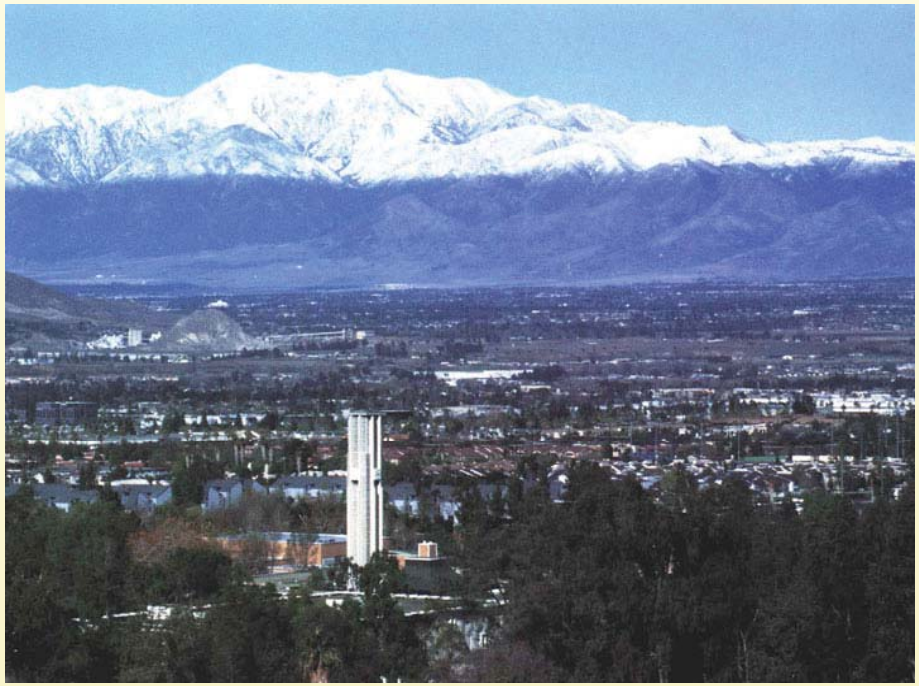
Surface Chemistry of Copper Amidinates on Metal Surfaces



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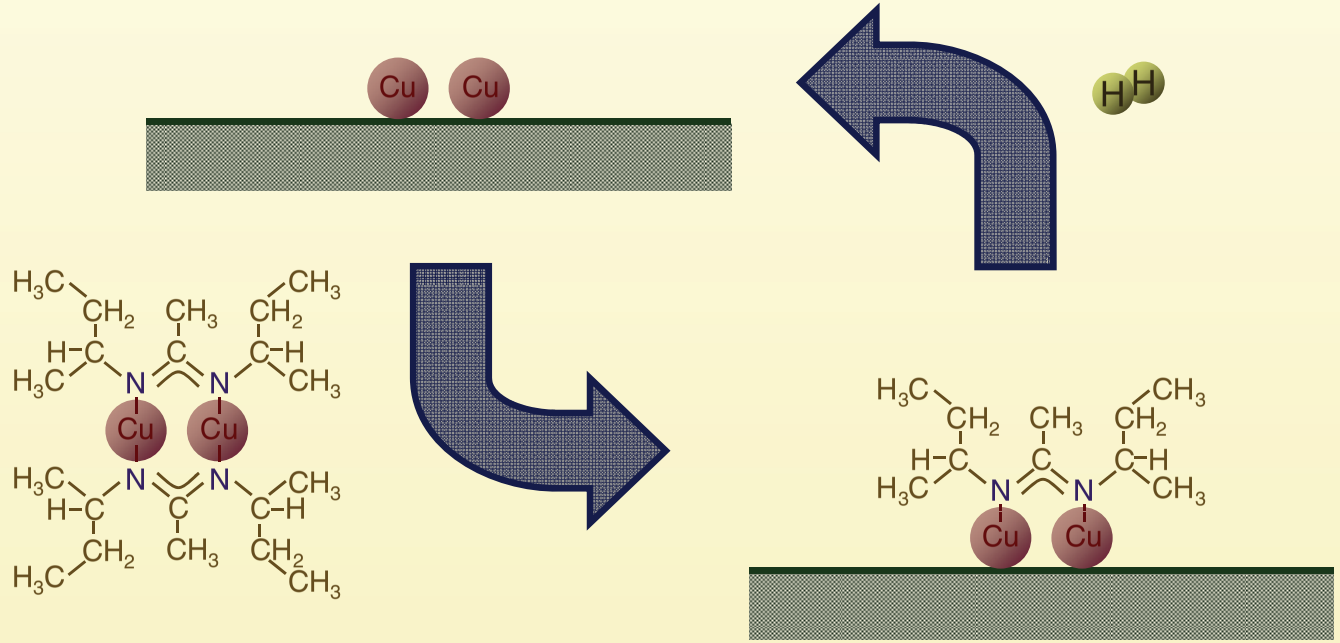
Introduction

Atomic Layer Deposition

Separate chemistry into two self-limiting and complementary reactions for more control



Outline

- Cu Amidinate Uptake
- Effect of Coadsorbed Hydrogen
- Cu Amidinate Surface Chemistry

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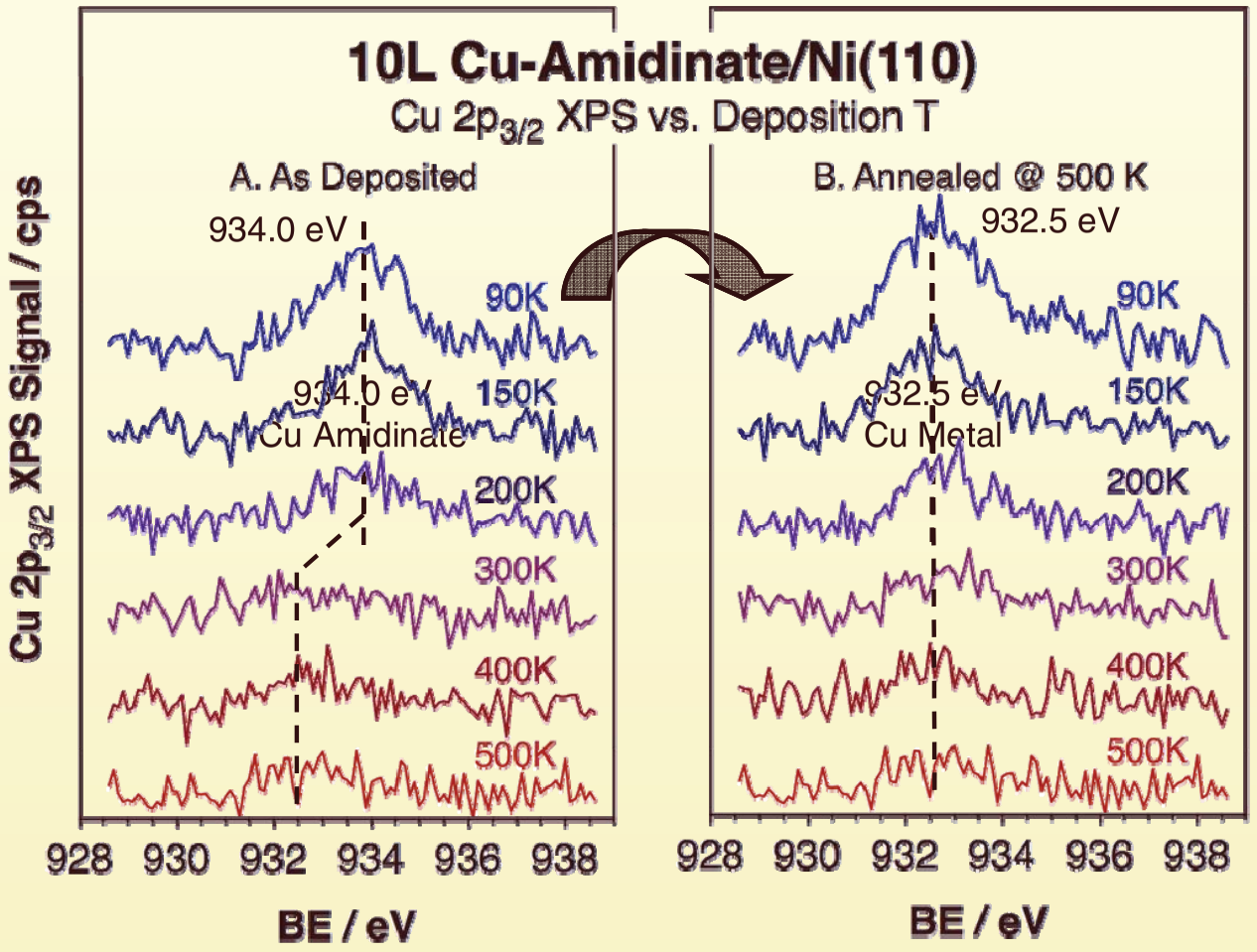
Cu Amidinate Uptake

XPS versus Adsorption Temperature



Molecular adsorption converts to Cu metal upon annealing

Already adsorbed as Cu metal, but lower sticking

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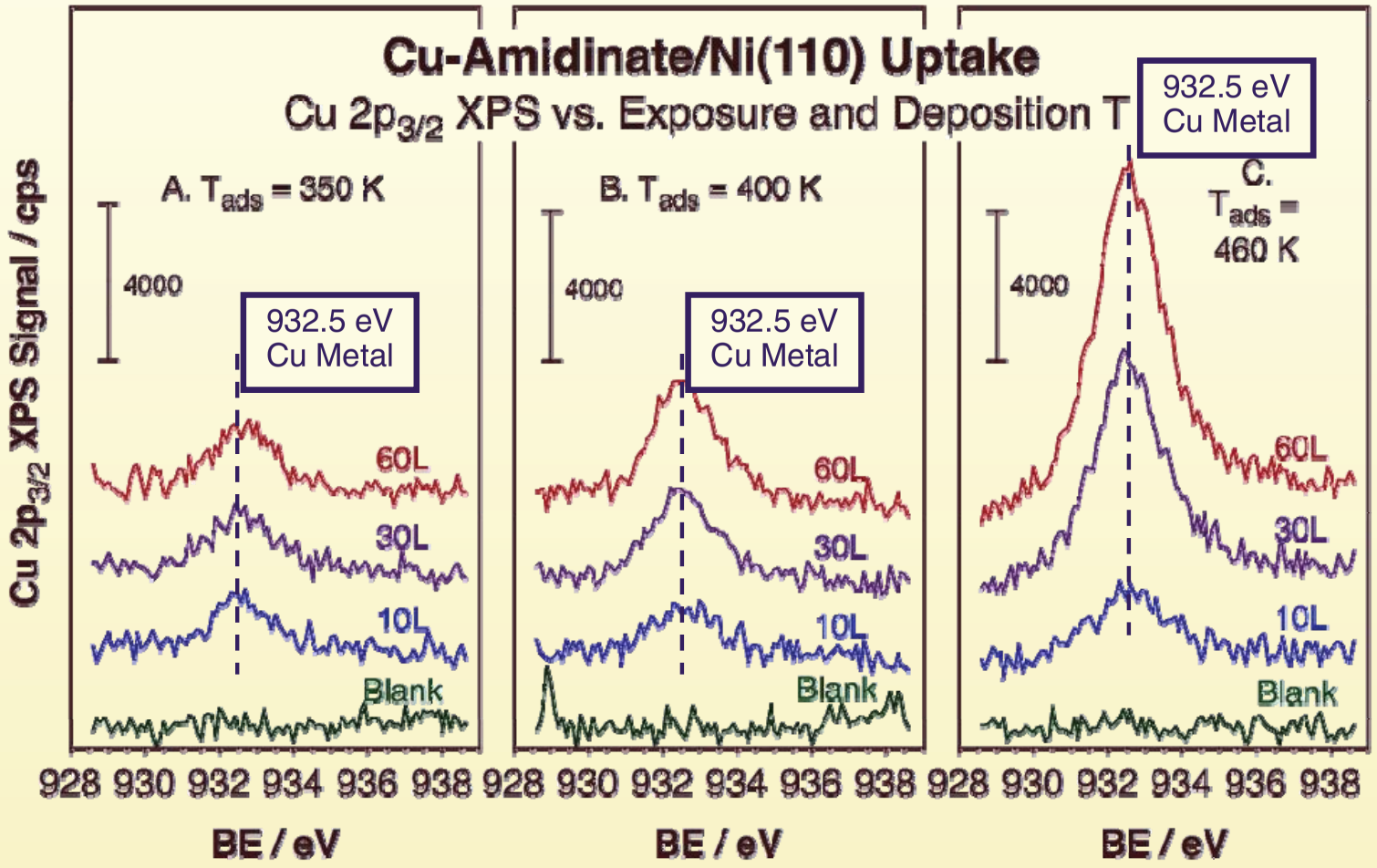
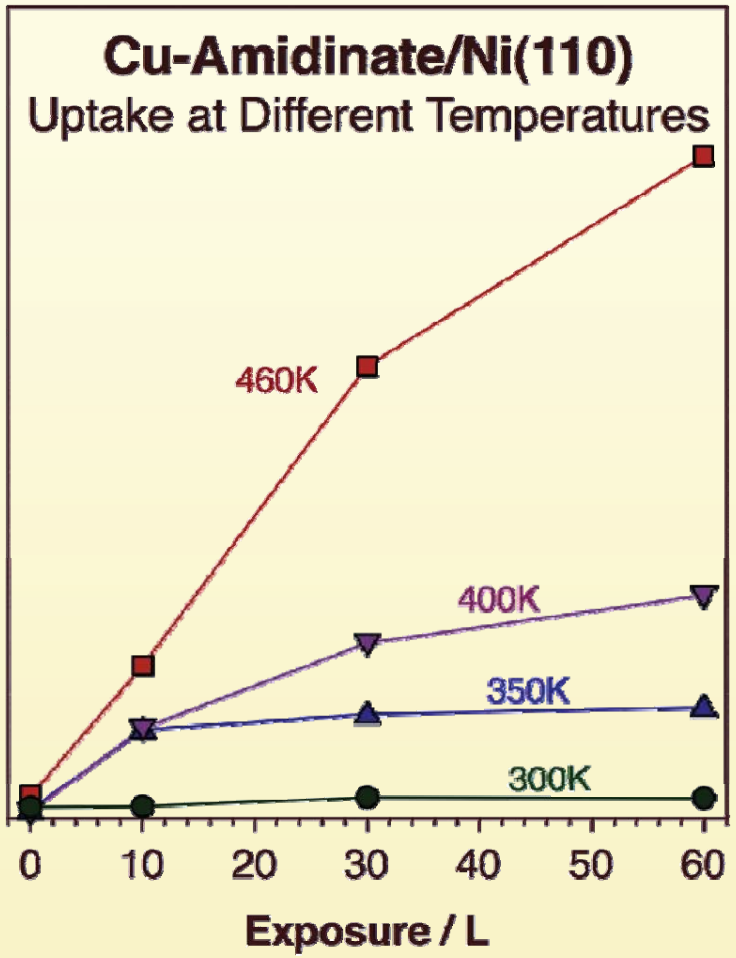
XPS versus Exposure at ALD Temperatures



Uptake increases with increasing T

Cu Amidinate Uptake

XPS versus Exposure at ALD Temperatures

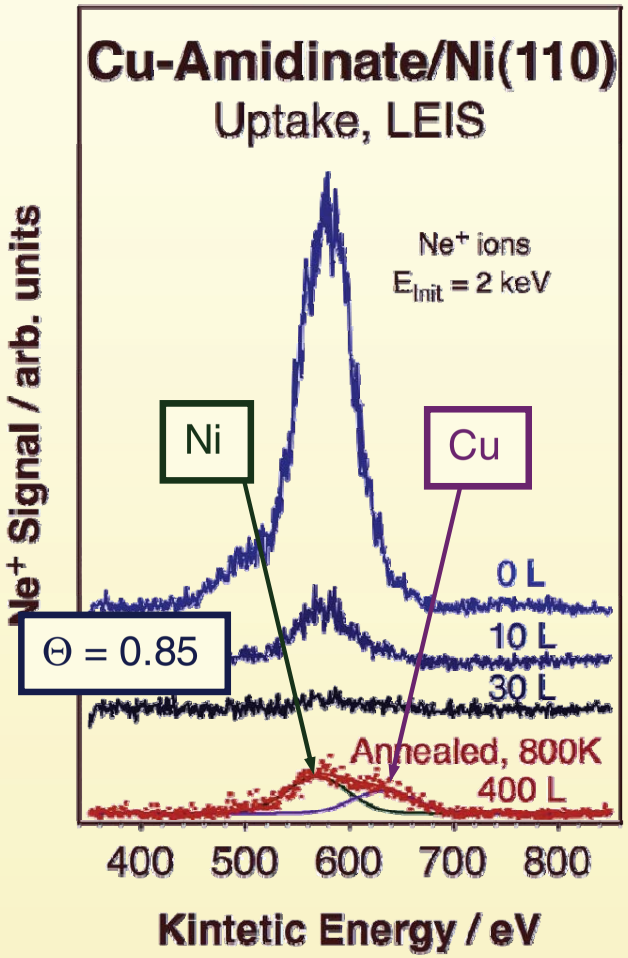


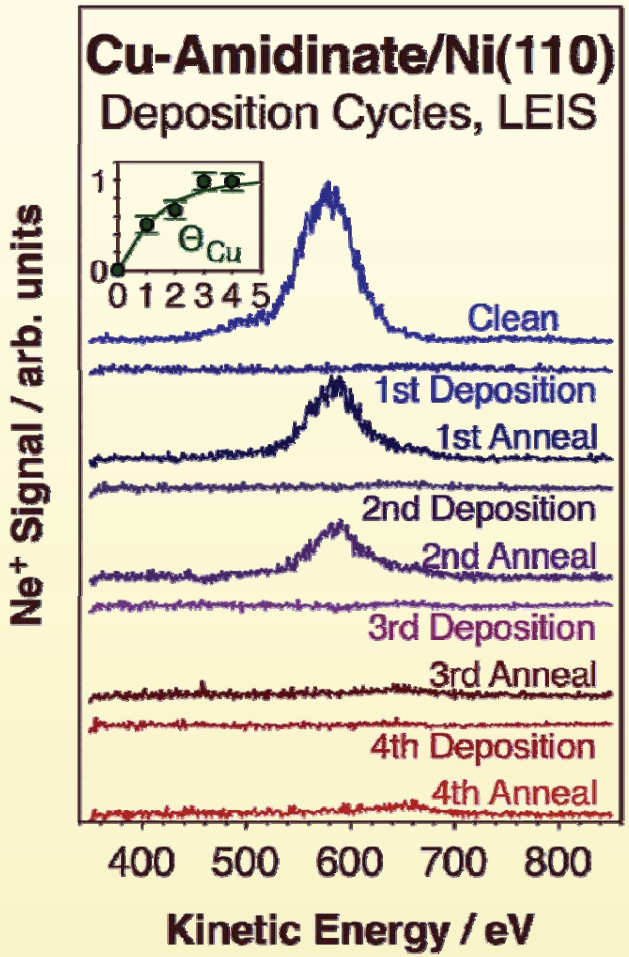
Fast and continuous uptake above 450 K. Possible CVD

Uptake past monolayer above 400 K

No uptake below 300 K

LEIS versus Exposure



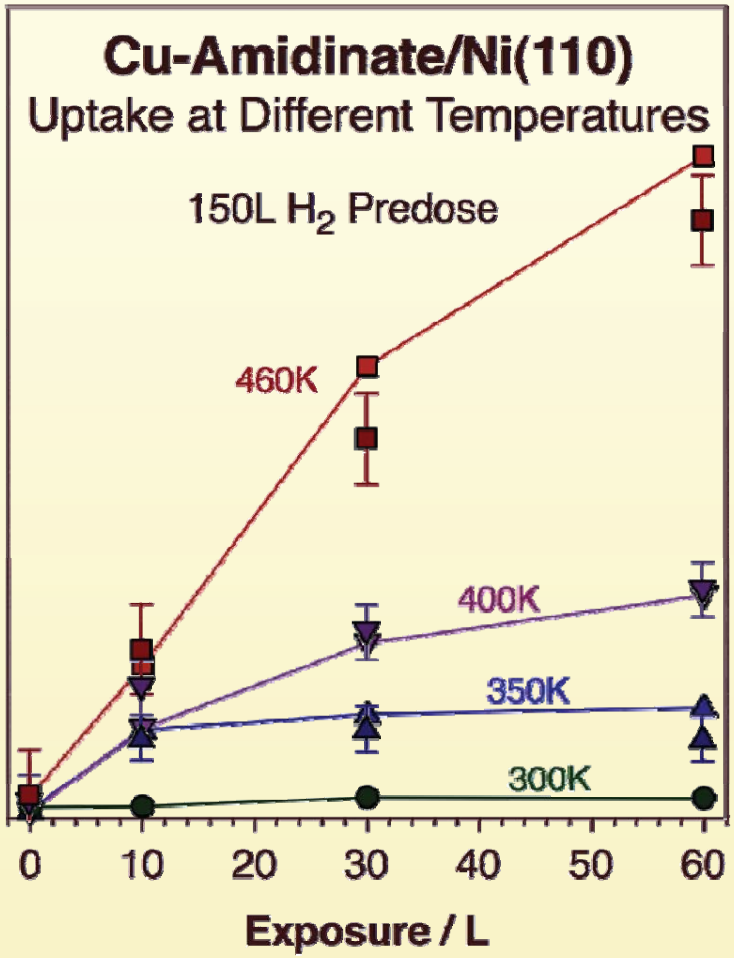


Saturation at ~ 15 L
Some surface uncovered upon annealing

~ 3 Cycles/ML
required for Cu ALD

Effect of Hydrogen

Cu Amidinate Uptake on Clean and H-Saturated Ni



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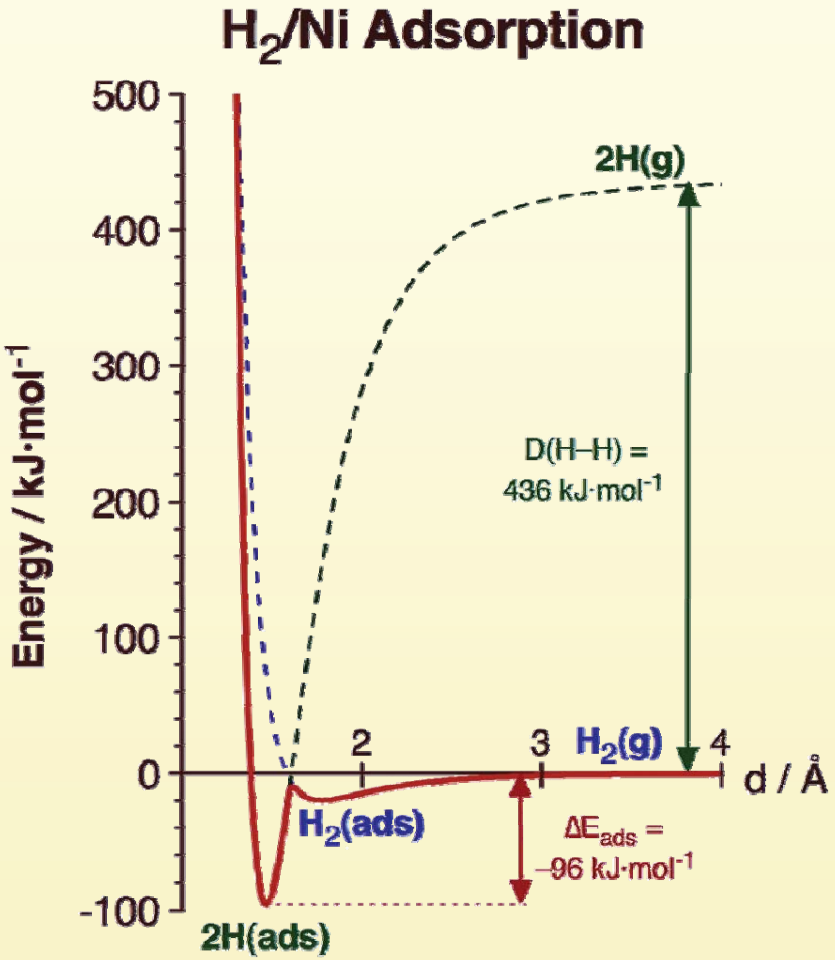
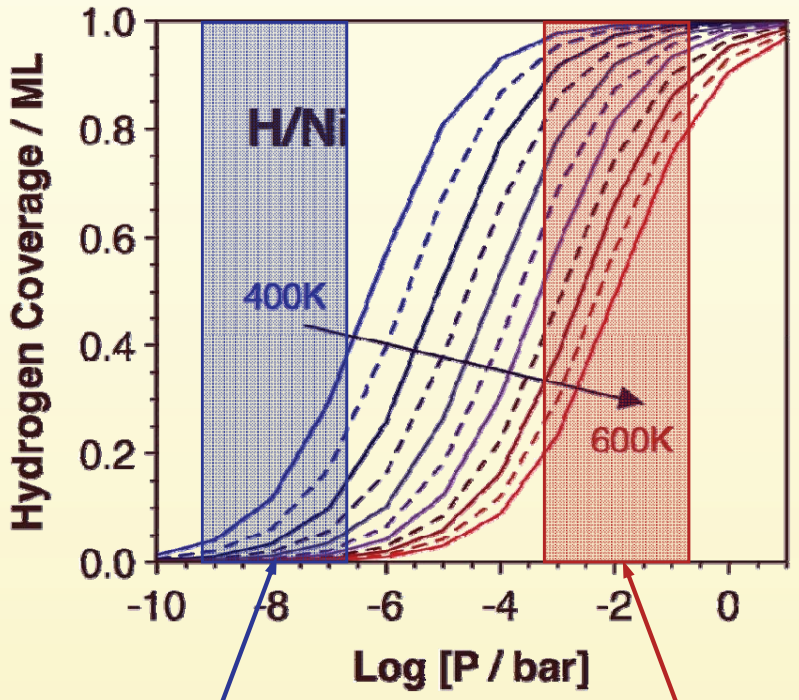
Hydrogen Adsorption Kinetics on Ni



Activated H_2 Desorption → Less H(ads) at higher Ts



Not enough H once H_2 is pumped away

Reasonable H coverages under ALD conditions

- Cu Amidinate Uptake
- Effect of Coadsorbed Hydrogen
- Cu Amidinate Surface Chemistry

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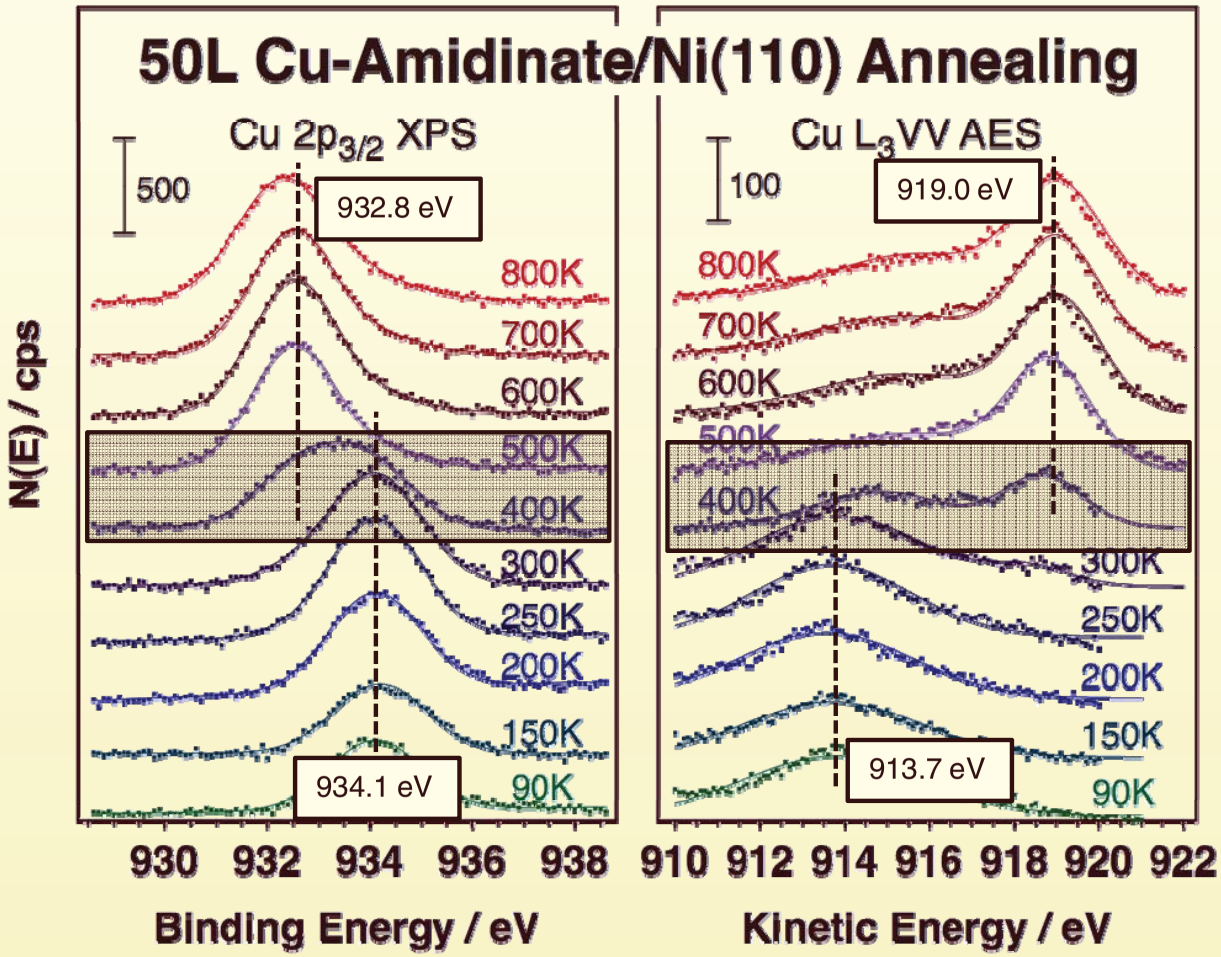
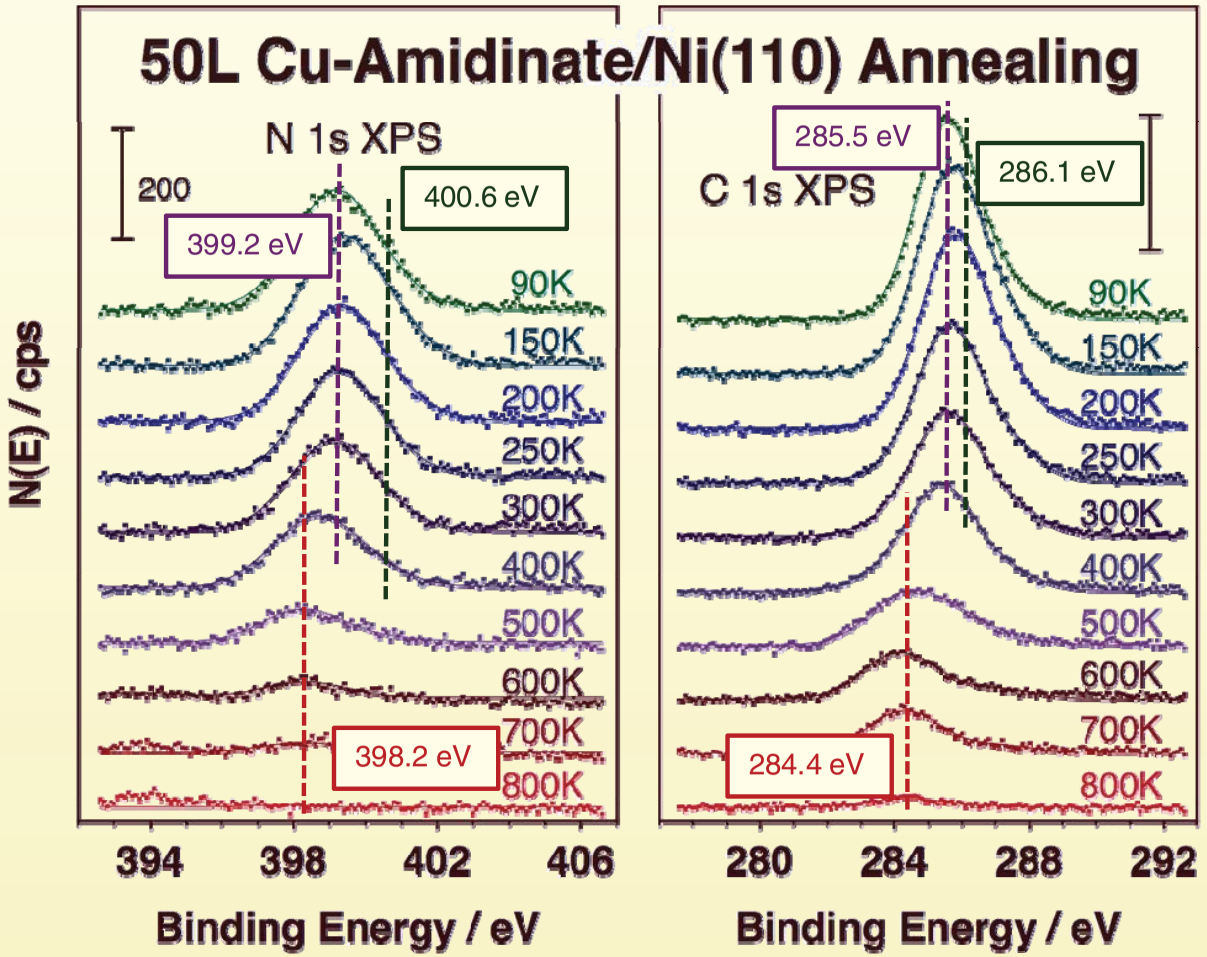
Cu Amidinate Thermal Chemistry



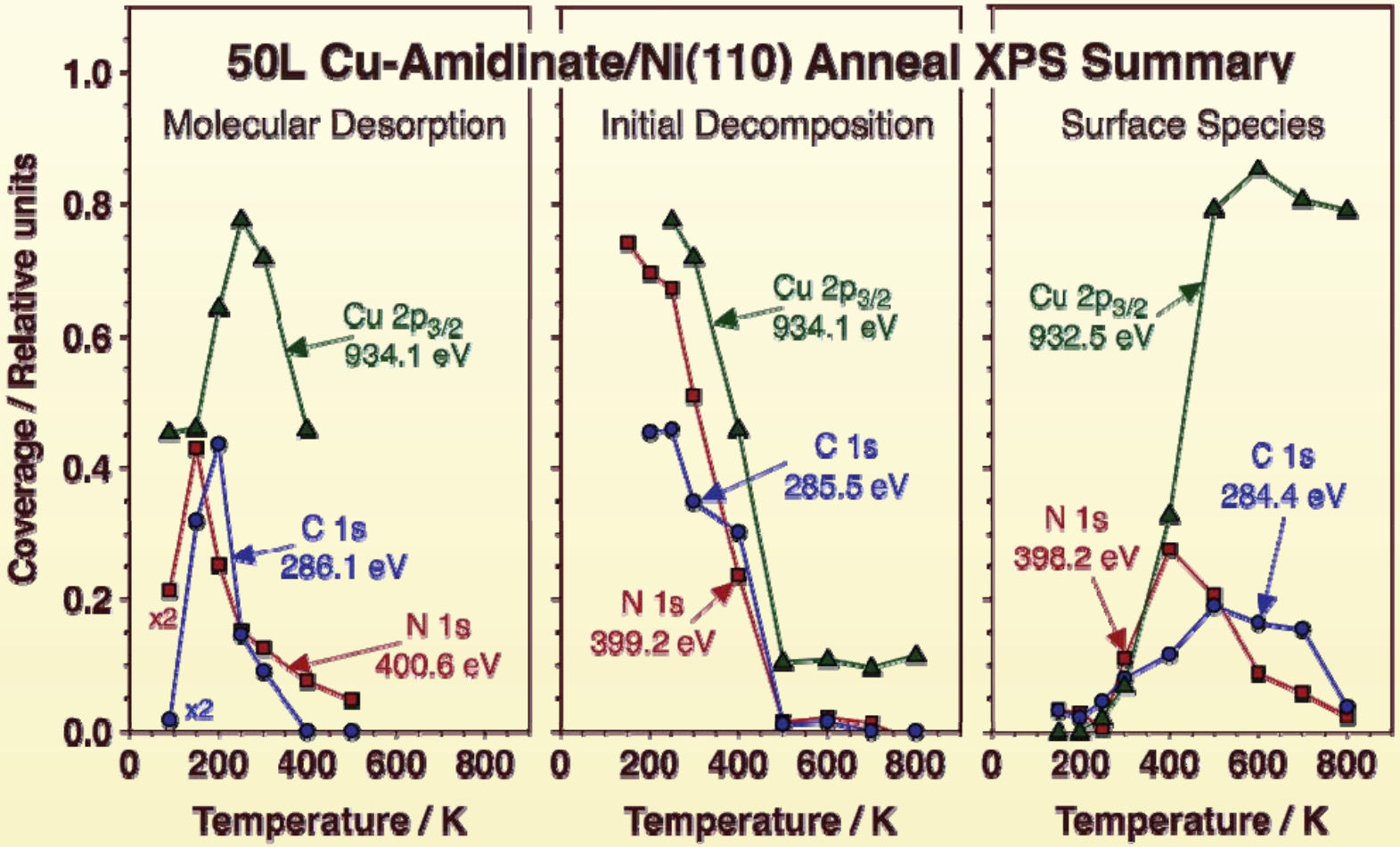
Surface reaction around 400 K
Direct conversion from Cu(I) to Cu(0)

C 1s and N 1s XPS versus Annealing Temperature

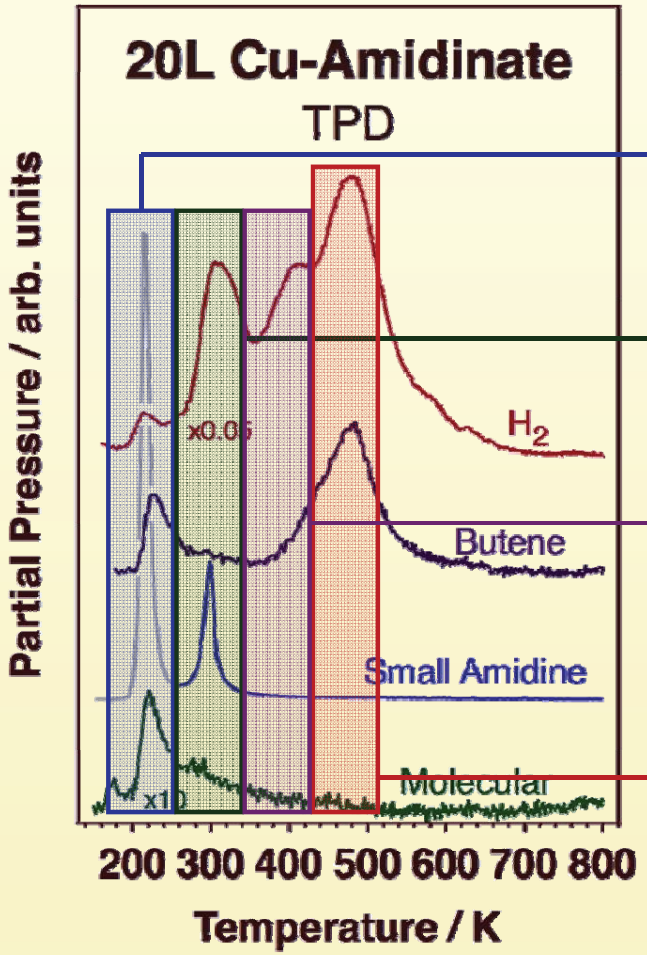


At least three temperature regimes
Carbon and nitrogen changes slightly dephased

XPS versus Annealing Temperature, Summary



Multilayer desorption below 250 K	Cu and N track each other C displays two stages	New C species between 400 & 700K



220 K
Molecular desorption

300 K
114 amu desorption, Amidine
^{s}But–NH–C(CH_3)=NH_2?

405 K
Additional dehydrogenation
Surface amine?

480 K
β-Hydride elimination
From N-containing species?
Sets upper limit for ALD

- Cu Amidinate Uptake
  - Direct Cu(I) to Cu(0) conversion upon adsorption
  - Activated adsorption, starts at T ~ 350K
  - Possible CVD at T > 450 K
  - ~ 3 Cycles/ML for ALD
- Effect of Coadsorbed Hydrogen
  - No appreciable changes under UHV
  - Need P > 1 mbar to reach significant steady-state Θ_H
  - Surface species need to survive Cu-Amidinate $\leftrightarrow$ H_2 transition
- Cu Amidinate Surface Chemistry
  - T < 250 K Molecular desorption
  - T ~ 300 K Amidine desorption, Surface amine formation
  - T ~ 405 K Amine decomposition
  - T ~ 480 K β-Hydride elimination, butene desorption

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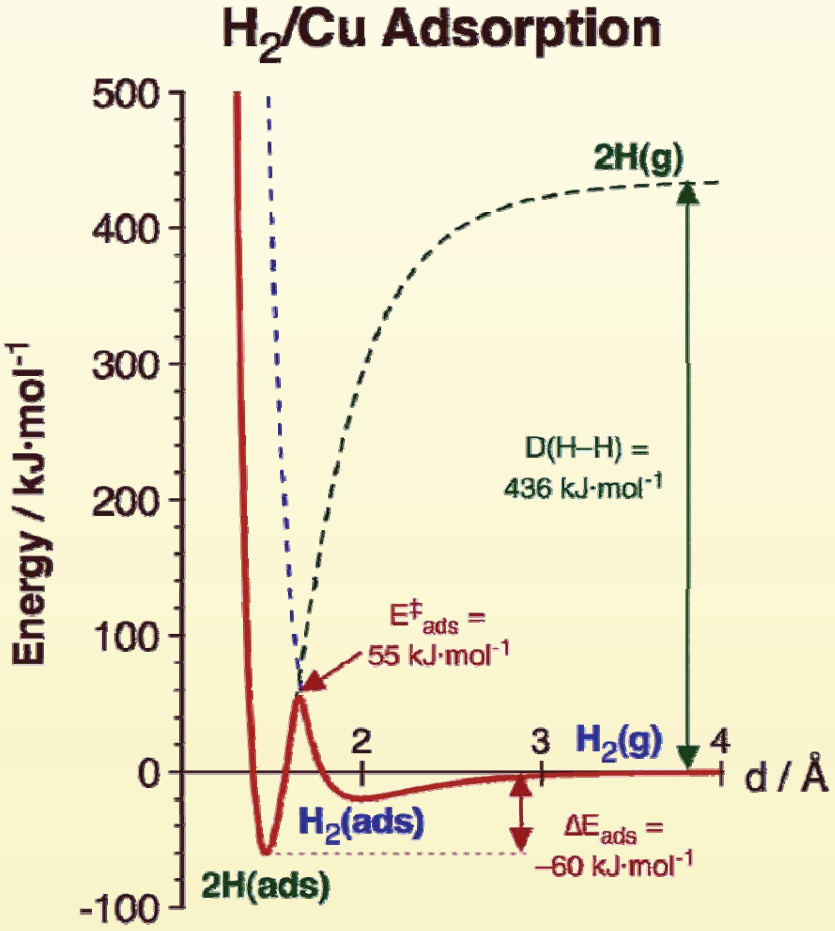

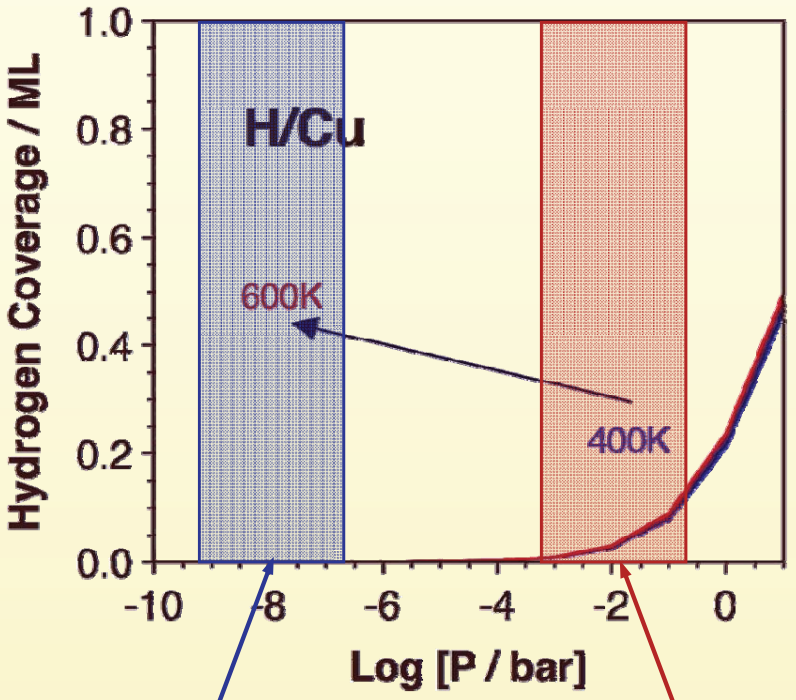

Not enough H once H_2 is pumped away

Not enough H under ALD conditions

Activated H_2 Adsorption → no H(ads) at any T

Cu Amidinate must produce hydrogenatable surface intermediates during adsorption