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)

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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

STM

A

B

C

D

Ag 140K 25x25 nm²

Al first then Ni

STM

E

F

KMC

Al first then Ni

Ni first then Al

• **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
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  
\[ E_d = 0.28 \text{eV (Au), 0.27 eV (Ag)} \]

Ni and Al on NiAl(110):  
...both prefer Ni-br site  
(which is the wrong site for Ni)  
...Ni diff.n by diag. hops: \[ E_d=0.40\text{eV} \]  
...Al anisotropic diff.n: \[ E_d=0.5, 0.3\text{eV} \]
Ag(110) & Au(110) on NiAl(110): near-perfect lattice-match

Top view: NiAl(110)

Top view: Ag(110)

Au(110)-(1x1)
Ag on NiAl(110): rectangular bilayer Ag(110) islands

STM Image
300 K deposition
500 x 500 nm²
0.2 BL Ag

bilayer Ag(110) islands with elongated growth shapes

Measured island height = 0.33 nm

Side view of model

0.34 nm (DFT)

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

- **Ag**

  Deformation

- **Ni**
  - **Al**
  - **B**
  - **C**
  - **D**
  - **A**
  - **E**
  - **S**
  - **O**
  - **X**
  - **Y**
  - **Z**

- **Terrace Diffusion**
  - $E_d = 0.27\text{eV}$

- **Hop up**
  - $E_d + E_{bw} + \delta$

- **Detach**
  - $E_d + E_{bs}$

- **Hop Down**
  - $E_d + \delta + \Delta E_{QSE}$

- **Edge Diffn**
  - $E_{es} = 0.29\text{eV}$
  - $E_{ef} = 0.13\text{eV}$

- **Detach**
  - $E_d + E_{bs}$

- **Fast Vert.**
  - Edge diff

- **E_d**

- **Ag(110)/NiAl(110) 200 K 20% covered**

- **Island Height: 0.33nm @ all T**

- **100x100 nm² 200 K**

- **Han et al. PRL 100 (2008) 116105**

- **Deposition**

- **E_{bs} = 0.09\text{eV} (stronger attraction)**
  - **E_{bw} = 0.03\text{eV} (WEAK attraction)**

- **\Delta E_{QSE} = 0.04-0.05\text{eV}**

- **stronger adsorption**

- **substrate**

- **1-layer island**
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:**

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

**INSTEAD, we use…**

**Modified “initial value approximation” (IVA) approach:**

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

For **terrace diff.n, attachment & detachment**, \( E_o = E_d(\text{terrace diff.n barrier}) \)

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.
STM & KMC images of Ag islands on NiAl(110) are $27 \times 19 \text{ nm}^2$.
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 |
|--------------------|---------------------|---------------------|---------------------|
| STM: 0.14BL        | KMC: 0.07BL         | KMC: 0.14BL         | KMC: 10 min later   |
KMC simulation: elongated Ag bilayer island growth shapes

175 K  50x30 nm² (a-c)

(a)  (b)  (c)  (d)

15x15 nm²

14th Summer School on Crystal Growth (AIP Conf. Proc. 2010)
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

Relative surface energy $\alpha$ [eV/site]

Au coverage [ML]

1 $\times$ 1 Ag/NiAl(110)
1 $\times$ 1 Au/NiAl(110)
2 $\times$ 1 Au/NiAl(110)
3 $\times$ 1 Au/NiAl(110)

PNAS (2010)
Ag vs. Au on NiAl(110): similar metals, different behavior

Energy, eV

Ag

Au

Reaction Coordinate for Ag Diffusion

Reaction Coordinate for Au Diffusion
Ag and Au on NiAl(110): multi-site LG model energetics
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

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

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

$h = \nu \exp(-E_{\text{act}}/kT)$

thermally activated hop

$E_{\text{act}} = E_{\text{TS}} - E_{\text{init}}$
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).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(b)-Ni(3)</td>
<td>0.25</td>
</tr>
<tr>
<td>Al(b)-Al(3)</td>
<td>0.29</td>
</tr>
<tr>
<td>Ni(b)-Al(3)</td>
<td>0.71</td>
</tr>
<tr>
<td>Al(b)-Ni(3)</td>
<td>0.62</td>
</tr>
<tr>
<td>Al(t)-Al(2)</td>
<td>−1.00</td>
</tr>
<tr>
<td>Al(t)-Ni(2)</td>
<td>−0.44</td>
</tr>
<tr>
<td>Ni(b)-Ni(5)</td>
<td>0.14</td>
</tr>
<tr>
<td>Al(b)-Al(5)</td>
<td>0.40</td>
</tr>
<tr>
<td>Ni(b)-Al(5)</td>
<td>0.28</td>
</tr>
<tr>
<td>Al(b)-Ni(5)</td>
<td>0.24</td>
</tr>
<tr>
<td>Al(t)-Al(3)</td>
<td>−12.00</td>
</tr>
<tr>
<td>Al(t)-Ni(3)</td>
<td>−6.50</td>
</tr>
<tr>
<td>Ni(b)-Ni(6)</td>
<td>0.30</td>
</tr>
<tr>
<td>Al(b)-Al(6)</td>
<td>0.45</td>
</tr>
<tr>
<td>Ni(b)-Al(6)</td>
<td>0.85</td>
</tr>
<tr>
<td>Al(b)-Ni(6)</td>
<td>0.73</td>
</tr>
<tr>
<td>Al(t)-Al(4)</td>
<td>0.12</td>
</tr>
<tr>
<td>Al(t)-Ni(4)</td>
<td>0.06</td>
</tr>
<tr>
<td>Ni(b)-Ni(8)</td>
<td>0.18</td>
</tr>
<tr>
<td>Al(b)-Al(8)</td>
<td>0.20</td>
</tr>
<tr>
<td>Ni(b)-Al(8)</td>
<td>0.14</td>
</tr>
<tr>
<td>Al(b)-Ni(8)</td>
<td>0.18</td>
</tr>
<tr>
<td>Al(t)-Al(7)</td>
<td>0.02</td>
</tr>
<tr>
<td>Al(t)-Ni(7)</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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

Experimental STM images (100 × 100 nm²)  

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

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

STM image of Ni on NiAl(110)

DFT calculations

Experiment

Side view
1 ML Ni on NiAl(110)

Side view
2 ML Ni on NiAl(110)

50 × 50 nm² @ 300 K
0.90 ML

0.19 nm

0.19 nm

0.19 nm

0.2 nm

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

<table>
<thead>
<tr>
<th>Temperature</th>
<th>KMC</th>
<th>STM</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>450 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **300 K:**
  - KMC: Elongated irregular diagonal edges favored
  - STM: Octagon-like

- **400 K:**
  - KMC: 6-sided (octagon less 2 sides)
  - STM: 6-sided (octagon less 2 sides)

- **450 K:**
  - KMC: 6-sided (octagon less 2 sides)
  - STM: Octagon-like

- **600 K:**
  - KMC: Equilibrium Shape

Han et al., submitted
**Effective dimer binding**

\[
E_{\text{bdiag}} = 0.34 \text{ eV} - (\Delta E_{\text{ads}} = 0.15) = 0.19 \text{ eV}
\]

...not strong enough for i=1 @ 300K

\[
N_{\text{isl}}(\text{expt}) = 4 \times 10^{-3} \text{ nm}^{-2} \quad N_{\text{isl}}(i=1 \text{ KMC}) = 9 \times 10^{-3} \text{ nm}^{-2}
\]

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**ISLAND GROWTH SHAPES**

Edge diffusion active along diagonal steps at 300K with barrier of $E_{\text{edge}} \sim 0.35$ 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)**

![Diagram of Ni and Al dimers](image)

- $E_{by} = 0.05$ eV
- $E_{bx} = 0.00$ eV
- $E_{bdiag} = 0.34$ eV

**Effective dimer binding**

\[
= (E_{bdiag}=0.34) -(\Delta E_{\text{ads}}=0.15) = 0.19 \text{ eV}
\]

...not strong enough for i=1 @ 300K
Al on NiAl(110): Island Shapes at 300 K (KMC vs. Expt.)

STM

STM images of Al on NiAl(110) with dimensions 87×100 nm² and 44×51 nm².

KMC

KMC simulations showing island shapes with numbers 116, 608, 120, and 226.
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

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

Duguet, Han, Yuen, Jing, Unal, Evans, Thiel, PNAS (2010)
Ni and Al on NiAl(110): Sequential co-deposition

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)

- Ni atom
- Al atom

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.
SUBMONOLAYER ISLAND FORMATION

- **Beyond-Mean-Field Theory** for island size (ISD) & capture zone area (CZD) distributions
  
  \[ ISD \ f(x=s/s_{av}) : -zx \frac{df}{dx} + (1-2z)f = \text{growth terms}; \quad \text{CZD} \ g(a=A/A_{av}) : \ a \frac{dg}{da} + 2 g = \text{nuc. terms} \]

  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**...
  
  \[ \frac{dn}{dt} = F + D \frac{dn}{dx} = 0 \] with \( D \frac{dn}{dx} = K(n-n_{eq}) + P \delta n \) …kinetic coefficients \( K = ? \), \( P = ? \)

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

UNSTABLE MULTILAYER GROWTH (MOUNDING DUE TO ES BARRIER)

- **Coarse-graining of step-dynamics models to obtain continuum PDE**
  
  \[ \frac{d}{dt} h(x, t) = F - \frac{d}{dx} J \] where \( J \) = non-equilibrium surface diffusion current = ?

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

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