Realistic multi-site multi-component lattice-gas modeling …epitaxial growth of metal films on binary alloy surfaces

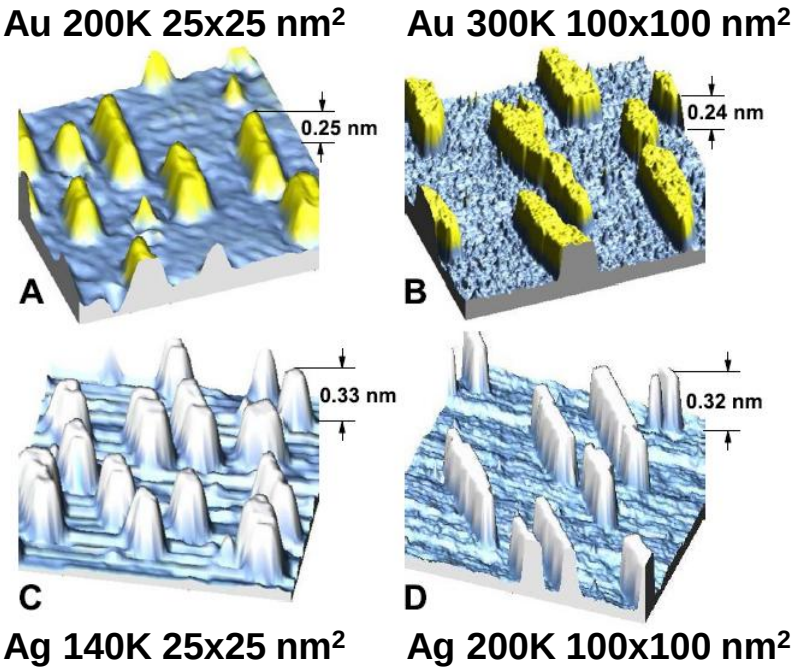
Au versus Ag on NiAl(110) ***Ni + Al on NiAl(110)***

DFT & KMC Modeling: Yong Han, Da-Jiang Liu, Jim Evans

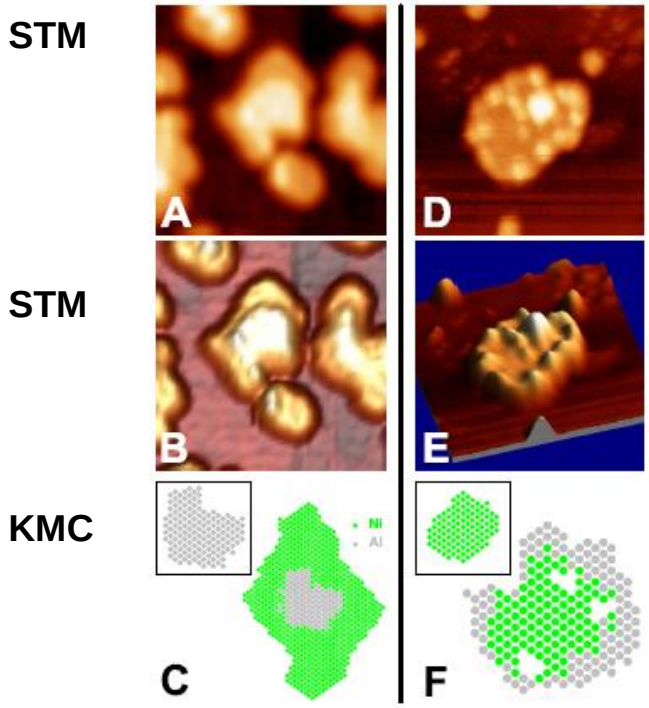
Experiment: Dapeng Jing, Baris Unal, Chad Yuen, Thomas Duguet, Patricia Thiel

Iowa State University **$$ NSF Grant CHE ♦ 0809472**

COMPARISON OF Au AND Ag ON NiAl(110): SIMILAR LATTICE-MATCHED METALS …DISTINCT BEHAVIOR



CO-DEPOSITION OF Ni AND Al ON NiAl(110): DEVIATIONS FROM PERFECT ALLOY ORDER



Duguet, Han, Yuen, Jing, Unal, Evans, Thiel, Proc. Nat. Acad. Sci. (2010)

Overview: Goals, Challenges, Approach, Systems

- **Goal:** realistic atomistic-level modeling of formation of epitaxial metal nanostructures during deposition on binary alloy surfaces *.....far-from-equilibrium nanostructures access vast phase-space of morphologies and local compositions for multi-component deposition*

- **Challenges:** binary alloy surfaces can offer multiple adsorption sites and diffusion paths even for isolated adatoms. In addition, realistic modeling requires accurate description of edge diffusion and attachment-detachment processes for all island edge configurations.

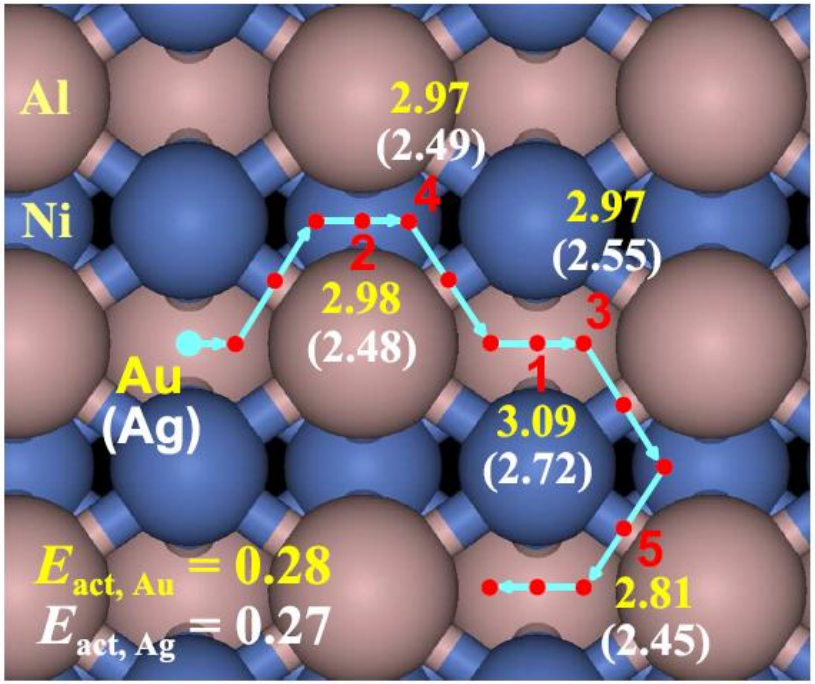
- **Approach:** multi-site lattice-gas modeling with realistic energetics & hopping barriers guided by DFT (ideally sampling adatom interactions at both adsorption sites and transition states). Analysis via KMC.

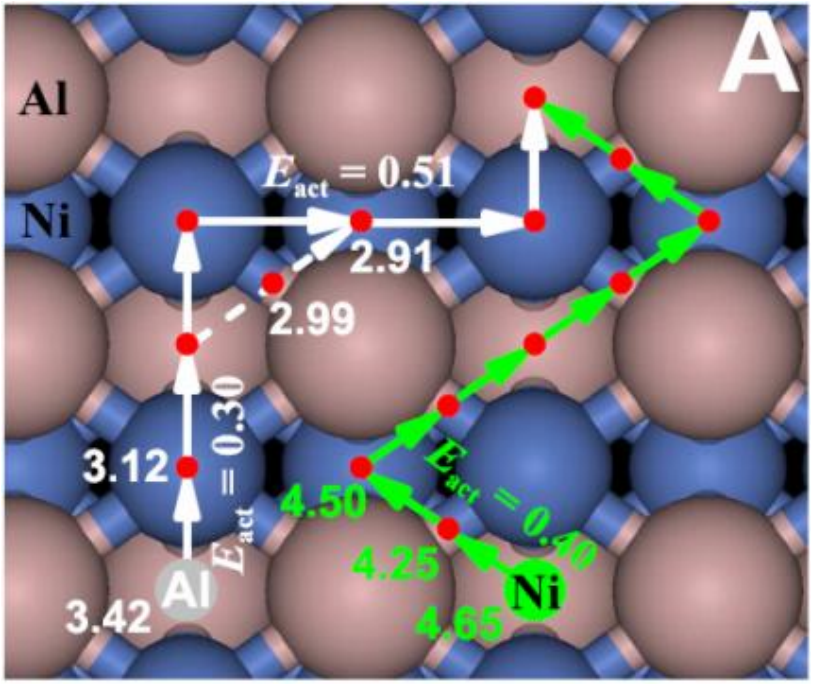
Focus of this presentation:

Au/NiAl(110) vs. Ag/NiAl(110): similar systems, different structures

Ni+Al on NiAl(110): fundamental study of (deviations from) alloy self-growth

Isolated adatoms: adsorption energies & diffusion paths





Au and Ag on NiAl(110):

…both prefer Ni-bridge (Ni-br) site

…isotropic diff.n by diagonal hops between Ni-br and Al-br sites

E_d = 0.28eV (Au), 0.27 eV (Ag)

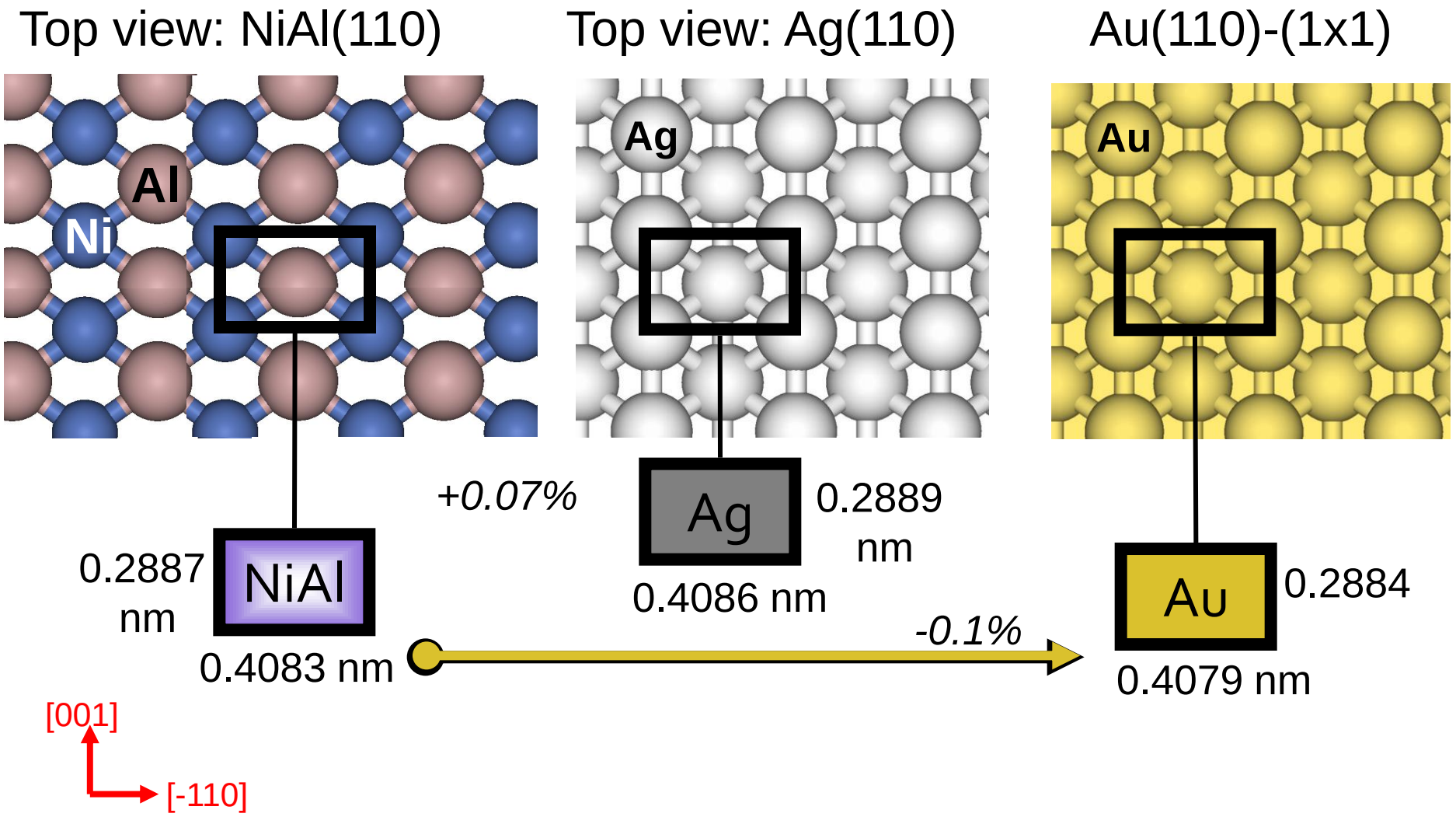
Ni and Al on NiAl(110):

…both prefer Ni-br site (which is the wrong site for Ni)

…Ni diff.n by diag. hops: E_d=0.40eV

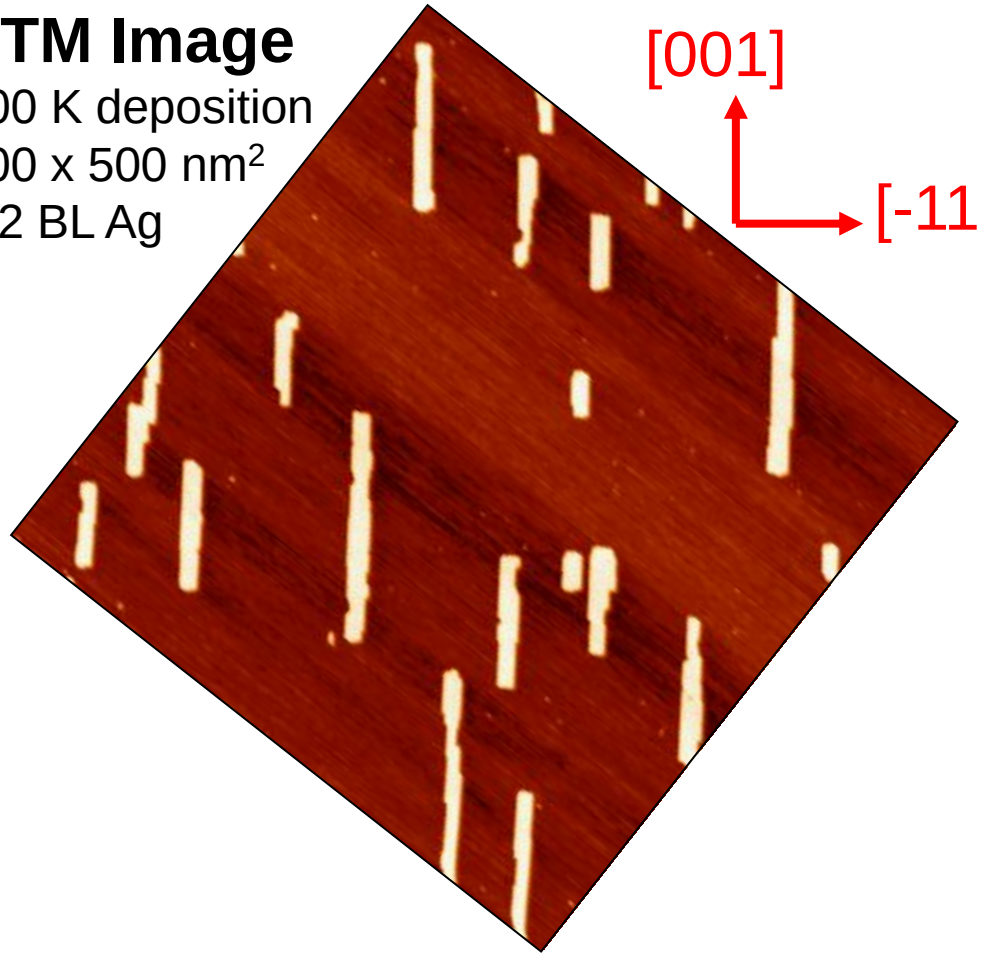
…Al anisotropic diff.n: E_d=0.5,0.3eV

Ag(110) & Au(110) on NiAl(110): near-perfect lattice-match



Ag on NiAl(110): rectangular bilayer Ag(110) islands

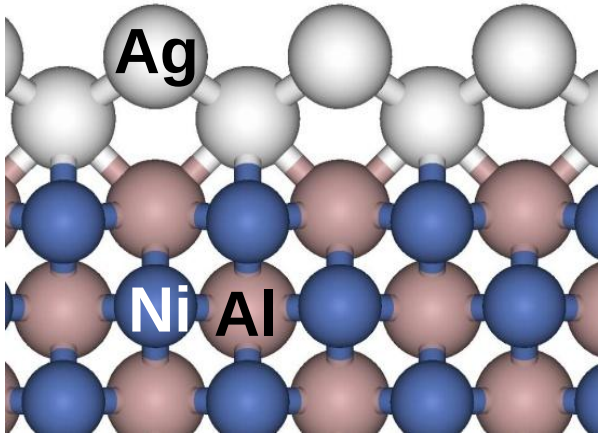
STM Image
300 K deposition
500 x 500 nm^2
0.2 BL Ag



Measured island height = 0.33 nm

Side view of model

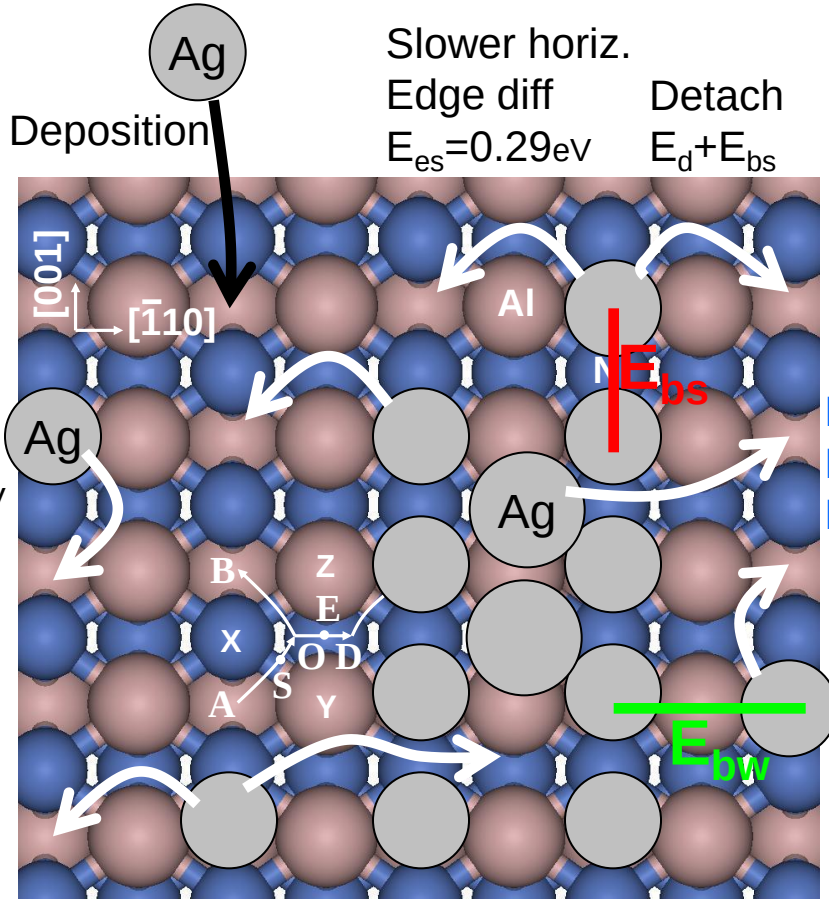
0.34 nm
(DFT)

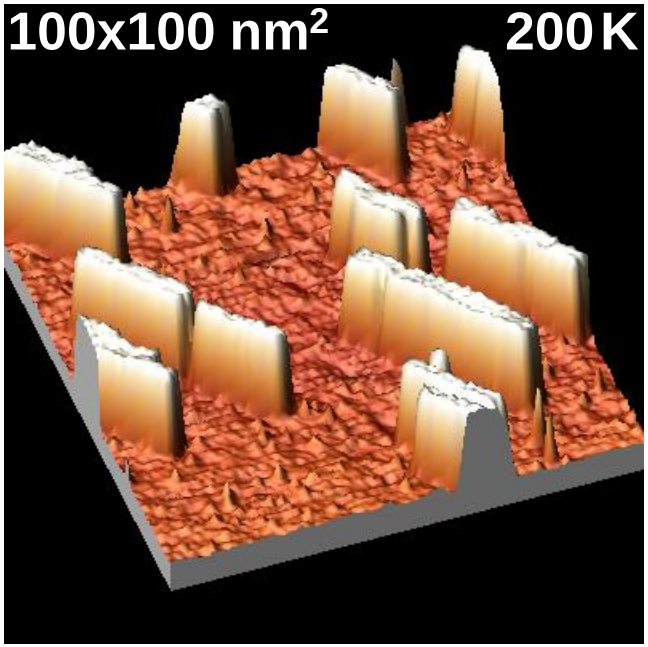


bilayer Ag(110) islands with elongated growth shapes

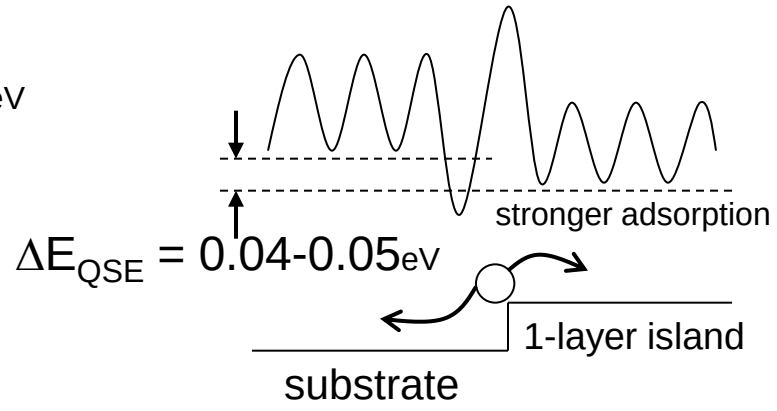
Ünal, Qin, Han, Liu, Jing, Layson, Jenks, Evans, Thiel, PRB (2007).
Han, Unal, Jing, et al., PRL (2008); PRB **81** (2010) 115462.

Single-site LG modeling: Ag(110) bilayer island formation





Ag(110)/NiAl(110) 200 K 20% covered
Island Height: 0.33nm @ all T



E_{bs} = 0.09eV (stronger attraction)
E_{bw} = 0.03eV (WEAK attraction)

Han et al. PRL 100 (2008) 116105

Hopping barrier selection: single-site model, geometric islands

Any legitimate choice must satisfy **detailed-balance**..
We will NOT use…

Standard "initial value approximation" (IVA) approach:

E_{act} = E_d(terrace diffusion barrier) + E_{int}(lateral interactions in initial state)

INSTEAD, we use…

Modified "initial value approximation" (IVA) approach:

E_{act} = E_o(appropriate diff.n barrier) + E_{int}(lateral int. in initial state) where…

For terrace diff.n, attachment & detachment, E_o = E_d(terrace diff.n barrier)

For edge diffusion (where the adatom is at edge before and after hop), E_o = selected to recover barrier along straight horizontal (vertical) edges for hops in the horizontal (vertical) direction $\Rightarrow$ $E_o = E_{eh(ev)} - E_{bv(bh)}$

For interlayer diffusion, difference in E_o for upward and downward hops equals difference in isolated adatom adsorption energies for different layers, and magnitude of E_o also reflects any step edge barrier.

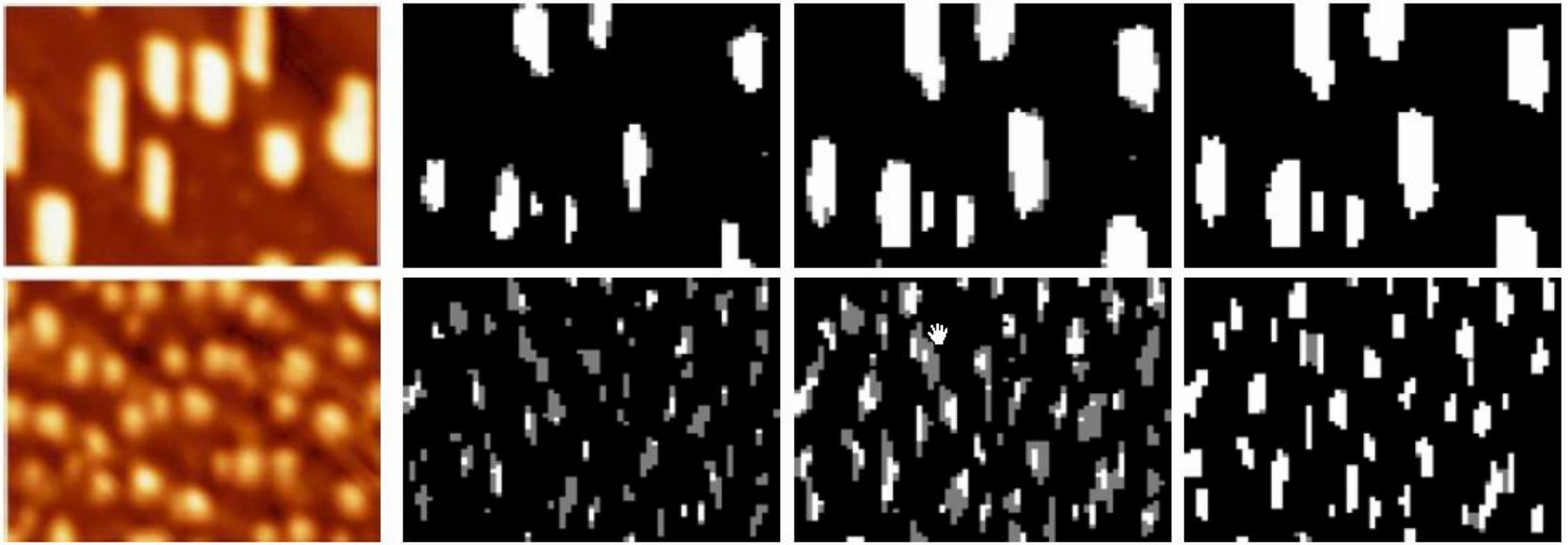
KMC simulation: facile Ag bilayer island formation on NiAl(110)

STM & KMC images of Ag islands on NiAl(110) are 27×19 nm^2
KMC images: grey = 1st layer; white = 2nd layer Ag adatoms

Han et al.,
PRL (2008), PRB (2010)

TOP: DEPOSITION OF Ag ON NiAl(110) AT 140K WITH LOW F =0.003BL/S

STM: 0.2BL **KMC: 0.1BL** **KMC: 0.2BL** **KMC: 10 min later**



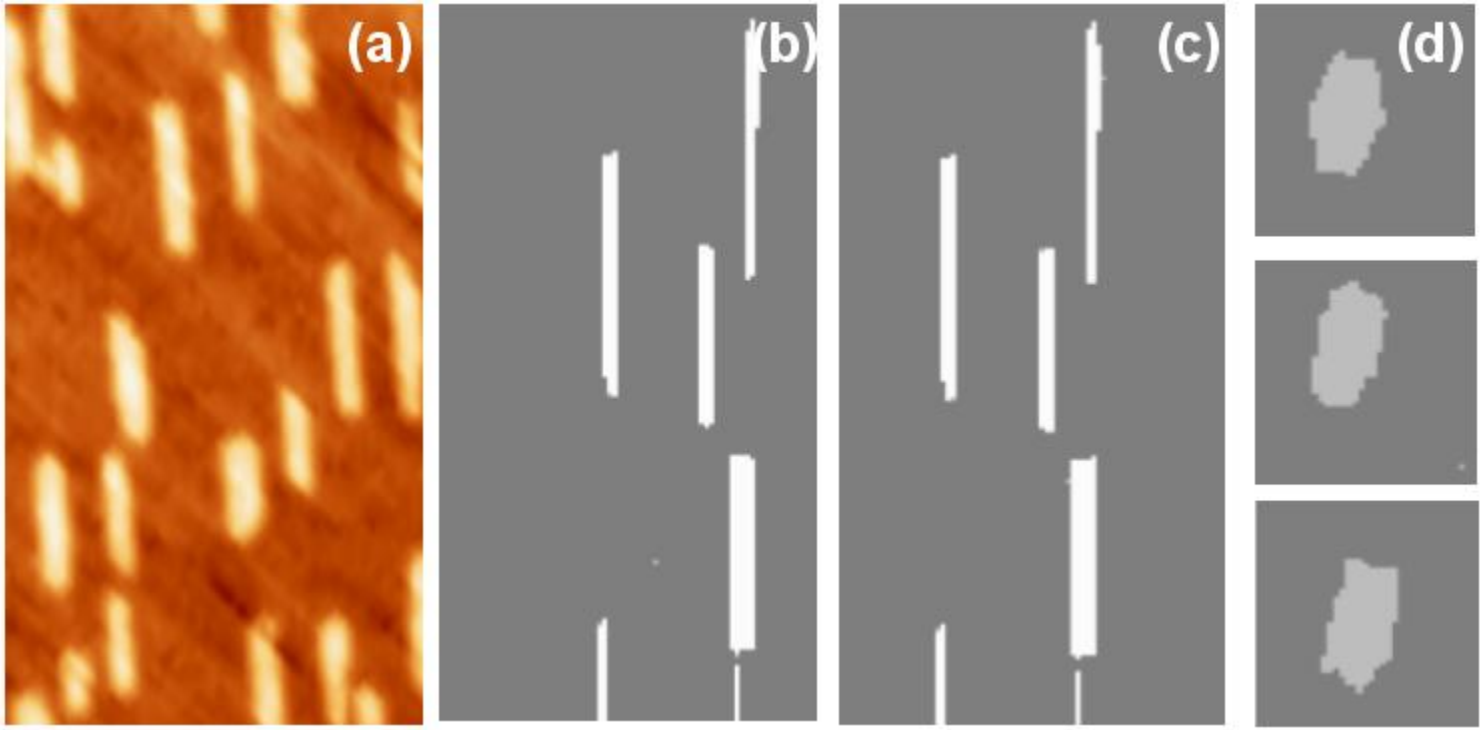
STM: 0.14BL **KMC: 0.07BL** **KMC: 0.14BL** **KMC: 10 min later**

BOTTOM: DEP.N OF Ag ON NiAl(110) AT 130K WITH HIGH F =0.03 BL/S

KMC simulation: elongated Ag bilayer island growth shapes

175 K **50x30 nm^2 (a-c)**

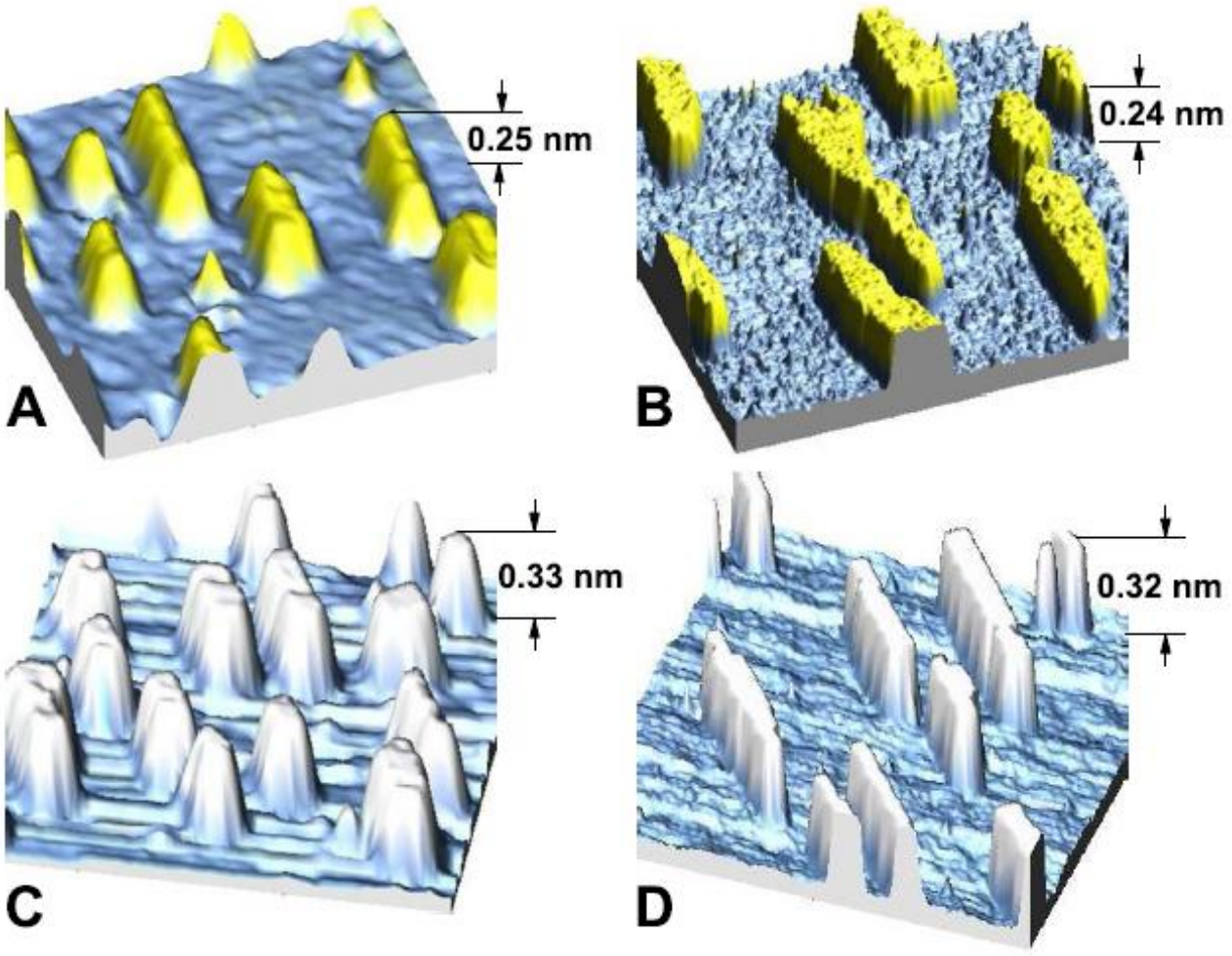
15x15 nm^2



Ag vs. Au on NiAl(110): similar metals, different behavior

Au 200K 25x25 nm²

Au 300K 100x100 nm²

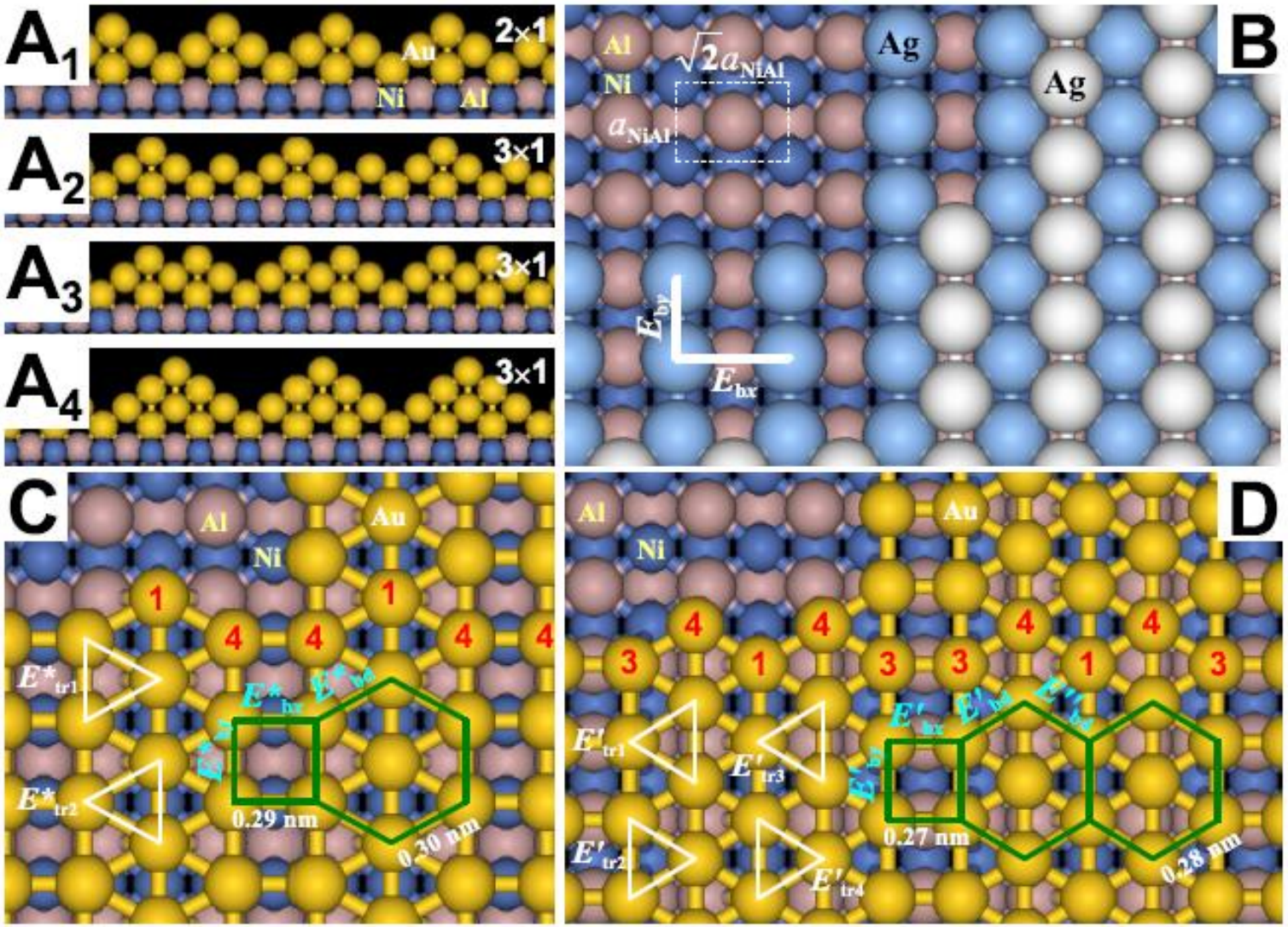


Ag 140K 25x25 nm²

Ag 200K 100x100 nm²

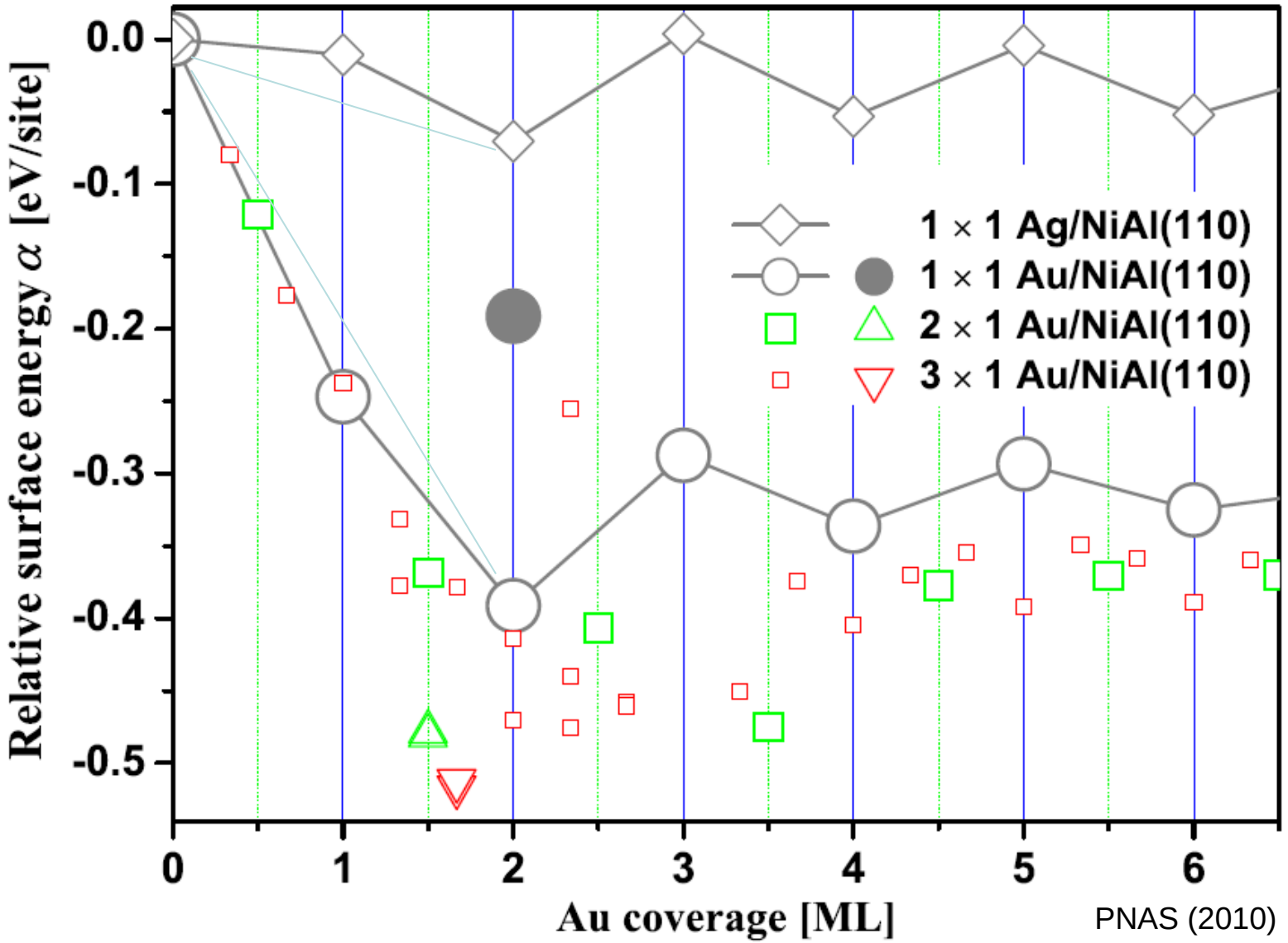
PNAS (2010)

Au on NiAl(110): viable low-energy structures



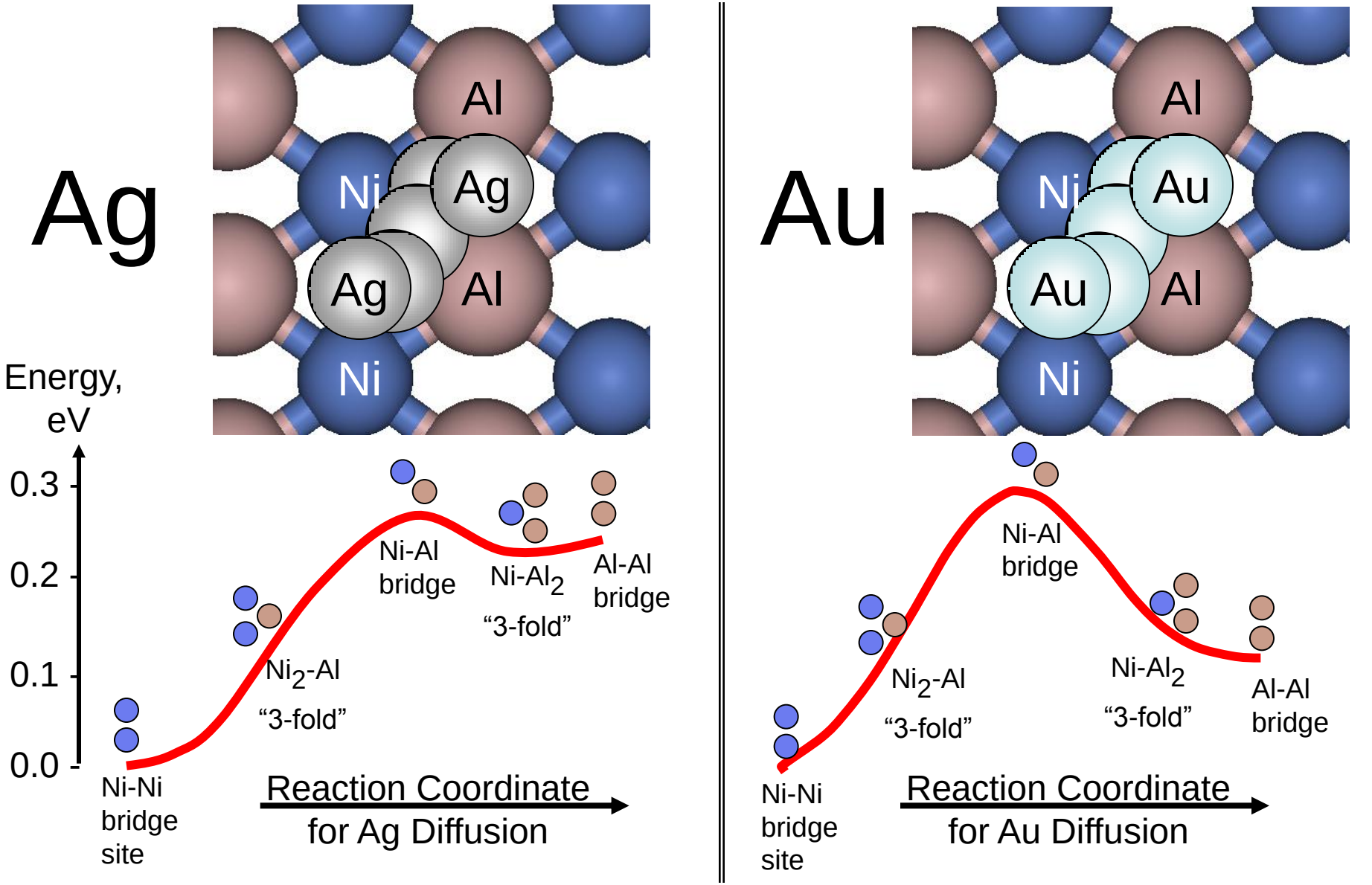
PNAS (2010)

Au on NiAl(110): viable low-energy structures

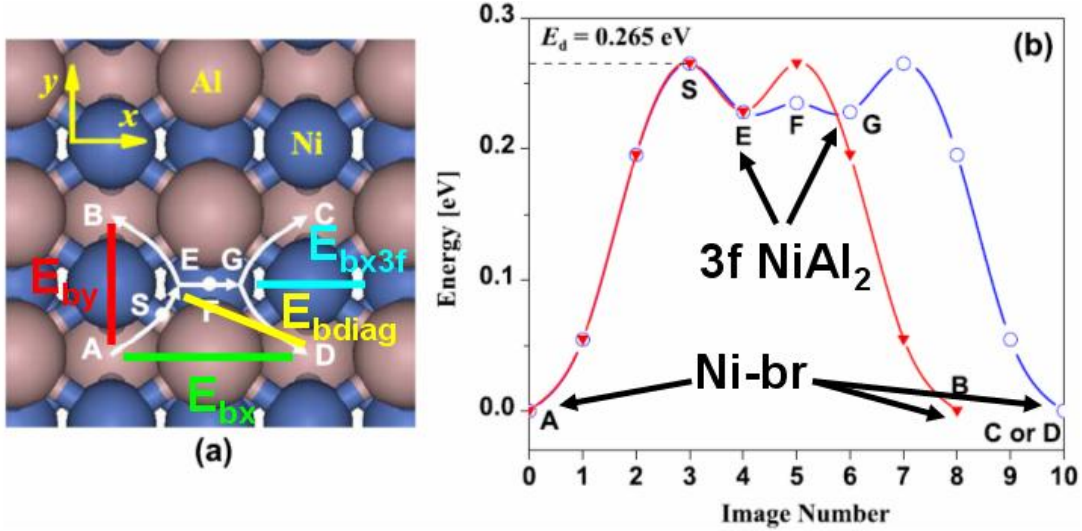


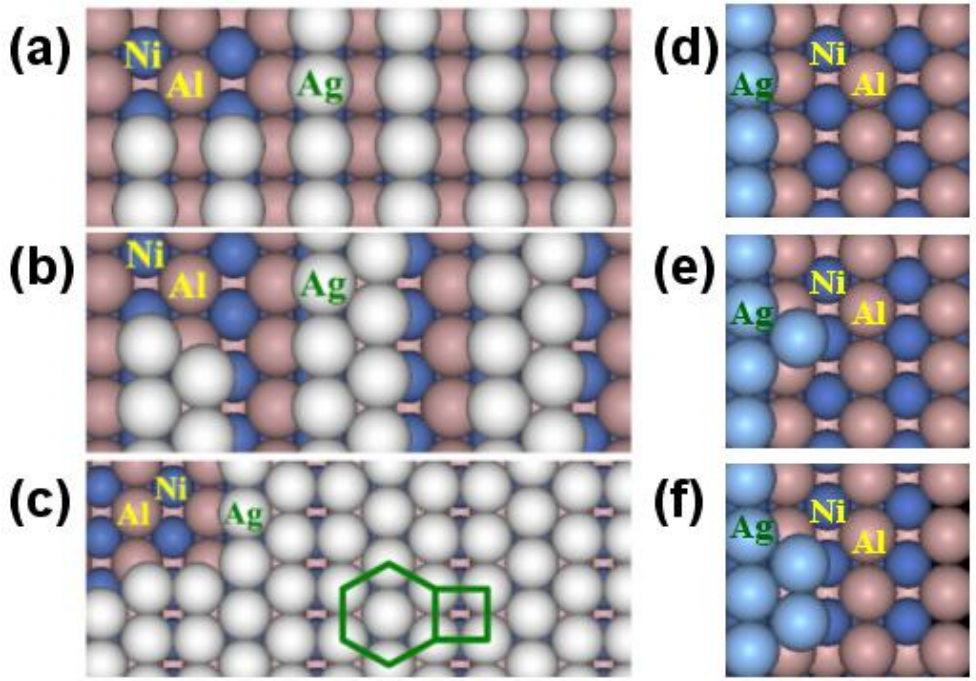
PNAS (2010)

Ag vs. Au on NiAl(110): similar metals, different behavior

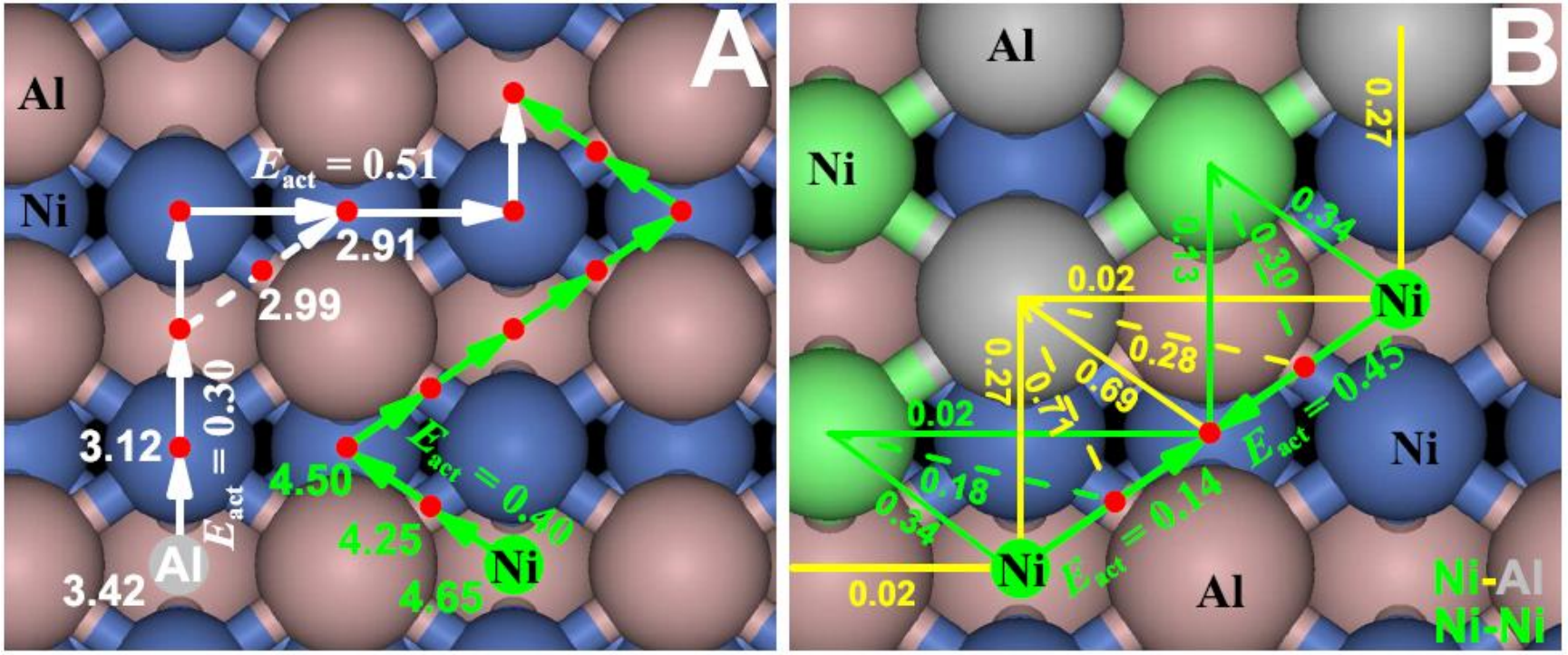


Ag and Au on NiAl(110): multi-site LG model energetics



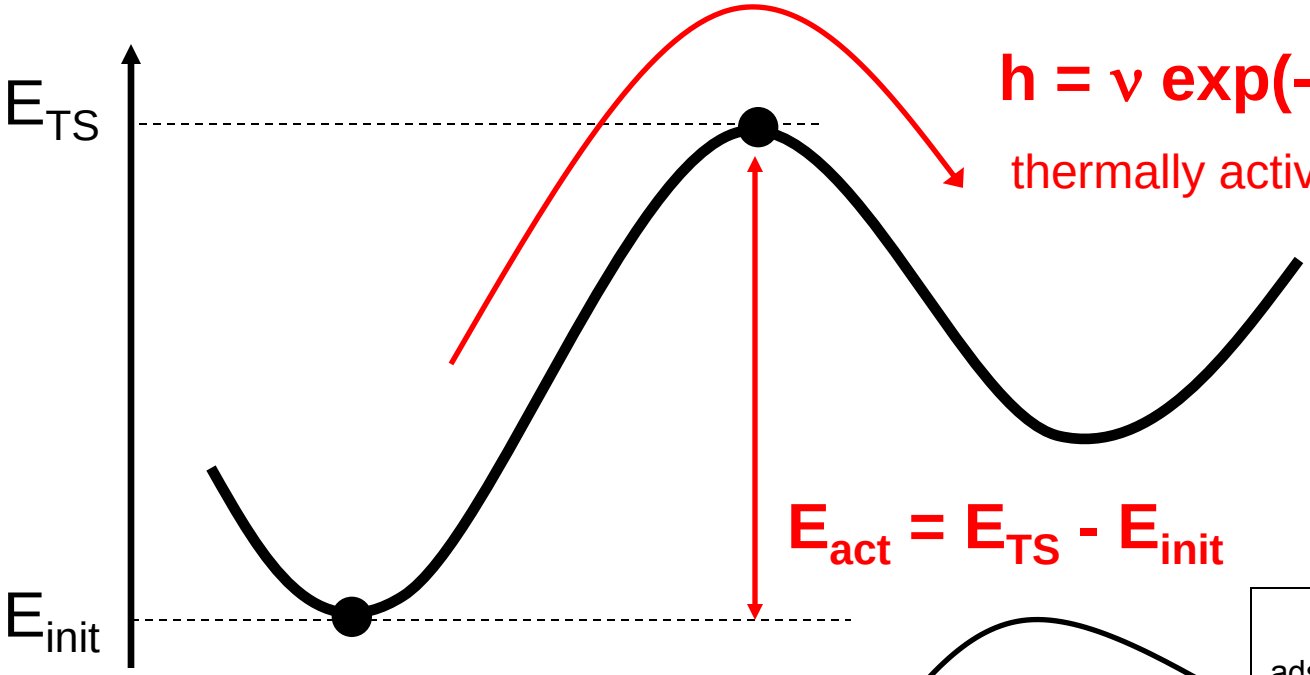


Ni and Al on NiAl(110): diffusion & detach/attach kinetics



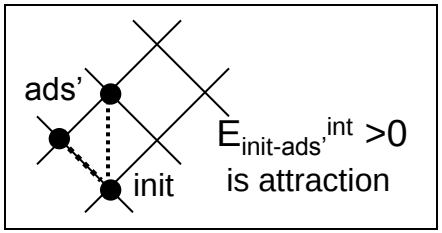
In addition to terrace diffusion of isolated adatoms,
must accurately describe edge diffusion
and detachment /reattachment kinetics
for a vast number of edge configurations

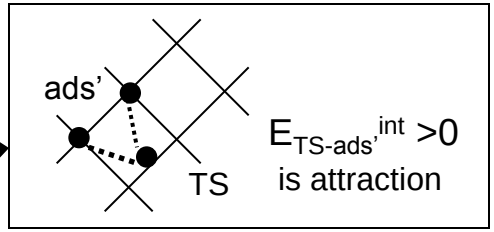
Ni and Al on NiAl/NiAl(110): General Treatment of Diffusion



$$E_{init} = E_{init}^{ads} - \sum_{ads'} E_{init\text{-}ads'}^{int}$$

$$E_{TS} = E_{TS}^{ads} - \sum_{ads'} E_{TS\text{-}ads'}^{int}$$

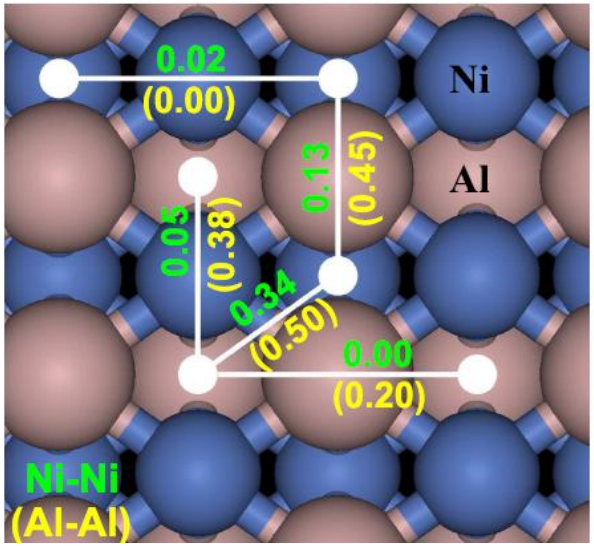


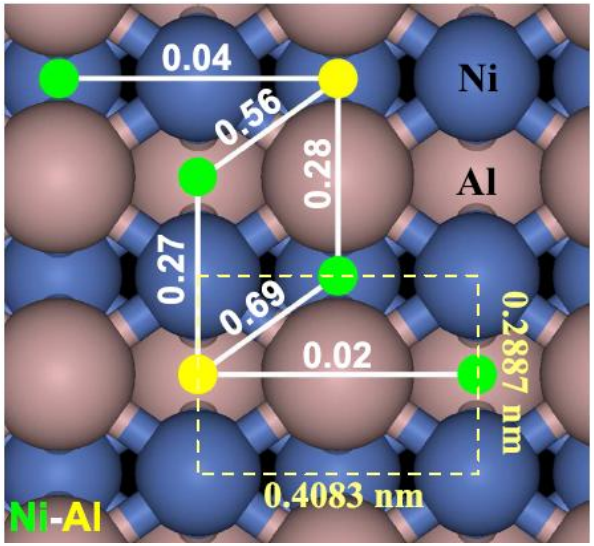


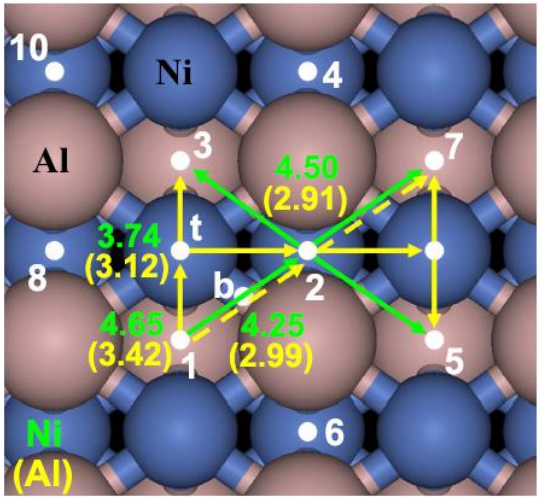
Ni and Al on NiAl(110): adatom interaction energies

Both adatoms at adsorption sites…

16 values







One adatom at a TS (Ni-Al-br = b, or Ni-top = t) and the other at an adsorption site…

TABLE I: Interactions in eV (attraction > 0) between adatoms with one adatom is at an adsorption site (Ni-br sites 1, 3, ...; Al-br sites 2, 4, ...) and another is at a TS (approximated as a Ni-top site t or Ni-Al bridge site b). See Fig. 2(a).

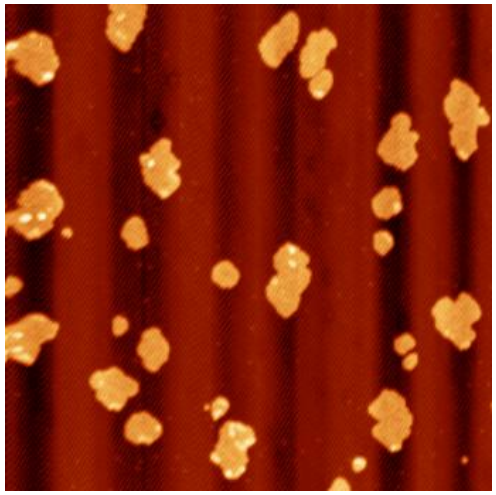
Ni(b)-Ni(3)	0.25	Al(b)-Al(3)	0.29	Ni(b)-Al(3)	0.71	Al(b)-Ni(3)	0.62	Al(t)-Al(2)	−1.00	Al(t)-Ni(2)	−0.44
Ni(b)-Ni(5)	0.14	Al(b)-Al(5)	0.40	Ni(b)-Al(5)	0.28	Al(b)-Ni(5)	0.24	Al(t)-Al(3)	−12.00	Al(t)-Ni(3)	−6.50
Ni(b)-Ni(6)	0.30	Al(b)-Al(6)	0.45	Ni(b)-Al(6)	0.85	Al(b)-Ni(6)	0.73	Al(t)-Al(4)	0.12	Al(t)-Ni(4)	0.06
Ni(b)-Ni(8)	0.18	Al(b)-Al(8)	0.20	Ni(b)-Al(8)	0.14	Al(b)-Ni(8)	0.18	Al(t)-Al(7)	0.02	Al(t)-Ni(7)	0.01

24 values

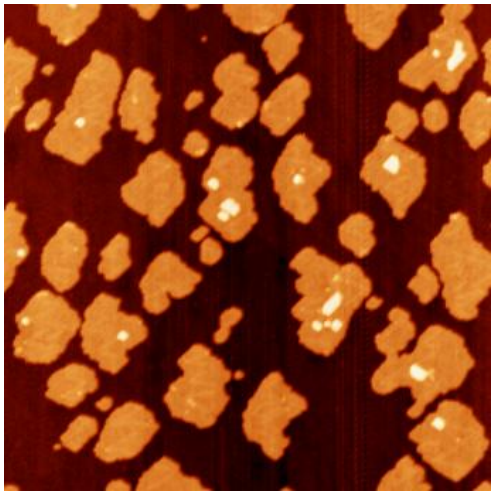
Ni on NiAl(110): Growth Shapes vs. Equilibrium Shape

Experimental STM images (100 × 100 nm^2) **F = 3×10^{-3} ML/s**

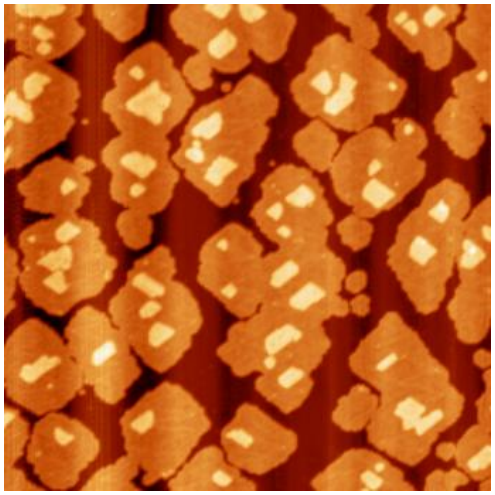
300 K Deposition



0.12 ML

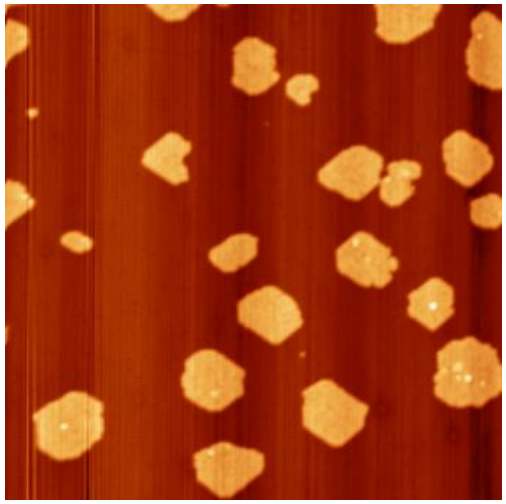


0.48 ML



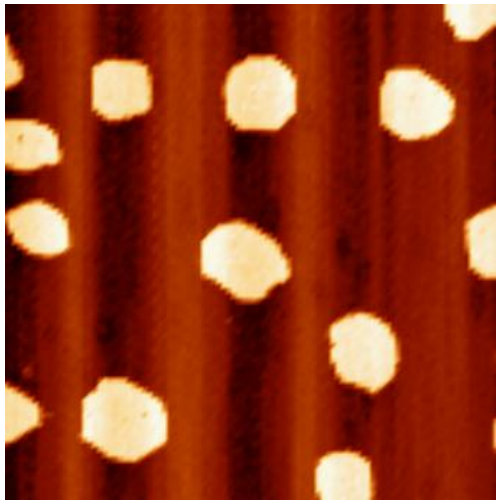
0.90 ML

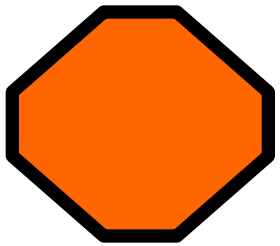
400 K Deposition



0.18 ML

500 K annealing

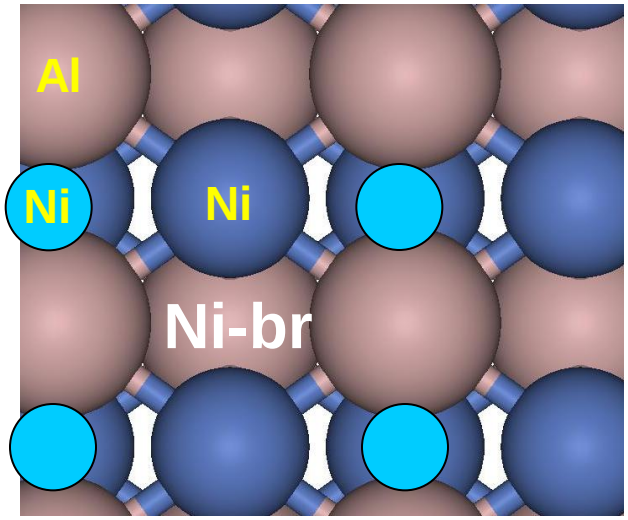




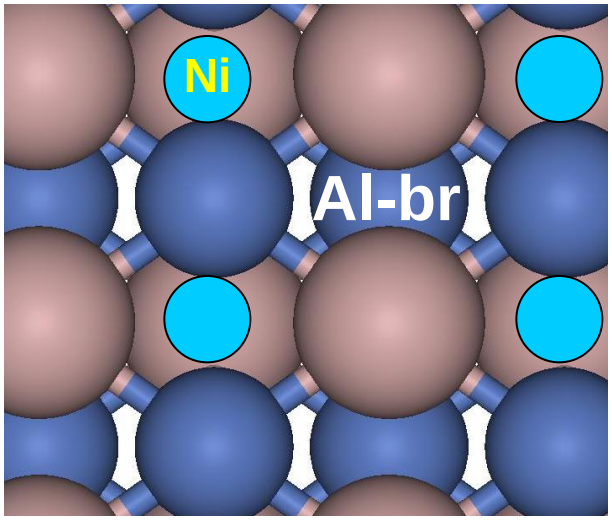
Equilibrium Shape

Ni on NiAl(110): Formation of 'Dense' Submonolayer Islands

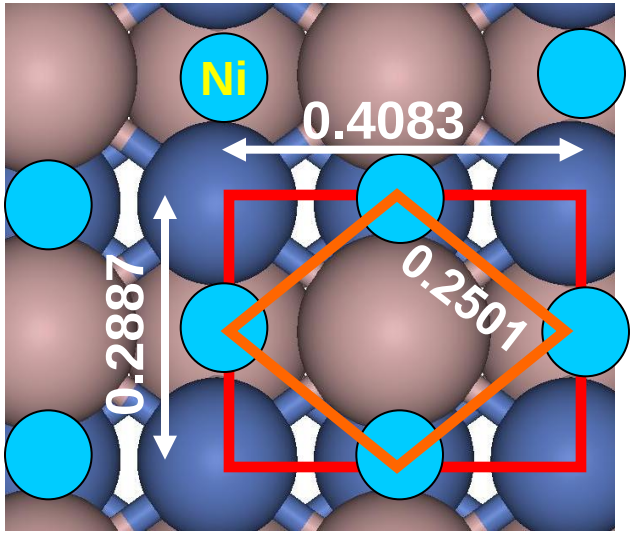
DFT calculations for monolayer binding energy per atom: E_{mb}



E_{mb} = 4.70 eV (natural site least favored)



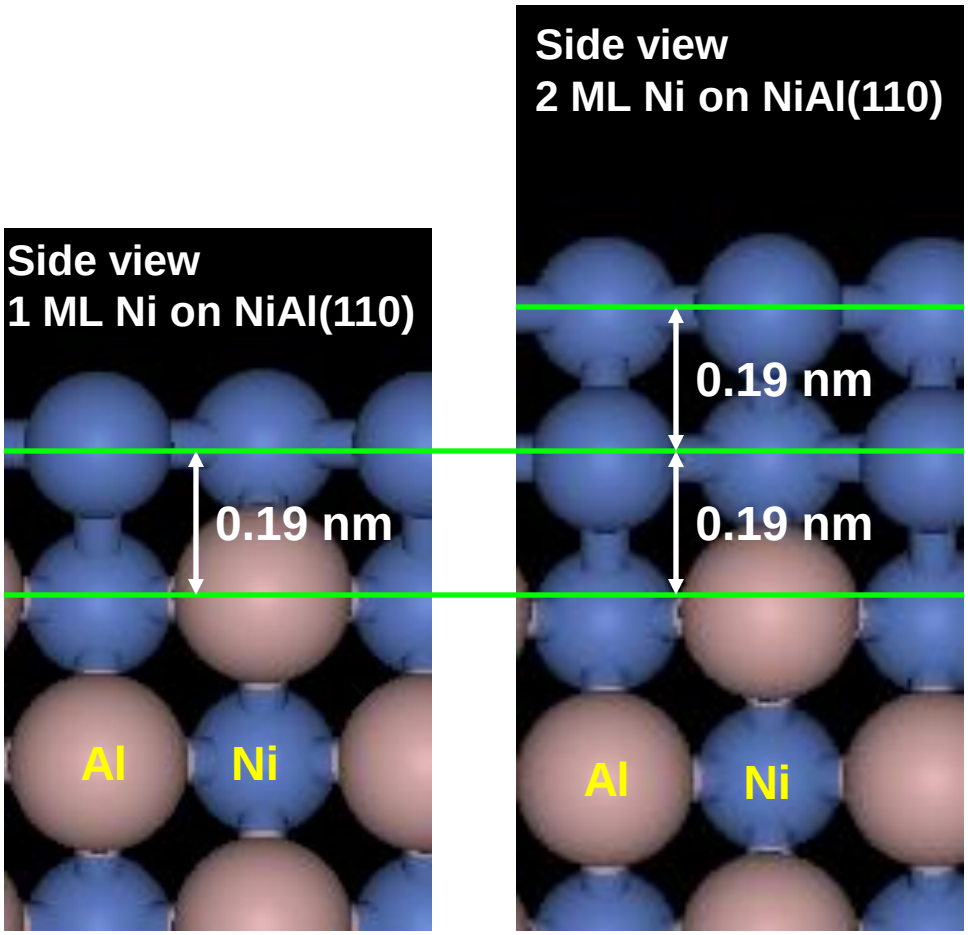
E_{mb} = 4.79 eV



E_{mb} = 5.45 eV

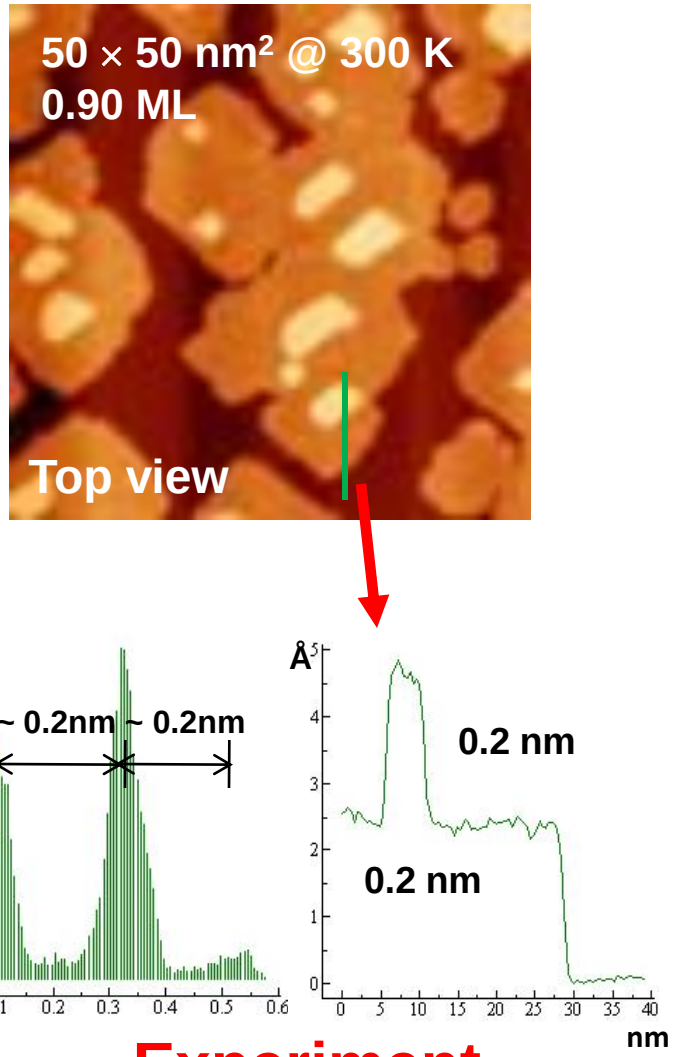
- Dense overlayer preferred with both Ni-br and Al-br sites populated (cf. Ag, Au: dilute)
- Surface lattice constant for Ni(100): 0.2489 nm
- Dense Ni adlayer suffers <u>little</u> strain

Ni on NiAl(110): Interlayer Spacing of Submonolayer Islands



DFT calculations

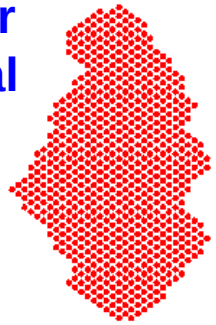
STM image of Ni on NiAl(110)

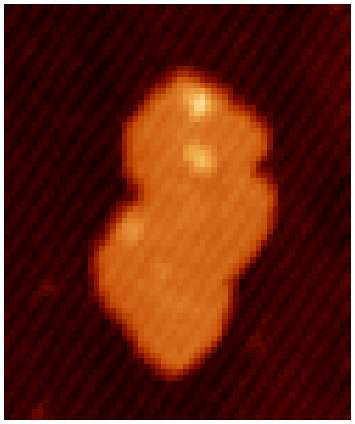


Experiment

Ni on NiAl(110): Island Shapes at 300-600 K (KMC vs. Expt.)

Elongated irregular diagonal edges favored

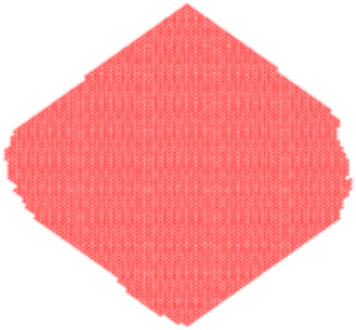


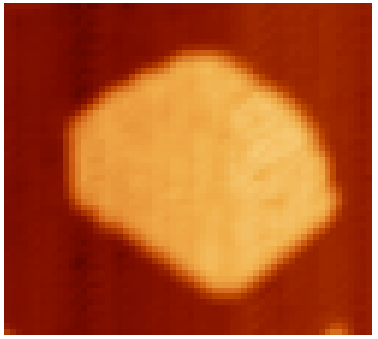


KMC STM

300 K

6-sided (octagon less 2 sides)

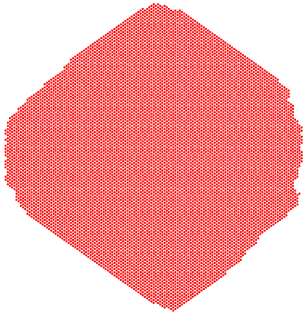




KMC STM

400 K

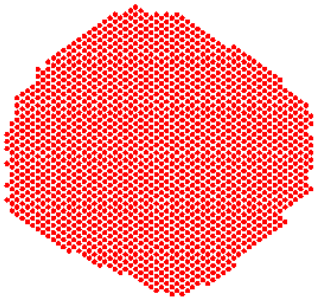
6-sided (octagon less 2 sides)

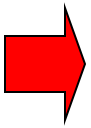


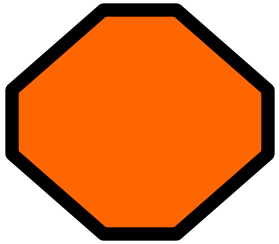
KMC STM

450 K

Octagon-like







KMC

600 K

Equilibrium Shape

Han et al., submitted

Ni on NiAl(110): More details on Ni island nucleation & shapes

ISLAND GROWTH SHAPES

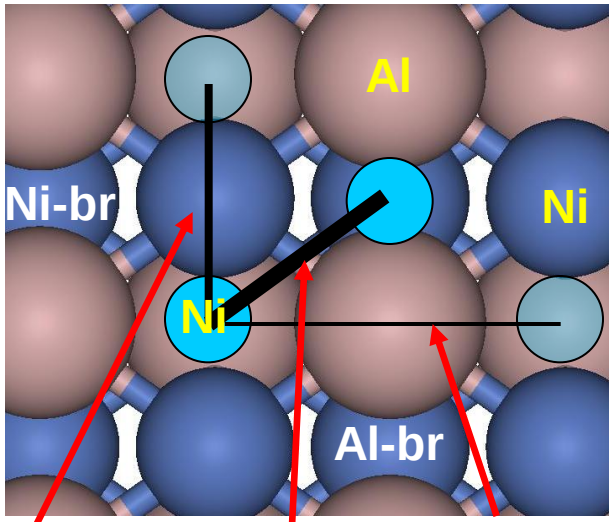
Edge diffusion active along diagonal steps at 300K with barrier of E_{edge} ~ 0.35 eV. but not along horiz/vert steps

…hence preference for diagonal steps [cf. square islands in metal(100) homoepi]

..why vertical elongation: anistropic corner rounding: easier from diagonal to horiz. (versus vertical) steps

…at higher T, horiz/vert edge diffusion becomes Active & anisotropic corner Rounding gives 6-sided islands

Most stable dimer mediating nucleation at low T (i=1)



E_{by}= 0.05 eV

E_{bx}= 0.00 eV

E_{bdiag}= 0.34 eV

Effective dimer binding

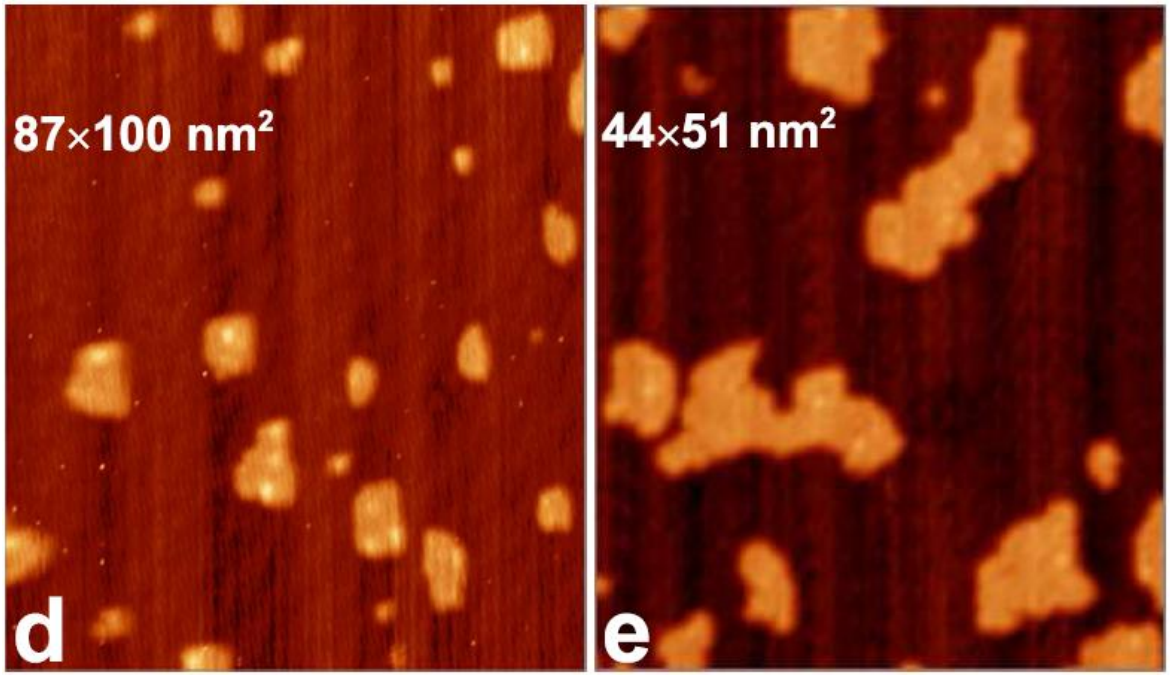
= (E_{bdiag}=0.34)–(ΔE_{ads}=0.15)= 0.19 eV

…not strong enough for i=1 @ 300K

N_{isl}(expt) = 4×10^{-3} nm^{-2} N_{isl}(i=1 KMC) = 9×10^{-3} nm^{-2}

Al on NiAl(110): Island Shapes at 300 K (KMC vs. Expt.)

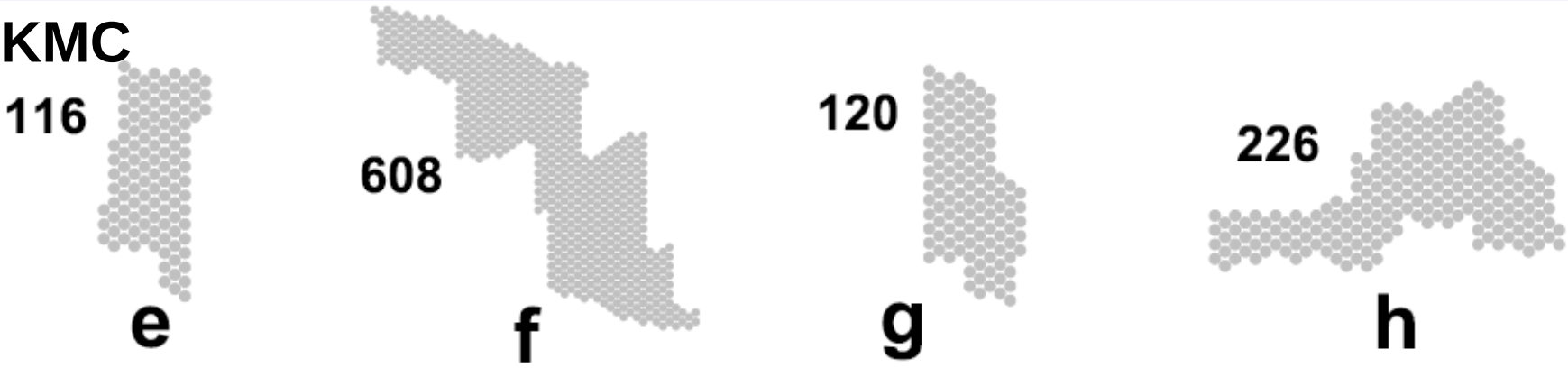
STM



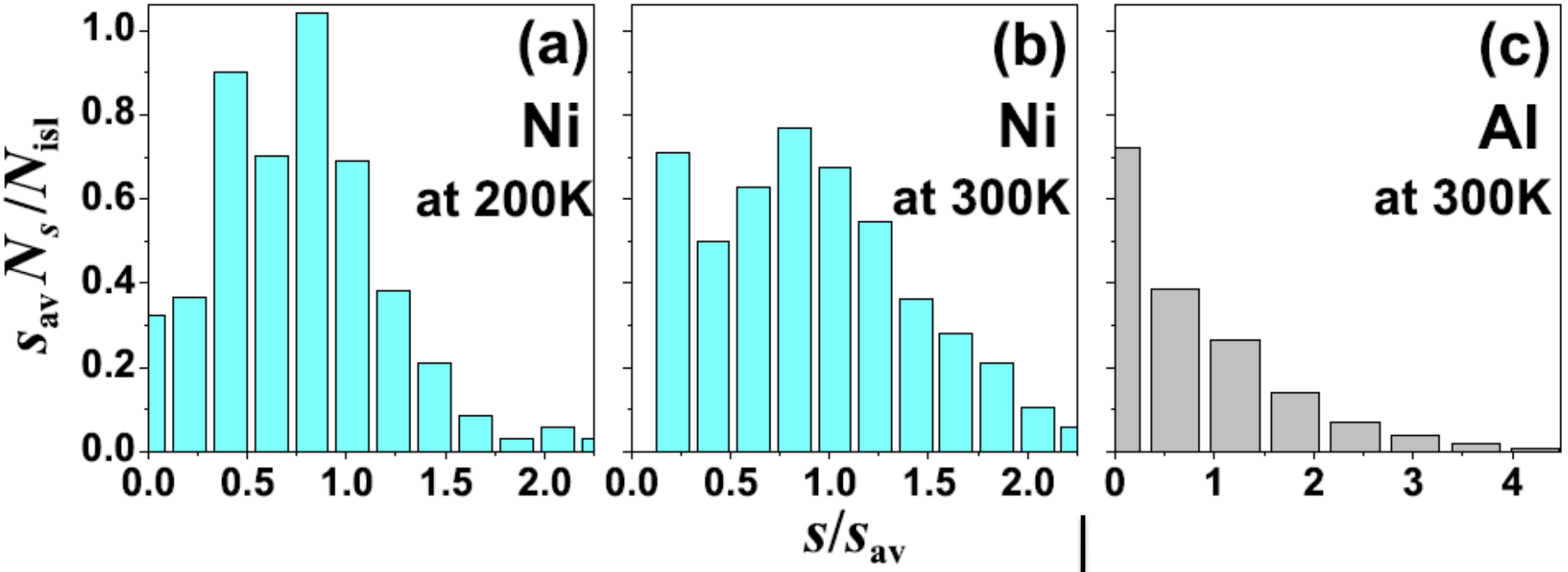
Al on NiAl(110)

Han et al., submitted

KMC



Ni on NiAl(110) & Al on NiAl(110): island size distributions (ISD)



Expt. monomodal ISD broadens with increasing T

BUT for homogeneous nucleation, monomodal ISD sharpens with increasing T corresponding to Increasing reversibility in island nucleation.

..implies some defect-mediated nuc. at least at 300K

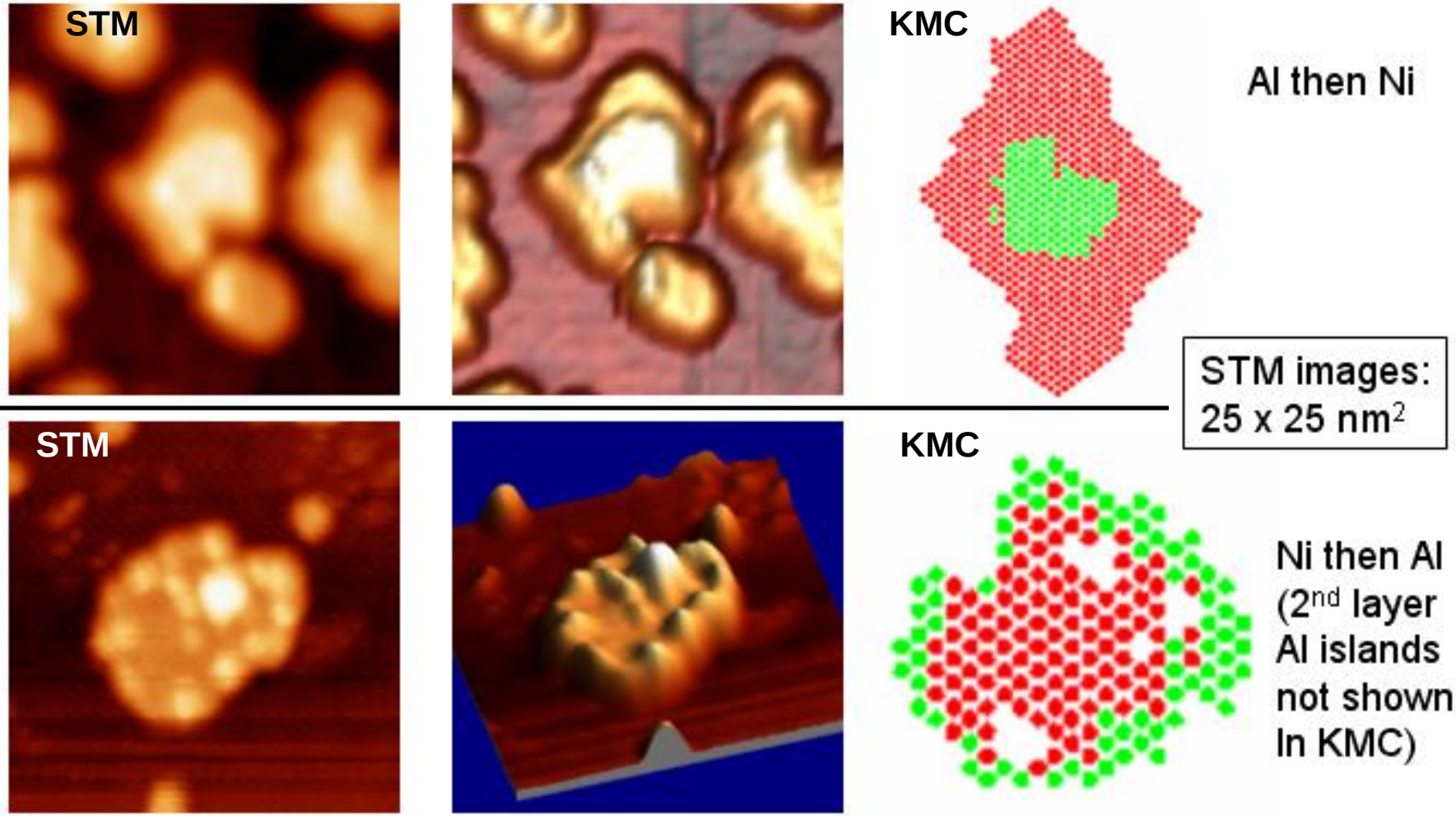
Monotonically decreasing ISD…

implies dominance of defect-mediated nucleation

Ni and Al on NiAl(110): Sequential co-deposition at 300 K

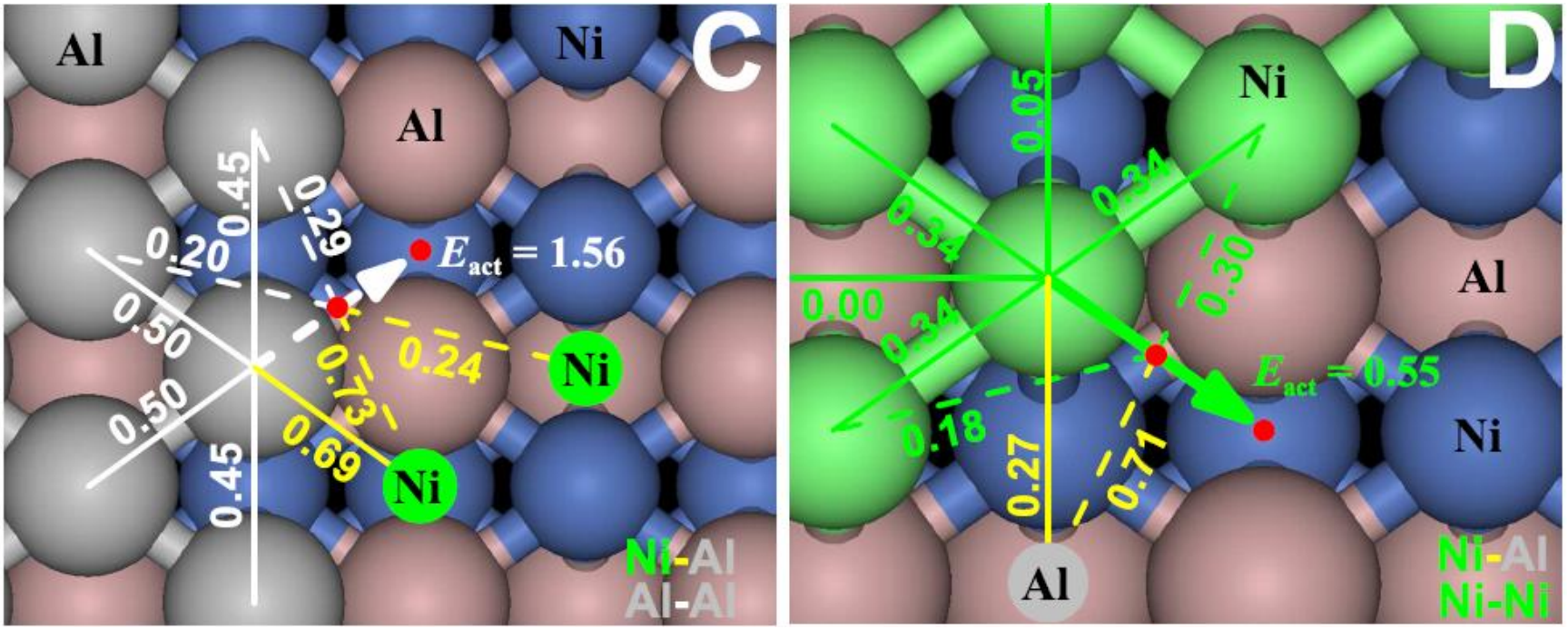
Duguet, Han, Yuen, Jing, Unal, Evans, Thiel, PNAS (2010)

KMC simulations
$F = 8.8 \times 10^{-3}$ ML/s, T = 300 K



Ni and Al on NiAl(110): Sequential co-deposition

PNAS (2010)

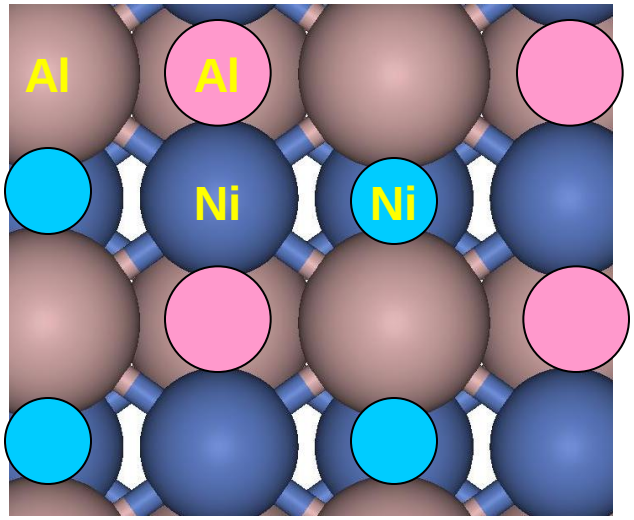


Al core in [Al-core Ni-ring] islands is robust against extraction of Al aided by peripheral Ni

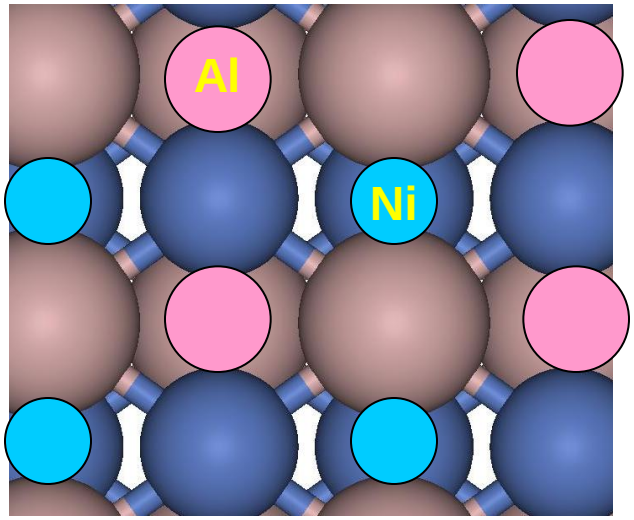
Ni core in [Ni-core Al-ring] islands is susceptible to extraction of Al aided by peripheral Ni

Ni and Al on NiAl(110): Mixed adlayer thermodynamics

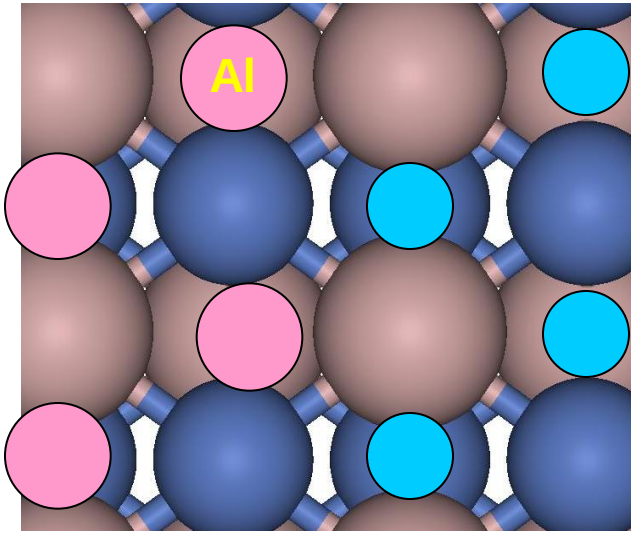
DFT calculations for monolayer binding energy per Al-Ni pair: E_p



E_p = 11.41 eV (perfect order) (correct sites)



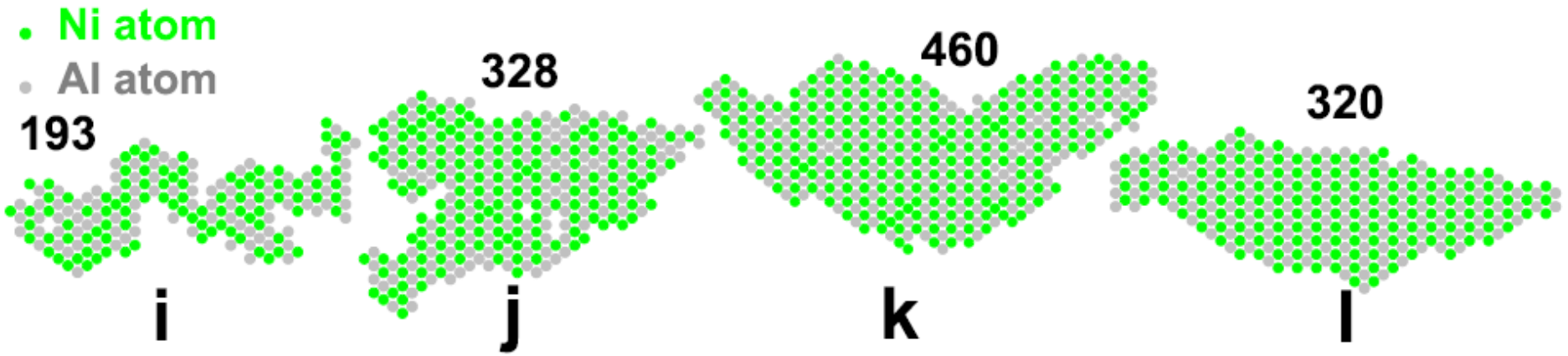
E_p = 10.30 eV (perfect order) (wrong sites)



E_p = 10.04 eV (components separated)

- Perfect alloy ordering on correct sites preferred over wrong sites
- Perfect alloy ordering preferred over separated dense domains of Ni and Al

Simultaneous stoichiometric codeposition of Ni+Al on NiAl(110)



300 K **400 K** **500 K** **600 K**

CONCLUSIONS

Ag versus Au on NiAl(110):

. Near perfect lattice-match of fcc(110) unit cell and that of NiAl(110)
. Bilayer Ag(110) growth on NiAl(110) mediated by QSE
. Both Ag and Au can select from a variety of low energy adlayer structures – lower penalty for Au to populate near Al-br sites leads to selection of complex monolayer structures…

Ni/NiAl(110):

- **isotropic terrace diffusion; dense Ni(100)-like island structure.**
- **multi-site LG model describes growth shape transitions + equil.**

Al/NiAl(110):

- **anis. terrace diff.n; multi-site LG models describe dense irregular islands**

Ni+Al/NiAl(110):

- **Multi-site LG model used to describe simultaneous and sequential co-deposition of Ni and Al on NiAl(110)**
- **LG model predicts ring structures for sequential co-deposition and evolution from poor to good alloy ordering from 300K to 600 K.**

FUNDAMENTAL CHALLENGES FOR (HOMO-) EPITAXIAL THIN FILM GROWTH

SUBMONOLAYER ISLAND FORMATION

- **Beyond-Mean-Field Theory** for island size (ISD) & capture zone area (CZD) distributions

  ISD $f(x=s/s_{av})$: $-zx\, df/dx + (1-2z)f =$ *growth terms*; CZD $g(a=A/A_{av})$: $a\, dg/da + 2g =$ *nuc. terms*

  Joint Probability Distribution (JPD) for island sizes and CZ areas $P(x,a)$ satisfies PDE…

- **Boundary Conditions for coarse-grained BCF type Step-Dynamics Models…**

  $dn/dt = F + D\,\Delta n = 0$ with $D\, dn/dx = K(n-n_{eq}) + P\,\delta n$ …kinetic coefficients K = ?, P = ?

- **Step edge diffusion current**: $J = J_{equil}$(Mullins) + $J_{nonequil}$ ….needs rigorous derivation

UNSTABLE MULTILAYER GROWTH (MOUNDING DUE TO ES BARRIER)

- **Coarse-graining of step-dynamics models to obtain continuum PDE**

  $d/dt\, h(\underline{x}, t) = F - d/d\underline{x}\, \underline{J}$ where $\underline{J}$ = non-equilibrium surface diffusion current = ?

- **Mound coarsening dynamics: deterministic vs. stochastic evolution**

- **Deviations from mean-field nucleation in higher layers**