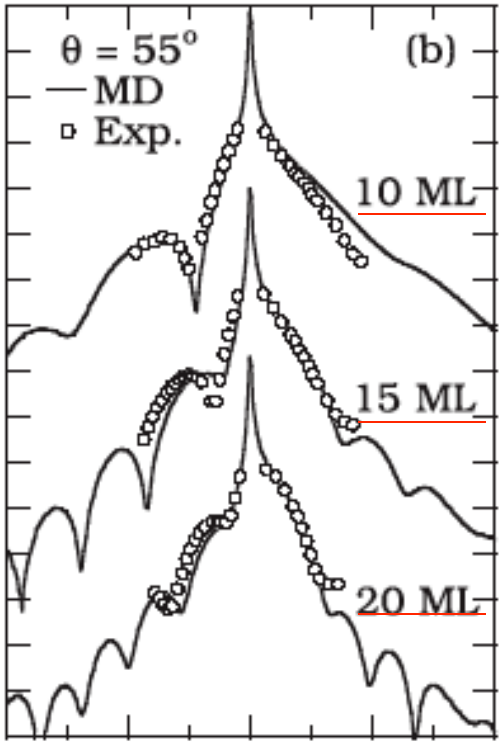
7 ML

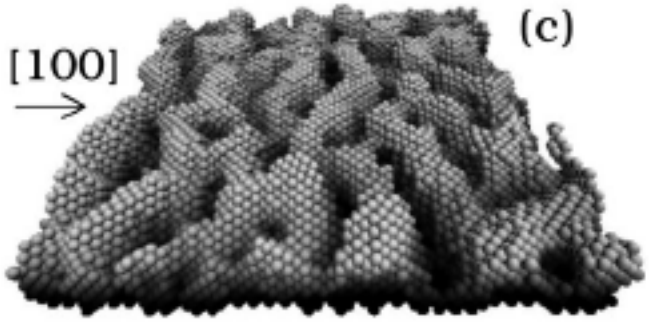




Good agreement with experimental XRD

Oblique incidence

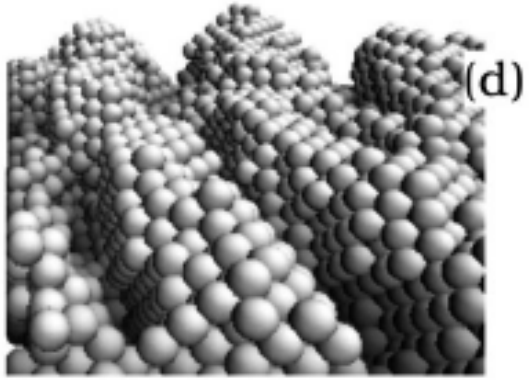




ParTAD simulations of Cu/Cu(100) growth at low T

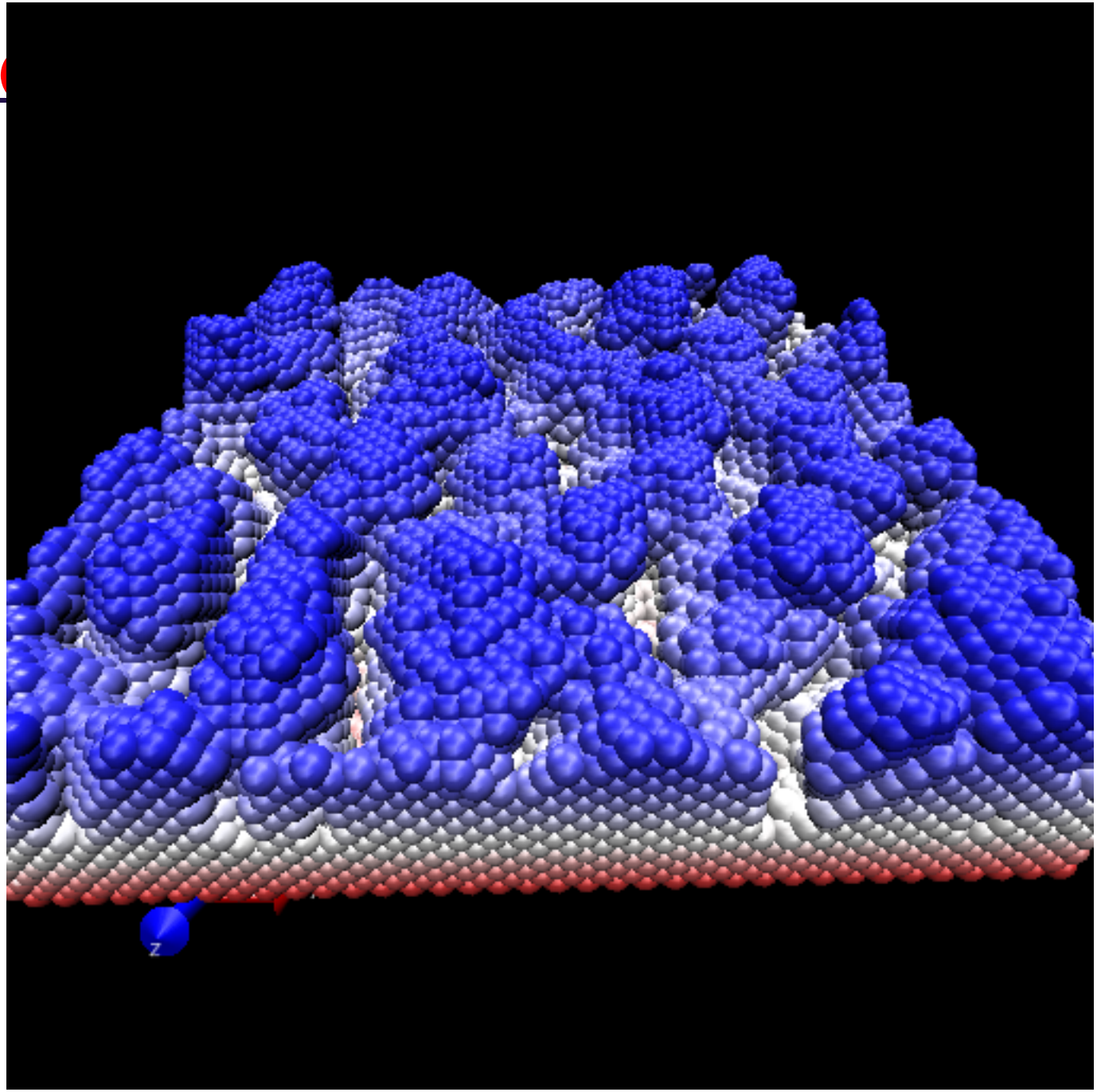
Y. Shim et al, PRL (2008)

- Key factor responsible for observed compressive strain in low-temperature films is **not vacancies** but rather the existence of **nanoscale surface roughness** as well as **presence of (100) cliffs (overhangs)**



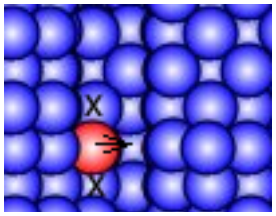
=> Increased nanoscale roughness at large deposition angles is due to combination of ***shadowing due to oblique incidence and suppressed activated 'downward-funneling' (DF) events at low T*** *(prevents filling in of valleys)*

Cu

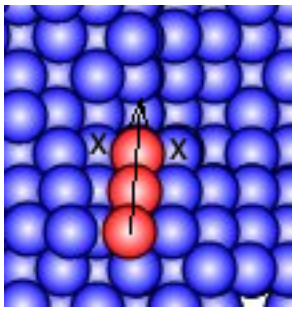


Can we use parTAD simulations to predict Tc?

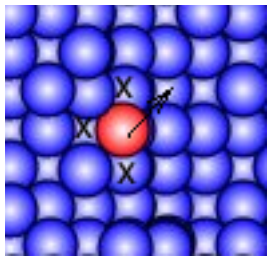
=> need to determine activation barriers for DF-like activated events



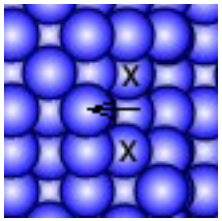
(1) 0.4239 eV, 0.7554 eV



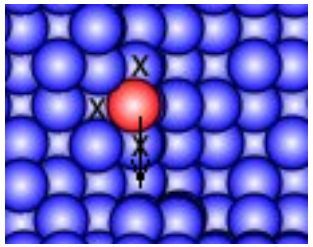
(2) 0.4183 eV, 1.4014 eV



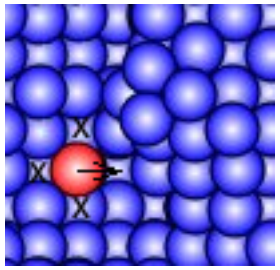
(3) 0.3938 eV, 0.9810 eV



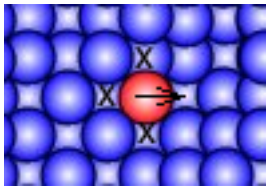
(4) 0.3853 eV, 0.0643 eV



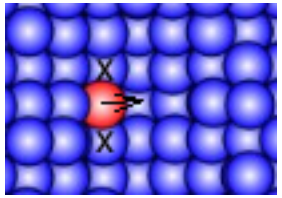
(5) 0.3080 eV, 0.9470 eV



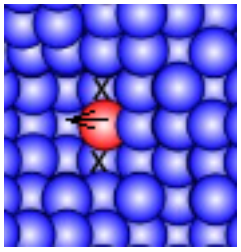
(6) 0.3497eV, 0.4020 eV



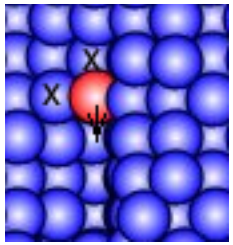
(7) 0.2813 eV, 0.7640 eV



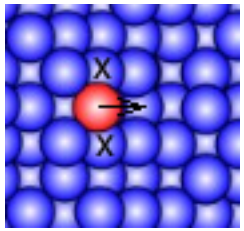
(8) 0.3172 eV, 0.8445 eV



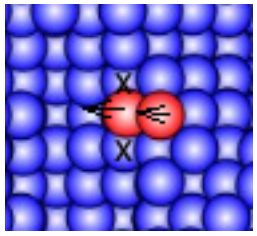
(9) 0.3902 eV, 0.8716 eV



(10) 0.212 eV, 0.5545 eV

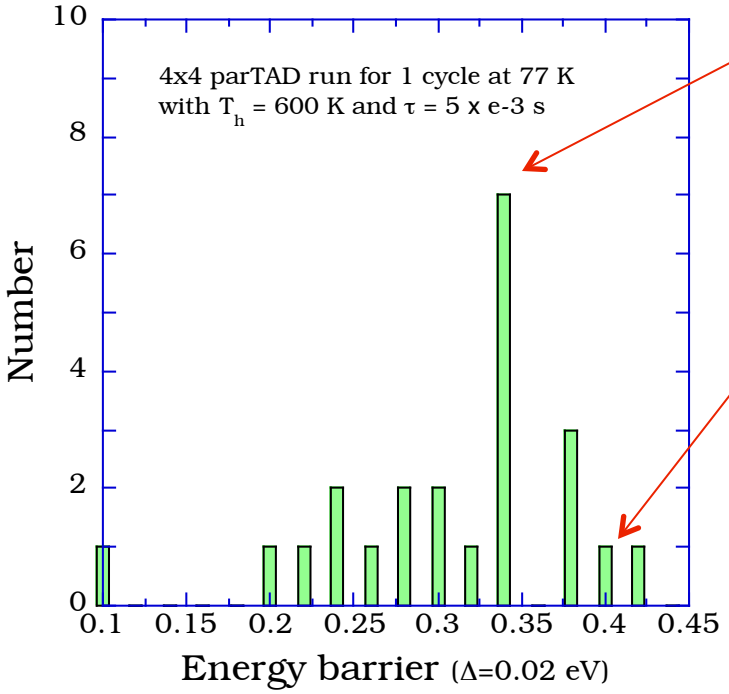


(11) 0.2729 eV, 0.2308 eV



(12) 0.348 eV, 0.7395 eV

Histogram of DF energy barriers obtained from parTAD (annealing) simulations



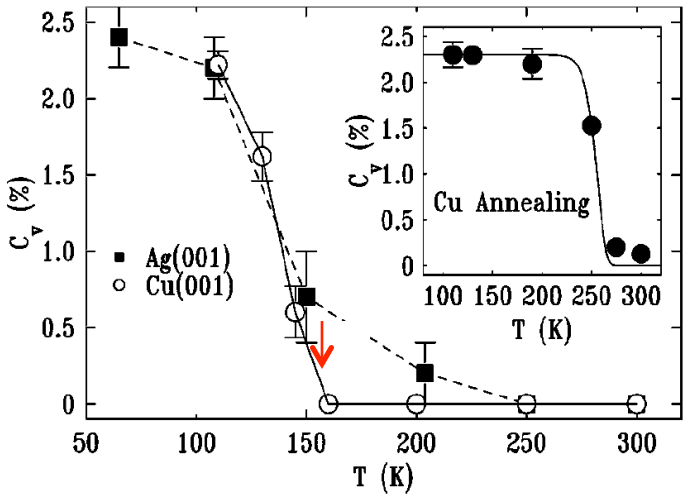
$E_{pk} \approx 0.33$ eV

$E_{max} \approx 0.42$ eV

Taking into account experimental deposition rate leads to estimated range of transition temperatures for onset of strain:

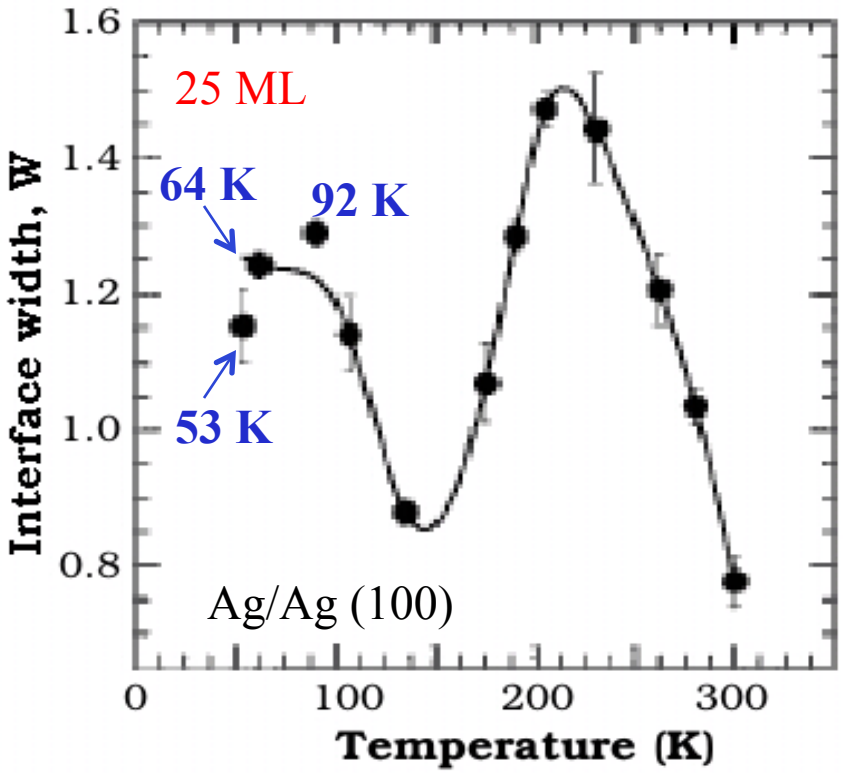
$T_c \approx 120$ - 150 K

Good agreement with experiment!



Low T Ag/Ag(100) growth: dependence of roughness on T

(Stoldt et al, PRL 85 (2000))



How to explain non-monotonic temperature dependence ?

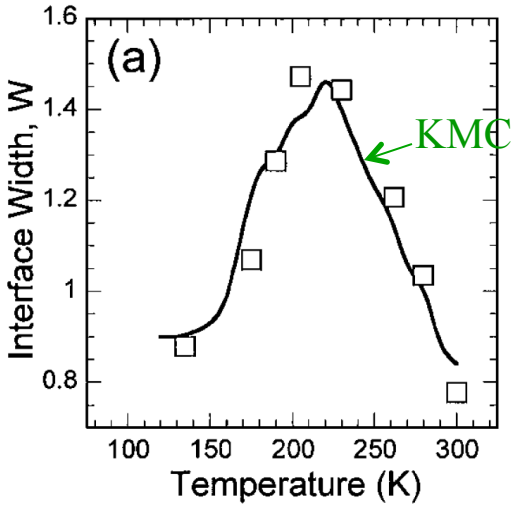
Simple KMC model (Stoldt et al) explains high T behavior

-Assume *infinitely fast island relaxation*

with small Ehrlich-Schwoebel (ES) barrier

to interlayer diffusion

-High T behavior explained by competition between monomer and interlayer diffusion

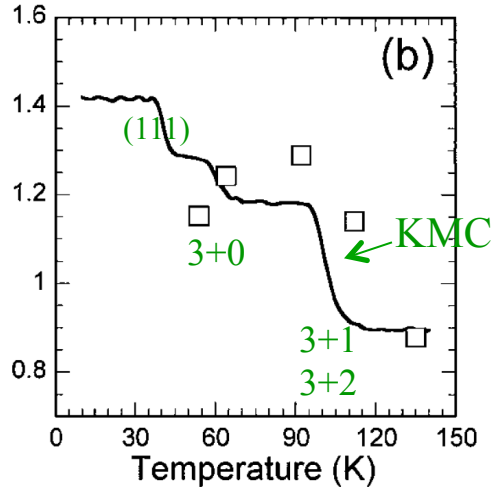


High T

How to explain low-T behavior (T < 120 K)?

-Restricted downward funneling (RDF) for atoms at non-fourfold hollow sites

⇒ Poor agreement with expt. at low T



Low T

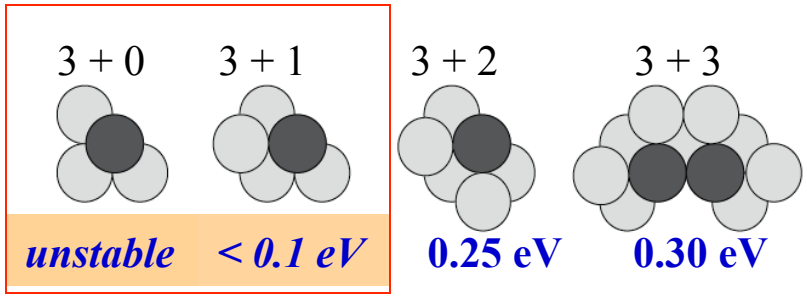
⇒ Model predicts very high (30%) vacancy density at low T,

in disagreement with parTAD simulations of low T Cu/Cu(100) growth

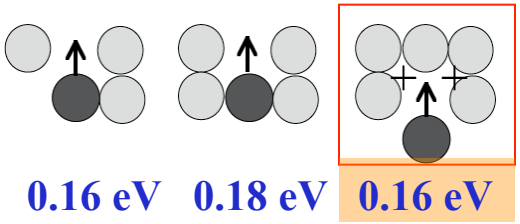
Low T Ag/Ag(100) growth revisited: ***Model I (T = 50 - 110 K)***

Key Elements:

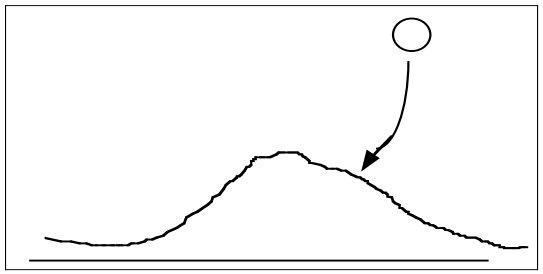
(1) Restricted DF - barriers obtained from EAM/parTAD/DFT



(2) Low barrier edge-zipping (converts unstable 3-fold to stable 4-fold site)
(EAM, Mehl et al, PRB 60, 1999)



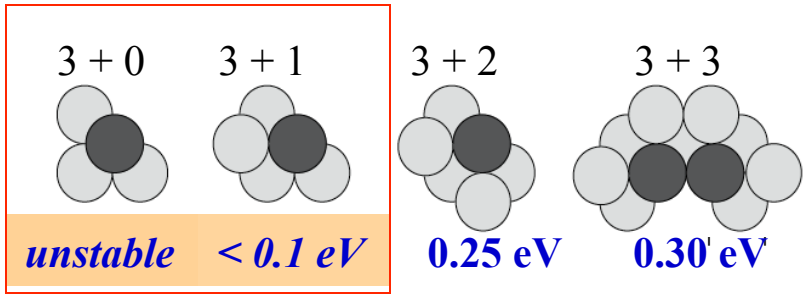
(3) SR attraction of depositing atoms to substrate – include by carrying out hybrid MD-KMC simulations



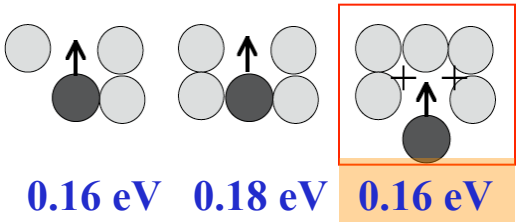
Low T Ag/Ag(100) growth revisited: ***Model I (T = 50 - 110 K)***

Key Elements:

(1) Restricted DF - barriers obtained from EAM/parTAD/DFT

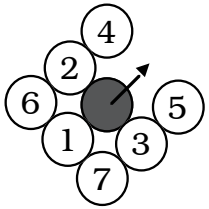


(2) Low barrier edge-zipping (converts unstable 3-fold to stable 4-fold site)
(EAM, Mehl et al, PRB 60, 1999)

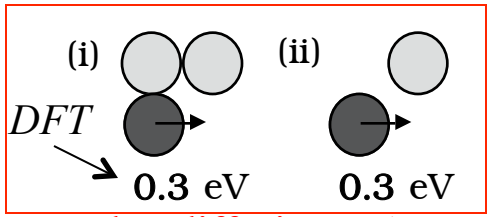


(3) SR attraction of depositing atoms to substrate – include by carrying out hybrid MD-KMC simulations

(4) Edge-diffusion, atom-attraction and higher barrier processes (T > 110 K)



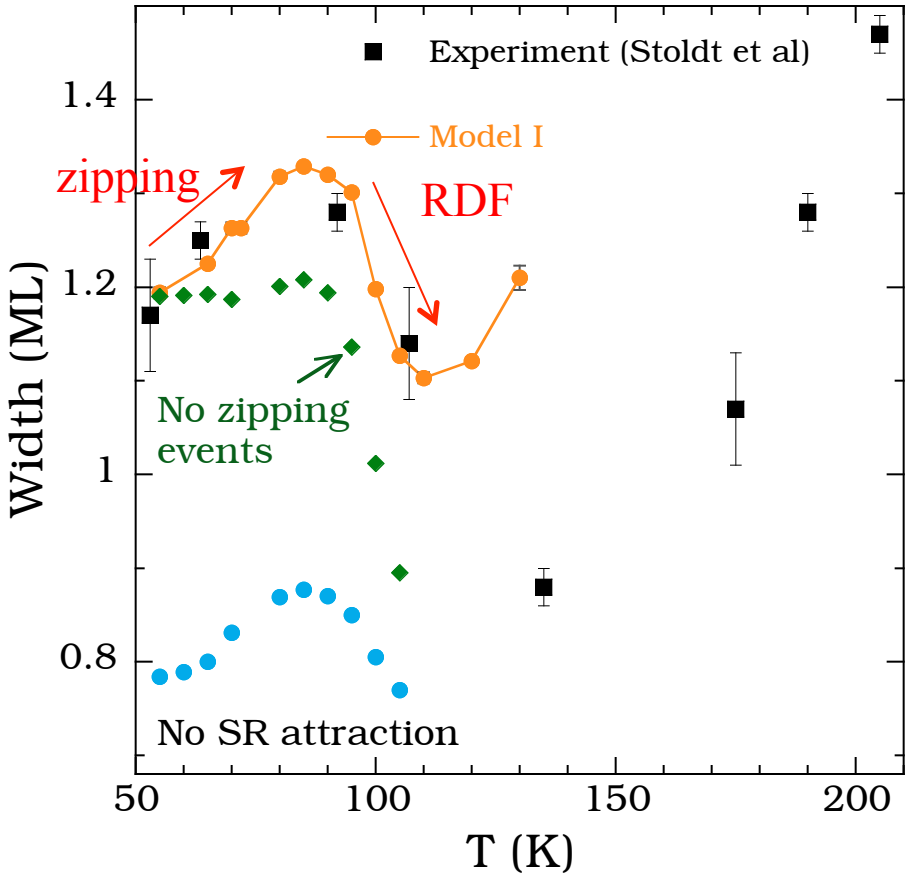
(EAM, Mehl et al, PRB)



Edge-diffusion Atom-attraction

Note: monomer diffusion (0.45 eV) not active until at least 160 K !

Simulation results: Model I

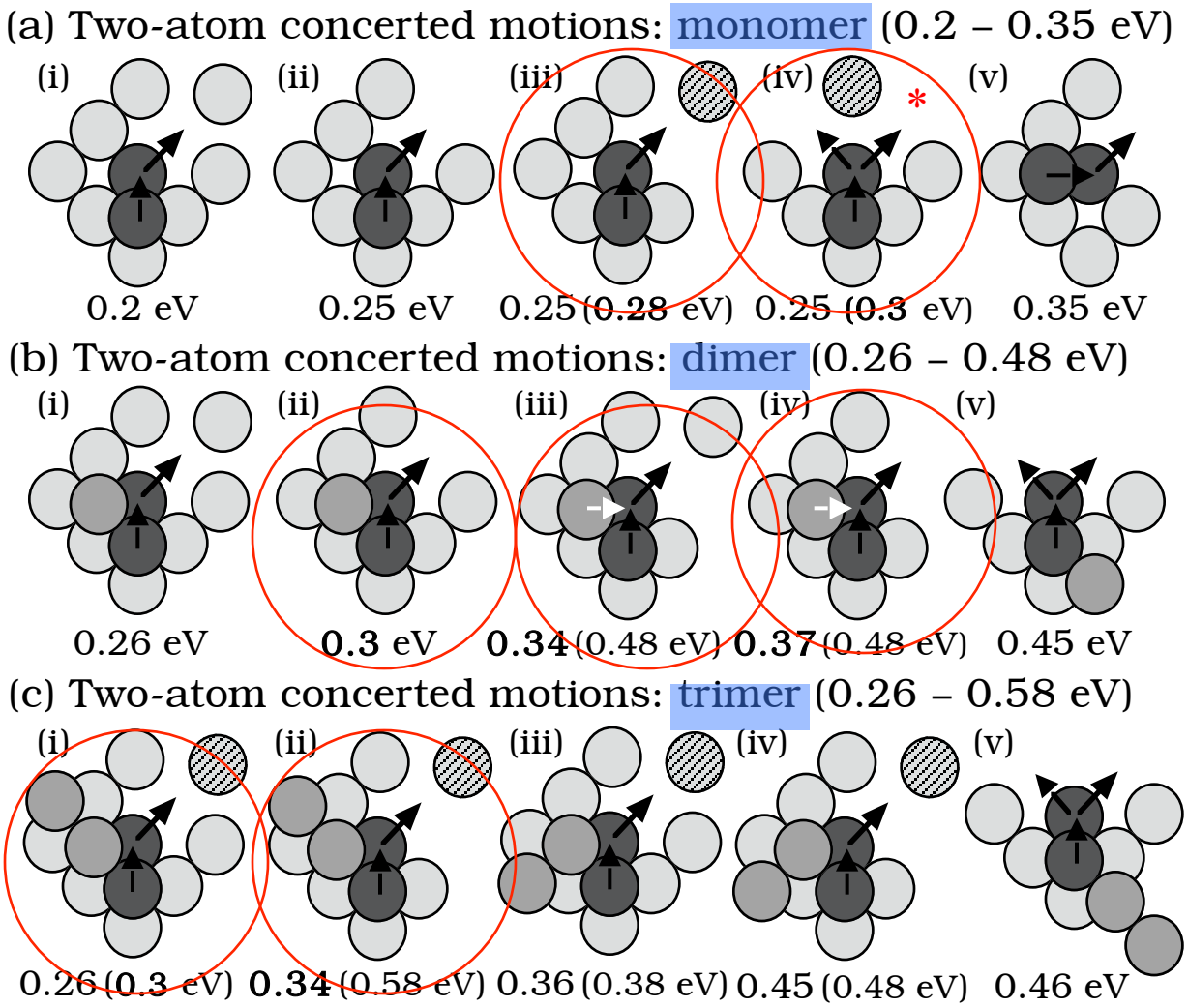


*How to explain experimentally observed **decrease** in roughness above 110 K?*

Some other pathway for smoothing becomes active above 110 K?

*Carry out **parTAD annealing** simulations of representative KMC configurations*

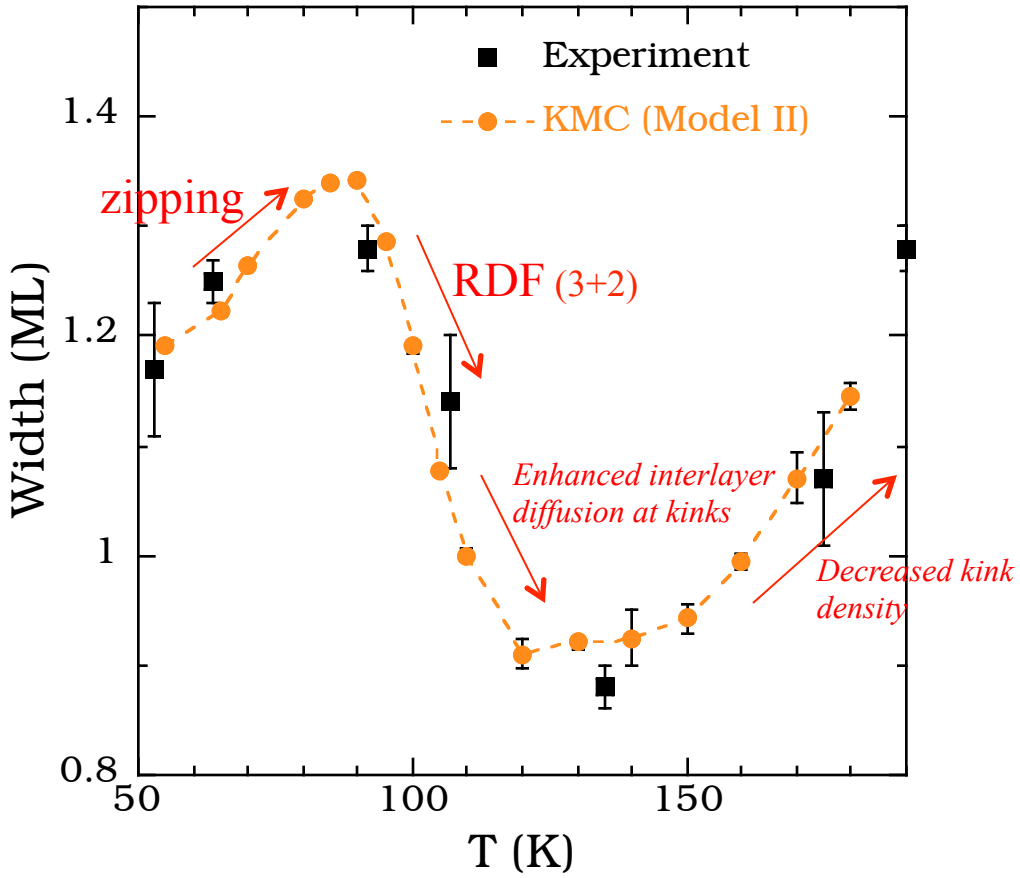
Low-barrier interlayer diffusion processes at kinks!



* *Exchange at open-step (U. Kurpick and T. Rahman, PRB 1998)*

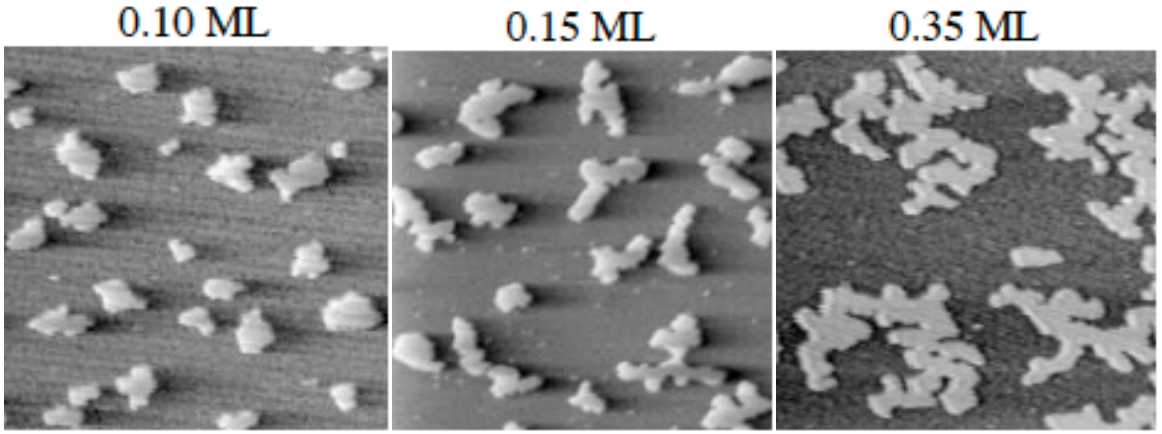
Simulation results (Model II)

Y. Shim & JGA, PRB (2010)



Shape transitions in submonolayer Cu/Ni(100) growth

Müller, Surf. Rev. Lett. 8 (2001), Müller et al. PRL 80 (1998)



T = 345 K

Ramified islands (with selected arm-width 22 b) observed over wide range of temperatures T = 250 – 345 K

- How to explain ramified Cu islands on Ni(100)?
- What are effects of strain (ε = 2.7 %) on island morphology?

Müller et al. argued that shape transition is not of kinetic origin but instead due to equilibrium energetic effects (continuum elasticity theory)

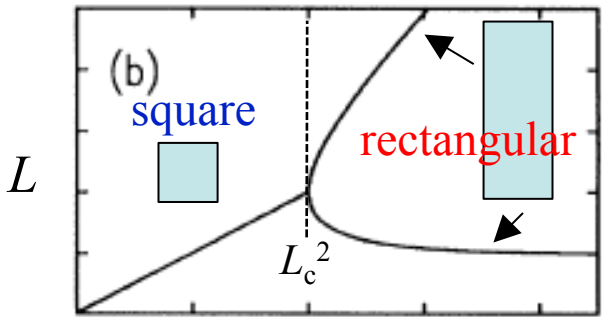
Continuum elasticity approach

(Tersoff and Tromp, PRL 1993, Li, Liu, Lagally, PRL 2000)

- Competition between step free energy γ (compact islands) and strain-energy E_u (anisotropic islands) leads to shape transition at critical island-size

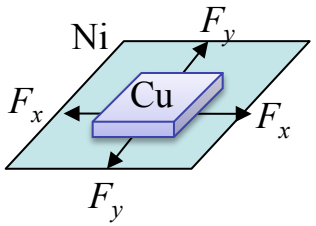
- For island-size $A < L_c^2$ step energy dominates (square-islands) while strain energy dominates for $A > L_c^2$ (anisotropic islands with width $w = L_c$)

- Selected arm-width $L_c = b\ exp\ [\frac{\gamma/E_u + 2}{2(1-\nu)} + 1.30]$ where E_u = 'unit strain energy'



Energetics calculations (DFT)

Li, Liu, Lagally, PRL 85 (2000)



$$L_c = b\ exp\ [\frac{\gamma/E_u + 2}{2(1-\nu)} + 1.30]$$

where $E_u = \frac{1+\nu}{2\pi\mu}F^2$

- **Step energy:** $\gamma = 0.044$ eV/Å

  Force monopole $F = \sigma^f_{xx} - \sigma^s_{xx} = -0.134$ eV/Å^2

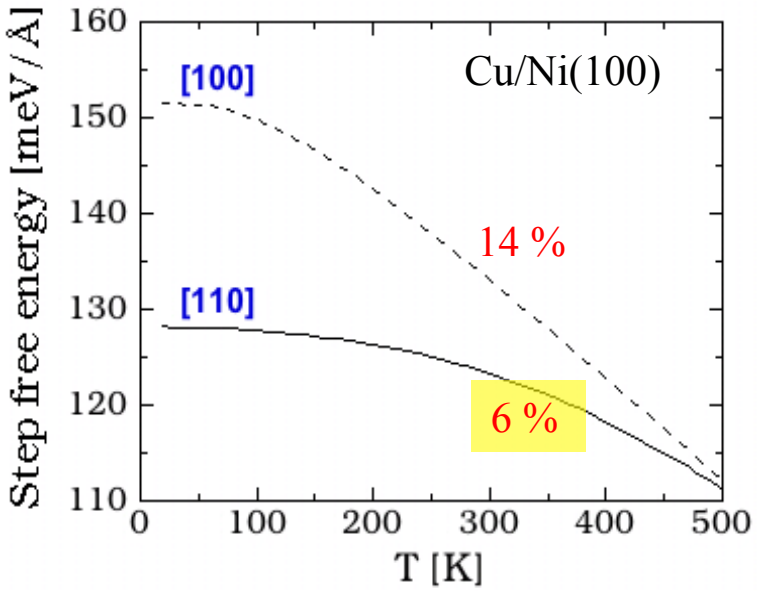
- **Unit strain energy:** $E_u = 3.0 \times 10^{-3}$ eV/Å

- **Critical island size:** $L_c \sim 6.5 \times 10^5\ b$ >> expt. armwidth 22 b

Shape transition not due to energetics !

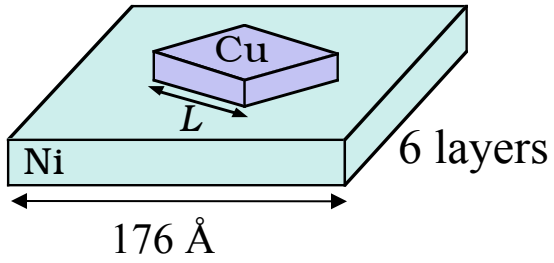
Effects of finite-temperature (EAM)

SOS model for free energy as function of n.n. and n.n.n pair-interactions E_1 and E_2



Relatively weak temperature dependence

Atomistic energy calculations (continued)

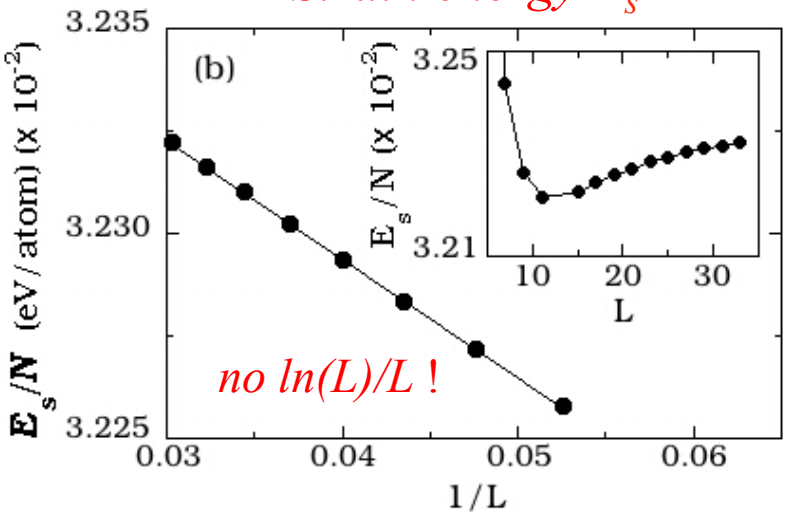


Cu-Ni EAM potentials:

Bonny et al. Phil. Mag. 89 (2009)
- Cu-Cu: Mishin et al. PRB 63 (2001)
- Ni-Ni: Voter & Chen (1987)

(1) Cu/Ni (100): $a_{Cu} = 3.615$ Å, $a_{Ni} = 3.52$ Å
(2) Cu/matched Ni (100): $a_{Cu} = a_{Ni} = 3.615$ Å

Strain energy E_s



$E_s(L)/N = 0.0324$ eV $- 0.0029$ eV$/L$

Theoretical prediction (LLL):

$$\frac{E_s}{N} = E_{sat} + \frac{10.56\ E_u a_0 [1 - 0.52\ ln(L)]}{L}$$

$$= E_{sat} + 0.1eV \frac{[1 - 0.52\ ln(L)]}{L}$$

Atomistic $E_{sat} = 0.032$ eV !

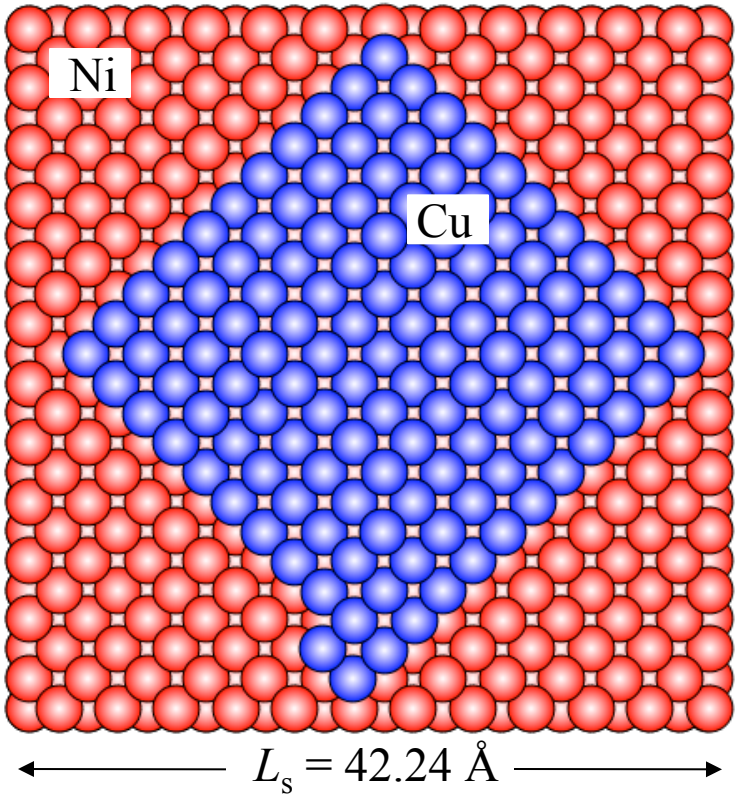
Continuum prediction: $E_{sat} = \mu_{Cu}\epsilon^2(\frac{a^3}{2\sqrt{2}})(1-\nu_{Cu}) = 0.022eV$

Temperature-accelerated dynamics (TAD) simulations

Sorensen & Voter, JCP, 112 (2000), Shim & Amar, JCP 134 (2011)

Annealing of Cu island on Ni(100)

T = 300 K



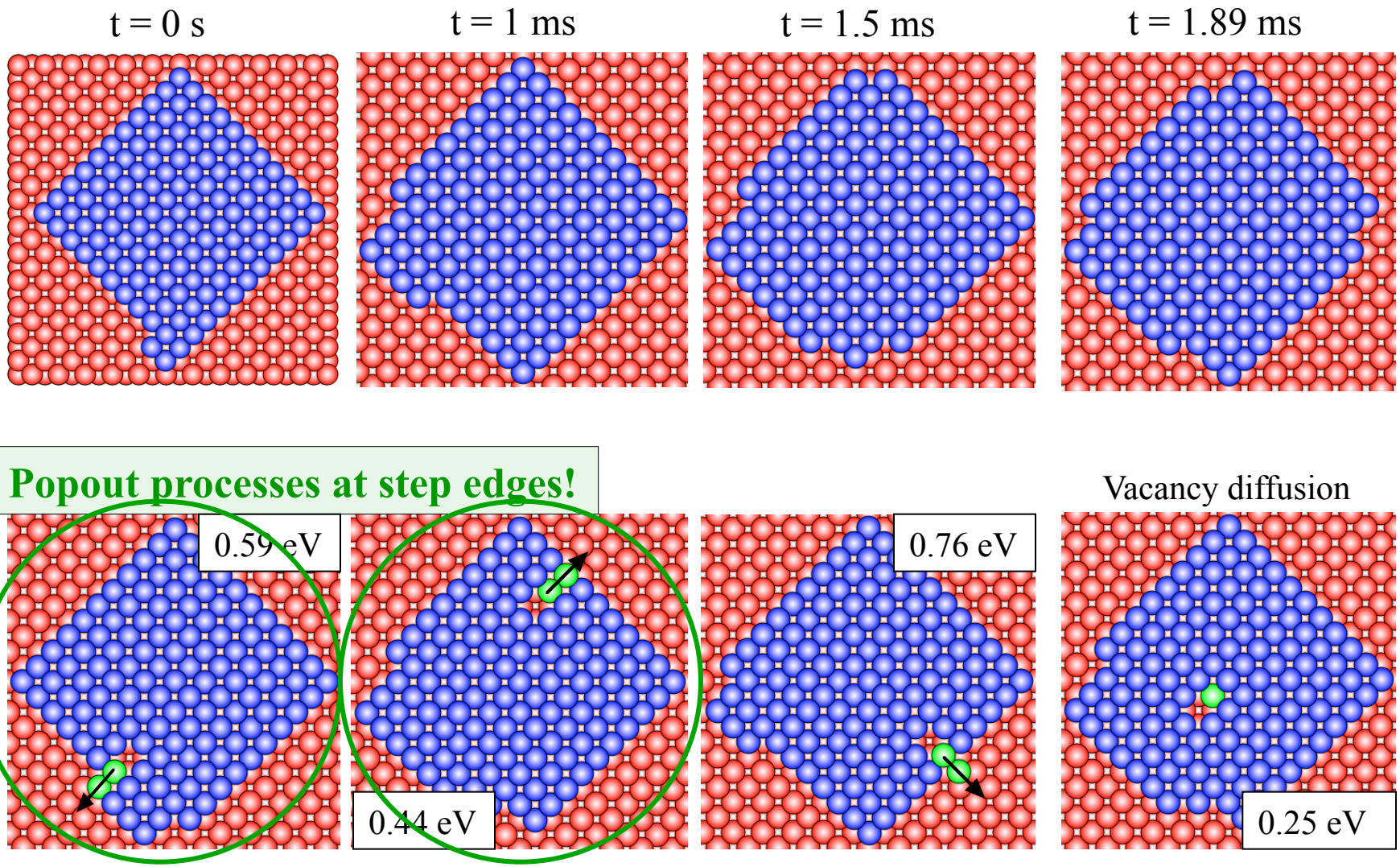
$$t_{i,\mathrm{low}} = t_{i,\mathrm{high}} \exp\left[E_i \left(\frac{1}{k_B T_{\mathrm{low}}} - \frac{1}{k_B T_{\mathrm{high}}}\right)\right]$$

1. Cu-Ni EAM potentials:

   a_{Cu} = 3.615 Å, a_{Ni} = 3.52 Å

- Substrate thickness: 4 layers
- Cu island: 123 Cu atoms
- T_{low} = 300 K, T_{high} = 900 K
- Simulation time: *t = 1.94 ms*

TAD simulation of Cu/Ni(100): T = 300 K (ε = 2.7 %)

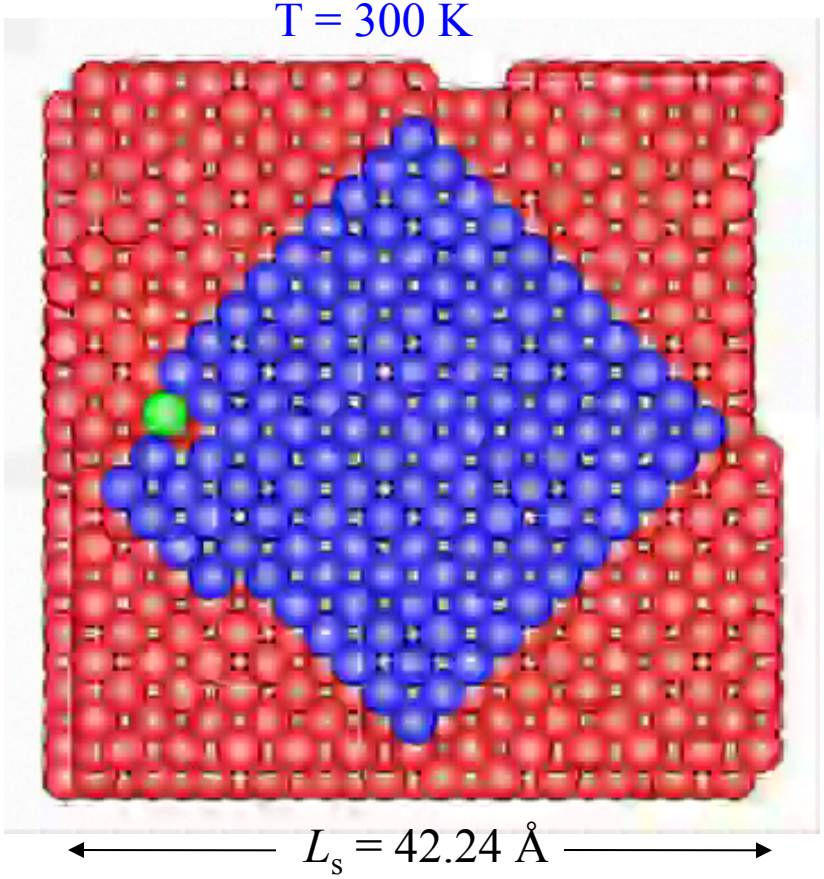


Temperature-accelerated dynamics (TAD) simulations

Shim & Amar, PRL (2012)

Annealing of Cu island on Ni(100)

T = 300 K



Temperature-accelerated dynamics (TAD) simulations

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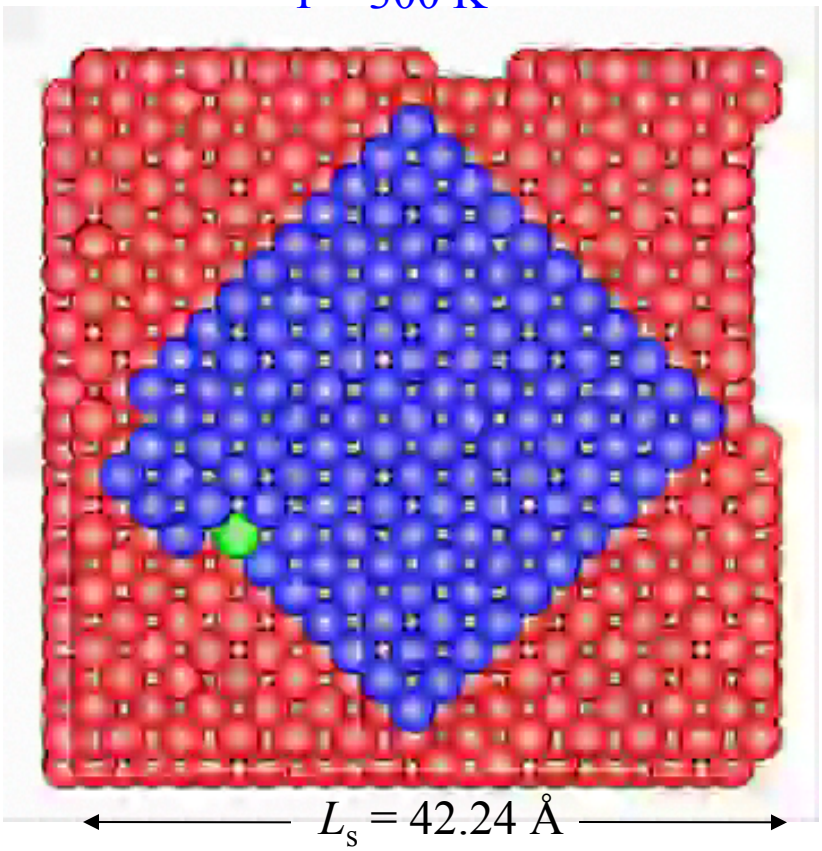
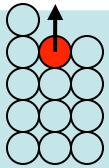
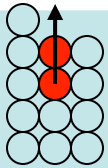
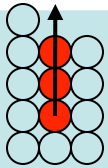
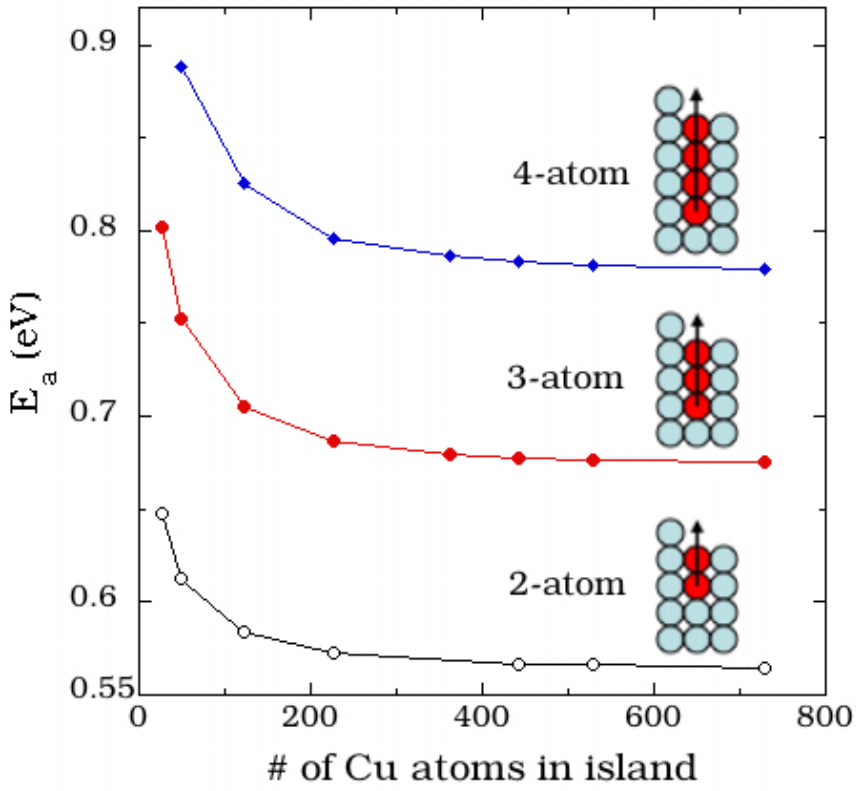


Activation barrier calculations: popout processes

Popout processes at kink *(11 x 11 island)*

			
Cu/Ni(100) ε= 2.7 %	0.47 eV	0.59 eV	0.72 eV
Cu/Ni(100) ε= 5.0 %	0.34 eV	0.37 eV	0.41 eV
Cu/Cu(100)	0.70 eV	0.86 eV	1.04 eV
Ni/Ni(100)	0.98 eV	1.17 eV	1.41 eV

Island size dependence

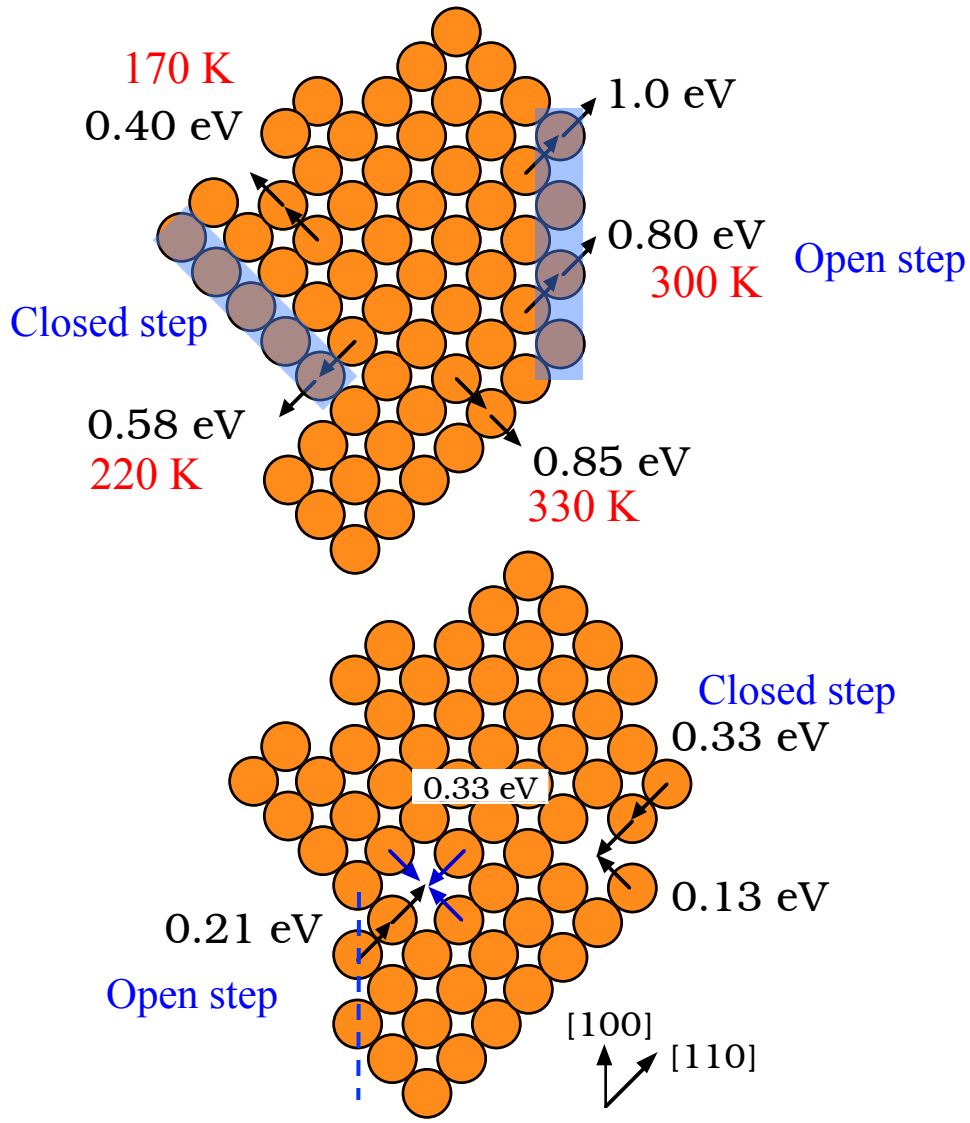


Similar results obtained for other types of `popout' events at [110] and [100] steps

Pop-out events: competition between open and closed steps

Pop-out processes

Reverse processes



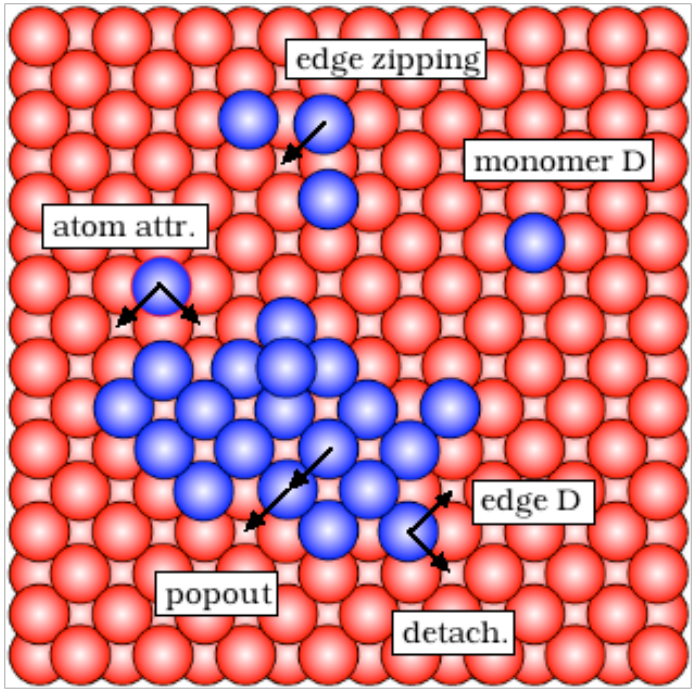
KMC model of Cu/Ni(100) submonolayer growth

I. Deposition:

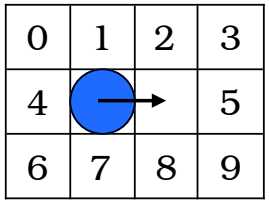
Flux = 6.3 x 10^{-3} – 1.5 x 10^{-3} ML/s

II. Surface diffusion:

DFT and EAM barrier calculations (AFW, MVC, Zhou, and Voter EAM)



1. Single atom diffusion: 0.17 – 0.90 eV



(1) Embed in 11 x 11 Cu island

(2) EAM potential

- 544 independent config. out of 1024 config.

Edge zipping: E_{zip} = 0.17 eV (DFT)

Edge diffusion: E_e = 0.35 eV (DFT)

Monomer diffusion: E_m = 0.41 eV (Expt.)

Corner diffusion: E_c = 0.56 eV

2. ES step barrier:

- $E_{[110]}$ = 0.0 eV, $E_{[100]}$ = -0.04 eV (exchange)

3. Vacancy diffusion:

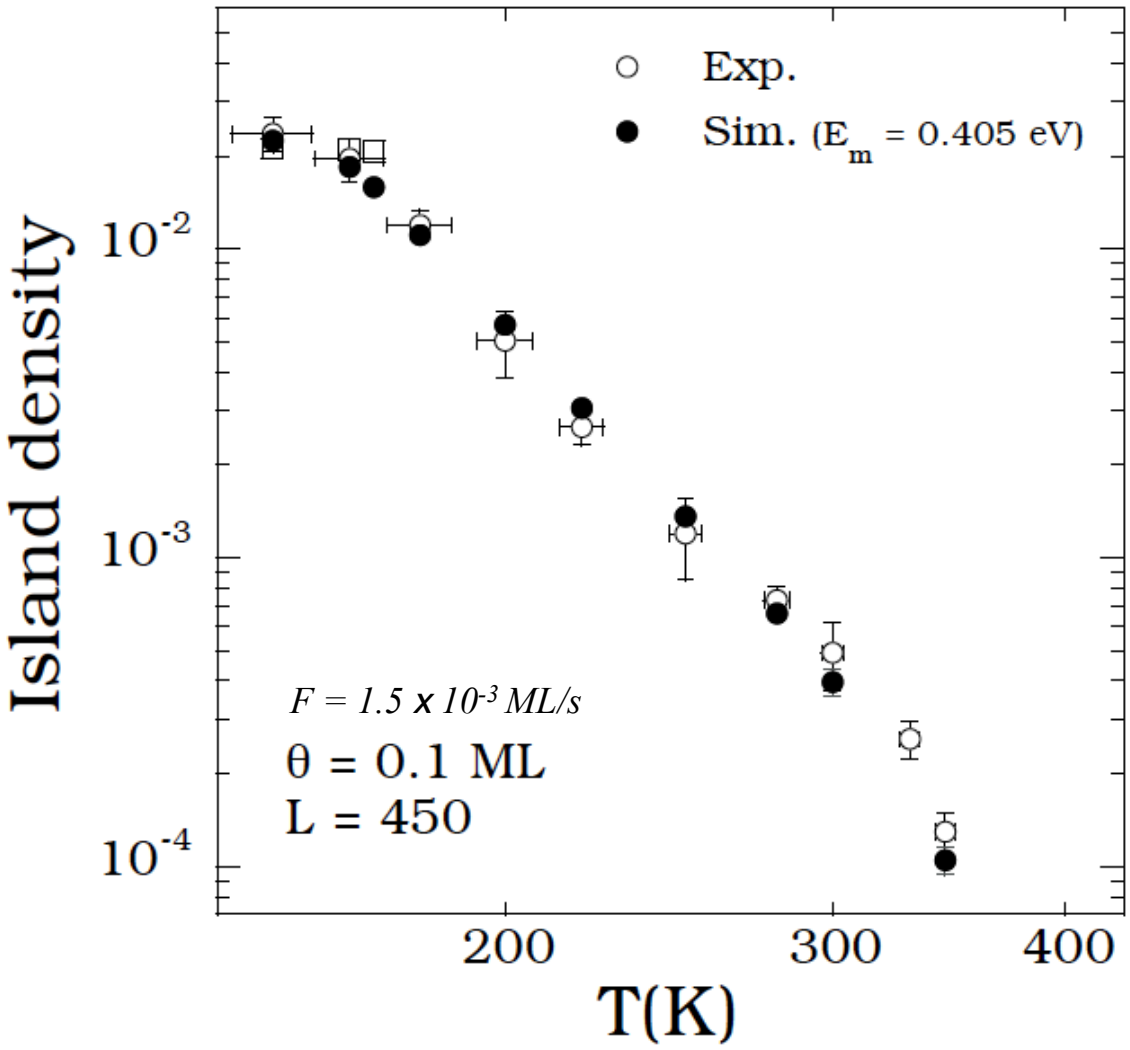
- Single (0.33 eV: DFT), dimer (0.46 eV)

4. Multiatom diffusion: 0.23 – 1.1 eV

- 35 popout processes including reverse processes: 2-atom and 3-atom popout at [100], [110] and other types of steps

Island density: Cu/Ni(100) submonolayer growth

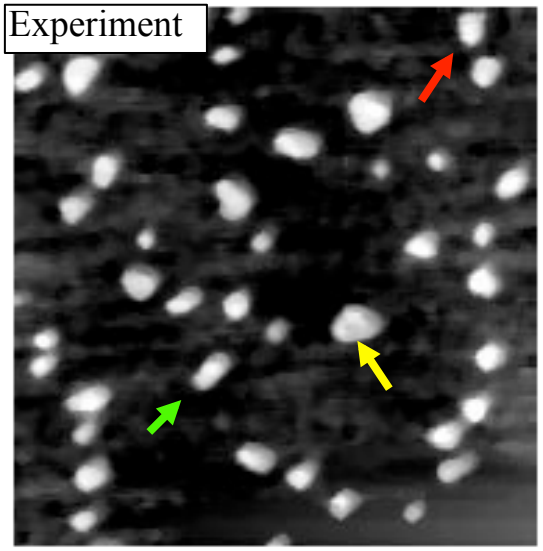
[1]Müller, Surf. Rev. Lett. 8 (2001)

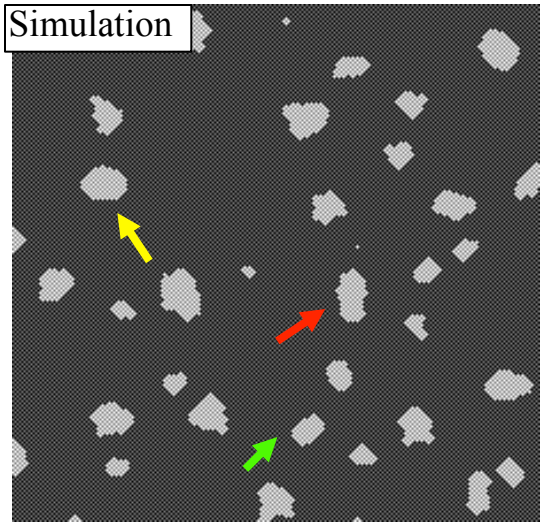


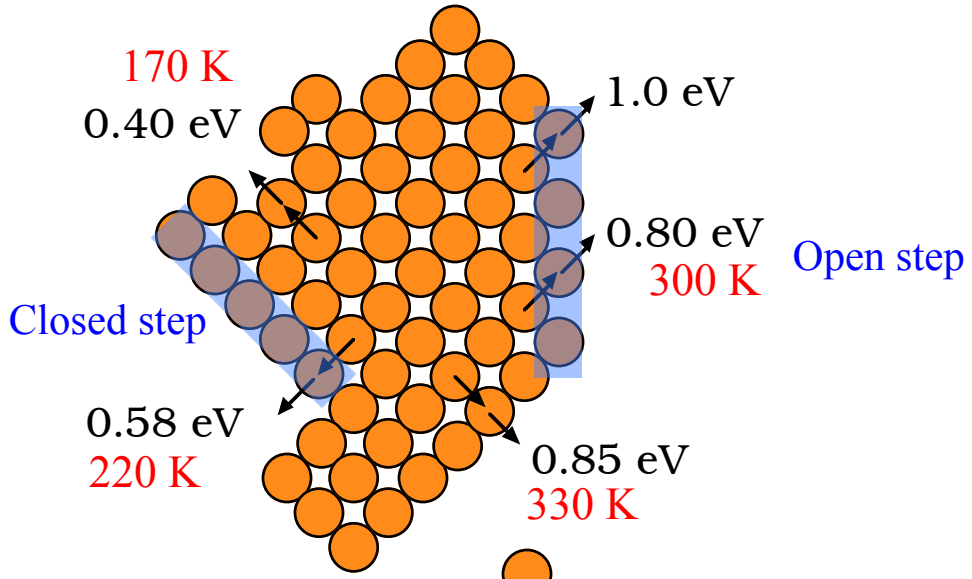
Comparison of island morphology with experiment

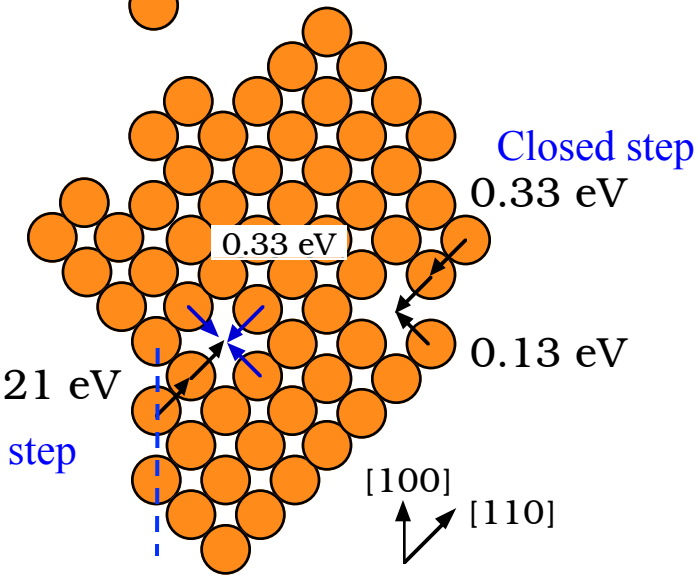
T = 250 K

θ = 0.09 ML (F = 0.0015 ML/s)





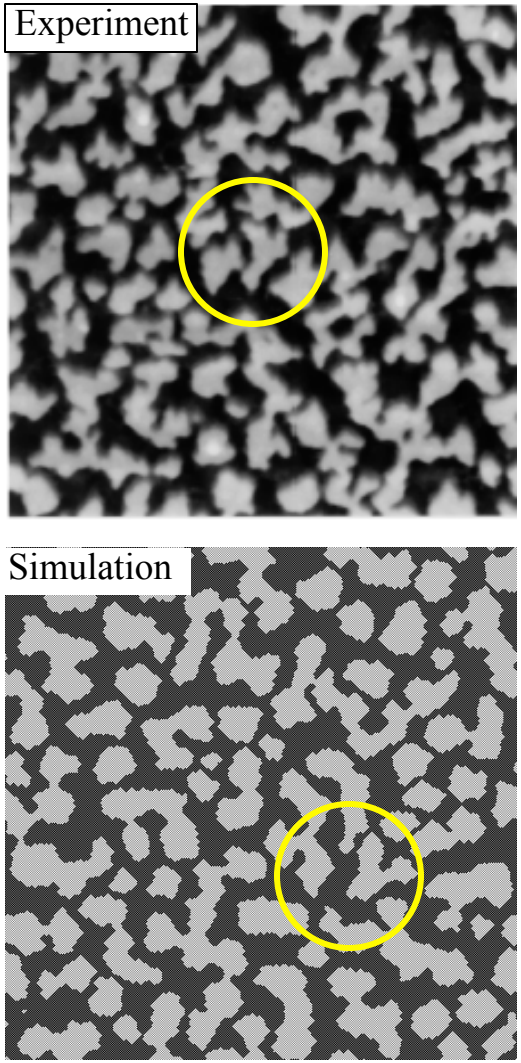


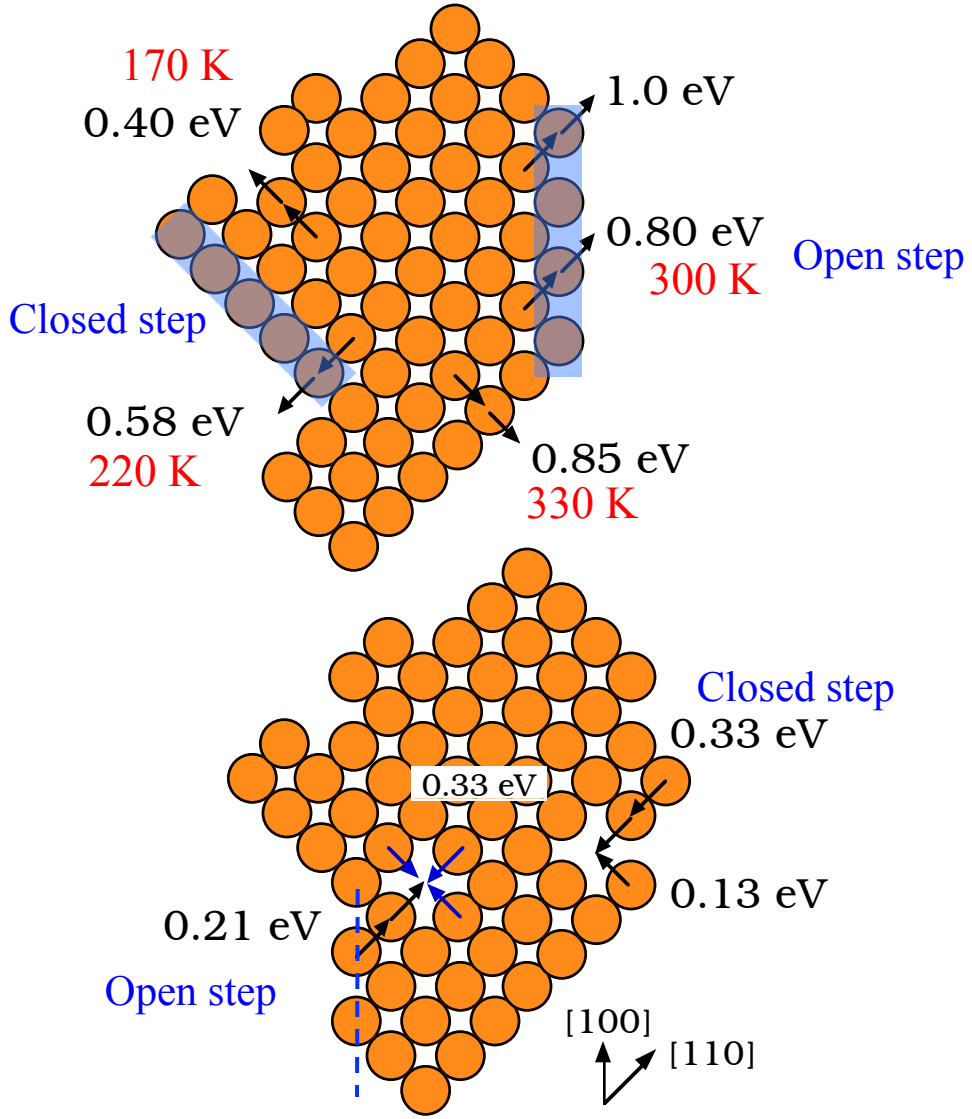


Comparison of island morphology with experiment

T = 250 K

θ = 0.5 ML (F = 0.0015 ML/s)



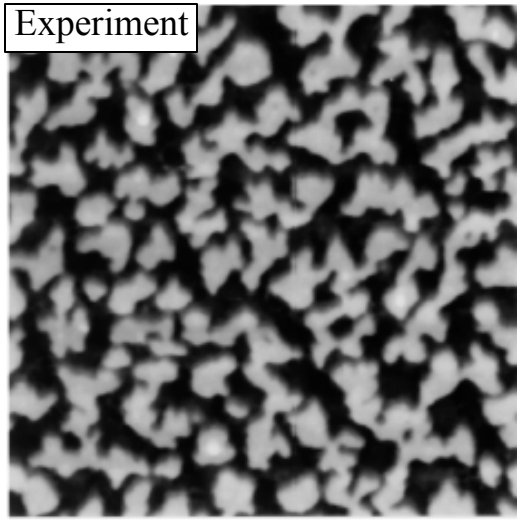


Comparison of island morphology with experiment

T = 250 K

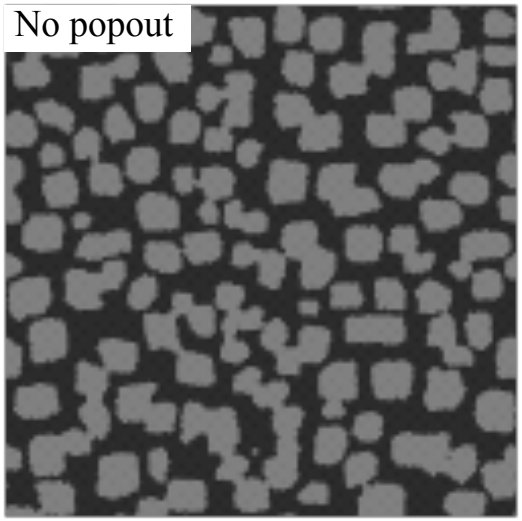
θ = 0.5 ML (F = 0.0015 ML/s)

Experiment

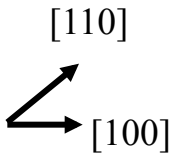


Open and closed steps

No popout



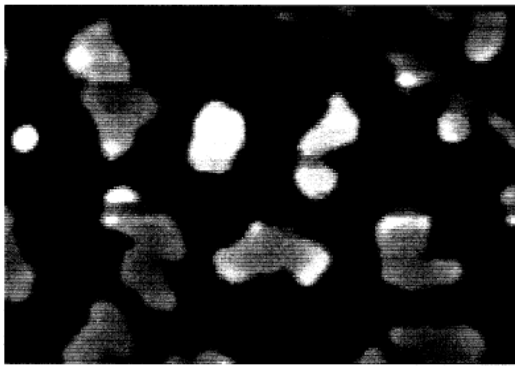
Open steps dominate



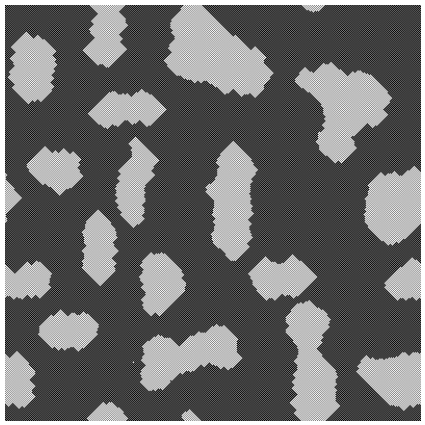
Comparison of island morphology with experiment

T = 300 K, θ = 0.3 ML

Experiment



Simulation

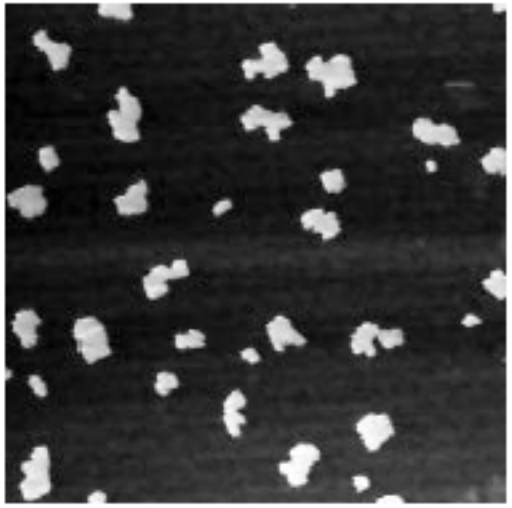


[110]
[100]

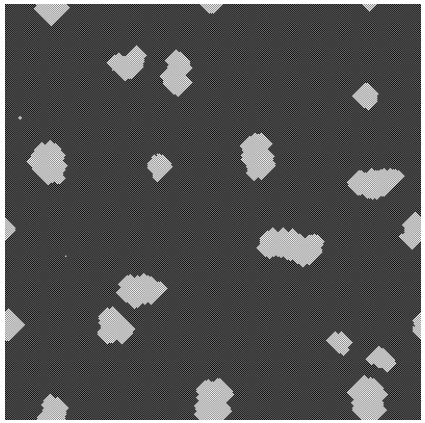
Good qualitative agreement

Comparison of island morphology with experiment

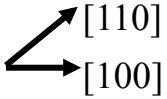
T = 345 K, θ = 0.09 ML



(F = 6.3 x 10^{-3} ML/s)



(F = 6.0 x 10^{-3} ML/s)



Summary

- **Ramified islands** and **selected arm width** in Cu/Ni(100) submonolayer growth ***cannot*** be explained by continuum elasticity theory

  => elasticity theory prediction for L_c too large!

  => strain energy shows significant deviations for finite islands

- TAD/KMC results indicate that formation of ramified islands due to ***competition between open and closed steps mediated by strain***

  => novel kinetic mechanisms ("pop-out") play key role

  => activation barriers for "pop-out" affected by island-size

Summary

- At higher T = 345 K (θ = 0.32 ML) KMC simulations lead to elongated rather than ramified islands as observed in experiment

  => Additional processes may become active at 345 K

  => Need to take into account size-dependence of activated processes

Conclusions

- By carrying out *temperature-accelerated dynamics* and parallel TAD (parTAD) simulations (combined with *DFT calculations* and *KMC simulations*) we have made significant progress in understanding ***submonolayer and multilayer metal epitaxial growth***

- Competition between variety of different and unexpected relaxation mechanisms plays key role in determining growth behavior

  - *shadowing/DF in low T Cu/Cu(100) growth*

  - *RDF/edge-zipping/interlayer-diffusion in Ag/Ag(100) growth*

  - *strain-mediated popout events in submonolayer Cu/Ni(100) growth*

- Understanding metal epitaxial growth requires multiscale simulations in both length- and time